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Microstructure–Surface Properties Correlation of LPBF–Manufactured Alloys

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Abstract

La manifattura additiva (AM) di leghe metalliche, in particolare la tecnologia Laser Powder Bed Fusion (L-PBF), rappresenta un approccio trasformativo per la progettazione e la produzione di componenti ad alte prestazioni. La possibilità di ottenere geometrie near-net-shape e un livello senza precedenti di libertà progettuale ha aperto nuove prospettive nell'utensileria, nell'aerospazio e nelle applicazioni per la termoregolazione. Le condizioni estreme di solidificazione tipiche della L-PBF generano tuttavia microstrutture e popolazioni di difetti significativamente diverse da quelle ottenute con tecnologie convenzionali. Architetture cellulari colonnari, segregazioni di soluto, tensioni residue e specifiche classi di porosità (mancata fusione, keyhole, pori gassosi) influenzano in modo critico l'integrità e la durabilità dei componenti. Comprendere la correlazione tra microstruttura, condizione superficiale e risposta ambientale è quindi essenziale per valutare l'affidabilità delle leghe AM in condizioni di servizio gravose, dove usura e corrosione costituiscono le principali cause di danneggiamento.

La tesi analizza tali fenomeni in due leghe metalliche con diverso grado di maturità applicativa: l'acciaio maraging 18Ni300 (1.2709) e l'ottone bifasico CuZn42 (CW510L). Gli acciai maraging, già impiegati negli inserti con canali di raffreddamento conformati per stampi da pressocolata, sono tra le leghe ad alta resistenza più compatibili con la L-PBF, ma le loro prestazioni in contatto con leghe di alluminio fuso e il loro comportamento in condizioni operative severe, in quanto materiali per inserti con raffreddamento conformato, sono ancora poco caratterizzati. Gli ottoni, al contrario, presentano sfide di processabilità legate alla volatilità dello zinco, all'ampio intervallo di solidificazione e alla segregazione degli elementi di lega, ma risultano promettenti come alternative senza piombo per componenti per conduzione di fluidi e per applicazioni di design.

La prima parte del lavoro esamina sistematicamente l'acciaio maraging L-PBF attraverso confronti con l'equivalente materiale forgiato e acciai per stampi. Sono valutati la resistenza alla corrosione a contatto con leghe Al-Si allo stato fuso, il comportamento all'usura, la resistenza alla corrosione in ambienti acquosi e la

risposta all'erosione per cavitazione. I risultati mostrano un'elevata resistenza al contatto con alluminio fuso, con velocità di corrosione comparabili a quelle degli acciai da utensili a caldo per brevi esposizioni. Nei test relativi ai circuiti di raffreddamento, cavitazione e usura evidenziano il ruolo dominante dell'austenite residua come sito preferenziale di nucleazione del danneggiamento. Un'analisi di cedimento su un inserto con canali di raffreddamento conformati per pressocolata conferma l'elevata qualità strutturale del componente L-PBF, ma sottolinea la necessità di un controllo accurato dell'acqua di raffreddamento per evitare sinergie tra criccate meccaniche e ambiente corrosivo, riconducibili a fenomeni di corrosione-fatica.

La seconda parte della tesi riguarda l'ottone CuZn42 prodotto mediante L-PBF. Confronti con il materiale estruso permettono di valutare erosione per cavitazione, corrosione elettrochimica e resistenza alla dezincificazione. Sebbene i tempi di incubazione in cavitazione siano simili, la variante AM raggiunge più rapidamente il regime stazionario e mostra una perdita di materiale più uniforme ma accelerata, guidata dalla porosità interstrato e dall'anisotropia microstrutturale. In soluzioni clorurate, la corrosione è fortemente localizzata: le sezioni lungo la direzione di crescita risultano più attive rispetto a quelle nel piano di scansione, più simili al materiale laminato. Immersioni prolungate favoriscono la dezincificazione in corrispondenza dei pit, con campioni AM che sviluppano strati alterati più profondi. Prove standardizzate confermano questa tendenza e consentono una classificazione quantitativa dei campioni. L'analisi indica che, sebbene l'ottone AM risulti nominalmente ricco in fase α per via dell'evaporazione dello zinco, è la topologia dei difetti, più che la sola frazione di fase, a governare la risposta alla corrosione. Nel complesso, gli studi su acciaio maraging e ottone convergono verso un messaggio unificato: nelle leghe L-PBF, la durabilità superficiale in ambienti corrosivi o soggetti a usura dipende meno dalle proprietà meccaniche di bulk e più dalla topologia, connettività e chimica dei difetti prossimi alla superficie. Contestualizzando le osservazioni microstrutturali attraverso test rappresentativi delle condizioni di esercizio, la tesi definisce una correlazione microstruttura–superficie–prestazioni applicabile a diverse classi di leghe, fornendo indicazioni pratiche per l'impiego affidabile di componenti L-PBF in ambienti severi.

Contents

Additive manufacturing (AM) of metallic alloys, in particular Laser Powder Bed Fusion (L-PBF), is an increasingly transformative approach for the design and production of high-performance components. The ability to obtain near-net-shape geometries and an unprecedented degree of design freedom has opened new opportunities in tooling, aerospace, and thermal-management applications. However, the extreme solidification conditions inherent to L-PBF generate microstructures and defect populations that differ markedly from those produced by conventional technologies. Columnar cellular architectures, solute segregation, residual stresses, and characteristic classes of porosity (lack-of-fusion, keyhole, and gas pores) critically influence component integrity and durability. Understanding the correlation between microstructure, surface condition, and environmental response is therefore essential for assessing the reliability of AM alloys in demanding service environments, where wear and corrosion are major causes of damage or premature failure.

This thesis investigates several corrosion- and wear-related phenomena in two metallic alloys that differ in industrial maturity: maraging steel 18Ni-300 (1.2709) and the duplex brass CuZn42 (CW510L). The selection reflects both technological opportunities and scientific challenges. Maraging steels, already employed in inserts with conformal cooling channels for high-pressure die-casting molds, are among the high-strength alloys most compatible with L-PBF. However, their performance in contact with molten aluminum alloys and their behavior under severe operating conditions, as materials used for conformally cooled inserts, are still poorly characterized. Brasses, conversely, present significant processability challenges due to zinc volatility, a wide solidification interval, and alloying-element segregation, yet they are attracting interest as lead-free alternatives for fluid-handling components traditionally manufactured by machining, as well as for design-oriented applications in fashion and luxury sectors where the design freedom of AM is particularly appealing.

The first part of the work examines L-PBF maraging steel. Comparative studies with forged steels and reference tool steels enable the evaluation of its corrosion resistance in contact with molten Al-Si foundry alloys (representative of mold filling), its wear performance, its corrosion resistance in aqueous environments, and its behavior under cavitation erosion (representing coolant-flow effects). The results show that the alloy exhibits high resistance to molten aluminum, with corrosion rates comparable to those of conventional hot-work tool steels for short exposure times. In tests simulating potential damage mechanisms in water-cooled channels, cavitation and wear highlight the dominant role of localized retained austenite, which acts as a preferential site for wear nucleation. A failure analysis conducted on a maraging-steel die-casting insert further confirms the high structural quality of the L-PBF component, while underscoring the need for careful control of cooling water to avoid synergies between mechanical cracking and corrosive environments. The observed damage is primarily attributable to corrosion-fatigue mechanisms.

The second part of the thesis focuses on L-PBF CuZn42 brass. Comparative tests with the extruded counterpart assess cavitation erosion, electrochemical corrosion, and dezincification resistance. Although both materials show similar incubation times under cavitation, the AM variant reaches the steady-state regime more rapidly and exhibits a more uniform yet accelerated material loss, driven by interlayer porosity and microstructural anisotropy. In chloride-containing solutions, corrosion is strongly localized: sections along the build direction display higher activity than those in the scan plane, which behave more similarly to the wrought material. Prolonged immersion promotes pit-centered dezincification, with AM samples developing deeper altered layers. Standardized dezincification tests confirm this trend and allow quantitative classification of the specimens. The analysis indicates that although AM brass is nominally richer in α phase (due to zinc evaporation), it is the topology of defects, rather than phase fraction alone, that governs corrosion response.

Overall, the studies on maraging steel and brass converge toward a unified message: in L-PBF alloys, the surface durability of components exposed to corrosive or wear-intensive environments is governed less by bulk mechanical properties or nominal phase fractions, and more by the topology, connectivity, and chemistry of

near-surface defects. By contextualizing microstructural observations through tests representative of service conditions – exposure to molten aluminum, cavitation erosion, corrosion-fatigue, and dezincification – the thesis establishes a microstructure-surface-performance correlation applicable across different alloy classes. This framework provides practical guidance for the deployment of L-PBF alloys in environments where wear and corrosion resistance are critical to component reliability.

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SECTION 1.

1. Background and State of the Art

1.1. Additive Manufacturing of Metallic Alloys

Additive Manufacturing (AM) of metallic materials represents a paradigm shift in the design and production of engineered components. By building parts layer by layer directly from digital models, AM removes many of the geometric and tooling constraints associated with conventional processes such as casting, forging, or machining. This enables unprecedented design freedom, greater material efficiency, and the integration of multiple functions into a single component, reducing assembly complexity and enhancing performance [1, 2].

Among the various metal AM technologies, Laser Powder Bed Fusion (L-PBF) is the most mature and widely adopted, with major applications in aerospace, biomedical, and tooling industries. Its origins can be traced to selective laser sintering of polymers in the late 1980s, later extended to metals as selective laser melting with the advent of fiber lasers and precision scanning systems [3]. Today, L-PBF is a refined process with well-established control over powder spreading, laser energy delivery, and inert gas atmospheres [4]. In L-PBF, thin layers of metal powder (typically 20–60 μm) are selectively melted by a focused laser beam following the geometry defined in the digital model. After solidification of each layer, the build platform is lowered, and a fresh powder layer is spread. The process takes place in a sealed chamber with an inert gas flow (argon or nitrogen) to suppress oxidation and contamination.

To orient the reader across the powder-to-part chain, **Figure 1-1** synthesizes the coupled *science* and *technology* challenges in L-PBF and links them to performance-relevant design targets. On the science side (left, green), the figure foregrounds powder attributes and heat-source/powder interactions, the resulting heat transfer and vaporization phenomena, and the emergence of hierarchical microstructures and defect populations; it closes the loop with quantitative metallography for model calibration and feedback. On the technology side (right, blue), the emphasis shifts to process parameter optimization and path planning, in-situ monitoring, post-build heat treatment, non-destructive qualification, and the scaling/throughput needed for industrial components. At the center, a radar chart encodes the design trade-space: additive manufacturability must be advanced without compromising static and dynamic mechanical properties, microstructural stability, environmental resistance, or cost and density.

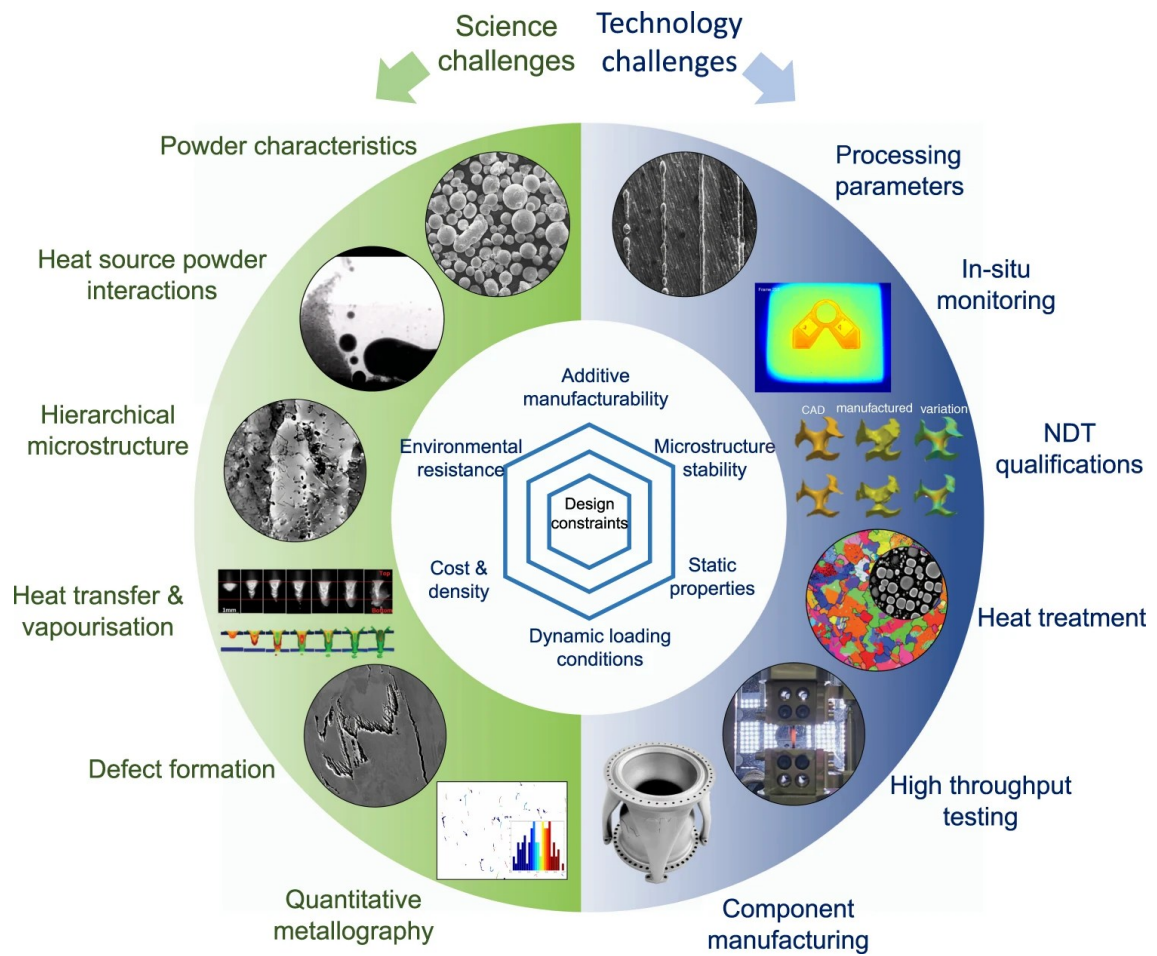


Figure 1-1 Key challenges in science (left, green) and technology (right, blue) for digitally designed metal 3D printing, and the central design trade-space. Reprinted from [5].

The process is characterized by extreme thermal gradients (10^5 – 10^7 K·m⁻¹) and very high cooling rates (10^3 – 10^6 K·s⁻¹). These conditions produce microstructures markedly different from those obtained by traditional manufacturing. A common feature is the formation of columnar grains aligned with the build direction [6]. Rapid solidification also promotes fine cellular substructures, dense dislocation networks, metastable phases, and microsegregation of alloying elements [1]. Defects are generated in parallel with these microstructural features. Three main pore families are typically distinguished: lack-of-fusion voids, caused by insufficient overlap or low energy density; keyhole pores, formed by unstable collapse of vapor cavities at excessive energy density; and gas pores, arising from entrapped shielding gas or feedstock porosity. At free surfaces, capillary instabilities such as balling and humping, along

with spatter redeposition and denudation, create rough and re-entrant topographies **Figure 1-2**. These defects co-evolve with the thermal history and strongly influence downstream performance by concentrating stresses, enlarging the true metal–environment interface, and generating occluded geometries that may accelerate localized corrosion [7].

Another unique characteristic of L-PBF is the repeated thermal cycling imposed by successive layers. Each new track partially remelts or reheats the underlying material, inducing tempering, grain coarsening, and secondary precipitation [8]. This layered thermal history produces a complex microstructural evolution that directly impacts fatigue performance, corrosion resistance, and mechanical strength [9]. In addition, steep temperature gradients and rapid cooling generate tensile residual stresses that can exceed the local yield strength, causing distortion or cracking. Two crack types are most common: hot or solidification cracks, which form during the final stages of solidification in constrained regions; and cold or residual-stress cracks, which develop during post-solidification contraction. Process strategies such as base plate preheating and optimized scan paths can reduce residual stress, but these must be balanced against porosity control to maintain density [7].

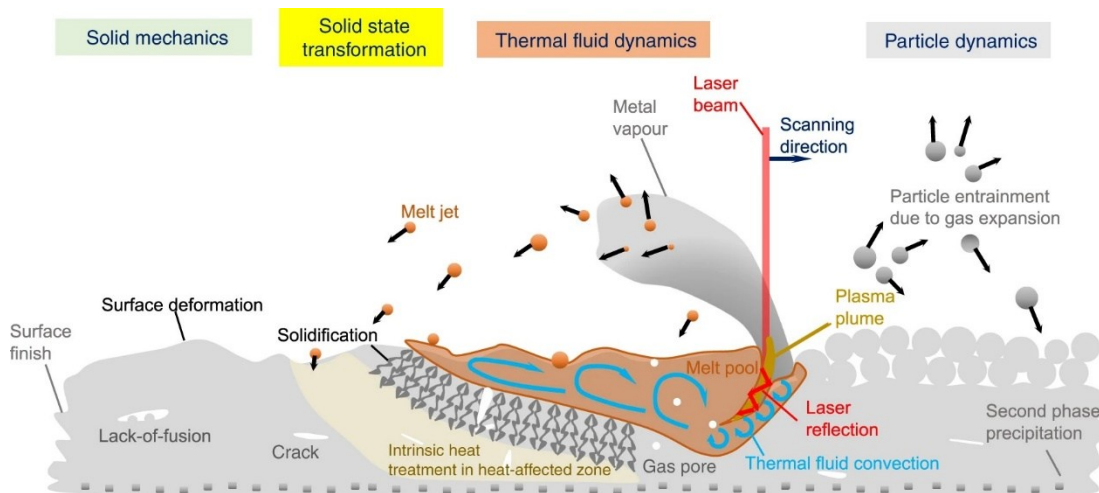


Figure 1-2. Schematization of the thermophysical phenomena in a single track-scan. Reprinted from [5]

Most L-PBF applications still rely on legacy alloys originally developed for casting or forging but found to be compatible with the process. Examples include:

- 316L stainless steel, valued for its corrosion resistance and weldability.

- AlSi10Mg, a near-eutectic aluminum alloy with excellent castability and low hot-cracking sensitivity.
- Ti-6Al-4V, widely used in aerospace and biomedical sectors.
- Maraging steels, which can be precipitation-hardened after printing to achieve high strength.

Although these alloys perform reasonably well in L-PBF, their behavior differs from conventionally processed counterparts [10]. In AlSi10Mg, rapid solidification generates a continuous silicon network that enhances hardness but increases susceptibility to localized corrosion [11]. In maraging steels, the as-built supersaturated martensite responds differently to aging treatments because of the fine substructure introduced by AM [12]. For alloys containing volatile elements (e.g., Zn, Mg, Sn), high melt-pool temperatures may drive selective evaporation and re-condensation, shifting composition and altering properties relevant to wear and corrosion (hardness, phase balance, passivity). Oxide films and inclusions, exacerbated by spatter and oxygen pickup, can further degrade interlayer bonding, promote balling, and act as brittle third bodies at the surface. Such process induced effects are strongly alloy-dependent and must be considered when comparing AM with conventional processing [13].

To address these challenges, research has increasingly focused on AM-specific alloy design. These alloys are tailored to rapid solidification kinetics and thermal histories, with strategies including:

- narrowing solidification ranges to reduce hot cracking [14, 15];
- adding grain refiners (e.g., TiC, Zr) to promote equiaxed growth [16];
- controlling segregation and porosity [17];
- designing compositions tolerant to oxygen pickup and powder reuse [18].

This design philosophy enables alloys that better exploit AM's potential for functional performance and geometric complexity [19]. In parallel, novel material classes such as high-entropy alloys, bulk metallic glasses, and compositionally graded alloys are being explored for their compatibility with L-PBF and their ability to deliver superior or unconventional properties. Coupled with advances in real-time monitoring,

computational modeling, and machine learning, these developments are driving AM toward a predictive and performance-oriented discipline [20].

Nevertheless, most feedstock materials used in L-PBF remain legacy alloys such as 316L stainless steel, AlSi10Mg, and Ti-6Al-4V, which have transitioned relatively smoothly from conventional to powder-based processing [21]. While mechanical properties such as strength and fatigue resistance have been extensively investigated as a function of process parameters and post-processing treatments, the implications of L-PBF for less-studied functional properties, particularly wear and corrosion resistance, remain incompletely understood. Current evidence indicates that the complex interplay among process parameters, thermal history, and alloy chemistry produces highly variable tribological and corrosion responses, making predictions and controlling an ongoing challenge [22].

To connect these fundamentals with surface related properties impacting corrosion and wear resistance, the following subsection introduces a microstructure–surface–defect map that will serve as a framework throughout the chapter.

1.1.1. A microstructure-surface-defect map for L-PBF

Pore families, surface roughness, residual stresses, and inclusions all originate from the same thermal–fluidic conditions that define microstructure. A unified process–structure–defect–surface–environment map is therefore essential to predict wear and corrosion pathways in L-PBF components.

The solidification process in L-PBF shares many similarities with welding metallurgy. In both cases, the material is exposed to a moving, highly concentrated heat source, which induces rapid melting and solidification under steep thermal gradients [23]. As a result, the microstructure formed within a single laser track provides valuable insight into the mechanisms that govern solidification in this process.

A distinctive feature of L-PBF is the coexistence of columnar and equiaxed grains. Columnar grains typically grow epitaxially from the underlying solidified layer, extending along the direction of the temperature gradient and reflecting a directional solidification mode. By contrast, equiaxed grains can form in interlayer regions, where

constitutional undercooling and local solute enrichment reduce the thermal gradient and encourage heterogeneous nucleation.

The transition between columnar and equiaxed growth is strongly influenced by the G/R ratio, defined as the temperature gradient (G) divided by the solidification front velocity (R). High G/R values promote columnar morphologies, whereas lower values favor the development of equiaxed structures, as shown in **Figure 1-3**. Given the extreme conditions of L-PBF, with cooling rates on the order of 10^4 – 10^6 K/s, the resulting microstructures are generally very fine, with reduced dendritic arm spacings [24]. Under such conditions, some alloys may also exhibit metastable or supersaturated phases that would not normally form during conventional solidification routes.

The way heat is delivered and removed during scanning controls solidification and, ultimately, functional performance. Steep directional heat flow promotes heterogeneous nucleation at melt-pool boundaries and epitaxial growth along the temperature gradient, producing columnar grains often with a $\langle 001 \rangle$ texture in cubic alloys. The G–R framework describes the transition from planar to cellular or dendritic morphologies and sets the sub-micrometric cell size typical of as-built metals. Solute rejection enriches cell and dendrite boundaries as well as melt-pool borders, establishing chemical and crystallographic anisotropy from the micrometer to the sub-micrometer scale.

Layer-wise reheating imposes multiple thermal cycles on this substructure. Each new track partially remelts or tempers the underlying material, while expansion and contraction between hot top layers and cooler underlayers generate residual stress. Two regimes dominate: temperature-gradient stresses during scanning, and cool-down mismatch after solidification. Together, they cause distortion, tensile residual stress, and the activation of cracking modes.

Ultimately, this unique solidification behavior plays a central role in determining the performance and surface properties of L-PBF components.

Melt-pool hydrodynamics (recoil pressure, Marangoni flow), combined with track overlap, dictate which defect class prevails. Excessive energy density destabilizes the keyhole, producing near-spherical pores upon collapse. Insufficient overlap or poor wetting creates lack-of-fusion (LoF) voids at hatch and layer interfaces. Gas entrapment and incomplete backfilling at high scan speeds leave open or re-entrant

pores along track wakes. These pore families and their parameter sensitivities have been consolidated through in-situ imaging and modeling.

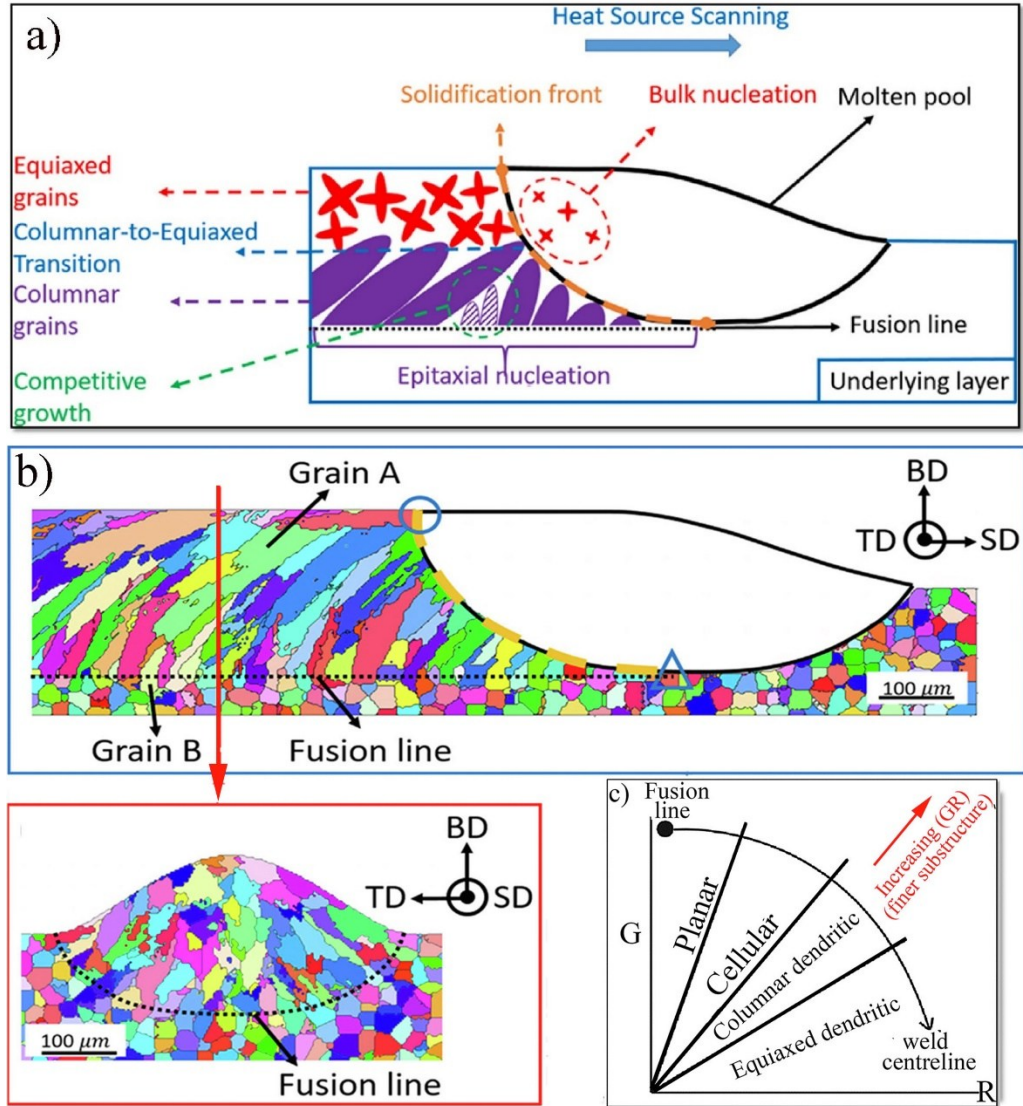


Figure 1-3. (a) Solidification features on the mid-plane across the scan path, indicating plausible nucleation and growth routes; (b) simulated single-pass grain morphology during build with bulk nucleation suppressed (BD: Building Direction, TD: Transversal Direction, SD: Scanning Direction); and (c) schematic illustrating how the temperature gradient (G) and solidification rate (R) control the resulting grain structure. Reprinted from [24].

1.1.2. Pore Types in L-PBF Alloys: Morphology and Surface Effects

Porosity is one of the most widespread defect classes in L-PBF and strongly influences both mechanical and environmental durability. Three main types are distinguished (Figure 1-4):

- **Lack-of-fusion (LoF) pores**, LoFs mainly form due to insufficient overlap between adjacent melt pools, between layers or laser tracks, which can be the result of insufficient energy input or excessively large hatch distance. Irregular and elongated along melt-pool boundaries, they increase effective surface area, disrupt passive films, and act as strong stress concentrators [25, 26].
- **Keyhole (KH) pores**, KHs form in overheating conditions due to the “pinch-off” from the bottom of the depression inside the melt pool. They are rounded voids from unstable vapor-cavity collapse [27, 28].
- **Gas-entrapped (GEP) pores** are essentially “bubbles” of inert gas inside/between powder particles entrapped within the melt pool due to the combined action of buoyancy, Marangoni force, the turbulence due to vapor recoil, and the rapidly moving solidification. Smooth and near-spherical, usually isolated; their effect is minor unless they intersect the surface or exceed critical sizes, where they can trigger pit-to-crack transitions. GEPs cannot be avoided and are typically present even under optimum processing conditions [28, 29].

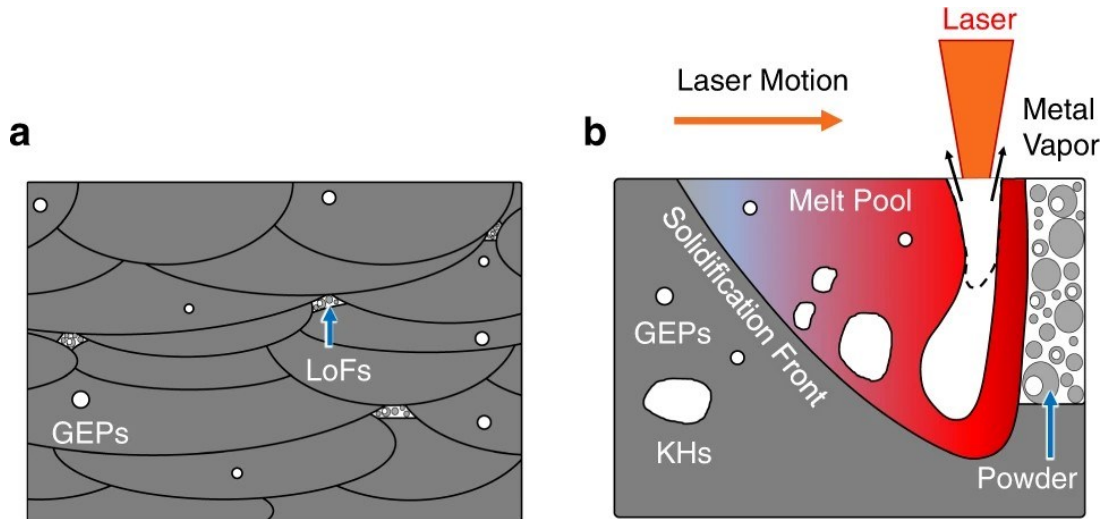


Figure 1-4. Formation of LoFs and GEPs. b Formation of KVs and GEPs. Reprinted from [30].

Distinct pore classes, defined by their shapes and formation routes, are key to interpreting surface related properties in L-PBF components. In this process, volumetric flaws often trap shielding gases (e.g., argon) that are largely insoluble in the metal. Their subsequent removal is extremely difficult, if not unfeasible, because it would require complete venting of the gas from the solid [30]. Non-destructive qualification increasingly employs micro-computed tomography (μ -CT) to detect near-surface and internal defects. Combined with extreme-value statistics, μ -CT allows estimation of the most harmful flaw size for a given gauge volume and supports the definition of design stresses at specific failure probabilities. Together with post-processing, HIP for internal pores, machining or polishing for surface regularization, these methods link process control to performance [7]. Indeed, internal gas pressure can drive pore reopening or growth during post-HIP heat treatments [31]. Hence, rather than relying on remedial post-processing, the priority should be to tune AM parameters to suppress both the size and number of pores during fabrication, thereby safeguarding the structural integrity of the parts.

The combined effects of melt-pool dynamics, powder–laser interactions, and layer-by-layer deposition determine the formation and morphology of both surface and subsurface defects. Typical features include balling, satellites, LoF voids, keyholes and gas pores, and spatter redeposition, all contributing to the characteristic roughness and heterogeneity of as-built surfaces. To summarize these relationships, **Table 1-1**

outlines the main process-induced defects, their surface expressions, and their impact on functional performance.

Table 1-1. Main defect families generated during L-PBF processing, their typical surface manifestations, and implications for wear and corrosion behavior.

Origin / Process Feature	Defect Type	Surface Expression	Primary Impact on Performance
Insufficient energy density or poor overlap	Lack-of-fusion (LoF) pores	Irregular, elongated surface depressions along hatch or layer boundaries	Crack initiation sites; stress concentration; crevice corrosion cells
Excessive energy density	Keyhole pores	Rounded or near-spherical cavities	Internal defect; fatigue initiation; reduced density
High scan speed / gas entrapment	Gas pores	Smooth, isolated spherical pits	Minor effect unless surface-connected
Melt-pool instability	Balling droplets	Bead-like discontinuous tracks	Increased roughness; reduced layer bonding
Powder adhesion / spatter redeposition	Satellites and spatter	Fused particles and re-entrant topographies	Elevated roughness; occluded micro-zones promoting localized corrosion
Layer-wise geometry and overlap variation	Stair-step and overlap defects	Faceted or terraced surfaces	Friction increase; turbulent flow; wear intensification

Mitigation requires a chain of interventions. Base-plate preheating, optimized scan strategies (e.g., orthogonal hatching), and in-situ laser remelting reduce thermal gradients, stabilize melt pools, and heal near-surface porosity. Carefully tuned parameter windows prevent both keyhole collapse and under-melting. Clean powders and a controlled atmosphere minimize spatter and denudation. Post-processing further enhances performance: hot isostatic pressing collapses internal pores and relieves stress, while machining, polishing, and passivation remove surface asperities and regularize chemistry [32]. Collectively, these steps densify and homogenize the near-surface region where wear and corrosion initiate.

In conclusion, although volumetric porosity and microstructural heterogeneity are central to mechanical integrity, their translation into surface features, such as re-entrant topographies, exposed pores, and inclusion-rich zones, establishes the primary pathways for localized corrosion and wear initiation. This interplay underscores the need for an integrated process–structure–surface framework to predict and mitigate these degradation mechanisms in L-PBF components.

1.2. Critical issues for Wear and Corrosion in L-PBF Components

Despite the significant technological progress of Laser Powder Bed Fusion (L-PBF), several inherent challenges continue to limit its full potential, particularly regarding the wear and corrosion performance of printed components. These challenges arise from the extreme thermal conditions intrinsic to the process, namely rapid solidification, steep thermal gradients, and layer-by-layer deposition, which together generate complex microstructures, high residual stresses, and surface conditions that differ markedly from those produced by conventional manufacturing routes [8, 33].

A major issue is the high surface roughness of as-built L-PBF parts. This originates from partially fused powder particles adhering to the surface and from the “stair-step” effect inherent to the layer-wise strategy, especially along inclined or curved surfaces. Typical roughness values often exceed 10–30 μm (Ra), far higher than those achieved with conventional finishing [34]. Such roughness accelerates wear by increasing friction, promoting debris accumulation, and enlarging the real contact area. From a corrosion perspective, rough surfaces trap aggressive ions and create microenvironments that favor localized attacks such as pitting and crevice corrosion, particularly in chloride-rich solutions [9].

Another critical limitation is porosity, which can arise from incomplete fusion between scan tracks, gas entrapment, or keyhole instability under excessive energy input [30]. Pores reduce mechanical strength and fatigue resistance while also serving as initiation sites for corrosion. For example, in 316L stainless steel, even isolated pores can disrupt the protective chromium-oxide film, accelerating corrosion in otherwise resistant alloys [9]. Moreover, porosity enlarges the effective surface area exposed to the environment, amplifying galvanic interactions within the microstructure.

Residual stress is another unavoidable outcome of the rapid and directional solidification in L-PBF. Steep thermal gradients induce tensile stress in some regions and compressive stress in others, depending on geometry, heat input, and scanning strategy. These stresses can promote crack initiation under mechanical loading and may also influence electrochemical behavior by modifying oxide-film formation and stability. Excessive residual stress may ultimately lead to distortion, warping, or premature failure of critical parts.

In addition, microstructural inhomogeneities inherent to L-PBF exacerbate wear and corrosion risks. As abovementioned, rapid solidification promotes columnar grains, dendritic or cellular structures, and solute segregation at submicron scales. Such features, especially melt-pool boundaries and enriched regions, can act as local galvanic couples that accelerate corrosion [9]. For instance, the fine silicon network in AlSi10Mg increases hardness but also promotes micro-galvanic corrosion in saline environments. Similarly, in Ti-6Al-4V, α/β phase segregation may drive electrochemical instabilities and degradation [35].

The influence of process parameters, laser power, scan speed, hatch spacing, and layer thickness, is particularly critical. Improper control worsens surface morphology, increases porosity, and results in inconsistent mechanical and chemical properties across the component [4, 10].

Given these challenges, post-processing strategies may be indispensable for restoring or enhancing functional performance. Among the most effective, hot isostatic pressing eliminates internal porosity and reduces residual stress, significantly improving fatigue and corrosion resistance [36]. Surface-focused treatments such as laser polishing or electropolishing decrease roughness, remove adhered particles, and improve surface integrity. Additional techniques, shot peening, passivation, or tailored heat treatments, further refine the microstructure and surface chemistry, optimizing performance under corrosive or tribological conditions. That said, post-processing does not universally resolve AM-specific surface issues. Internal and tortuous features (e.g., conformal cooling) limit access for machining or laser polishing; electropolishing and chemical deburring can suffer from non-uniform current density, risking over- or under-treatment [37]; coatings with line-of-sight deposition may not conformally cover occluded geometries; and while HIP densifies internal pores, it does not close surface-connected LoF networks and at high temperatures sealed porosity could reopen. Consequently, the durability of non-machinable regions remains dominated by as-built roughness and defect topology, reinforcing the need for process-window control upstream and, where feasible, truly conformal finishing strategies downstream.

Recent studies show that a synergistic combination of thermal, mechanical, and chemical post-processing is often required to raise L-PBF components to the level of conventionally manufactured parts, or even beyond. Increasingly, these treatments are

viewed not as optional enhancements, but as essential phases of the additive manufacturing workflow [32].

1.2.1. Mechanism-based implications of process-induced defects

- **Wear:** Porosity, especially planar LoF networks aligned with hatch/layer interfaces (see Table 1-1), acts as a potent internal stress concentrator that promotes subsurface fatigue-crack nucleation under sliding or impact loading [38]. Elevated as-built roughness and hard, brittle inclusions (e.g., oxides, nitrides) enhance third-body abrasion and micro-chipping, shifting crack initiation toward the surface at modest contact pressures. Consistently with this picture, it has been demonstrated that wear rates scale with porosity: less-dense builds exhibit $\approx 6\text{--}17\%$ higher wear than dense ones, whereas fully dense and surface-smoothed parts can match or surpass conventionally processed alloys [39].
- **Corrosion:** Surface-connected pores and inter-track gaps behave as occluded cells that foster chloride accumulation and local acidification, a classic pathway toward crevice-type attack. Rough, particle-laden skins increase pit-nucleation frequency and sustain stagnant micro-environments [40]. At the microstructural level, solute-enriched cell walls and melt-pool boundaries introduce galvanic heterogeneity that biases passive-film stability [9]. Superposed tensile residual stress adds a mechanical driver for environmentally assisted cracking. Superposed tensile residual stress provides a mechanical driver for environmentally assisted cracking, linking process-imposed stress fields to localized corrosion and crack advance. These elements frame the mitigation hierarchy: (i) prevention of surface-connected porosity and re-entrant topographies (process window, scan strategy, atmosphere/powder cleanliness), (ii) stress management (preheating, path planning, post-build stress relief/HIP), and (iii) surface chemistry regularization (finishing + passivation), with **Table 1-1** serving as a navigation map between defect origin, surface expression, and failure mode.

1.3. Maraging Steels in Additive Manufacturing

Maraging steels are a distinctive class of high-strength alloys whose properties arise from a unique metallurgical concept: a low-carbon martensitic matrix strengthened by precipitation hardening during aging. Developed in the early 1960s to meet demanding aerospace requirements, they take their name from the combination of *martensite* and *aging*. Unlike conventional martensitic steels, which derive strength from high carbon content and carbide precipitation, maraging steels achieve exceptional performance through the precipitation of intermetallic phases such as $\text{Ni}_3(\text{Ti}, \text{Mo})$ and Fe_2Mo in a soft, ductile low-carbon matrix [41, 42]. The typical composition of 18% Ni maraging steels includes nickel, cobalt, molybdenum, and titanium; their controlled precipitation during aging drives the increase in hardness and tensile strength.

Traditionally, maraging steels are solution-annealed and quenched to form supersaturated martensite, followed by artificial aging at $\approx 480\text{--}500\text{ }^\circ\text{C}$. Owing to their very low carbon content ($<0.03\%$), the as-quenched martensite is relatively soft ($\sim 300\text{ HV}$) but strengthens dramatically upon aging, when finely dispersed intermetallic, chiefly Ni_3Mo , Ni_3Ti , Ni_3Al , and Fe_2Mo , precipitate at high volume fraction [43, 44]. Conventional production routes, whether ingot casting with hot working or powder metallurgy with consolidation, have long been optimized to deliver homogeneous microstructures, low defect levels, and predictable property profiles.

The advent of AM has opened new possibilities for these alloys. The layer-by-layer approach of AM enables geometries and internal features unattainable or uneconomical with traditional manufacturing. Among AM processes, Laser Powder Bed Fusion and Wire + Arc Additive Manufacturing have received the most attention for maraging steels, owing to their ability to process high-strength alloys with reasonable control over heat input and solidification [45].

The selection of maraging steels for AM is not coincidental: their low carbon content minimizes cracking during rapid solidification, a frequent limitation in other high-strength steels. Furthermore, the as-built microstructure, a fine cellular martensitic matrix with high dislocation density, responds strongly to post-build aging, enabling

manufacturers to achieve target properties without extensive hot working [46, 47]. A practical advantage is that near-net-shape components can be printed in the soft, machinable as-built state and then aged to peak performance. With advances in powder quality and process control, L-PBF maraging steels now achieve properties competitive with conventional alloys, while offering unmatched design freedom and high material efficiency [48]. Consequently, 18Ni maraging steels are routinely selected for duty in defense, aerospace, die-casting, and tooling applications that impose stringent performance requirements. However, legacy fabrication chains, often involving multiple remelts, hot working, extensive machining and welding, and several heat-treatment stages, are cost-intensive. To meet rising performance demands while controlling cost and lead time, the field has steadily shifted toward advanced manufacturing routes that compress the workflow and raise efficiency when AM's resolution, size, and surface constraints are acceptable. In this context, additive manufacturing provides a direct pathway to near-net-shape components with reduced waste and post-processing, aligning with these objectives and complementing the alloys' strong age-hardening response.

1.3.1. Microstructural Features

Processing by L-PBF involves cooling rates of 10^3 – 10^6 K/s which refine martensitic laths and suppress equilibrium phases during solidification [49]. The resulting microstructure consists of fine columnar grains aligned along the build direction, subdivided into cellular substructures defined by solute segregation at cell boundaries (**Figure 1-5a-e**) [50]. Retained austenite may also be present, depending on composition and local thermal histories (**Figure 1-5f**) [51]. Microsegregation (e.g., enrichment) can stabilize retained austenite at room temperature, with fractions reported up to ~11 vol% [52]. Hence, rapid solidification produces a cellular martensitic matrix with nanoscale segregation of Ni, Mo, and Ti at cell walls; these features can persist after direct aging due to limited recovery at typical tooling heat treatments (~480–500 °C).

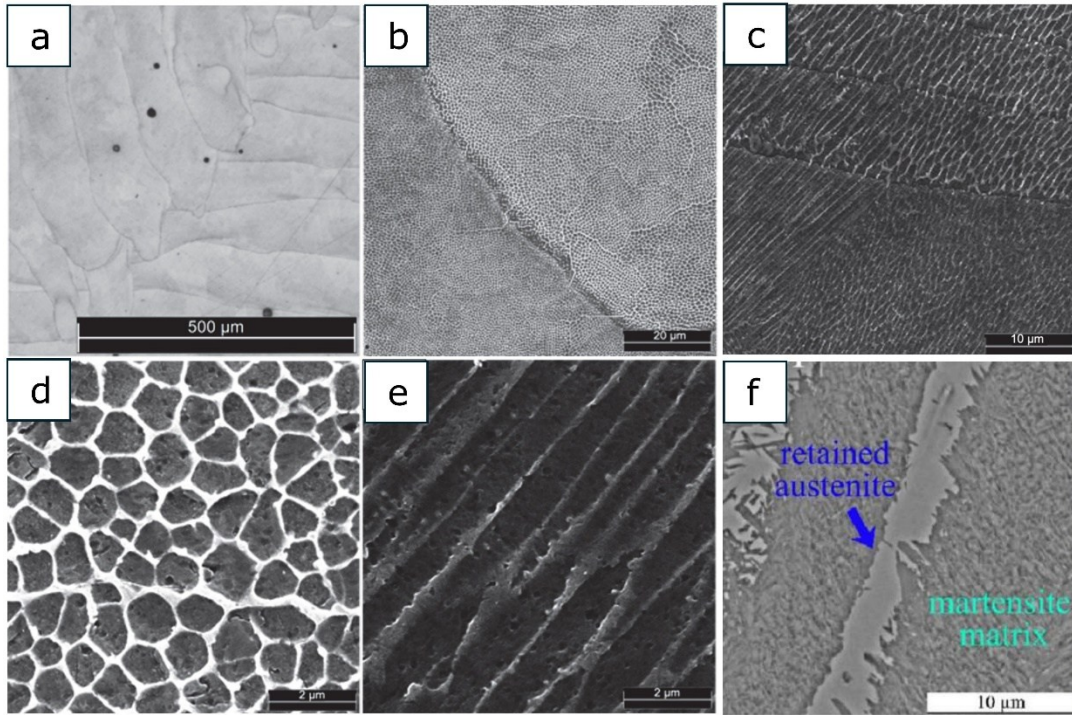


Figure 1-5. Microstructure of 18Ni300 maraging steel after etched with Nital for 1 min. (a) Optical micrograph; (b) SEM micrographs showing the grain boundaries and the welding paths; (c) high-magnification SEM micrographs showing grains across different welding paths; (d,e) high-magnification SEM micrographs showing the cellular dendrites of LPBF-processed parts [53]. (f) SEM image of austenite formed in as-built C250 maraging steel [54].

The layer-wise strategy introduces anisotropy between planes normal to the build (BD) and scan (SD) directions. Compared to forged material, where lath packets are clearly bounded by prior-austenite grains, L-PBF martensite is extremely fine and prior-austenite boundaries are less distinct [55]. Melt-pool boundaries, influenced by segregation and residual-stress gradients, may act as weak paths under combined mechanical and corrosive loading. After heat treatment, the extent of retained or reversed austenite can reach ~20%, depending strongly on Ni content and aging conditions; this fraction can influence crack growth and corrosion response [56]. Repeated reheating during layer deposition further modifies the microstructure. Partial recovery, nanoscale precipitation prior to formal aging, and substructure coarsening have all been reported [57]. Consequently, the as-built state is not equivalent to the solution-annealed condition of conventional processing, which may affect both mechanical properties and secondary characteristics such as wear and corrosion

1.3.2. Heat treatment and Mechanical Properties

Aging remains the critical step to unlock the high strength of maraging steels. In AM builds, aging at 480–500 °C promotes the precipitation of Ni_3Ti and Fe_2Mo , raising hardness from ~350 HV in the as-built state to >550 HV [46]. Due to the refined substructure and local segregation patterns, precipitation kinetics may differ from conventionally processed alloys [58]. This can result in faster hardening but also a narrower window before over-aging, where precipitate coarsening reduces strength and ductility. In L-PBF 18Ni-class maraging steels, direct aging at ~490 °C routinely achieves ~54 HRC with accelerated kinetics compared to wrought material, reflecting high dislocation density and dense nucleation of $\text{Ni}_3\text{Ti}/\text{Fe}_2\text{Mo}$. However, modest over-aging causes accelerated softening [59, 60].

Unlike forged alloys, a separate solution treatment before aging is often unnecessary in L-PBF maraging steels, since the as-built state is already a supersaturated solid solution due to high cooling rates. Literature consistently shows little additional benefit from solutionizing compared to direct aging [57].

As-built AM maraging steels exhibit relatively high strength compared to other AM alloys, typically with yield strengths around 1000 MPa and elongations of 8–12% [47]. Aging can increase tensile strength beyond 2000 MPa while retaining 3–5% ductility [46]. This combination of strength, machinability in the soft state, and post-processing flexibility makes them attractive for tooling, aerospace structures, and defense applications. Conventionally, alloy compositions are balanced to set M_s/M_f and minimize retained austenite; after aging, yield strength depends on the fraction of hardening elements and can reach ≈ 2000 MPa. High Ni contents (≈ 17 –26 wt%) with very low C ensure excellent ductility and toughness [44]. Forged maraging steels typically show lath martensite packets within prior-austenite grains, with lath thickness around 0.5 μm and high dislocation density [61]. Reported tensile strengths above 2 GPa after aging, with 3–5% elongation, have been achieved in L-PBF 300-grade maraging steels. In contrast, as-built states usually exhibit ~1 GPa yield strength and 8–12% ductility. Aging schedules must be adapted to AM-specific substructures to avoid embrittling austenite reversion pathways [60]. Overall, multiple studies confirm that, after aging, tensile strengths in L-PBF 18Ni-300 maraging steels are comparable

to conventional counterparts, though anisotropy and austenite content can influence fracture and fatigue behavior. **Figure 1-6** summarize the effect of different heat treatments on the ultimate tensile strength and elongation.

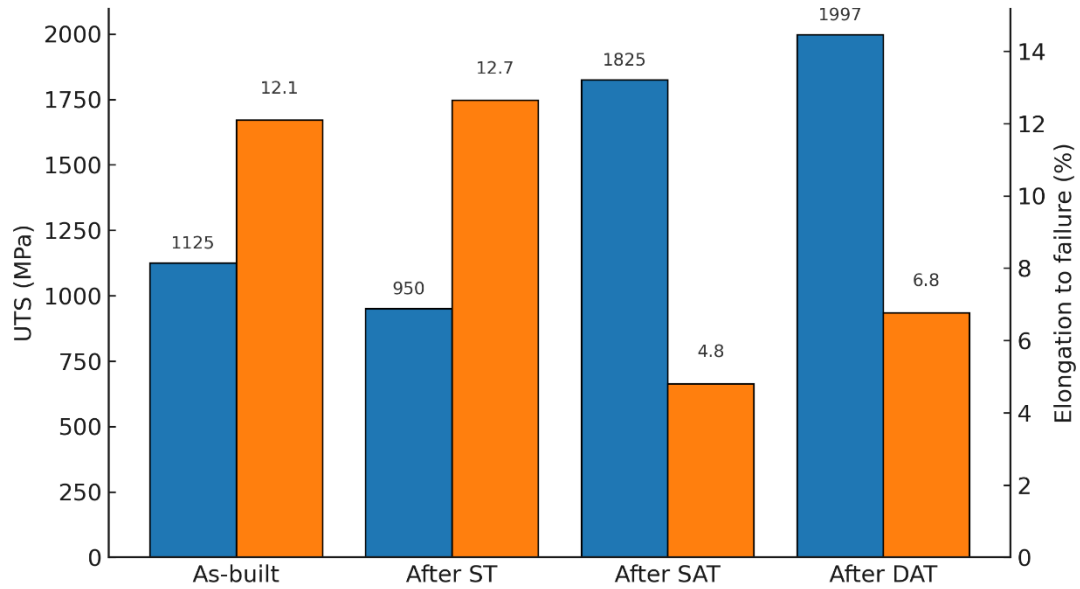


Figure 1-6. Effect of the heat treatments (ST: solution treatment; SAT: solution-aging treatment; DAT: direct aging treatment) on UTS and elongation. Data from [62, 63]

1.3.3. Wear and Corrosion considerations

While mechanical properties of AM maraging steels are well established, their wear and corrosion resistance remain less understood especially for new applications enabled by AM. The refined microstructure, residual stresses, and segregation patterns introduced by L-PBF may affect wear resistance through changes in hardness distribution and strain hardening, while corrosion behavior can be influenced by segregation at cell boundaries, retained austenite content, and potential micro-galvanic coupling [9, 57]. Initial studies indicate that maraging steels retain good corrosion resistance in neutral environments, but AM variants may display distinct tendencies due to their unique microstructures. Systematic studies directly linking AM parameters, microstructural features, and wear/corrosion performance remain scarce, representing a significant knowledge gap.

Recent tribological investigations add two clarifications that are directly relevant to AM design. First, friction appears largely insensitive to building orientation, sliding

direction, and standard heat treatments; by contrast, wear is strongly orientation dependent. Under abrasive contacts (e.g., hard counter-bodies), horizontally built specimens tested in-plane generally show the lowest material loss, whereas vertical builds, particularly when sliding across or along layer interfaces, exhibit markedly higher wear. Under adhesive contacts (e.g., steel-on-steel), the optimum can invert: vertical builds sliding along layers often reduce material removal relative to inclined builds sliding across layers. Second, heat treatment trades anisotropy for durability in nuanced ways: direct aging reduces but does not erase process-imposed directionality, whereas solution treatment followed by aging homogenizes the microstructure and mechanical response (beneficial for toughness and qualification), but can raise adhesive wear relative to aging alone [64].

Despite their high strength and dimensional stability, AM maraging steels, particularly grade 1.2709, face additional challenges in demanding environments. In high-pressure die casting (HPDC) tooling, L-PBF enables tooling insert with conformal cooling channels (CCCs) that improve thermal management and reduce cycle time (**Figure 1-7**); however, the tighter radii and directional changes of CCCs introduce geometric stress concentrators and reduce cross-sectional robustness.

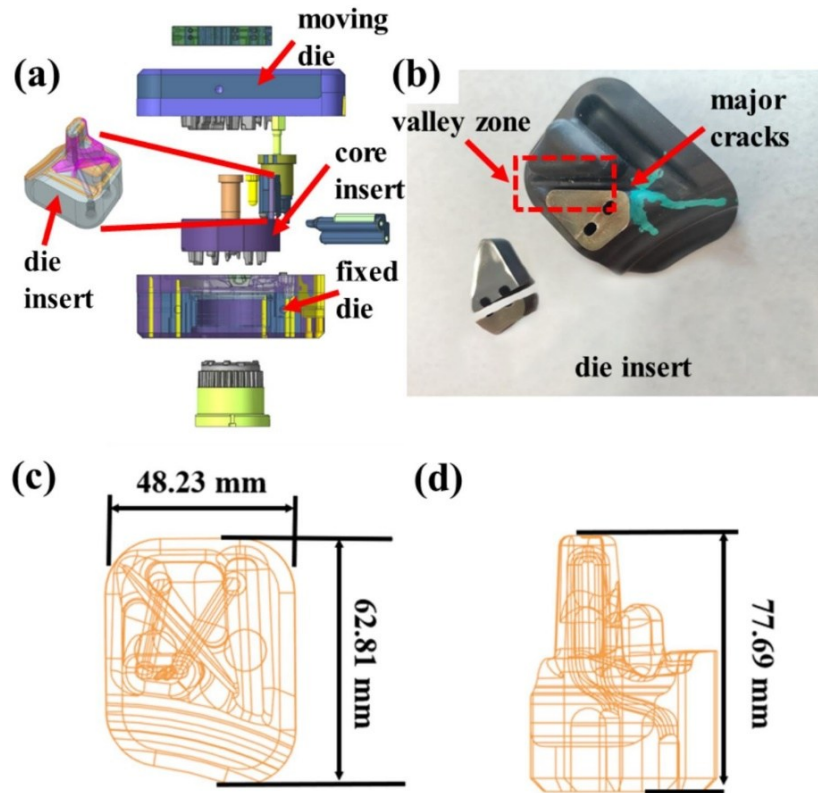


Figure 1-7. L-PBF tooling insert with CCC reprinted from [65]. Geometry, location and dimensions of the die insert: (a) the assembly of dies insert, ejector die, cover die and other components; (b) valley zone and major crack locations in the die insert; (c) top view of die insert; (d) front view of die insert.

Moreover, the internal channel surfaces are typically left in the as-built state, with roughness and partially fused particles that cannot be mechanically polished, providing preferential sites for localized corrosion in aggressive or poorly inhibited water circuits [66-68]. In hydraulically constrained CCCs, rapid pressure transients and two-phase flow can also trigger cavitation; the collapse of vapor bubbles generates microjets and shock waves that both erode asperities and disrupt passive films. Consequently, cavitation erosion, often acting synergistically with corrosion, emerges as a dominant surface-damage mechanism, especially at constrictions, elbows, and near inlets/outlets. These as-built features amplify the interaction between microstructure, flow-assisted depassivation, and cyclic thermal-mechanical stresses, creating a pathway for environmentally assisted damage. In addition, such inserts operate in contact with molten aluminum, where interfacial reactions promote die soldering (and, in severe cases, washout), further degrading surface integrity. The literature on HPDC die failure mechanisms and protection strategies is extensive; however, it concerns the

typical hot-work tool steels (e.g., H11/H13, 1.2343/1.2344) rather than maraging grades. The two families differ fundamentally: tool steels are medium- to high-carbon Cr–Mo–V martensites strengthened by dense carbide populations and secondary hardening upon tempering, whereas maraging steels are ultra-low-C, Ni-rich alloys hardened by intermetallic precipitation (e.g., $\text{Ni}_3(\text{Ti}, \text{Mo}, \text{Al})$) after solution treatment and aging [69-71]. Consequently, their damage and protection maps are not interchangeable, direct extrapolation to 18Ni-300 requires caution and dedicated testing under AM-relevant microstructures.

Notably, maraging steels, such as 18Ni-300, are reported to be susceptible to stress corrosion cracking (SCC) under specific conditions. SCC typically occurs in steels with low carbon content exposed to mildly aggressive aqueous environments and subjected to tensile stresses from either external loading or residual stresses. Under such conditions, even mildly corrosive environments may initiate cracking. For example, Diwakar et al. reported that the crack growth rate of maraging steel in water was approximately 40 times higher than in hydraulic oil, underlining the detrimental effect of water exposure. Furthermore, while crack propagation in hydraulic oil and 2% dichromate solutions followed straight paths, branching occurred in water and 0.5% dichromate solutions, indicative of transgranular fracture under environments with low inhibitor content [72]. Bagchi et al. identified two main mechanisms underlying environmentally assisted cracking in 18Ni-250 weldments: anodic dissolution and hydrogen embrittlement [73]. Common ionic species in cooling water, such as chloride (Cl^-) and sulfide (S^{2-}), can accelerate corrosion processes for such material-environment combination, particularly under elevated temperatures and dynamic flow conditions, where passive oxide layers are continually disrupted. These conditions favor both SCC and corrosion fatigue, which can critically compromise the integrity of the material [74].

Beyond these general trends, three complementary investigations documented in this thesis help bridge L-PBF–induced heterogeneities with service-relevant degradation modes. First, cavitation-erosion tests show that damage localization and mass-loss kinetics are governed primarily by the topology and connectivity of near-surface defects (e.g., lack-of-fusion ligaments opened by cyclic pressure waves) rather than by frictional properties per se. When open porosity is minimized and the microstructure

is rendered more homogeneous (via parameter optimization and appropriate heat treatment), the performance gap with conventional material narrows, reinforcing the idea that controlling layer interfaces and defect architecture is a dominant lever. Second, corrosion–erosion under contact with molten aluminum highlights the role of chemically driven reactions at the steel–aluminum interface and their mechanical consequences: reaction-layer formation, repeated depassivation, and particle detachment accelerate material removal relative to purely mechanical wear, with susceptibility modulated by microsegregation, retained austenite, and surface condition. Third, a failure analysis of an LPBF-fabricated HPDC insert with conformal cooling channels reveals environmentally assisted initiation and propagation along as-built internal surfaces: roughness, partially fused particles, and inhibitor-poor water chemistry combine with cyclic thermo-mechanical stresses to promote crack nucleation at stress concentrators, oxide-filled wake development, and mixed SCC/corrosion-fatigue morphologies.

1.4. Conventional and L-PBF Brass

Brasses are copper–zinc alloys containing up to ~45 wt% Zn, with minor additions of elements such as Sn, Al, Si, Mn, Ni, or Pb typically below 4 wt%. Increasing Zn reduces cost and raises strength, but at the expense of corrosion resistance, melting point, and electrical conductivity. The Cu–Zn phase diagram **Figure 1-8a** shows that copper dissolves up to ~39 wt% Zn at 454 °C; higher Zn promotes formation of the ordered β' phase (CuZn), which is hard and brittle at room temperature but transforms into a more ductile disordered β phase at elevated temperatures. Consequently, α brasses (single-phase solid solution) are soft, ductile, and suitable for cold working, whereas $\alpha+\beta'$ brasses are harder and generally processed hot, with machinability often enhanced by Pb additions. Strength peaks near 44 wt% Zn, but ductility decreases as β' develops, limiting cold formability **Figure 1-8b** [75].

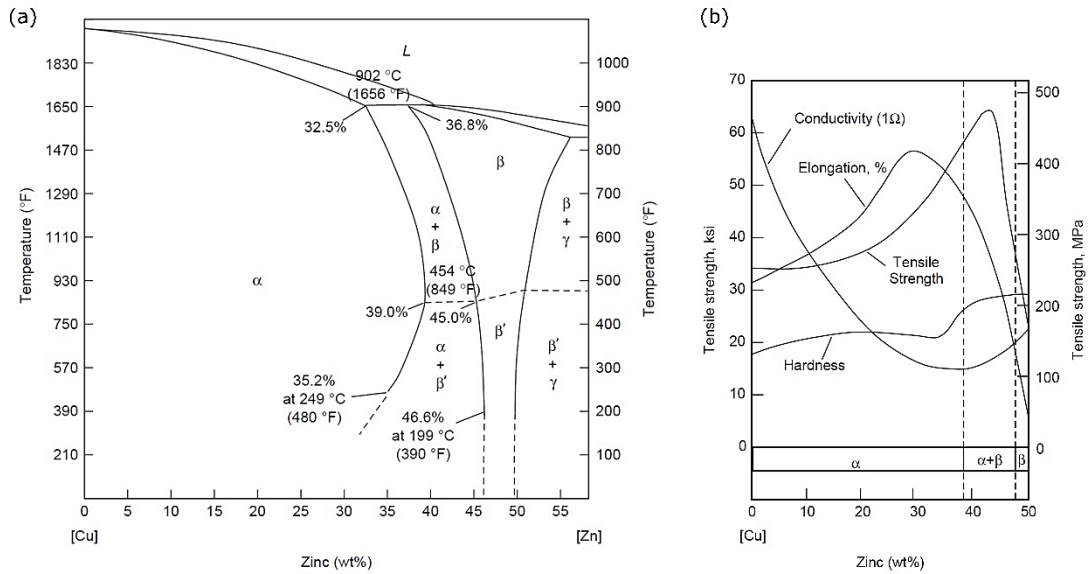


Figure 1-8. (a) Cu–Zn phase diagram; (b) Effect of zinc on properties of copper [75].

Biphasic ($\alpha + \beta$) brasses are engineered to balance strength, formability, and machinability by combining a softer, Cu-rich α matrix with a harder, Zn-rich β -derived constituent. In traditional free-cutting grades, lead provided a softer phase at the tool–chip interface, enabling short, well-controlled chips, lower forces, and high productivity [76]. The current regulatory context for potable water and other sensitive uses has accelerated the shift toward low-Pb or Pb-free solutions and toward processes capable of delivering complex shapes without relying on lead additions [77]. This is not a purely administrative shift: it reframes machinability as a material–process–tooling problem rather than an alloying shortcut.

Biphasic brasses are typically manufactured through routes that deliberately tune microstructure to property targets. Unlike single-phase α -brass, $\alpha + \beta$ brasses generally cannot be formed at room temperature; higher-temperature processing is required to activate favorable slip and transformation mechanisms [76]. In practice, shops exploit a cooling-through-work window where the microstructure is pliable yet stable enough to avoid coarsening. An effective range is cooling from ~ 750 to 650 °C, where α precipitates and is mechanically fragmented by deformation. This progressive fragmentation is a practical lever to raise strength and stabilize machinability in the final product.

Among forming routes, hot forging remains central for $\alpha+\beta$ brasses [78]. During forging and subsequent cooling, the transformation $\beta\rightarrow\alpha$ may occur directly if material is brought rapidly from the all- β field, through $\alpha+\beta$, into α [79].

By analogy with secondary steelmaking, re-melting steps can be applied to brasses to improve cleanliness, deoxidize, trim composition, and adjust microstructure. Although less documented than in steel, available evidence shows that this route can uplift mechanical and chemical properties when used judiciously [80]. One enabler is inclusion engineering. For example, non-metallic particles such as Al_2O_3 introduced via quartz-tube suction may react with ZnO to form ZnAl_2O_4 (spinel) with plate-like or spherical morphologies; these morphologies can influence flow, chip nucleation sites, and corrosion behavior downstream [81].

On the regulatory front, RoHS and ELV have tightened allowable Pb contents for electronic and automotive uses. Lead brasses have enjoyed temporary exemptions due to the lack of drop-in alternatives, but these are time-limited, catalyzing development of Pb-free $\alpha+\beta$ brasses that retain hallmark machinability and strength without Pb [82].

1.4.1. Microstructural Characteristics

At service temperature, biphasic brass contains α (fcc, Cu-rich) and β -derived constituents. On cooling, β orders to B2 (β'); thus, the room-temperature β -derived phase in $\alpha+\beta$ brasses is typically ordered β' rather than disordered β . The relative fractions and spatial distribution of α and β_1 govern elastic/plastic response and machining: the β -derived constituent is harder and promotes chip segmentation, while α provides ductility and stabilizes machinability. Pb-free $\alpha+\beta$ brasses often target a balanced α fraction ($\approx$ mid-range); several modern developments cite $\sim 55\%$ α as a practical target for strength–chip control compromise.

Crystal-structure contrast carries process implications: α (fcc) offers many slip systems and work-hardens steadily; ordered β' exhibits different dislocation behavior and being harder, supports shear localization that seeds chip fragmentation. Hence machinability

in $\alpha+\beta$ brasses is not reducible to hardness alone—both phase balance and β' connectivity matter for chip mechanics [83].

A central feature of $\alpha+\beta$ brasses is the interplay between diffusion-controlled and diffusion-less transformations during processing. In hot-forged brasses with ~61–62.5% Cu, a direct $\beta\rightarrow\alpha$ transformation can occur upon rapid cooling through the $\alpha+\beta$ range into α . Cooling rate dictates whether α precipitates and coarsens (slow) or whether rapid crossing suppresses extensive partitioning, locking in a fine, transformation-driven morphology (fast). Superimposed on this is β ordering: at ~468 °C, β can transform by diffusion via a martensitic-like step ($\beta\rightarrow\beta'$) [76]; subsequent cooling may, depending on chemistry and stress, lead to close-packed martensite variants. For engineering purposes, the thermal path (forge finish, hold, quench/air-cool) maps directly to room-temperature phase balance. Against this transformation background, silicides, especially Mn-rich M_5Si_3 and Fe-bearing particles, are a structurally persistent constituent introduced mainly during solidification and then redistributed or coarsened by later thermal history; their presence at α/β interfaces modulates local constraint and crack initiation, so near-surface integrity depends strongly on silicide size and bonding [84].

Moreover, processing parameters strongly shape microstructure and properties. Cooling rate governs transformation paths: rapid cooling from the all- β field through $\alpha+\beta$ into α promotes direct $\beta\rightarrow\alpha$ without major composition change, whereas slow cooling favors α precipitation with progressive de-Cu-ing of β . Operating in the 750–650 °C hot-work window encourages α precipitation into small, fragmentable pieces that can be refined mechanically during forging/rolling. For additively manufactured $\alpha+\beta$ brasses, rapid solidification and segregation fields can refine α/β spacing yet also fragment β or concentrate hard particles and as-built defects near interfaces; as a result, qualification should target connectivity and inclusion morphology (not just bulk hardness) to avoid long, continuous shear paths in α and brittle, poorly supported islands in β' .

1.4.2. Effect of Alloying Elements

Alloying remains a powerful microstructure tool in $\alpha+\beta$ brasses. Silicon is particularly relevant: small additions reduce stacking-fault energy and cutting resistance, favoring planar slip and stable chip segmentation; phosphorus at modest levels further assists chip breaking through dispersed, brittle compounds that act as local stress concentrators during cutting. In combination, Si+P provides a compositional route to recover chip control in Pb-free brasses. Beyond Si and P, additions such as Al, Mn, Ni, Fe, and Sn are used to tune strength, corrosion behavior, and high temperature.

Here, partitioning tendencies matter: Fe is only sparingly soluble in the matrix and enters almost exclusively as silicides (often together with Mn and sometimes Ni), while Mn contributes both to strengthening and to Mn-rich M_5Si_3 ; Al supports more protective oxide films; Ni improves resistance to environmentally assisted cracking. The practical consequence is that alloying changes not only phase fractions but also the nature and morphology of intermetallic inclusions, which in turn condition wear, machinability, and corrosion by altering α/β connectivity and interface quality [84].

1.4.3. Corrosion Properties

Dezincification is a form of selective corrosion in which Zn is preferentially dissolved from the brass matrix, leaving a porous, Cu-rich structure [85]. Although the residual Cu network retains nearly the same volume as the original alloy, its mechanical integrity is severely compromised, with marked losses in ductility, hardness, and strength. Under optical microscopy, dezincified regions appear reddish due to the enrichment in copper. Different mechanisms have been proposed to explain the phenomenon: selective dissolution of Zn owing to its lower nobility compared with Cu, producing vacancy-rich porous Cu; simultaneous dissolution of both Cu and Zn followed by re-deposition of Cu, leading to a porous Cu network; or a combination of these processes occurring together [86].

To mitigate dezincification, arsenic is commonly added in α -brasses as an internal inhibitor. Its protective effect relies on being dissolved in solid solution within the α -

phase, although the precise mechanism remains debated. One proposed explanation is that As hinders Cu re-deposition by forming a thin protective film around anodic regions. The efficiency of As, however, is sensitive to the presence of other alloying elements (e.g., Fe, Al, Mn, Ni, Co), which is particularly relevant given that brass is frequently recycled, and impurities are difficult to eliminate economically [87].

Other microalloying elements such as Sb and P have been reported to provide similar protective effects, though they have been studied far less extensively. High Sb contents are known to embrittle brass, complicating processing steps such as extrusion and cold drawing, while the protective role of P may depend on alloy chemistry, particularly the amounts of Al and Fe. Since Al is often intentionally added to casting brasses and Fe is a common impurity, the sensitivity of P-containing brasses to these elements must be carefully considered in the context of dezincification resistance [88].

Dezincification is the headline risk for brasses in drinking-water service. While certain α -rich plumbing brasses are engineered for dezincification resistance, β -phase-dominated brasses generally cannot be made dezincification resistant, limiting the use of strongly β -leaning or β -dominated chemistries in potable-water fixtures. The usual strategy in $\alpha+\beta$ brasses is therefore to select compositions and thermal paths that safeguard corrosion performance while retaining $\alpha+\beta$ benefits. Newer Pb-free $\alpha+\beta$ formulations (e.g., around CuZn42 with targeted minor additions) explicitly aim to maintain corrosion behavior while addressing machinability via phase balance and SFE-tuning rather than Pb.

Dezincification, as previously discussed, is a selective corrosion process in which zinc is dissolved from the brass matrix, leaving behind a porous, mechanically weakened Cu-rich network **Figure 1-9a**. This degradation not only reduces strength and ductility but also provides sites that can facilitate further damage mechanisms. In practice, dezincification often acts synergistically with stress corrosion cracking (SCC), making brasses particularly vulnerable under certain water chemistries [89]. Although brasses are generally considered corrosion resistant, numerous failures have been reported in service due to the combined action of SCC (**Figure 1-9b**) and selective corrosion. While the statistical probability of failure per component remains low, the associated consequences, such as uncontrolled water leakage, can be severe. For this reason,

many manufacturers of taps and fittings have progressively shifted to copper–tin–zinc–lead alloys (gunmetals), which show higher resistance to both SCC and dezincification. Beyond the economic implications, preventing such failures is critical for ensuring safety in domestic and industrial water systems.

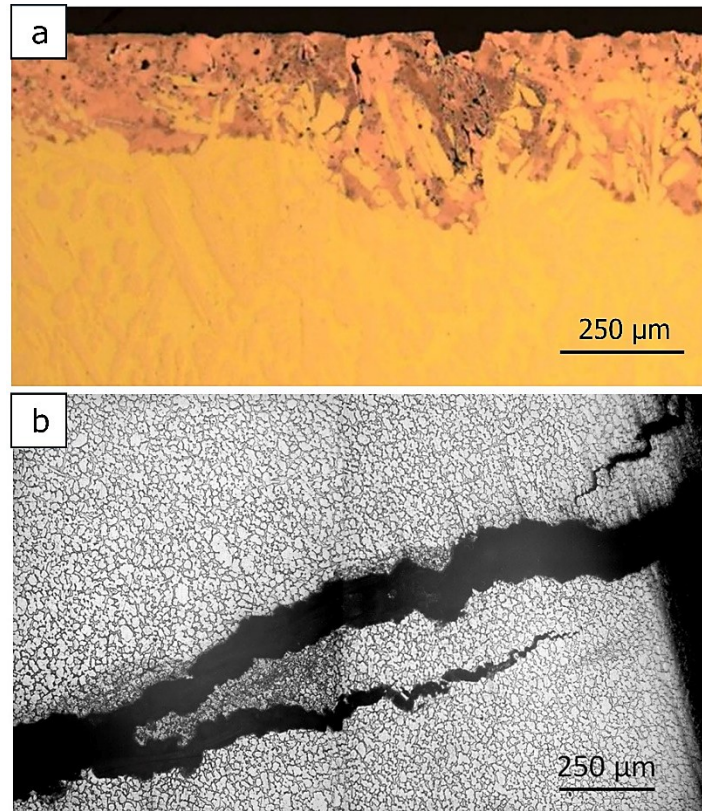


Figure 1-9. (a) Optical microscope observation of the dezincification structure of CuZn42 following an ISO 6509 dezincification test. The red defect-rich structure on the cross section is the dezincification structure [90]. (b) Microstructure showing SCC cracks in a biphasic brass alloy [82].

The role of environmental factors in SCC remains debated. According to DIN EN 12502-T2 [91], high concentrations of nitrite and/or ammonia in tap water are the main drivers of cracking. E. Brandl et. al [89] investigated α – β brasses, finding that even modest ammonia levels (~15 ppm) significantly increase the risk of dezincification, which in turn promotes crack initiation and accelerates SCC propagation. This observation supports the view that ammonia acts as a key environmental factor by amplifying the interplay between selective corrosion and mechanical stresses, rather than as an isolated trigger for SCC. At the same time, the reduced crack propagation observed at higher ammonia concentrations (~30 ppm) in As-containing alloys echoes

literature reports of a possible inhibiting effect under specific chemical conditions, likely linked to passive film stability. These contrasting trends highlight that the influence of ammonia cannot be generalized, but must be evaluated in relation to alloy composition, phase constitution, and the chemistry of the local environment, particularly with respect to chloride and carbonate balance.

Stress-corrosion cracking (SCC) can also be mitigated microstructurally. Multiphase brasses that distribute local stresses, e.g., $\alpha+\kappa+\gamma$ microstructures in certain commercial grades, have shown good SCC resistance in service-like environments. Although outside the $\alpha+\beta$ focus here, the design message carries across: tailoring phase inventory and morphology is a viable route to manage corrosion–mechanical coupling.

1.4.4. Wear Resistance

As previously mentioned, brass is commonly used in water-delivery components and marine applications (e.g., pumps and valves) [92]. In such contexts, a frequent degradation mechanism is cavitation erosion, where cavitation bubbles damage the material through shock wave generation and intense microstreaming during bubble collapse, particularly when collapse occurs close to the surface [93].

Under acoustic cavitation in chloride solution, $\alpha-\beta'$ brass exhibits a staged, phase-selective response that couples mechanical and electrochemical damage. In the early stage, discrete lead inclusions are removed from the surface and redeposited as lead-rich corrosion products, altering the electrochemical state and exposing fresh brass. As cavitation progresses, the β' constituent, richer in zinc and mechanically less accommodating, recedes preferentially through cavitation-enhanced corrosion and interfacial attack, while the α matrix absorbs most of the near-surface plastic strain, evolving from shallow flow and dimpling to roughened, strain-hardened layers. With prolonged exposure, depassivation caused by bubble collapse, increased roughness, and an expanding effective area sustain higher corrosion activity during sonication. Once sonication ceases, the plastically altered surface repassivates more readily, indicating modified film-formation kinetics. The net effect is a time-dependent

synergy in which phase chemistry and micromechanics jointly govern material removal and the electrochemical response [94].

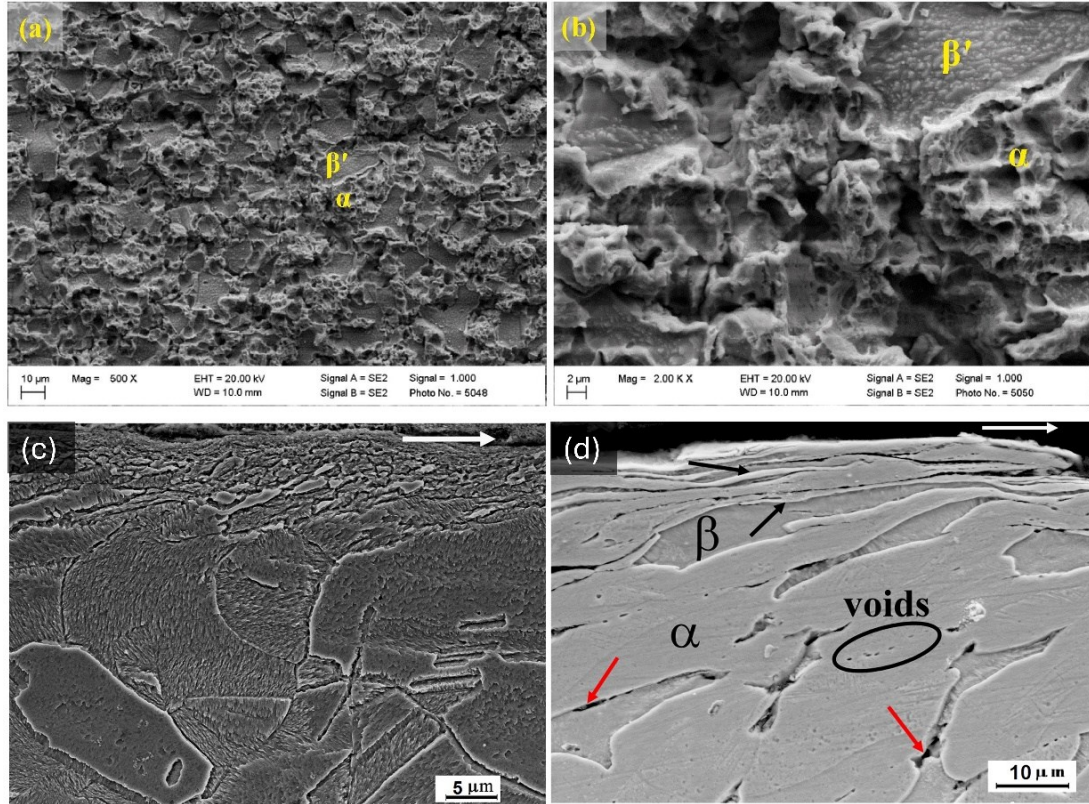


Figure 1-10. Scanning electron micrographs of CuZn38Pb3 after 15 min of ultrasonic cavitation in NaCl (open-circuit conditions; ASTM G32 indirect setup). (a) Overview of the cavitated surface showing a clear phase-selective relief: Zn-rich β' regions have sunk relative to the α matrix, producing step-like rims and exposing α/β' boundaries. (b) Higher-magnification view highlighting the onset of plastic flow in α , visible as waviness and localized shear, adjacent to comparatively undeformed β' islands [94]. SEM images of cross-sectional ranges in the direction of friction for Cu (c) ($P=1750\text{ N}$, $\mu=0.08$) and for brass (d) ($P=650\text{ N}$, $\mu=0.18$). Shear bands are noted by black arrows. The cracks in the boundaries of α - and β -phases are depicted by red arrows (on the bottom of (a)). Some voids formed during a shearing are also noted in (a)[95].

Sliding wear is a critical aspect in the performance of $\alpha+\beta$ brasses, as their dual-phase nature makes them particularly sensitive to how frictional stresses are partitioned between α and β . In practical applications, such as bushings and bearing components, contact conditions frequently oscillate between full-film and boundary lubrication, making the onset of sliding wear unavoidable. Unlike single-phase Cu, biphasic brasses do not deform uniformly: the α matrix and β skeleton respond differently, giving rise to complex subsurface strain fields and distinctive wear modes. This makes

sliding wear not merely a matter of hardness but a direct manifestation of phase topology and interfacial integrity.

Under lubricated sliding, $\alpha+\beta$ brasses partition deformation unevenly between phases: the α matrix accommodates most of the near-surface strain by intragranular slip and shear-banding, while the β -derived constituent remains comparatively rigid and often serves as a locus for interfacial cracking. As lubrication degrades toward boundary conditions, brass tends to shift into this shear-band-controlled regime earlier than single-phase Cu, and the delamination debris that forms reflects the thickness of the sheared α layers. The subsurface zone affected in brass is markedly thicker than in Cu, and work-hardening is more pronounced, consistent with the low-SFE, f.c.c. character of α and the limited plasticity of β at the modest contact temperatures typical of boundary lubrication. These mechanisms elevate phase topology over simple phase fraction: a well-connected β skeleton can support load and resist ploughing but intensifies stresses at α/β interfaces, whereas a continuous α network improves toughness yet favors long-run shear-banding and sheet-like delamination when lubrication is marginal [95].

Experimental studies on microcrystalline and sub microcrystalline brass confirm that delamination is the dominant wear mechanism under dry sliding, with wear resistance depending strongly on both grain size and phase constitution [96]. Microcrystalline $\alpha+\beta$ structures produced by deformation–heat treatments exhibit significantly lower wear intensity, about 1.5–2 times less than quenched β -phase brass and ~30% less than coarse-grained states, demonstrating that grain refinement coupled with a balanced α/β morphology can stabilize subsurface deformation and delay large-scale delamination. The refinement of α and β grains to the 2–3 μm scale enhances hardness while still preserving phase complementarity, thereby limiting debris formation to thinner, more stable sheets.

For LPBF $\alpha+\beta$ brasses, wear–corrosion performance may depend less on bulk hardness and more on how the process modifies the connectivity and interface quality of α and β' near the surface. Microstructures that might extend shear paths in α or generate brittle, poorly supported β' islands, particularly when combined with as-built porosity,

could be more prone to delamination and interfacial cracking under cavitation or boundary-like lubrication. Conversely, if L-PBF were to promote a finely recrystallized $\alpha+\beta$ distribution, wear resistance might approach that of conventionally treated microcrystalline brass, thereby narrowing the performance gap with coarse-grained alloys. In this perspective, both excessive β continuity and discontinuous or over-segregated β might exert unfavorable effects, either by amplifying interfacial stresses or by weakening load transfer. Thus, design strategies for AM brasses may need to emphasize α/β topology and interface integrity, seeking to interrupt long shear paths in α without embrittling phase boundaries, while also considering the possible influence of galvanic or inclusion-driven local cells.

1.4.5. L-PBF of biphasic brasses

Building on Pb-free motivations and the conventional strategies above, LPBF offers a route that reduces dependence on chip-forming while delivering lead-free brass components. Cu–Zn systems pose two core challenges: copper’s low near-IR absorptivity and zinc’s low boiling point, which together promote spatter, plume-driven mass loss, and composition drift [97-99]. These couple with melt-pool instabilities, so parameter selection must explicitly control energy input and scan-track stability.

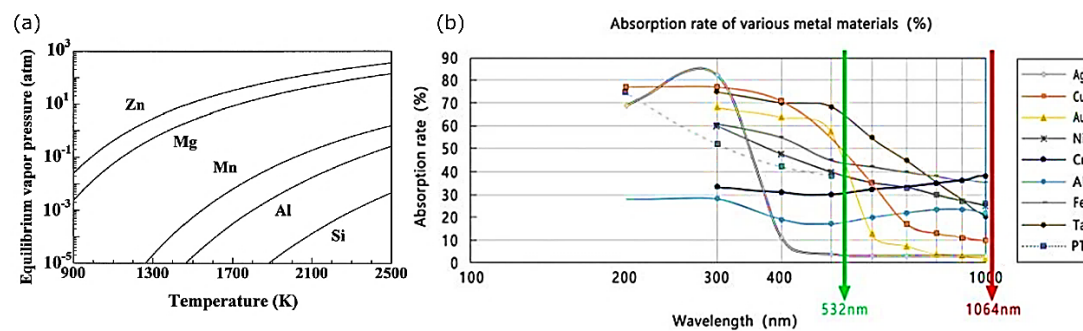


Figure 1-11. (a) Equilibrium vapor pressure of metals at different temperatures. Reprinted from [100]. (b) Absorption rate of different metals [101].

A practical control variable for Cu–Zn is the surface energy density (SED), defined as $SED = P/Vh$ where P is the laser power, V the laser scanning speed and h the hatch distance. SED better reflects the energy imparted to the active track than volume

energy density (VED), which can be misleading in LPBF because the effective remelted geometry spans multiple layers [102, 103]. A., Gatto *et al.* [104] used SED to develop a robust process window for CuZn42 of roughly 2–10 J mm⁻², within which near-full density ($\approx 99.2\%$) was achieved at 190 W / 200 mm s⁻¹ with $h \approx 0.10$ mm; outside this window, lack-of-fusion or over-melting defects dominated [25, 104]. However, as shown in TABLE, high densification still led to a shift in phase composition i.e. the only full dense sample was no more biphasic but constituted by 91 wt.% of α phase. All the other combination of different laser power and scan speed led to mainly β phase materials and extremely low relative density values. Showing how keeping the powder composition and/or the expended phases after the process can be a challenge for this class of alloy.

Table 1-2. Printing parameters, XRD Rietveld analysis, relative density for CuZn42 powder (PW) and samples from full factorial tests. Retrieved from [104].

Sample	P [W]	V [mm/s]	Es [J/mm ²]	α -Cu _{0.64} Zn _{0.36} (wt.%)	β -CuZn (wt.%)	γ -Cu ₅ Zn ₈ (wt.%)	Ortho-Cu _{0.61} Zn _{0.39} (wt.%)	Relative density (%)	SD
P190V200	190	200	9.5	91.2 ± 0.1	8.8 ± 0.1	—	—	99.2	0.3
P190V600	190	600	3.2	18.1 ± 0.1	72 ± 1	—	10.2 ± 0.9	85.7	0.5
P190V800	190	800	2.4	1.62 ± 0.05	98 ± 3	—	—	85.6	0.2
P270V200	270	200	13.5	12.5 ± 0.3	88 ± 2	—	—	86.21	0.04
P270V600	270	600	4.5	11.1 ± 0.5	74 ± 1	—	14.8 ± 0.5	86.40	0.06
P270V800	270	800	3.4	1.23 ± 0.05	92.3 ± 0.9	—	5.8 ± 0.2	88.6	0.3
PW	—	—	—	4.3 ± 0.4	78 ± 3	17 ± 1	—	—	—

LPBF imprints a clear composition–phase signature because Zn selectively evaporates. In-situ fumes and filter residues are Zn-rich; compensating by Zn-enriching the feedstock partially helps restore target chemistry in part [104]. As processed, CuZn42 components are predominantly $\alpha+\beta$, with α fraction increasing as SED (and Zn loss) rises; in the densest condition, α approached ≈ 90 wt%, coherently reflecting a lower Zn/Cu ratio. Independent studies on Cu–Zn and Cu alloys corroborate the central roles of vaporization, plume dynamics, and adequate absorbed power to stabilize the pool [105, 106].

At the microstructural scale, XRD shows that γ -brass present in the powder tends to disappear after LPBF.

When comparing LPBF parts with extruded/forged analogues, report: (i) densification metrics and defect morphology; (ii) post-build composition (Zn/Cu) and phase fractions (α/β); and (iii) the SED/scan-speed context (i.e., location on the process map). Variability across builds is a known contributor to property scatter in LPBF [25]; this framing ties processing to microstructure and properties in a way consistent with both brass-specific physics and broader LPBF best practices.

1.5. Introduction to the Investigations

In the introductory portion of this thesis, is established the foundational motivations and challenges associated with applying laser powder bed fusion (L-PBF) to a well-established high-performance material: maraging steel. This alloy is well recognized for its printability and mechanical robustness, which have enabled its adoption in additive manufacturing (AM) of tooling components. However, its deployment in harsh service environments, such as exposure to molten aluminum in die-casting or under combined corrosive and mechanical loads, poses severe challenges for which the alloy was not originally designed. To address these issues, several studies were carried out, including investigations of corrosion resistance of L-PBF and conventionally produced steels in molten aluminum alloys (Metallurgical and Materials Transactions A, 2025), cavitation erosion of L-PBF maraging steel (Procedia Structural Integrity, 2024), corrosion behavior of maraging steel 1.2709 in Al-alloys (Procedia Structural Integrity, 2024), and comparative studies of wear and corrosion of 18Ni-300 maraging steel fabricated by both additive and conventional routes (Procedia Structural Integrity, 2022). These works collectively highlight the duality of L-PBF maraging steel: surprising resistance towards contact with molten aluminum and potential vulnerabilities coming from its application

The central body of this thesis extends this line of inquiry by focusing on another technologically relevant alloy system: biphasic brass CuZn42 (CW510L). The overarching aim remains consistent evaluating the wear and corrosion performance of additively manufactured alloys in comparison with their conventionally processed counterparts. Unlike maraging steels, brasses present intrinsic challenges for L-PBF due to their wide solidification intervals, the high vapor pressure of zinc, and strong segregation tendencies, all of which contribute to porosity and compositional inhomogeneity. Nevertheless, industrial interest in L-PBF brass arises primarily from the opportunity to eliminate lead from its chemical composition, thereby reducing the health-related risks associated with traditional brass grades. These considerations motivate its exploration within AM despite the inherent process difficulties. This effort culminated in the study *Cavitation erosion and corrosion behavior of LPBF and conventional produced CuZn42 alloy*, which systematically investigates the

relationship between processing route, microstructure, and surface degradation mechanisms.

Taken together, the maraging steel and brass investigations represent two facets of the same overarching objective: to establish a microstructure–surface–performance framework for L-PBF alloys, with particular attention to corrosion and wear phenomena under service-like conditions.

1.6. References

1. Liu Z, Zhao D, Wang P, Yan M, Yang C, Chen Z, et al. Additive manufacturing of metals: Microstructure evolution and multistage control. *Journal of Materials Science & Technology*. 2022; 100:224-36. doi: <https://doi.org/10.1016/j.jmst.2021.06.011>.
2. Gibson I, Rosen D, Stucker B. *Additive Manufacturing Technologies*. Springer. 2015.
3. Kruth JP, Levy G, Klocke F, Childs THC. Consolidation phenomena in laser and powder-bed based layered manufacturing. *CIRP Annals*. 2007;56(2):730-59. doi: <https://doi.org/10.1016/j.cirp.2007.10.004>.
4. Narasimharaju SR, Zeng W, See TL, Zhu Z, Scott P, Jiang X, et al. A comprehensive review on laser powder bed fusion of steels: Processing, microstructure, defects and control methods, mechanical properties, current challenges and future trends. *Journal of Manufacturing Processes*. 2022; 75:375-414. doi: <https://doi.org/10.1016/j.jmapro.2021.12.033>.
5. Panwisawas C, Tang YT, Reed RC. Metal 3D printing as a disruptive technology for superalloys. *Nature Communications*. 2020;11(1):2327. doi: 10.1038/s41467-020-16188-7.
6. Thijs L, Verhaeghe F, Craeghs T, Humbeeck JV, Kruth JP. A study of the microstructural evolution during selective laser melting of Ti–6Al–4V. *Acta Materialia*. 2010;58(9):3303-12. doi: 10.1016/j.actamat.2010.02.004.
7. Acharya R, Sharon JA, Staroselsky A. Prediction of microstructure in laser powder bed fusion process. *Acta Materialia*. 2017;124.
8. Qiu C, Panwisawas C, Ward M, Basoalto HC, Brooks JW, Attallah MM. On the role of melt flow into the surface structure and porosity development during selective laser melting. *Acta Materialia*. 2015; 96:72-9. doi: <https://doi.org/10.1016/j.actamat.2015.06.004>.
9. Sander G, Thomas S, Cruz V, Jurg M, Birbilis N, Sha G, et al. Corrosion of Additively Manufactured Alloys: A Review. *Corrosion*. 2018;74(12):1318-40. doi: 10.5006/2926.
10. Gong H, Rafi K, Gu H, Starr T, Stucker B. Analysis of defect generation in Ti–6Al–4V parts made using powder bed fusion additive manufacturing processes. *Additive Manufacturing*. 2014;1-4:87-98. doi: <https://doi.org/10.1016/j.addma.2014.08.002>.

11. Lorenzi S, Cabrini M, Carrozza A, Gritti L, Nani L, Pastore T, et al. On the selective corrosion mechanism of LPBF-produced AlSi10Mg: Potentiostatic polarization effects. *Electrochimica Acta*. 2023; 470:143354. doi: <https://doi.org/10.1016/j.electacta.2023.143354>.
12. Conde FF, Avila JA, Oliveira JP, Schell N, Oliveira MF, Escobar JD. Effect of the as-built microstructure on the martensite to austenite transformation in an 18Ni maraging steel after laser-based powder bed fusion. *Additive Manufacturing*. 2021; 46:102122. doi: <https://doi.org/10.1016/j.addma.2021.102122>.
13. Chowdhury S, Yadaiah N, Prakash C, Ramakrishna S, Dixit S, Gupta LR, et al. Laser powder bed fusion: a state-of-the-art review of the technology, materials, properties & defects, and numerical modelling. *Journal of Materials Research and Technology*. 2022; 20:2109-72. doi: <https://doi.org/10.1016/j.jmrt.2022.07.121>.
14. Amon A, Bean GE, Forien JB, Voisin T, Hammons JA, Moore EE, et al. Alloy design for additive manufacturing: Continuously reinforced Al-Ce nanocomposites. *Materials & Design*. 2025; 250:113595. doi: <https://doi.org/10.1016/j.matdes.2025.113595>.
15. Plotkowski A, Rios O, Sridharan N, Sims Z, Unocic K, Ott RT, et al. Evaluation of an Al-Ce alloy for laser additive manufacturing. *Acta Materialia*. 2017; 126:507-19. doi: <https://doi.org/10.1016/j.actamat.2016.12.065>.
16. Zhao K, Gao T, Yang H, Hu K, Liu G, Sun Q, et al. Enhanced grain refinement and mechanical properties of a high-strength Al-Zn-Mg-Cu-Zr alloy induced by TiC nano-particles. *Materials Science and Engineering: A*. 2021; 806:140852. doi: <https://doi.org/10.1016/j.msea.2021.140852>.
17. Sabzi HE, Maeng S, Liang X, Simonelli M, Aboulkhair NT, Rivera-Díaz-del-Castillo PEJ. Controlling crack formation and porosity in laser powder bed fusion: Alloy design and process optimisation. *Additive Manufacturing*. 2020; 34:101360. doi: <https://doi.org/10.1016/j.addma.2020.101360>.
18. Dietrich K, Diller J, Dubiez-Le Goff S, Bauer D, Forêt P, Witt G. The influence of oxygen on the chemical composition and mechanical properties of Ti-6Al-4V during laser powder bed fusion (L-PBF). *Additive Manufacturing*. 2020; 32:100980. doi: <https://doi.org/10.1016/j.addma.2019.100980>.
19. Yap CY, Chua CK, Dong ZL, Liu ZH, Zhang DQ, Loh LE, et al. Review of selective laser melting: Materials and applications. *Applied Physics Reviews*. 2015; 2:041101. doi: [10.1063/1.4935926](https://doi.org/10.1063/1.4935926).
20. Bandyopadhyay A, Heer B. Alloy design via additive manufacturing: Advantages, challenges, applications and perspectives. *Materials Today*. 2022; 52:52-70. doi: [10.1016/j.mattod.2021.11.026](https://doi.org/10.1016/j.mattod.2021.11.026).
21. DebRoy T, Wei HL, Zuback JS, Mukherjee T, Elmer JW, Milewski JO, et al. Additive manufacturing of metallic components – Process, structure and properties. *Progress in Materials Science*. 2018; 92:112-224. doi: [10.1016/j.pmatsci.2017.10.001](https://doi.org/10.1016/j.pmatsci.2017.10.001).

22. Zhang H, Yang L, Zhang Z, Chen Z, Song Z, Wang C, et al. Effect of spherical Mo metal particles on microstructure and properties of 316L stainless steel during laser powder bed fusion. *Materials Research Express*. 2025;12(1):016519. doi: 10.1088/2053-1591/ada5b9.
23. Oliveira JP, Santos TG, Miranda RM. Revisiting fundamental welding concepts to improve additive manufacturing: From theory to practice. *Progress in Materials Science*. 2020; 107:100590. doi: <https://doi.org/10.1016/j.pmatsci.2019.100590>.
24. Abd-Elaziem W, Elkatatny S, Abd-Elaziem A-E, Khedr M, Abd El-baky MA, Hassan MA, et al. On the current research progress of metallic materials fabricated by laser powder bed fusion process: a review. *Journal of Materials Research and Technology*. 2022; 20:681-707. doi: <https://doi.org/10.1016/j.jmrt.2022.07.085>.
25. Gordon JV, Narra SP, Cunningham RW, Liu H, Chen H, Suter RM, et al. Defect structure process maps for laser powder bed fusion additive manufacturing. *Additive Manufacturing*. 2020; 36:101552.
26. Shrestha R, Shamsaei N, Seifi M, Phan N. An investigation into specimen property to part performance relationships for laser beam powder bed fusion additive manufacturing. *Additive Manufacturing*. 2019; 29:100807. doi: <https://doi.org/10.1016/j.addma.2019.100807>.
27. Kiss AM, Fong AY, Calta NP, Thampy V, Martin AA, Depond PJ, et al. Laser-Induced Keyhole Defect Dynamics during Metal Additive Manufacturing. *Advanced Engineering Materials*. 2019;21(10):1900455. doi: <https://doi.org/10.1002/adem.201900455>.
28. Martin AA, Calta NP, Khairallah SA, Wang J, Depond PJ, Fong AY, et al. Dynamics of pore formation during laser powder bed fusion additive manufacturing. *Nature Communications*. 2019;10(1):1987. doi: 10.1038/s41467-019-10009-2.
29. Du C, Zhao Y, Jiang J, Wang Q, Wang H, Li N, et al. Pore defects in Laser Powder Bed Fusion: Formation mechanism, control method, and perspectives. *Journal of Alloys and Compounds*. 2023; 944:169215. doi: <https://doi.org/10.1016/j.jallcom.2023.169215>.
30. Poudel A, Yasin MS, Ye J, Liu J, Vinel A, Shao S, et al. Feature-based volumetric defect classification in metal additive manufacturing. *Nature Communications*. 2022;13(1):6369. doi: 10.1038/s41467-022-34122-x.
31. Zhang B, Meng WJ, Shao S, Phan N, Shamsaei N. Effect of heat treatments on pore morphology and microstructure of laser additive manufactured parts. *Material Design & Processing Communications*. 2019;1(1):e29. doi: <https://doi.org/10.1002/mdp2.29>.
32. Malakizadi A, Mallipeddi D, Dadbakhsh S, M'Saoubi R, Krajnik P. Post-processing of additively manufactured metallic alloys – A review. *International Journal of Machine Tools and Manufacture*. 2022; 179:103908. doi: <https://doi.org/10.1016/j.ijmachtools.2022.103908>.
33. Gunenthiram V, Peyre P, Schneider M, Dal M, Coste F, Fabbro R. Analysis of laser–melt pool–powder bed interaction during the selective laser melting of a stainless steel. *Journal of Laser Applications*. 2017;29(2):022303. doi: 10.2351/1.4983259.
34. Zhang D, Qi X, Chiu YL, Liu Y. Metal Alloys for Fusion-Based Additive Manufacturing. *Advanced Engineering Materials*. 2018;20(5):1700952. doi: 10.1002/adem.201700952.

35. AlMangour B, Grzesiak D, Yang J-M. Rapid fabrication of bulk-form TiB₂/316L stainless steel nanocomposites with novel reinforcement architecture and improved performance by selective laser melting. *Journal of Alloys and Compounds*. 2016; 680:480-93. doi: <https://doi.org/10.1016/j.jallcom.2016.04.156>.
36. Malakizadi A, et al. Post-processing of additively manufactured metallic alloys – A review. *International Journal of Machine Tools and Manufacture*. 2022; 179:103908. doi: [10.1016/j.ijmachtools.2022.103908](https://doi.org/10.1016/j.ijmachtools.2022.103908).
37. Mu J, Sun T, Leung CLA, Oliveira JP, Wu Y, Wang H, et al. Application of electrochemical polishing in surface treatment of additively manufactured structures: A review. *Progress in Materials Science*. 2023; 136:101109. doi: <https://doi.org/10.1016/j.pmatsci.2023.101109>.
38. Barrionuevo GO, Walczak M, Ramos-Grez J, Sánchez-Sánchez X. Microhardness and wear resistance in materials manufactured by laser powder bed fusion: Machine learning approach for property prediction. *CIRP Journal of Manufacturing Science and Technology*. 2023; 43:106-14. doi: <https://doi.org/10.1016/j.cirpj.2023.03.002>.
39. Gong S, Takata N, Kobashi M, Shin SE. Wear properties of aluminum alloys fabricated by laser powder bed fusion. *Tribology International*. 2023; 187:108769. doi: <https://doi.org/10.1016/j.triboint.2023.108769>.
40. Vukkum VB, Gupta RK. Review on corrosion performance of laser powder-bed fusion printed 316L stainless steel: Effect of processing parameters, manufacturing defects, post-processing, feedstock, and microstructure. *Materials & Design*. 2022; 221:110874. doi: <https://doi.org/10.1016/j.matdes.2022.110874>.
41. Floreen S. The Physical Metallurgy of Maraging Steels. *Metallurgical Reviews*. 1968; 13:115-28. doi: [10.1179/mtlr.1968.13.1.115](https://doi.org/10.1179/mtlr.1968.13.1.115).
42. Vasudevan VK, Kim SJ, Wayman CM. Precipitation reactions in maraging steels. *Metallurgical Transactions A*. 1990;21A:2655-68. doi: [10.1007/BF02646949](https://doi.org/10.1007/BF02646949).
43. Mouritz AP. *Introduction to Aerospace Materials*. Woodhead; 2012.
44. Durand-Charre M. *Microstructure of Steels and Cast Irons*. Springer; 2004.
45. Xu X, Ganguly S, Ding J, Guo S, Williams S, Martina F. Microstructural evolution and mechanical properties of maraging steel produced by wire + arc additive manufacturing. *Materials Characterization*. 2018; 143:152-62. doi: [10.1016/j.matchar.2018.04.006](https://doi.org/10.1016/j.matchar.2018.04.006).
46. Tan C, Zhou K, Kuang M, Ma W, Kuang T. Microstructural evolution, nanoprecipitation behaviour and mechanical properties of maraging steel produced by selective laser melting. *Science and Technology of Advanced Materials*. 2018; 19:746-58. doi: [10.1080/14686996.2018.1522625](https://doi.org/10.1080/14686996.2018.1522625).
47. Bodziak S, Al-Rubaie KS, Valentina LD, Lafratta FH, Santos EC, Zanatta AM, et al. Microstructural evolution and mechanical behaviour of maraging steel produced by additive manufacturing. *Materials Characterization*. 2019; 151:73-83. doi: [10.1016/j.matchar.2019.02.012](https://doi.org/10.1016/j.matchar.2019.02.012).

48. Biffi CA, Tuissi A. Stato dell'arte sulle tecniche di produzione additiva per metalli. *La Metallurgia Italiana*. 2017(1).
49. Kürnstener P, Wilms MB, Weisheit A, Barriobero-Vila P, Jägle EA, Raabe D. Massive nanoprecipitation in an Fe-19Ni-xAl maraging steel triggered by the intrinsic heat treatment during laser metal deposition. *Acta Materialia*. 2017; 129:52-60. doi: <https://doi.org/10.1016/j.actamat.2017.02.069>.
50. Jägle EA, Sheng Z, Wu L, Lu L, Risse J, Weisheit A, et al. Precipitation Reactions in Age-Hardenable Alloys During Laser Additive Manufacturing. *JOM*. 2016;68(3):943-9. doi: 10.1007/s11837-015-1764-2.
51. Bai Y, Wang D, Yang Y, Wang H. Effect of heat treatment on the microstructure and mechanical properties of maraging steel by selective laser melting. *Materials Science and Engineering: A*. 2019; 760:105-17. doi: <https://doi.org/10.1016/j.msea.2019.05.115>.
52. Bajaj P. Steels in additive manufacturing: A review of their microstructure and properties. *Materials Science and Engineering: A*. 2020;772.
53. Cerezo PM, Aguilera JA, Garcia-Gonzalez A, Lopez-Crespo P. Microhardness and Microstructure Analysis of the LPBF Additively Manufactured 18Ni300. *Materials*. 2024 doi: 10.3390/ma17030661.
54. Guo L, Zhang L, Andersson J, Ojo O. Additive manufacturing of 18% nickel maraging steels: Defect, structure and mechanical properties: A review. *Journal of Materials Science & Technology*. 2022; 120:227-52. doi: <https://doi.org/10.1016/j.jmst.2021.10.056>.
55. Takata N. Crystallographic Features of Microstructure in Maraging Steel Fabricated by Selective Laser Melting. 2018.
56. Hemmasian Ettefagh A, Guo S, Raush J. Corrosion performance of additively manufactured stainless steel parts: A review. *Additive Manufacturing*. 2021; 37:101689. doi: <https://doi.org/10.1016/j.addma.2020.101689>.
57. Casati R, Lemke JN, Tuissi A, Vedani M. Aging Behaviour and Mechanical Performance of 18-Ni 300 Steel Processed by Selective Laser Melting. *Metals*. 2016 doi: 10.3390/met6090218.
58. Mugwagwa L, Yadroitsev I, Matope S. Effect of Process Parameters on Residual Stresses, Distortions, and Porosity in Selective Laser Melting of Maraging Steel 300. *Metals*. 2019 doi: 10.3390/met9101042.
59. Conde FF, Escobar JD, Rodriguez J, Afonso CRM, Oliveira MF, Avila JA. Effect of Combined Tempering and Aging in the Austenite Reversion, Precipitation, and Tensile Properties of an Additively Manufactured Maraging 300 Steel. *Journal of Materials Engineering and Performance*. 2021;30(7):4925-36. doi: 10.1007/s11665-021-05553-2.
60. Oliveira AR, Diaz JAA, Nizes ADC, Jardini AL, Del Conte EG. Investigation of Building Orientation and Aging on Strength–Stiffness Performance of Additively Manufactured Maraging Steel. *Journal of Materials Engineering and Performance*. 2021;30(2):1479-89. doi: 10.1007/s11665-020-05414-4.

61. Castro Güiza GM, Oliveira CAS. Microstructural changes produced by hot forging in a C300 maraging steel. *Materials Science and Engineering: A*. 2016; 655:142-51.
62. Mooney B, Kourousis KI, Raghavendra R. Plastic anisotropy of additively manufactured maraging steel: Influence of the build orientation and heat treatments. *Additive Manufacturing*. 2019; 25:19-31. doi: <https://doi.org/10.1016/j.addma.2018.10.032>.
63. Becker T, Dimitrov D. The achievable mechanical properties of SLM produced Maraging Steel 300 components. *Rapid Prototyping Journal*. 2016.
64. Podgornik B, Šinko M, Godec M. Dependence of the wear resistance of additive-manufactured maraging steel on the build direction and heat treatment. *Additive Manufacturing*. 2021; 46:102123. doi: <https://doi.org/10.1016/j.addma.2021.102123>.
65. He X, Wang X, Vian C, Faezipour M. Numerical optimization of conformal cooling channels for thermal distribution and stress characterization in additively manufactured high pressure die casting die. *Engineering Failure Analysis*. 2025; 176:109620. doi: <https://doi.org/10.1016/j.engfailanal.2025.109620>.
66. Feng S, Kamat AM, Pei Y. Design and fabrication of conformal cooling channels in molds: Review and progress updates. *International Journal of Heat and Mass Transfer*. 2021; 171:121082. doi: <https://doi.org/10.1016/j.ijheatmasstransfer.2021.121082>.
67. Karakoc C, Dizdar KC, Dispinar D. Investigation of effect of conformal cooling inserts in high-pressure die casting of AlSi9Cu3. *International Journal of Advanced Manufacturing Technology*. 2022;121(11-12):7311-23. doi: 10.1007/s00170-022-09808-7.
68. Zhu J, Kokawa H, Feng K, Li Z. Unexpectedly high corrosion susceptibility near fusion boundaries of Inconel 625 manufactured by laser powder bed fusion. *Corrosion Science*. 2023; 223:111432. doi: <https://doi.org/10.1016/j.corsci.2023.111432>.
69. Song J, Wang X, DenOuden T, Han Q. Evolution of Intermetallic Phases in Soldering of the Die Casting of Aluminum Alloys. *Metallurgical and Materials Transactions A*. 2016;47(6):2609-15. doi: 10.1007/s11661-016-3454-2.
70. Chen ZW. Formation and progression of die soldering during high pressure die casting. *Materials Science and Engineering: A*. 2005;397(1):356-69. doi: <https://doi.org/10.1016/j.msea.2005.02.057>.
71. Tentardini EK, Kunrath AO, Aguzzoli C, Castro M, Moore JJ, Baumvol IJR. Soldering mechanisms in materials and coatings for aluminum die casting. *Surface and Coatings Technology*. 2008;202(16):3764-71. doi: <https://doi.org/10.1016/j.surfcoat.2008.01.019>.
72. Diwakar V, Arumugam S, Lakshmanan TS, Sarkar BK. Environmental stress intensity for maraging steel. *Journal of Materials Science*. 1986;21(6):1927-31. doi: 10.1007/BF00547927.
73. Bagchi A, Gope DK, Chattopadhyaya S, Wuriti G. A critical review on susceptibility of stress corrosion cracking in maraging steel weldments. *Materials Today: Proceedings*. 2020; 27:2303-7. doi: <https://doi.org/10.1016/j.matpr.2019.09.117>.

74. Kritzer P. Corrosion in high-temperature and supercritical water and aqueous solutions: a review. *The Journal of Supercritical Fluids*. 2004;29(1):1-29. doi: [https://doi.org/10.1016/S0896-8446\(03\)00031-7](https://doi.org/10.1016/S0896-8446(03)00031-7).
75. *Elements of Metallurgy and Engineering Alloys*. ASM International; 2008. doi: 10.31399/asm.tb.emea.9781627082518.
76. Davis JR. *Copper and Copper Alloys*. Materials Park, OH: ASM International; 2001.
77. World Health O. *Guidelines for Drinking-water Quality*. 4 ed. Geneva: WHO; 2011.
78. European Copper I. Publication 117 — Section 6: Types of Brass. 2016.
79. Ahlers M. Martensite and equilibrium phases in CuZn and CuZnAl alloys. *Progress in Materials Science*. 1986;30(3):135-86. doi: 10.1016/0079-6425(86)90007-1.
80. Siwiec JG. The Mechanism of Liquid Copper Deoxidation during Argon Blowing. *Metalurgija*. 2009; 48:75-7.
81. Jacob KT. Gibbs free energies of formation of ZnAl₂O₄ and ZnCr₂O₄. *Thermochimica Acta*. 1976;15(1):79-87. doi: [https://doi.org/10.1016/0040-6031\(76\)80094-9](https://doi.org/10.1016/0040-6031(76)80094-9).
82. Felli F, Brotzu A, Pilone D. Analysis of the fracture criticality of biphasic brass. *Procedia Structural Integrity*. 2016; 2:2959-65. doi: <https://doi.org/10.1016/j.prostr.2016.06.370>.
83. Vilarinho C, Davim JP, Soares D, Castro F, Barbosa J. Influence of the chemical composition on the machinability of brasses. *Journal of Materials Processing Technology*. 2005; 170:441-7.
84. Pugacheva NB. Structure of commercial $\alpha + \beta$ brasses. *Metal Science and Heat Treatment*. 2007;49(1):67-74. doi: 10.1007/s11041-007-0013-x.
85. Freudenberger J, Warlimont H. Copper and Copper Alloys. In: Warlimont H, Martienssen W, editors. *Springer Handbook of Materials Data*. Cham: Springer International Publishing; 2018. p. 297-305.
86. Claesson E, Rod O. The effect of alloying elements on the corrosion resistance of brass. *Materials Science and Technology*. 2016;32(17):1794-803. doi: 10.1080/02670836.2016.1254925.
87. Corcoran SG. Effects of Metallurgical Variables on Dealloying Corrosion. In: *Corrosion: Fundamentals, Testing, and Protection*. 13A. ASM International. 2003. p. 0. doi: 10.31399/asm.hb.v13a.a0003620. <https://doi.org/10.31399/asm.hb.v13a.a0003620>. Accessed 9/11/2025.
88. Karpagavalli R, Balasubramaniam R. Development of novel brasses to resist dezincification. *Corrosion Science*. 2007;49(3):963-79. doi: <https://doi.org/10.1016/j.corsci.2006.06.024>.
89. Brandl E, Malke R, Beck T, Wanner A, Hack T. Stress corrosion cracking and selective corrosion of copper-zinc alloys for the drinking water installation. *Materials and Corrosion*. 2009;60(4):251-8. doi: <https://doi.org/10.1002/maco.200805079>.
90. Zhou P, Hutchison MJ, Erning JW, Scully JR, Ogle K. An in situ kinetic study of brass dezincification and corrosion. *Electrochimica Acta*. 2017; 229:141-54. doi: <https://doi.org/10.1016/j.electacta.2017.01.078>.

91. Din. DIN EN 12502-2:2005-03 — Protection of metallic materials against corrosion— Guidance on the assessment of corrosion likelihood in water distribution and storage systems—Part 2: Influencing factors for copper and copper alloys. Berlin: DIN; 2005.
92. Hanke S, Fischer A, Beyer M, dos Santos J. Cavitation erosion of NiAl-bronze layers generated by friction surfacing. *Wear*. 2011;273(1):32-7. doi: <https://doi.org/10.1016/j.wear.2011.06.002>.
93. Al-Hashem A, Caceres PG, Riad WT, Shalaby HM. Cavitation Corrosion Behavior of Cast Nickel-Aluminum Bronze in Seawater. *Corrosion*. 1995;51(5):331-42. doi: 10.5006/1.3293598.
94. Abedini M, Reuter F, Hanke S. Corrosion and material alterations of a CuZn38Pb3 brass under acoustic cavitation. *Ultrasonics Sonochemistry*. 2019; 58:104628. doi: <https://doi.org/10.1016/j.ultsonch.2019.104628>.
95. Moshkovich A, Perfilyev V, Lapsker I, Rapoport L. Friction, wear and plastic deformation of Cu and α/β brass under lubrication conditions. *Wear*. 2014; 320:34-40. doi: <https://doi.org/10.1016/j.wear.2014.08.016>.
96. Sadykov FA, Barykin NP, Aslanyan IR. Wear of copper and its alloys with submicrocrystalline structure. *Wear*. 1999;225-229:649-55. doi: [https://doi.org/10.1016/S0043-1648\(98\)00374-3](https://doi.org/10.1016/S0043-1648(98)00374-3).
97. Bourell D, Kruth JP, Leu M, Levy G, Rosen D, Beese AM, et al. Materials for additive manufacturing. *CIRP Annals*. 2017;66(2):659-81.
98. Yin J, Zhang W, Ke L, Wei H, Wang D, Yang L, et al. Vaporization of alloying elements and explosion behavior during laser powder bed fusion of Cu–10Zn alloy. *International Journal of Machine Tools and Manufacture*. 2021; 161:103686.
99. Trapp J, Rubenchik AM, Guss G, Matthews MJ. In situ absorptivity measurements of metallic powders during laser powder-bed fusion additive manufacturing. *Applied Materials Today*. 2017; 9:341-9.
100. Zhao H, Debroy T. Weld metal composition change during conduction mode laser welding of aluminum alloy 5182. *Metallurgical and Materials Transactions B*. 2001;32(1):163-72. doi: 10.1007/s11663-001-0018-6.
101. W M. Using a Green Laser Facilitates 3D Printing of Pure Copper and Copper Alloys. *3Dnatives*. 2024.
102. Bertoli US, Wolfer AJ, Matthews MJ, Delplanque JPR, Schoenung JM. On the limitations of volumetric energy density as a design parameter for selective laser melting. *Materials & Design*. 2017; 113:331-40.
103. Yadroitsev I, Yadroitsava I, Bertrand P, Smurov I. Factor analysis of selective laser melting process parameters and geometrical characteristics of synthesized single tracks. *Rapid Prototyping Journal*. 2012; 18:201-8.
104. Gatto A, Gatto ML, Groppo R, Munteanu D, Mengucci P. Influence of laser powder bed fusion process parameters on the properties of CuZn42 components: case study of the laser surface energy density. *Progress in Additive Manufacturing*. 2023; 8:843-55. doi: 10.1007/s40964-022-00361-z.

105. Zhang S, Zhu H, Hu Z, Zeng X, Zhong F. Selective laser melting of Cu10Zn alloy powder using high laser power. Powder Technology. 2019; 342:613-20.
106. Popovich A, Sufiiarov V, Polozov I, Borisov E, Masaylo D, Orlov A. Microstructure and mechanical properties of additive manufactured copper alloy. Materials Letters. 2016; 179:38-41.

SECTION 2.

2. L-PBF Maraging Steel Characterization

2.1. Wear and corrosion behavior of 18Ni-300 maraging steel produced by laser-based powder bed fusion and conventional route

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2.1.1. Abstract

Maraging steels such as 18Ni-300 (1.2709) are characterized by high yield and tensile strength together with good toughness making them interesting materials for aerospace, automotive and tooling sectors as well as for bearing gears parts. The low carbon martensite matrix combined with the nanosized intermetallic precipitates are responsible for the peculiar mechanical properties. Thanks to the very low carbon content, these steels are easily weldable and therefore suitable for additive manufacturing (AM) techniques, such as laser-based powder bed fusion (LPBF). Indeed, this technique was recently adopted in tooling and molding industry to produce inserts with conformal cooling channels capable to improve inserts and cores lifetime enhancing productivity. These types of components usually undergo severe stress conditions, wear phenomena and even aggressive environments.

This work aims at comparing the tribological and corrosion behaviour of 1.2709 maraging steel samples produced by both forging and LPBF technique. Conventional samples were investigated after solution annealing and aging treatment while AM samples were directly aged. Aging parameters were chosen to achieve the same hardness values for both the production conditions. Samples sliding wear behaviour was investigated through pin-on-disc tests using 100Cr6 steel ball as counterpart (ASTM G99) at three different sliding velocities, while potentiodynamic polarization measurements (ASTM G3) were conducted in 3.5 wt % NaCl solution.

Microstructural analyses and hardness measurements were carried out on as-aged samples. The corrosion damage and the wear mechanism were investigated by means

of scanning electron microscope (SEM). For the considered heat treatment, results show only small differences in the wear and corrosion behaviors between forged and AM samples, despite differences in microstructural morphology, demonstrating the reliability of AM components.

2.1.2. Introduction

Maraging steels such as 18Ni-300 (1.2709) are characterized by high yield and tensile strength together with good toughness (Handbook 1993). The low carbon martensite matrix formed by cooling from the high Ni content-Fe solid solution, combined with the precipitation strengthening of nanosized intermetallics, such as Ni₃Ti (Pereloma et al. 2004), Ni₃Mo (Rao 2006), NiAl (Schnitzer et al. 2010), Ni₃Al (Shin, Jeong and Lee 2015), Fe₂Mo (Vasudevan, Kim and Wayman 1990), etc., obtained after aging at temperature of about 450-550 °C, are responsible for the peculiar mechanical properties. In fact, maraging steels are interesting materials for aerospace (Narayana Murty and Sharma 2022), automotive (Pennings, Hatanaka and Crebolder 2015) and tooling (Ferreira et al. 2021) sectors as well as for bearing gears parts (Kim et al. 1986). Furthermore, maraging steels present good dimensional stability and low coefficient of thermal expansion (Handbook 1993) that together with the very low content of interstitials alloying elements make this class of steels easy to weld (Lang and Kenyon 1971) and therefore suitable for additive manufacturing (AM) techniques, such as laser-based powder bed fusion (LPBF), also known as selective laser melting (SLM). LPBF is a 3D printing method that uses a powder bed of the chosen alloy and a laser source to selectively melt successive layers of powder obtaining the subsequent building of near-net-shape 3D parts from input CAD data (ISO/ASTM 2019). Nowadays, different metallic powders can be processed via LPBF technique. The most investigated alloys in the literature are Al-based (Aboulkhair et al. 2019), Ti-based (Zhang and Attar 2016), Co-based (Sing et al. 2016), Ni-based (Elahinia et al. 2016) and Fe-based (Zitelli, Folgarait and Di Schino 2019). Optimized printing parameters permit to obtain very dense parts with comparable mechanical properties to those of components realized by conventional production route. For example, in the case of maraging steels, thanks to the extremely high cooling rates (up to 108 K/s (Jägle et al.

2014)) typical of LPBF process that also promotes a sort of intrinsic solution heat treatment, the as-build parts develop a very fine cellular martensite microstructure, which only requires a final aging treatment to reach the mechanical properties of conventional manufactured parts (Casati et al. 2016). Furthermore, compared to forging process, LPBF technique allows much greater freedom of design and a lower need for subsequent machining operations, thus reducing material wastage. Indeed, this technique was recently adopted in tooling and molding industry to produce inserts with conformal cooling channels capable of improving inserts and cores lifetime, enhancing productivity. All these types of components usually undergo severe loads, wear phenomena and even aggressive environments. Thus, the aim of this work is to compare the wear and corrosion behavior of 18Ni-300 (1.2709) maraging steel produced by both AM technique and by conventional route.

2.1.3. Materials and methods

The maraging steels under investigation were industrially produced by Deutsche Edelstahlwerke Specialty Steel GmbH & Co. KG by both Additive Manufacturing techniques (AM) and conventional route (CR), consisting in the following steps: electric arc furnace melting, ladle furnace refinement, vacuum arc remelting and final forging.

The commercial powder namely Printdur® Powderfort (~1.2709) was chosen for building the AM samples. Concerning the particle size distribution, 3.4 vol.% of the powder is characterized by a diameter smaller than 20 μm , 45.6 vol.% smaller than 38 μm , and 98.2 vol.% smaller than 53 μm . The powder flow rate was 15.6 s/50g with an apparent density of 3.99 g/cm³. A commercially available laser-based powder bed fusion (LPBF) system was used to produce the maraging steel samples. The process parameters are confidential factory information that cannot be disclosed, as mentioned in other papers in the literature (Giovagnoli et al. 2021). AM samples are cylinders with a diameter of 57 mm and a height of 12 mm, manufactured, with the axis perpendicular to the building direction (BD).

The CR maraging steel was produced with the Cryodur®2709 commercial alloy. These samples were cut from a forged round bar with a diameter of 60 mm and machined to obtain the same dimensions of the AM samples.

Table 2-1 shows the mean chemical composition of the samples provided by the manufacturer and measured by optical emission spectroscopy.

Table 2-1. Samples mean chemical composition

Element (wt%)	C	Si	Mn	P	S	Cr	Mo	Ni	Co	Ti	N	O	Fe
AM	0.01	0.2	0.3	0.01	0.006	0.1	5	17.9	13.4	-	0.007	0.026	Bal.
CR	0.004	0.02	0.03	<0.003	0.0014	0.1	4.95	18.3	9.75	1.13	-	-	Bal.

The samples were heat treated to obtain the final mechanical properties. CR samples underwent solution treatment for 1 h at 820 °C, followed by air quenching and aging for 5 h and 30 min at 490 °C. Instead, only aging treatment was conducted on AM samples, holding the samples for 4 h at 490°C to promote the formation of precipitates (Casati et al. 2016). These heat treatment parameters were chosen on the basis of manufacturer experience to achieve the same hardness for both AM and CR samples. After heat treatment, all samples were machined to obtain discs with a diameter of 55 mm and a thickness of 10 mm. The flat surfaces were finished to a roughness of 0.4 µm.

Microstructural characterization of aged samples was carried out after polishing up to a mirror finish and etching with modified Fry's reagent or Nital 4% (E407 2017). An optical microscope (Leica DMI 5000M) and a scanning electron microscope (LEO EVO 40, Zeiss) equipped with an energy dispersive spectroscopy microprobe (EDS, Oxford Instruments) were used for microstructural analysis. Furthermore, X-ray diffraction (XRD, Phoenix S.N. 01-2018) measurements were carried out to quantify the retained austenite in the samples, by using a Mo $k\alpha$ radiation ($\lambda = 0.7107 \text{ \AA}$), a voltage of 45 KV and a current of 35 mA, in accordance with the ASTM E975 standard.

Rockwell hardness (HRC) of samples was measured following ASTM E18 standard by means of a Rupac 500 Mra hardness tester and the mean value was calculated as the average of 5 indentations.

The wear behavior of aged maraging steel samples was evaluated with pin-on-disk (PoD) dry wear test by using a THT tribometer (CSM Instruments) in accordance with the ASTM G99 standard and adopting as counterpart a 6 mm diameter 100Cr6 steel ball. The effect of three different sliding velocities on the wear mechanism was investigated. Tests were performed at 22.5 cm/s, 50 cm/s and 62 cm/s, applying a constant load of 5 N, on a distance of 1260 meters. During the tests, the coefficient of friction (CoF) was continuously recorded while, at the end of each test, a stylus profilometer (TRIBOtechnic) was used to measure the wear track profile. At least three tests were carried out for each velocity and material condition and five wear track profile measurements were performed to calculate the mean value of the worn surface for each test. The wear rate was then calculated using equation 1:

$$W = \frac{2 \pi r A}{F L} \quad (1)$$

where A is the average value of the worn surface (mm²), r is the radius of the wear tracks (i.e. 20 mm), F and L are the applied load (N) and the sliding distance (m) respectively.

To investigate the wear mechanisms, the worn surfaces (disc and counterpart) were analyzed by SEM-EDS technique at the end of each test.

The potentiodynamic polarization measurements (ASTM G3) were carried out at room temperature (25 °C) in a 3.5 wt % NaCl solution by means of a potentiostat (Model 7050 AMEL S.r.l.), by using a saturated calomel electrode (SCE) as reference electrode, two platinum wires as the counter-electrodes and the sample as working electrode. Samples were machined to fit into the sample holder that has an exposed circular surface of 5 mm in diameter. The specimens' surface was polished up to P1200 emery paper to remove any possible external oxide produced by the manufacturing process. The corrosion behavior of AM samples was investigated both on vertical (parallel to the BD) and horizontal (normal to the BD) section of the samples to identify the possible effect of the different orientation of the microstructure on the corrosion rate.

After 1 hour of samples immersion in the solution to stabilize the open circuit potential (E_{oc}), each test was performed at a scan rate of 0.25 mV/s from E_{oc} to E_{oc} – 300 mV

(cathodic polarization) and return to E_{oc} and again from E_{oc} up to $E_{oc} + 300$ mV (anodic polarization). During each test, electrochemical data was automatically acquired to plot the potentiodynamic polarization curves. The corrosion current density and the corrosion potential values were extrapolated by Tafel method.

2.1.4. Results and discussion

Figure 2-1 displays the optical microscope images of aged AM samples after etching with Nital 4%. Notwithstanding the aging heat treatment, the overlapped elongated scan tracks typical of as-built AM parts can be recognized in the horizontal cross-section (**Figure 2-1a**) as also the semi-elliptical melt pools in the vertical cross-section (**Figure 2-1b**) whose width and depth depend on the adopted laser parameters and building strategy (Song et al. 2019). No porosity was detected suggesting the achievement of a fully dense part. On the other hand, some unetched zones can be identified at the melt pool boundaries both vertical cross-section (**Figure 2-1b**) and in the horizontal (not presented here). According to the EDS analysis of **Figure 2-1c**, these zones correspond to positive segregations of Cr and Mo that form during solidification due to the partitioning of these elements into the last liquid that solidifies. This local enrichment of elements, typically located at cellular and dendritic boundaries but also at the boundaries of the scan tracks and melt pools, promotes the formation of retained austenite in AM maraging steel (Xu et al. 2018, Bai et al. 2019). In fact, despite Cr and Mo are ferrite stabilizer, their high concentration in the segregated zone locally decreases the martensite starting temperature (M_s) of steel to less than zero degree (-43 °C), as calculated by the empirical equation proposed by Liu et al. (Liu et al. 2001), resulting in the stabilization of austenite at room temperature. The aged AM microstructure at high magnification is shown in **Figure 2.1d**. As reported in other works (Yin et al. 2018, Casati et al. 2016, Bai et al. 2019), during the aging treatment, the very fine continuous cellular structure, typical of as-built parts, tends to blur with the increasing of holding time and temperature. At the same time the boundaries of the cells become non-continuous and irregular due to the precipitation of nano-sized Ni intermetallic phase and phase transformations can occur (e.g. formation of reverted austenite).

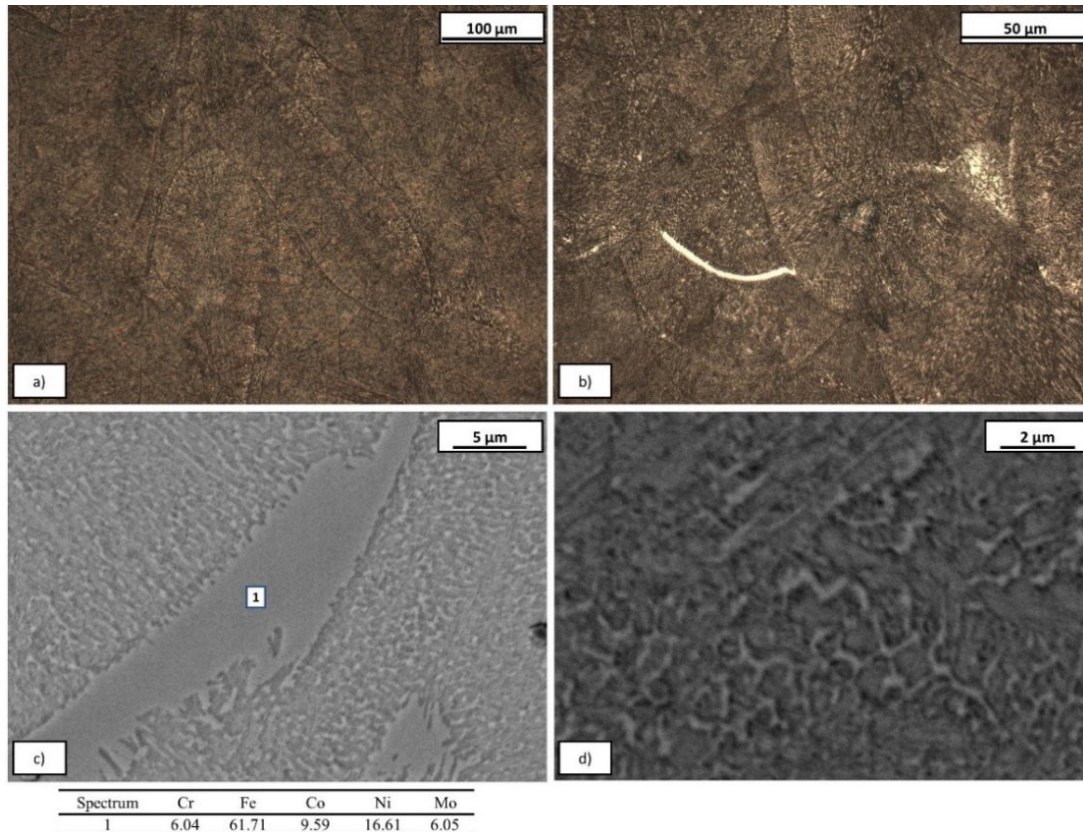


Figure 2-1. AM aged samples: a) horizontal and b) vertical cross-section; c) and d) SEM image and EDS analysis of AM vertical cross-section.

The microstructure of CR samples after solution treatment and aging is displayed in **Figure 2-2**. Samples etched with Nital 4% reveals packets or blocks of lath type martensite with very fine unetched boundaries that probably consist of reverse austenite (**Figure 2-2a**). Instead, etching with modified Fry's reagent puts in evidence the different orientation of martensite blocks (**Figure 2-2b**) (Morito et al. 2006).

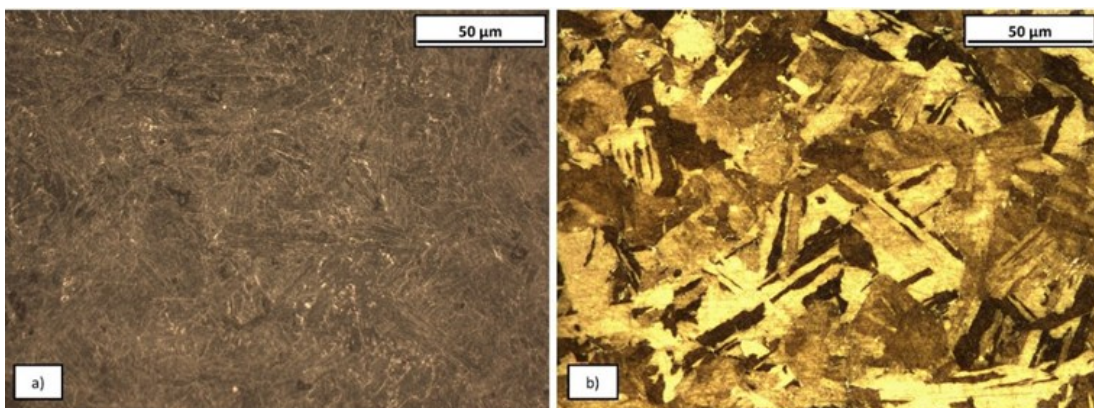


Figure 2-2. CR samples etched with a) Nital 4% and b) modified Fry's reagent

The presence of different quantities of austenite between AM and CR sample is further demonstrated by the results of XRD analysis (**Figure 2-3**). AM samples are characterized by a volume fraction of austenite that is 6.1% higher than in the CR samples, probably because of differences in their chemical composition and heat treatments. It is expected that the solution treatment experienced by CR samples has promoted the dissolution of alloying elements, minimizing segregations, and obtaining a martensitic matrix after cooling. During the following aging treatment, the matrix can revert into the more stable reverse austenite. Instead, AM samples underwent only aging treatment, and in this case, austenite can be both retained, promoted by the presence of micro segregation, and reversed, deriving from the reversion of martensite during the aging holding (Jäggle et al. 2014, Pereloma et al. 2004, Tan et al. 2017).

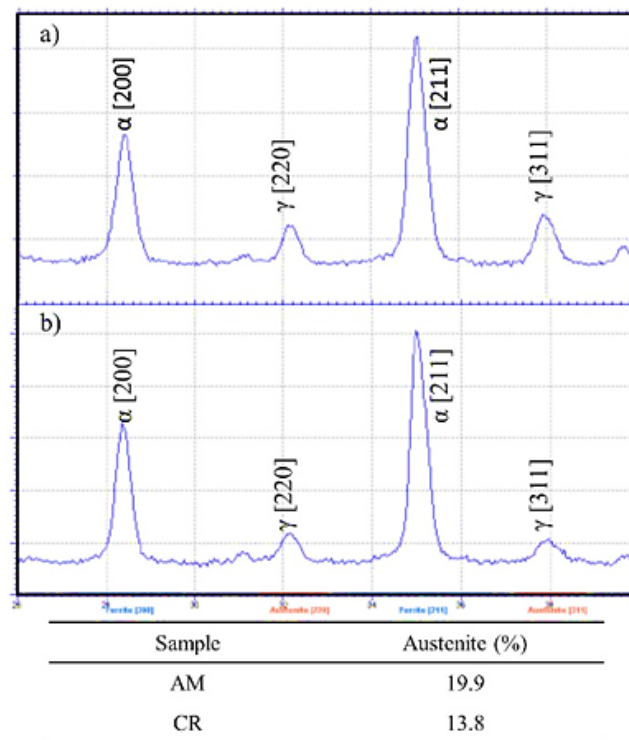


Figure 2-3. XRD analysis of samples a) AM and b) CR.

The hardness of CR samples (54.6 ± 0.2 HRC) is about 1% higher than that of AM samples (53.9 ± 0.2 HRC). This small difference confirms that the heat treatment parameters were properly chosen. As suggested by other authors (Jäggle et al. 2017), the slightly lower hardness of AM samples can be easily related to its highest content

of soft austenite. Furthermore, hardness differences between AM and CR samples can also have other sources: different grain size, shape, density, and chemical composition of intermetallic precipitates (e.g. the lack of Ti in the AM alloy composition, contrary to the CR samples, results in the lack of Ni₃Ti nanoprecipitates).

Figure 2-4 displays the Coefficient of Friction (CoF) with the sliding distance, for wear tests carried out on both AM and CR samples with three different sliding velocities: 22.5, 50 and 62 cm/s. There are no relevant differences between the CoF measured on AM and CR samples. In particular, for all the tested conditions, the CoF values quickly reach a steady state that remains more stable at the slower sliding speed (**Figure 2-4a**), with respect to the velocity of 62 cm/s (**Figure 2-4c**). Despite this difference, the average plateau values for the different samples remain very similar, close to 0.8, indicating that the sliding speed, in the considered range, has a negligible influence on the COF.

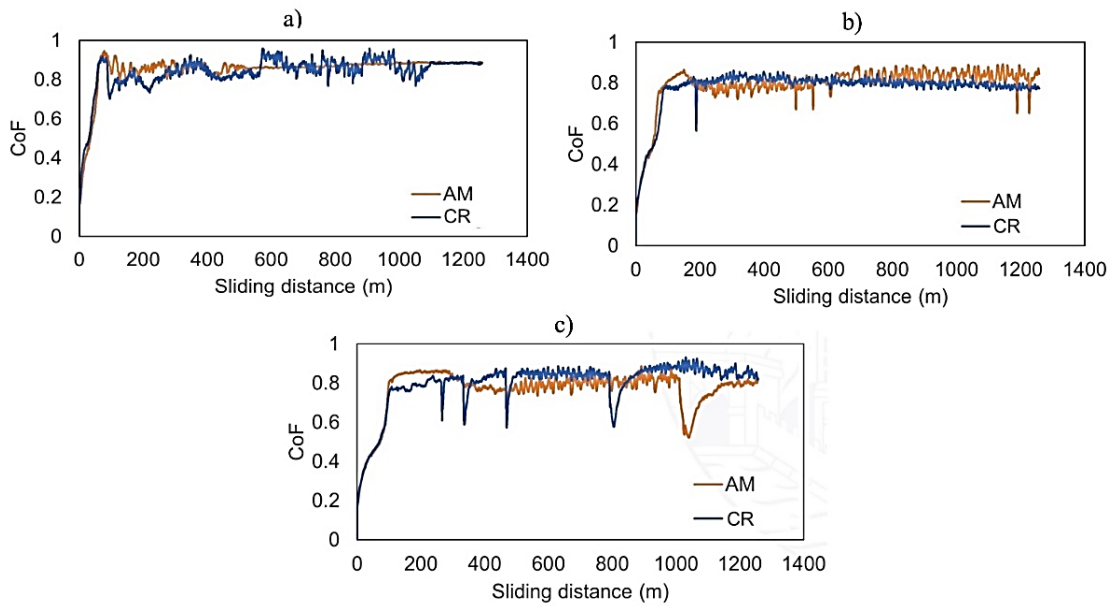


Figure 2-4. Coefficient of Friction (CoF) Vs sliding distance as a function of sliding velocity a) 22.5 cm/s, b) 50 cm/s and c) 62 cm/s

Figure 2-5 shows the samples wear rate (mm³/Nm) at the end of each test for all the considered conditions. Notwithstanding the difference in their microstructure, the AM and CR samples show wear rates that are very similar for each velocity, suggesting that the hardness plays a more significant role in the wear behavior compared to the

microstructural features of the samples. It can also be noted the increase in the wear rate with the sliding velocity, in accordance with the literature (Rai and Pathak 2004). In fact, the wear rate for the highest velocity results about 50% higher than for the tests carried out at 22.5 cm/s.

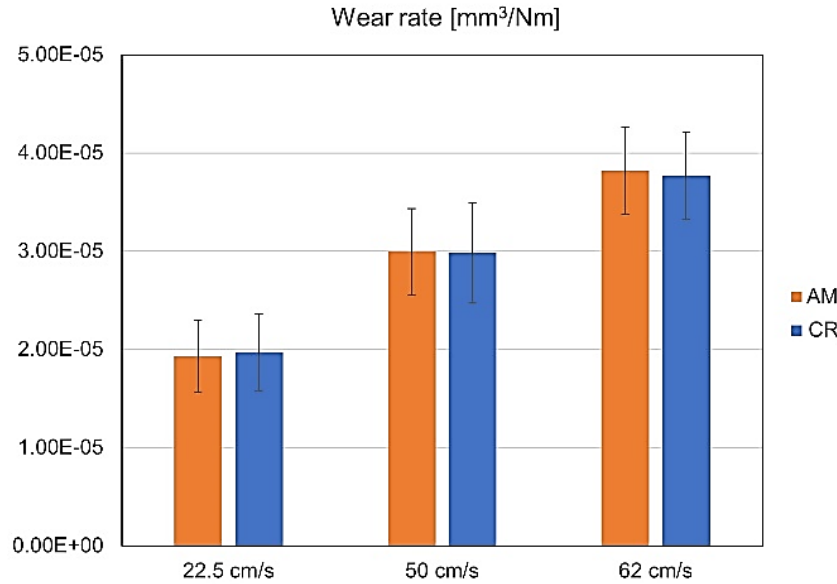


Figure 2-5. Wear rate ($\text{mm}^3 \text{N}^{-1} \text{m}^{-1}$) after 10000 laps of the tested samples

SEM analyses of the worn surfaces were carried out at the end of each test to investigate the wear mechanisms. These SEM images are presented in **Figure 2-6**. At the sliding velocity of 22.5 cm/s, both AM and CR samples show worn tracks with the presence of adhesion layers (**Figure 2-6a-b**), suggesting that the main wear mechanism is adhesion. Doubling the sliding speed from 22.5 to 50 cm/s, promotes the oxidation of the adhesive debris, embedded on the counterparts because the contact temperature is increased (Straffelini 2015), inducing two-body abrasion wear, as confirmed by the presence of ploughed grooves on the worn surfaces of both AM and CR samples (**Figure 2-6c-d**). A further increase of speed to 60 cm/s makes more evident this behavior, inducing the detachment of some embedded fragments from the steel ball and promoting a three-body abrasion mechanism. These oxidized wear fragments rest on the worn surfaces in form of thick layers unevenly distributed. The worn surface areas free from fragments show evident signs of adhesive wear and still abrasive grooves (**Figure 2-6e-f**).

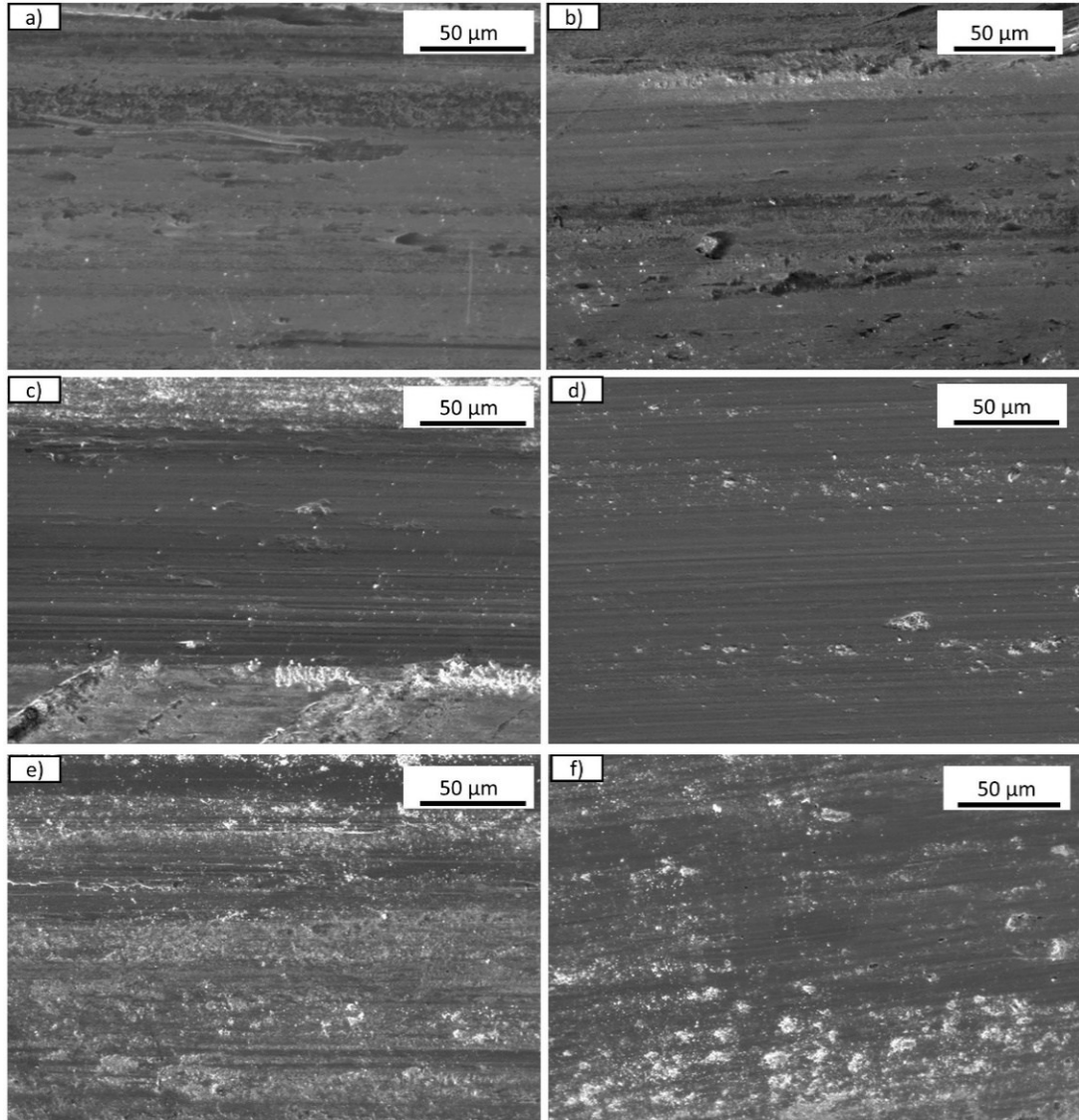


Figure 2-6. SEM images of wear tracks after 10000 laps for samples a) AM-22.5 cm/s b) CR-22.5 cm /s c) AM-50 cm/s d) CR-50 cm /s e) AM-62 cm/s and d) CR-62 cm /s

Finally, considering the result of corrosion tests, **Figure 2-7** shows the plot of corrosion potential (V) versus corrosion current density (A/cm²). The E_{corr} and I_{corr} values extrapolated from these plots with the Tafel method are summarized in **Table 2-2**. The results are in good agreement with data from literature (Suryawanshi et al. 2018). As can be noted, AM-horizontal and AM-vertical cross section exhibit a comparable corrosion behavior. Therefore, the anisotropy of the AM microstructure has a marginal role in the corrosion resistance to chlorine-bearing solutions. On the other hand, AM samples exhibit a nobler corrosion potential and a lower corrosion current density respect to the CR samples, indicating the better corrosion resistance of AM samples.

This behavior can be related to the slightly different chemical composition between AM and CR samples. Furthermore, as reported in the literature (Khan et al. 2022), the finer microstructure typical of LPBF components is often related to their better corrosion resistance respect to wrought samples. Moreover, this difference can be also related to the highest austenite volume fraction of AM samples that normally is a phase nobler than the martensitic matrix (Mahmood Khan et al. 2022).

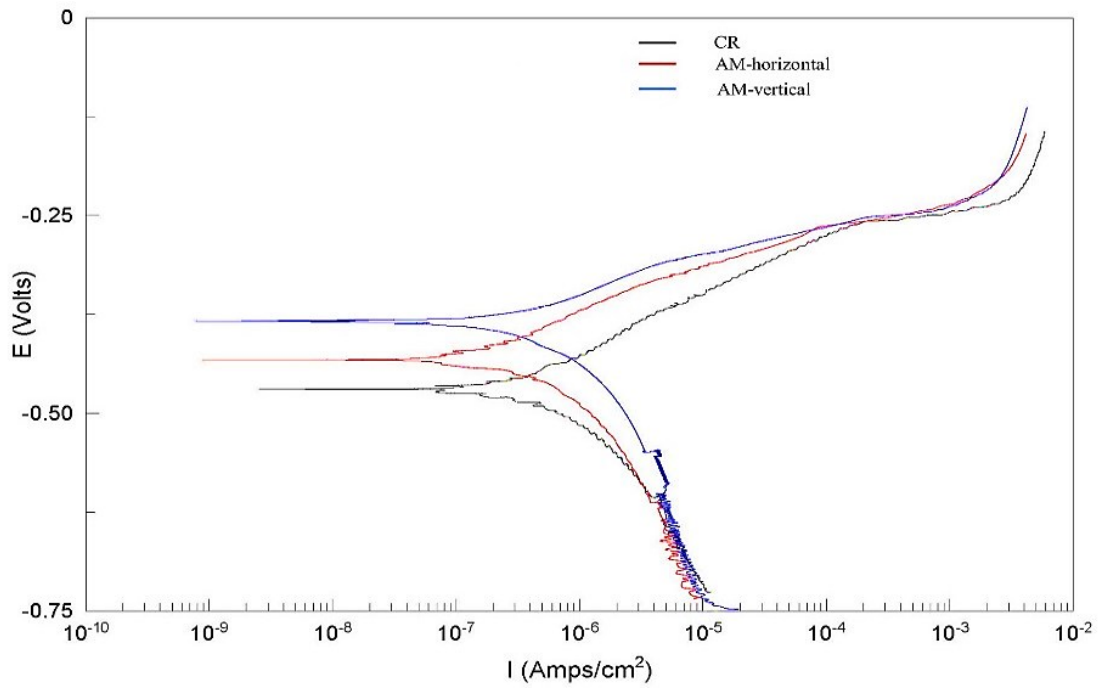


Figure 2-7 Potentiodynamic polarization tests results E_{corr} vs I_{corr}

Table 2-2 Average corrosion potential and corrosion current density values of the considered samples

Sample	E_{corr} (V)	I_{corr} ($\mu A/cm^2$)
AM-Vertical	-0.39	1.16
AM-Horizontal	-0.40	1.02
CR	-0.45	2.31

2.1.5. Conclusion

This work compares the sliding wear behavior and the corrosion resistance of 18Ni-300 maraging steel samples realized with two different manufacturing techniques: additive manufacturing and conventional forging route. The tests results showed that the AM components can compete with CR parts, notwithstanding the significant

differences in microstructure deriving from the different production routes. In particular, the microstructure of AM parts is a fully dense fine cellular martensitic structure with the boundary of the melt pools and scan tracks clearly visible also after the aging treatment, while CR microstructure consists of blocks of lath type martensite, with a resulting hardness of 53.9 ± 0.2 HRC and 54.6 ± 0.2 HRC respectively. XRD measurements permitted also to verify that AM samples have austenite content 6% more than CR samples. Notwithstanding these differences, the results of the sliding wear tests are very similar for AM and CR samples, in terms of COF and wear rate, suggesting that the microstructure plays a minor role on the wear behavior that is dominated by materials hardness. In particular, the wear mechanism detected on the worn surfaces was mainly adhesive, with the tendency to turn in abrasive at the increasing of the sliding speed, with a consequent increase of wear rate.

About polarization corrosion tests in chloride-bearing solution, AM samples showed better resistance with respect to CR ones, displaying nobler corrosion potentials and lower corrosion current densities with respect to CR ones. Again, the microstructural anisotropy of AM samples seems to have only marginal effect on corrosion resistance, as the AM-vertical and AM-horizontal produced similar figures.

2.1.6. Reference

- Aboulkhair, N. T., M. Simonelli, L. Parry, I. Ashcroft, C. Tuck & R. Hague (2019) 3D printing of Aluminium alloys: Additive Manufacturing of Aluminium alloys using selective laser melting. *Progress in Materials Science*, 106, 100578.
- Bai, Y., D. Wang, Y. Yang & H. Wang (2019) Effect of heat treatment on the microstructure and mechanical properties of maraging steel by selective laser melting. *Materials Science and Engineering: A*, 760, 105-117.
- Casati, R., J. N. Lemke, A. Tuissi & M. Vedani (2016) Aging Behaviour and Mechanical Performance of 18-Ni 300 Steel Processed by Selective Laser Melting. *Metals*, 6.
- E407, A. 2017. Standard Practice for Microetching Metals and Alloys. West Conshohocken, PA ASTM International.
- Elahinia, M., N. Shayesteh Moghaddam, M. Taheri Andani, A. Amerinatanzi, B. A. Bimber & R. F. Hamilton (2016) Fabrication of NiTi through additive manufacturing: A review. *Progress in Materials Science*, 83, 630-663.
- Ferreira, D. F. S., G. Miranda, F. J. Oliveira & J. M. Oliveira (2021) Predictive models for an optimized fabrication of 18Ni300 maraging steel for moulding and tooling by Selective Laser Melting. *Journal of Manufacturing Processes*, 70, 46-54.
- Giovagnoli, M., M. Tocci, A. Fortini, M. Merlin, M. Ferroni, A. Migliori & A. Pola (2021) Effect of different heat-treatment routes on the impact properties of an additively manufactured AlSi10Mg alloy. *Materials Science and Engineering: A*, 802, 140671.
- Handbook, A. 1993. *Properties and Selection: Irons, Steels, and High-Performance Alloys*.
- ISO/ASTM. 2019. ISO/ASTM 52911-1:2019, Additive manufacturing - Design - Part 1: Laser-based powder bed fusion of metals. West Conshohocken, PA: ASTM International.
- Jäggle, E. A., P.-P. Choi, J. Van Humbeeck & D. Raabe (2014) Precipitation and austenite reversion behavior of a maraging steel produced by selective laser melting. *Journal of Materials Research*, 29, 2072-2079.
- Jäggle, E. A., Z. Sheng, P. Kürsteiner, S. Ocylok, A. Weisheit & D. Raabe (2017) Comparison of maraging steel micro- and nanostructure produced conventionally and by laser additive manufacturing. *Materials*, 10.
- Khan, H. M., G. Özer, M. S. Yilmaz & E. Koc (2022) Corrosion of Additively Manufactured Metallic Components: A Review. *Arabian Journal for Science and Engineering*, 47, 5465-5490.
- Kim, Y. G., G. S. Kim, C. S. Lee & D. N. Lee (1986) Microstructure and mechanical properties of a cobalt-free tungsten-bearing maraging steel. *Materials Science and Engineering*, 79, 133-140.
- Lang, F. H. & N. Kenyon (1971) Welding of maraging steels. *Welding Research Council Bulletin*.
- Liu, C., Z. Zhao, D. O. Northwood & Y. Liu (2001) A new empirical formula for the calculation of MS temperatures in pure iron and super-low carbon alloy steels. *Journal of Materials Processing Technology*, 113, 556-562.
- Mahmood Khan, H., G. Özer, M. Safa Yilmaz & G. Tarakci (2022) Improvement of Corrosion Resistance of Maraging Steel Manufactured by Selective Laser Melting Through Intercritical Heat Treatment. *Corrosion*, 78, 239-248.

- Morito, S., X. Huang, T. Furuhashi, T. Maki & N. Hansen (2006) The morphology and crystallography of lath martensite in alloy steels. *Acta Materialia*, 54, 5323-5331.
- Narayana Murty, S. V. S. & S. C. Sharma (2022) Materials for Indian Space Program: An Overview. *Journal of the Indian Institute of Science*, 102, 513-559.
- Pennings, B., K. Hatanaka & L. Crebolder. 2015. Improved properties of high strength 18Ni maraging steels for pushbelt CVT applications by optimization of alloy compositions and surface hardening heat treatments. In *European Conference on Heat Treatment 2015 and 22nd IFHTSE Congress - Heat Treatment and Surface Engineering from Tradition to Innovation*.
- Pereloma, E. V., A. Shekhter, M. K. Miller & S. P. Ringer (2004) Ageing behaviour of an Fe–20Ni–1.8Mn–1.6Ti–0.59Al (wt%) maraging alloy: clustering, precipitation and hardening. *Acta Materialia*, 52, 5589-5602.
- Rai, D. & J. P. Pathak (2004) Influence of sliding velocity on wear behaviour of different microstructures of Ni-Cr-Mo-V steel. *Indian Journal of Engineering and Materials Sciences*, 11, 113-120.
- Rao, M. N. (2006) Progress in understanding the metallurgy of 18% nickel maraging steels. *International Journal of Materials Research*, 97, 1594-1607.
- Schnitzer, R., M. Schober, S. Zinner & H. Leitner (2010) Effect of Cu on the evolution of precipitation in an Fe-Cr-Ni-Al-Ti maraging steel. *Acta Materialia - ACTA MATER*, 58, 3733-3741.
- Shin, J.-H., J. Jeong & J.-W. Lee (2015) Microstructural evolution and the variation of tensile behavior after aging heat treatment of precipitation hardened martensitic steel. *Materials Characterization*, 99, 230-237.
- Sing, S. L., J. An, W. Y. Yeong & F. E. Wiria (2016) Laser and electron-beam powder-bed additive manufacturing of metallic implants: A review on processes, materials and designs. *Journal of Orthopaedic Research*, 34, 369-385.
- Song, J., Q. Tang, Q. Feng, S. Ma, R. Setchi, Y. Liu, Q. Han, X. Fan & M. Zhang (2019) Effect of heat treatment on microstructure and mechanical behaviours of 18Ni-300 maraging steel manufactured by selective laser melting. *Optics & Laser Technology*, 120, 105725.
- Straffelini, G. 2015. *Friction and Wear*. Springer Cham.
- Suryawanshi, J., T. Baskaran, O. Prakash, S. B. Arya & U. Ramamurty (2018) On the corrosion resistance of some selective laser melted alloys. *Materialia*, 3, 153-161.
- Tan, C., K. Zhou, W. Ma, P. Zhang, M. Liu & T. Kuang (2017) Microstructural evolution, nanoprecipitation behavior and mechanical properties of selective laser melted high-performance grade 300 maraging steel. *Materials & Design*, 134, 23-34.
- Vasudevan, V. K., S. J. Kim & C. M. Wayman (1990) Precipitation reactions and strengthening behavior in 18 Wt Pct nickel maraging steels. *Metallurgical Transactions A*, 21, 2655-2668.
- Xu, X., S. Ganguly, J. Ding, S. Guo, S. Williams & F. Martina (2018) Microstructural evolution and mechanical properties of maraging steel produced by wire+arc additive manufacture process. *Materials Characterization*, 143, 152-162.
- Yin, S., C. Chen, X. Yan, X. Feng, R. Jenkins, P. O'Reilly, M. Liu, H. Li & R. Lupoi (2018) The influence of aging temperature and aging time on the mechanical and tribological properties of selective laser melted maraging 18Ni-300 steel. *Additive Manufacturing*, 22, 592-600.
- Zhang, L.-C. & H. Attar (2016) Selective Laser Melting of Titanium Alloys and Titanium Matrix Composites for Biomedical Applications: A Review. *Advanced Engineering Materials*, 18, 463-475.

Zitelli, C., P. Folgarait & A. Di Schino (2019) Laser Powder Bed Fusion of Stainless Steel Grades: A Review. *Metals*, 9.

2.2. Cavitation erosion resistance of 1.2709 alloy produced via Laser-Powder Bed Fusion

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2.2.1. Abstract

Maraging steels, like 1.2709 (18Ni-300), are attractive materials for the aerospace, automotive, tooling, and bearing gear industries because of their high yield, tensile strength, and good toughness. The low-carbon martensite matrix and nanoscale intermetallic precipitates combine to provide distinctive mechanical properties. In particular, due to their low carbon content, these steels are easily weldable and are therefore appropriate for additive manufacturing (AM) processes like laser-based powder bed fusion (LPBF). The tooling and molding industry has just lately started using this fabrication technique to create inserts with conformal cooling channels that can extend the lifetime of the insert and core while boosting the cast quality. These parts are frequently exposed to high levels of stress, wear, and even aggressive conditions. In this context, this research focuses on a peculiar, and thus understudied, erosion phenomenon known as cavitation erosion. According to the ASTM G32 standard, the cavitation erosion resistance of 1.2709 maraging steel samples produced by additive manufacturing as well as by forging was investigated. Microstructural analyses were carried out to evaluate the effect of the different microstructures resulting from the different manufacturing techniques on erosion behavior. When compared to the forged maraging steel, the AM one shows less resistance to the initiation of the erosion phenomenon. Nevertheless, the wear rates of the two materials are comparable.

2.2.2. Introduction

In high-temperature applications, achieving rapid and uniform heat regulation within a component is of paramount importance. To control heat flow effectively, conformal cooling channels (CCCs) have gained widespread use in automotive and aerospace components. Furthermore, the integration of CCCs within mold inserts is increasingly prevalent in both plastic injection molding (PIM) and high-pressure die-casting (HPDC) processes. CCCs excel in maximizing heat extraction where conventional cooling systems often fall short, thereby enhancing process performance and the final quality of components (Venkatesh *et al.*, 2017). Mold thermoregulation is essential for producing high-quality parts as well as improving the die life and production cycle, which have a significant impact on the process' cost-effectiveness.

In the context of HPDC, these inserts are becoming fundamental for meeting the demands of modern lightweight automotive structural castings with a low carbon footprint, whose production requires larger and more intricate dies (Yang *et al.*, 2023). The fabrication of CCCs has been greatly simplified, thanks to significant advancements in additive manufacturing (AM) technologies. Complex geometries, tailored for cooling applications, can now be seamlessly produced using AM techniques (Brooks and Brigden, 2016). Particularly, laser-based AM methods, such as laser powder bed fusion (L-PBF), are commonly employed for manufacturing CCCs with intricate designs (Peças *et al.*, 2019).

Within this scenario, maraging steels emerge as a solution that can address both the challenges associated with mold inserts and the characteristics of the L-PBF process. In fact, maraging steels offer a unique blend of high ultimate tensile strength (UTS) even at high temperature, exceptional fracture toughness, good weldability, and dimensional stability (Piekło and Garbacz-Klempka, 2020). These two latter properties result fundamental for the processability by L-PBF where the powder material is melted and welded, undergoing extremely rapid cooling rate. Thus, these properties have led to the adoption of maraging steels, such as 1.2709, as mold inserts, even though they exhibit lower heat conductivity compared to traditional mold tool steels (e.g., H11). However, this limitation could become negligible with the implementation of CCCs.

While the mechanical properties required for the intended applications of these components are well-documented, there exists a notable gap in our understanding of the surface properties of additively manufactured (AMed) maraging components, despite their critical importance in various applications. Surface quality is particularly crucial in mold areas where it can influence performance significantly. Notably, cavitation erosion stands out as a prominent mechanism responsible for surface damage when a component interacts with a liquid experiencing rapid pressure fluctuations (Abdullah *et al.*, 2011).

2.2.3. Materials and methods

The maraging steels under examination were produced by Deutsche Edelstahlwerke Specialty Steel GmbH & Co. KG by using two distinct manufacturing techniques. The first manufacturing process encompassed several steps, including electric arc furnace melting, ladle furnace refinement, vacuum arc remelting, and final forging (named process F).

For the AM samples, a commercial powder known as Printdur® Powderfort, with a composition close to 1.2709 maraging steel was employed (named process AM). Regarding the particle size of the AM feedstock material, approximately 3.4 vol.% of the particles has a diameter smaller than 20 µm, 45.6 vol.% smaller than 38 µm, and a significant 98.2 vol.% smaller than 53 µm. The powder exhibits a flow rate of 15.6 s/50g and has an apparent density of 3.99 g/cm³. The fabrication of maraging steel samples through AM was accomplished using a commercially available laser-based powder bed fusion system which specific process parameters are classified information, as previously mentioned in the literature (Tonolini *et al.*, 2022). The resulting AM samples were discs, measuring 57 mm in diameter and 12 mm in height, with their axis oriented parallel to the building direction (BD).

In contrast, the forged maraging steel samples were derived from the Cryodur®2709 commercial alloy. These samples originated from a forged round bar with a diameter of 60 mm and were machined to match the sizes of the AM samples.

Table 2-3 shows the chemical composition of the AM and F maraging steels. The light difference in the percentage of alloying elements is related to the different manufacturing process requirements.

Table 2-3. Samples mean chemical composition.

El. (wt%)	C	Si	Mn	P	S	Cr	Mo	Ni	Co	Ti	N	O	Fe
AM	0.01	0.2	0.3	0.01	0.006	0.1	5	17.9	13.4	-	0.007	0.026	Bal.
F	0.004	0.02	0.03	<0.003	0.0014	0.1	4.95	18.3	9.75	1.13	-	-	Bal.

Moreover, to attain comparable ultimate mechanical properties, notwithstanding the different manufacturing procedures, the specimens underwent distinct heat treatment processes. For the forged samples, this involved a one-hour solution treatment at 820 °C, followed by rapid cooling at room temperature in air, and final aging for 5 hours and 30 minutes at 490 °C. Conversely, for the AM samples, only an aging treatment was implemented. This process consisted of holding the samples at 490 °C for 4 hours, promoting the formation of precipitates, following the methodology outlined by (Casati *et al.*, 2016). Notably, these specific heat treatment parameters were chosen based on the manufacturer's expertise to achieve equivalent hardness levels for both the AM and F samples.

Optical analyses were performed by Leica DMI 5000M (Wetzlar, Germany) optical microscope (OM). The metallographic analysis was performed by etching the mirror polished samples with modified Fry's reagent and Nital 4%. Samples porosities were characterized in terms of fraction of area through the analysis of 10 images (magnification 500x) by OM. The fraction of porosities (%) was determined as the ratio between the total area of porosities and the analysed area of samples.

HRC hardness measurements were performed using an LTF Galileo Ergotest Comp 25 testing machine (applied load of 1471 N) on the investigated samples.

Cavitation tests were conducted following the “stationary specimen method”, according to the ASTM G32-16 (2021) standard. The polished to mirror finish surface was exposed to cavitation. A Felisari GV2000 ultrasonic device with a vibration frequency of 20.0 kHz, a vibration amplitude of 50 µm, and a peak electrical power of 2 kW was utilized in the tests. The ultrasound probe (sonotrode) is composed of a

Ti6Al4V waveguide and an Inconel 625 horn with a final amplification diameter of 18 mm (Girelli *et al.*, 2018). The sample was obtained by cutting with a metallographic saw starting from the discs and was brought, by polishing, to a dimension such that it could be inserted into a specially designed sample holder. Due to the shape of the starting samples, the surface perpendicular to the BD was the one exposed to testing. The test was carried out with the sample immersed in a tank containing distilled water, at a distance of 0.50 mm from the surface of the tip of the sonotrode at the rest position. The positioning was achieved using a tab with a thickness equal to the previously indicated distance, ensuring that the sample was securely held by the gripping system. The ambient temperature was maintained at $23 \pm 2^\circ\text{C}$. Periodic interruptions of the test were made to measure the weight loss, with a precision of 0.1 mg, and observe the morphology of the eroded surface using a DMS300 digital microscope. The total test duration was set at 24 hours, upper time limit defined by the ASTM G32-16 standard, due to the high material resistance to erosion measured at early testing times.

The data were initially expressed as mean depth of erosion (MDE) and mean depth of erosion rate (MDER), as required by the standard. Additionally, for clarity, the results are presented in terms of cumulative mass loss over the test duration. Given the nearly identical densities of the materials, this presentation method was considered more suitable for the purpose of this study. For the calculation of MDE and MDER, the volume removed was determined based on the sample's density, while the surface of the material involved in the erosion was approximated as equal to the circular section of the tip of the sonotrode.

Low magnification images, obtained through a DSM300 digital microscope (Leica, Wetzlar, Germany), were used to analyse the erosion damage during the above reported steps. The displayed images are the result of digital merging of 9 shots per sample. In addition, cross sections of the samples at the end of the test were analysed by OM after polishing to mirror finish.

Finally, scanning electron microscope (LEO EVO 40, Carl Zeiss AG, Milan, Italy) was used for the analysis of the damaged surface after three selected test-time intervals (2, 4 and 8 hours).

2.2.4. Results and discussion

Fig. 2-8 presents optical microscope images, offering a representative view of the sections tested in the samples. **Fig. 2-8a** displays the microstructure of the forged samples after solution and aging treatment. When subjected to etching with Fry's reagent, a fully martensitic microstructure is revealed, characterized by martensite blocks with varying orientations. **Fig. 2-8b** showcases the surface of the additive manufactured sample. This surface is marked by cellular martensite, along with the recognizable overlapped and elongated scan tracks typically associated with as-built AM components. Importantly, after the aging treatment, the scan tracks remain observable. Additionally, the porosity detection from image analysis resulted in a 99.82 ± 0.08 % dense component. Whereas the F samples are considered fully dense. In contrast, areas that were left unetched can be identified at the boundaries of the melt pools and within the melt pools themselves. Earlier research findings support the assertion that these zones correspond to the positive segregation of Cr and Mo. This segregation takes place during solidification due to the partitioning of these elements into the final liquid phase to solidify. This phenomenon is typically observed at cellular and dendritic boundaries, as well as at the interfaces of scan tracks and melt pools. Such localization contributes to the formation of retained austenite within AM maraging steels (Tonolini *et al.*, 2022).

Interestingly, despite Cr and Mo working as ferrite stabilizers, their increased concentration within the segregated regions has a localized impact. This leads to a reduction in the martensite starting temperature (M_s) of the steel to approximately -43 °C, as calculated using the empirical equation introduced by (Liu *et al.*, 2001). Consequently, austenite is stabilized at room temperature within these regions.

Finally, it is worth noting that the hardness of the F samples, measured at 54.6 ± 0.2 HRC, is approximately 1% higher than that of the AM samples, which measured 53.9 ± 0.2 HRC. This observation serves as evidence that the chosen heat treatment parameters were aptly tailored to their respective materials.

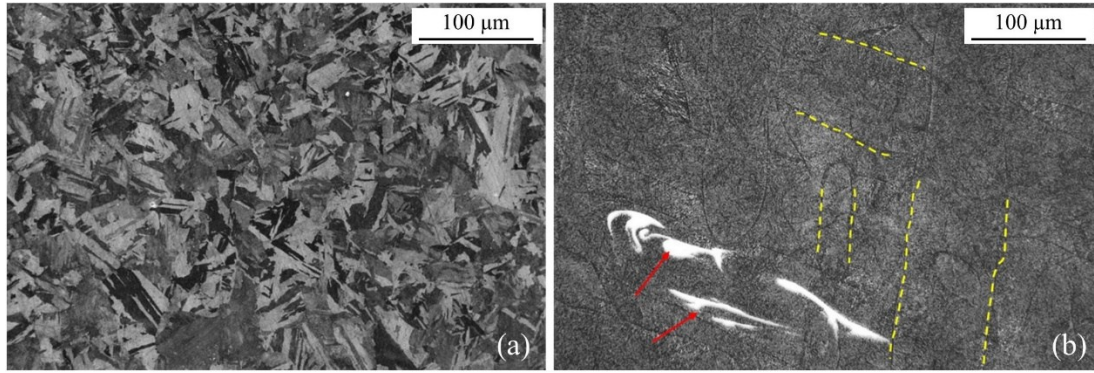


Fig. 2-8 – (a) Forged sample etched with Fry's reagent; (b) AMed sample etched with Nital 4%, the dashed yellow lines highlight some melt pool boundary, and the red arrows point at unetched zones that correspond to segregation of Cr and Mo.

The results from cavitation tests are represented in **Fig. 2-9**, illustrating MDE and MDER as a function of exposure time. These data represent the mean values obtained from two repetitions of the tests. In accordance with ASTM G32 standards, it is established that, the material accumulates plastic deformation and internal tensions before experiencing significant material loss (incubation period). This period corresponds to a time when the erosion rate is zero. Although the erosion rate values during the initial hours were not precisely zero, these were considered part of the incubation period due to the extremely low mass loss. This interpretation is further supported by the results of the analysis presented in **Fig. 2-10**, where the erosion rate is measured by plotting a linear regression in the steady-state period while the x-intercept of this linear regression is the incubation period (Taillon *et al.*, 2016). An incubation period of 4 hours and 7 hours was calculated for the AM and F alloys, respectively (**Fig. 2-10**). Furthermore, the analysis in **Fig. 2-10** also reveals that, following the incubation period, the erosion rate for both materials remains nearly constant, approximately at 0.67 mg/h in the steady-state erosion regime. After 24 hours of exposure, a total material loss of 13.5 ± 0.8 mg (MDE: 6.5 ± 0.4 μm) and 10.7 ± 2.9 mg (MDE: 5.2 ± 1.4 μm) is recorded for the AM and forged samples, respectively.

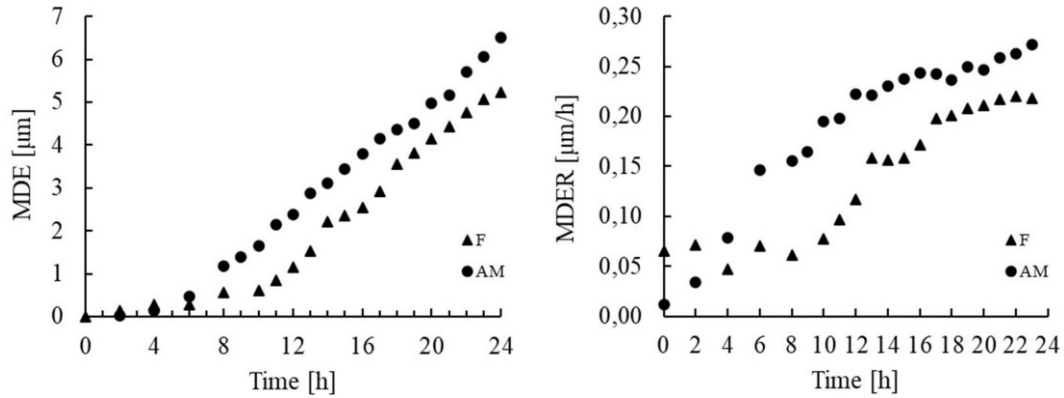


Fig. 2-9 – Mean Depth of Erosion (MDE) and Mean Depth of Erosion Rate (MDER) as functions of exposure time.

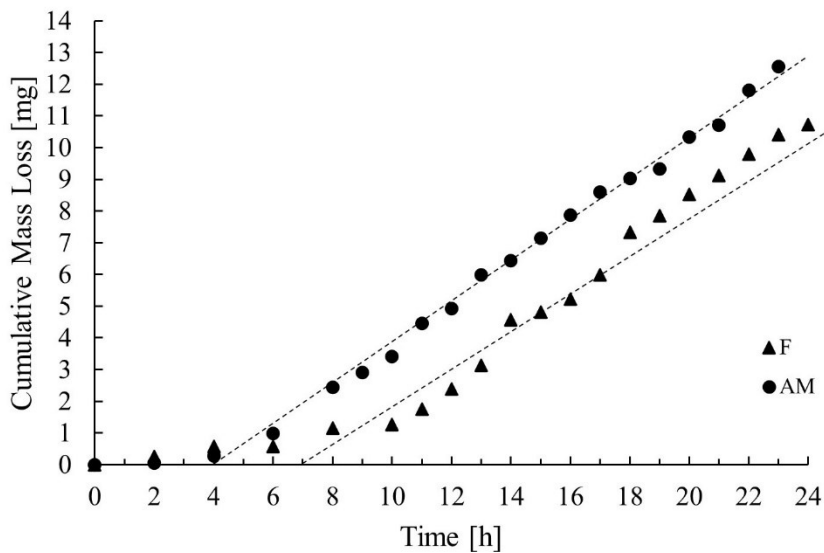


Fig. 2-10 – Cumulative mass loss as a function of exposure time.

In **Fig. 2-11** images from digital microscope reveal qualitatively how the erosion evolves over the samples surface. Since the total mass loss of the samples is low, few differences can be detected looking at the surface hour by hour with a low magnification optical analysis. Thus, just the observation made at 4h and 20h are presented. At 4h the surfaces appear already covered with a ring-like shaped grey shade. In fact, even though almost no mass loss was measured at this time interval, the surfaces were plastically deformed by the cavitation micro-jets and shock waves. On the other hand, at 20h the erosion process was fully developed. The erosion ring-like pattern is characteristic of the “stationary specimen method” (Chahine *et al.*, 2014; Astm, 2021).

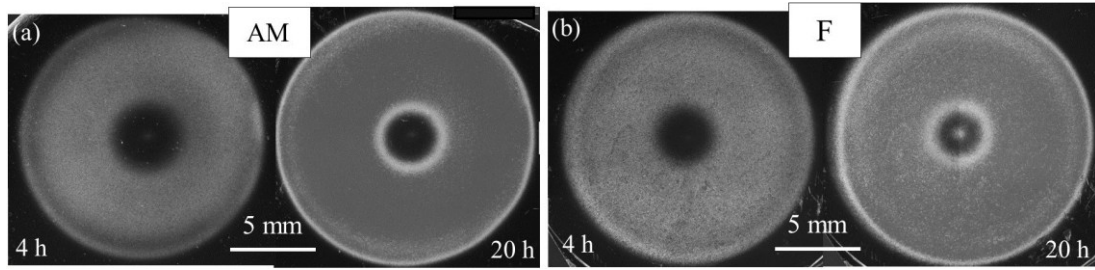


Fig. 2-11 – Stereomicroscopy images of (a) AM sample and (b) Forged sample after 4 and 20 hours of exposure to cavitation erosion.

The prior macroscopic observations provide limited insight into the underlying micro-damage mechanisms. However, upon conducting an optical microscopy analysis, the initial distinctions begin to emerge. **Fig. 2-12** displays unetched sections of AM and forged samples at the end of the testing period. In the case of the AM sample, cracks propagate perpendicular to the surface, and rounded crates associated with porosity are visible. Conversely, in the forged sample, cracks propagate parallel to the surface, eventually removing larger debris. In detail, when the total stress reaches the maximum stress bearable by the material surface, a crack form. The crack keeps expanding and deforming, in a fatigue like manner, with continued exposure to the cavitation erosion conditions (Tian *et al.*, 2022).

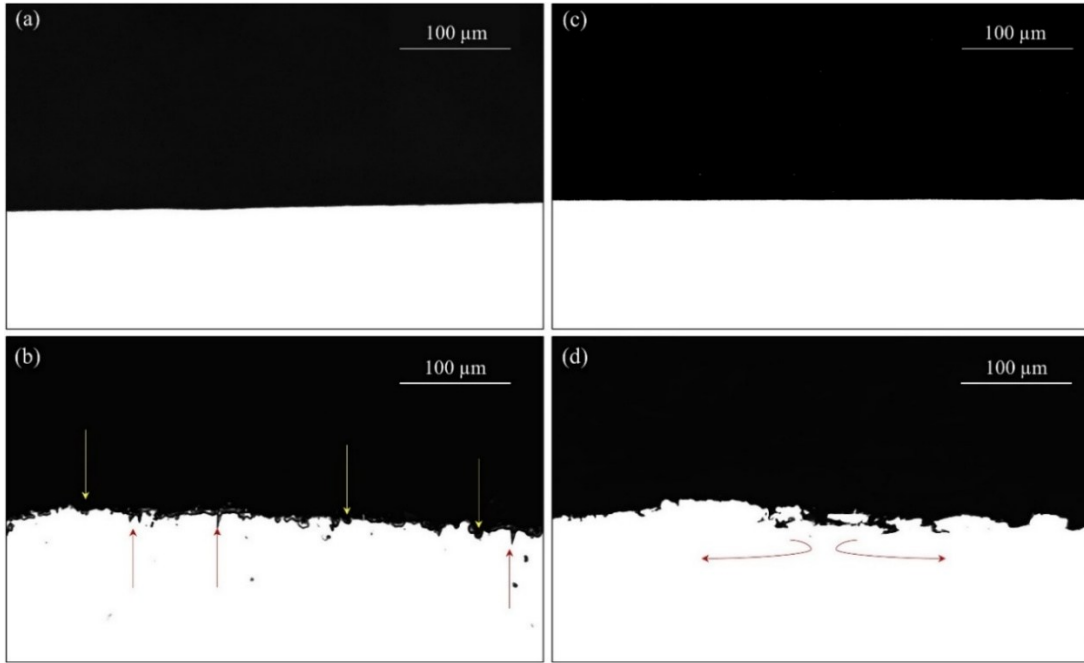


Fig. 2-12. (a) AM sample surface before testing (b) AM sample surface at the conclusion of testing period, the yellow arrows point at rounded crates while the red ones at sharp cracks; (c) forged sample surface before testing; (d) forged sample surface at the conclusion of testing period, the red arrows indicate the direction of cracks propagation.

At different testing intervals, SEM was employed to observe the morphology of the eroded surface. Following 2 hours of testing, several pits randomly emerged across the surface of both materials (**Fig. 2-13a, d**). Furthermore, the surface exhibited a progressively increasing roughness. These characteristics align with the typical early stages of cavitation erosion, marked by plastic deformation of the material rather than substantial mass loss (Heathcock *et al.*, 1982). The collapse of cavitation bubbles generates repetitive shock waves impacting the material's surface, inducing dislocation movements that result in plastic deformation and pitting, eventually leading to the removal of particles from the surface. Notably, the surface of the AM sample displayed a greater number of erosion initiation zones compared to the F sample.

At the 4-hour mark, corresponding to the incubation time of the AM samples, numerous larger and deeper craters emerged on the AM sample's surface (**Fig. 2-13b**). In contrast, as the forged sample had not yet reached its incubation time, its surface remained predominantly covered with small erosion pits, uniformly distributed, and exhibited only minor corrugations (**Fig. 2-13e**). Few craters were found, similar to the observations from the previous step. The more evident damage for the AM sample is

consistent with the shorter incubation periods as compared to the behaviour of F sample. Interestingly, several craters detected on the surface of AM sample followed preferential paths, consistent with some observations made at the 2-hour testing time. The shape and spatial distribution of the craters identified on the surface of the AM sample during these initial stages of cavitation erosion therefore indicates that certain microstructural features serve as preferential sites for erosion nucleation, as known for the grain boundaries (Bregliozzi *et al.*, 2005).

In fact, microstructural analysis (Fig. 1) revealed that the melt pool boundaries persisted even after the aging treatment, and areas of elements segregation may contribute to the presence of austenite, even at room temperature. These can represent weak points where erosion cavitation damage can more easily nucleates. This can be supported by SEM analysis, which highlighted a linear pattern in the formation of erosion craters that could be influenced by the presence of the melt pool boundaries within the microstructure of the AM samples. Furthermore, after 4 hours of testing, a notable number of holes resembling the unetched segregations observed in the metallographic analysis became clearly visible. In addition, the effect of porosities, even if they are scarce, cannot be neglected as known from previous studies (Tocci *et al.*, 2019).

On the other hand, the more even distribution of smaller-sized craters in the microstructure of the F samples is consistent with their lower microstructural imperfections.

After 8 hours of exposure, the surface had undergone uniform erosion for both tested materials (**Fig. 2-13c, f**). This suggests that prolonged exposure to cavitation eventually led to a stress level that result in microcracks and subsequent material removal. Once this mechanism is developed, the surface appears uniformly eroded and the role played by microstructural imperfection on the initiation of the material removal mechanism cannot be recognised. This is supported by the fact that, after the incubation time, the erosion rate was the same for both materials.

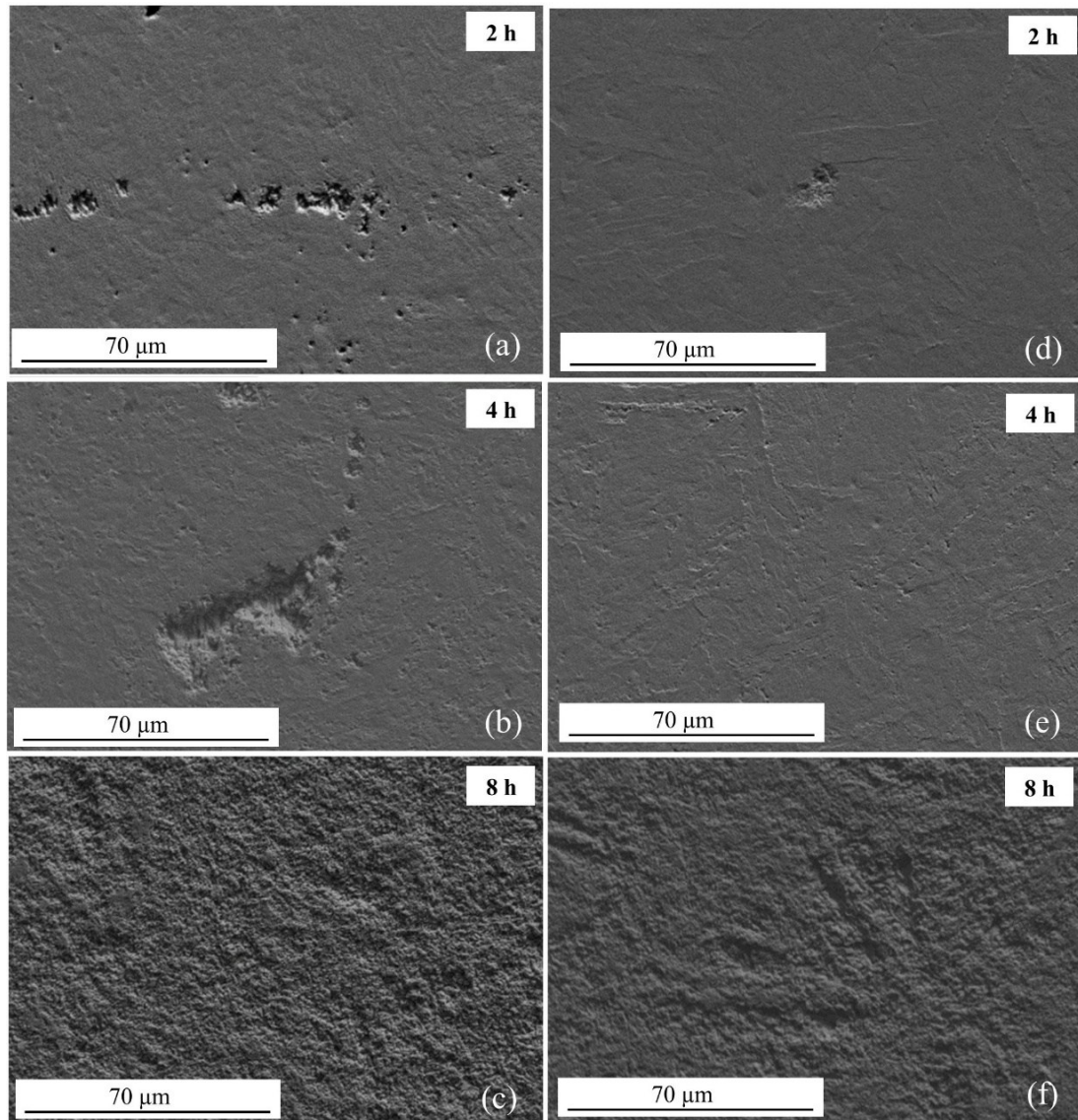


Fig. 2-13. SEM images of the eroded surface at different testing times; (a-b-c) images of the AM sample; (d-e-h) images of the F sample.

2.2.5. Conclusion

This investigation has undertaken a comparative assessment of the resistance to cavitation erosion in 1.2709 maraging steel specimens produced via two distinct manufacturing methodologies: additive manufacturing and the traditional forging process. The empirical findings substantiate the capacity of additive manufacturing components to effectively contend with their forged counterparts, notwithstanding marked disparities in microstructural characteristics stemming from their different production techniques. Specifically, the additively manufactured components manifest

a fully consolidated, fine-grained cellular martensitic structure, where the delineations of the melt pools and scan paths endure even post aging treatment. In contrast, the forged counterparts present a microstructure constituted by block of lath martensite. Notwithstanding these contrasting microstructural features, the outcomes of the cavitation erosion assessments manifest a remarkable similarity, implying that their respective hardness attributes, in fact equivalent, may be the determining factor of performance. In fact, the difference in material loss is statistically zero and the erosion rate in the steady-state erosion regime remain nearly constant, approximately at 0.67 mg/h for both materials, with the primary distinction being the shorter incubation time observed for the AM samples, which was 3 hours lower than that of the forged ones. Given the near-identical hardness of these parts, this phenomenon is likely attributed to microstructural features/defects at the surface that act as preferential sites for erosion nucleation, as indicated by a combination of optical microscopy and SEM analysis. Indeed, through SEM and metallographic analysis, it appears that microstructural imperfections, low-hardness austenite, melt pool boundaries and/or porosities may be responsible for the shorter incubation time of AM samples. Further research is essential to gain a deeper understanding of which specific defect clusters represent a greater risk for cavitation erosion. This understanding will enable the development for AM components with improved performance in the context of cavitation erosion resistance.

2.2.6. References

- Abdullah, A.; Malaki, M.; Baghizadeh, E. On the impact of ultrasonic cavitation bubbles. Proceedings of the Institution of Mechanical Engineers, Part C: Journal of Mechanical Engineering Science, v. 226, n. 3, p. 681-694, 2012/03/01 2011.
- ASTM. ASTM G32-16(2021) Standard Test Method for Cavitation Erosion Using Vibratory Apparatus 2021.
- Bregliozzi, G. et al. Cavitation wear behaviour of austenitic stainless steels with different grain sizes. Wear, v. 258, n. 1, p. 503-510, 2005.
- Brooks, H.; Brigden, K. Design of conformal cooling layers with self-supporting lattices for additively manufactured tooling. Additive Manufacturing, v. 11, p. 16-22, 2016.
- Casati, R. et al. Aging Behaviour and Mechanical Performance of 18-Ni 300 Steel Processed by Selective Laser Melting. Metals. 6 2016.
- Chahine, G. et al. Advanced Experimental and Numerical Techniques for Cavitation Erosion Prediction. 2014.
- Girelli, L. et al. Investigation of cavitation erosion resistance of AlSi10Mg alloy for additive manufacturing. Wear, v. 402-403, p. 124-136, 2018.
- Hattori, S. et al. Effect of liquid properties on cavitation erosion in liquid metals. Wear, v. 265, n. 11, p. 1649-1654, 2008.
- Heathcock, C. J.; Protheroe, B. E.; Ball, A. Cavitation erosion of stainless steels. Wear, v. 81, n. 2, p. 311-327, 1982.
- Liu, C. et al. A new empirical formula for the calculation of MS temperatures in pure iron and super-low carbon alloy steels. Journal of Materials Processing Technology, 2001, 1-3. p.556-562.
- Peças, P. et al. Chapter 4 - Additive Manufacturing in Injection Molds—Life Cycle Engineering for Technology Selection. Advanced Applications in Manufacturing Engineering: Woodhead Publishing, 2019.
- Piekło, J.; Garbacz-Klempka, A. Use of Maraging Steel 1.2709 for Implementing Parts of Pressure Mold Devices with Conformal Cooling System. Materials. 13 2020.
- Taillon, G. et al. Cavitation erosion mechanisms in stainless steels and in composite metal-ceramic HVOF coatings. Wear, v. 364-365, p. 201-210, 2016.
- Tian, Y. et al. In-situ SEM investigation on stress-induced microstructure evolution of austenitic stainless steels subjected to cavitation erosion and cavitation erosion-corrosion. Materials & Design, v. 213, p. 110314, 2022.
- Tocci, M. et al. Wear and Cavitation Erosion Resistance of an AlMgSc Alloy Produced by DMLS. Metals. 9 2019.
- Tonolini, P. et al. Wear and corrosion behavior of 18Ni-300 maraging steel produced by laser-based powder bed fusion and conventional route. Procedia Structural Integrity, 2022.
- Venkatesh, G.; Ravi Kumar, Y.; Raghavendra, G. Comparison of Straight Line to Conformal Cooling Channel in Injection Molding. Materials Today: Proceedings, v. 4, n. 2, Part A, p. 1167-1173, 01/01/2017.

Yang, Q.; Wu, X.; Qiu, X. Microstructural Characteristics of High-Pressure Die Casting with High Strength–Ductility Synergy Properties: A Review. *Materials*. 16 2023.

2.3. The corrosion resistance of maraging steel 1.2709 produced by L-PBF in contact with molten Al-alloys

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2.3.1. Abstract

Nowadays there is a growing interest in the use of secondary Al-alloys for high-pressure die casting to obtain structural parts. To guarantee appropriate performance, these alloys are characterized by a lower Fe content ($< 0.15\%$) than conventional secondary ones, commonly used in the production of non-structural parts. This makes them more susceptible to the phenomenon of die-soldering, thus resulting in a decrease in the service life of dies and inserts. The production of complex and demanding castings requires appropriate dies and materials, especially in high stressed areas where higher-performance steel inserts are used. Recently, maraging steel has been applied to these issues. Thanks to the good weldability of maraging steels, these alloys are nowadays also processed by additive manufacturing (AM) techniques, to obtain very complex parts like inserts with conformal cooling channels, able to extend the life of the inserts themselves, increasing productivity. In this context, this work aimed at the evaluation of the dissolution of maraging steel (1.2709) samples obtained via laser-based powder bed fusion (L-PBF) into molten AlSi7Mg (B356.2) through static immersion tests carried out at 720 °C for different times, to evaluate their response to the die-soldering phenomenon. For comparison, forged maraging steel samples were also considered, to investigate the effect of the different microstructures on the dissolution behavior. As well as a conventional H11 steel, to obtain benchmark data. The corrosion resistance of the samples was evaluated by measuring the samples' dimensional variation after the tests. Furthermore, SEM-EDS analysis was carried out to investigate the extent and the composition of the intermetallic layer formed on the samples' surface.

2.3.2. Introduction

In the context of industries such as automotive manufacturing, there is a discernible trend towards the substitution of traditional structural steel components with aluminum alloy counterparts. This transition is driven by the overarching goal of reducing the overall weight of transportation systems, thereby mitigating the environmental footprint (Cecchel *et al.*, 2018). Concurrently, there is a growing interest in the production of intricate, large-scale, and thin-walled structural components, particularly through High-Pressure Die Casting (HPDC) processes. The AlSi10Mg alloy has emerged as a prominent and extensively researched aluminum alloy for HPDC structural applications, owing to its industrial relevance. Nevertheless, at the European level, there is a concerted effort to diminish reliance on critical raw materials (European *et al.*, 2023). This has led to increased attention on aluminum alloys characterized by lower silicon content, with AlSi7Mg being a notable example, frequently employed in shell casting applications. Notably, the reduction in silicon content in these alloys results in elevated melting temperatures, which, in turn, accentuates the susceptibility of steel molds to corrosion. These considerations give rise to a compelling need to develop optimized molds capable of prolonging their operational lifespan. One prospective route for addressing this challenge involves the incorporation of high-performance inserts including conformal cooling channels, offering a potential solution to enhance die life (Venkatesh *et al.*, 2017).

The advent of additive manufacturing (AM) technologies has significantly simplified the fabrication of Conformal Cooling Channels (CCCs), enabling the seamless production of intricate geometries tailored for cooling applications. Laser-based AM methods, such as laser powder bed fusion (L-PBF), have become prevalent for crafting CCCs with complex designs (Brooks and Brigden, 2016). Within this framework, maraging steels emerge as a viable solution able to meet the challenges associated with mold inserts and the characteristics of the L-PBF process. Maraging steels exhibit a distinctive combination of attributes, including high ultimate tensile strength (UTS), exceptional fracture toughness, high weldability, and dimensional stability. Consequently, maraging steels like 1.2709 have found utility as mold inserts (Piekło and Garbacz-Klempka, 2020).

While the mechanical properties requisite for the intended applications of these components has been extensively documented, a noticeable knowledge gap exists concerning the hot-corrosion properties of additively manufactured (AMed) maraging components. This knowledge deficit is particularly significant, given the critical role of these properties across various applications. AMed maraging components, when exposed to molten aluminium without the presence of protective layers or in instances where these protective layers are damaged, undergo severe corrosion. This corrosion not only reduces mold longevity but also promotes die soldering and the undesired formation of brittle Fe-intermetallic particles within the cast part. In this context, the primary aim of this study is to assess and compare the hot-corrosion behaviour of maraging steel specimens produced with both the AM technique and the conventional forging process when immersed in molten aluminium alloy. For comparison, the H11 tool steel, widely adopted as mold material, was also investigated.

2.3.3. Materials and methods

Maraging steels considered in this study were produced by Deutsche Edelstahlwerke Specialty Steel GmbH & Co. KG with two distinct manufacturing processes, namely Additive Manufacturing (AM) and forging (F). The forged alloy underwent a series of sequential manufacturing steps, including electric arc furnace melting, ladle furnace refinement, vacuum arc remelting, and final forging. For the AM samples, a commercial powder known as Printdur® Powderfort, possessing a composition close to that of 1.2709 maraging steel, was utilized.

Regarding the particle size of the AM feedstock material, it was reported that approximately 3.4 vol.% of the particles had a diameter smaller than 20 μm , while 45.6 vol.% were smaller than 38 μm , with a substantial 98.2 vol.% exhibiting sizes smaller than 53 μm . The powder displayed a flow rate of 15.6 s/50g and possessed an apparent density of 3.99 g/cm³. The process for fabricating maraging steel samples through AM was executed using a commercially available laser-based powder bed fusion (L-PBF) system, whose specific process parameters were classified information. The resulting AM samples had a cylindrical shape, measuring 57 mm in

diameter and 12 mm in height, with their axis being oriented parallel to the building direction (BD).

In contrast, the forged maraging steel samples were derived from the Cryodur®2709 commercial alloy. These samples were obtained from a forged round bar with an original diameter of 60 mm and underwent machining to match the final dimensions of the AM samples. To achieve their ultimate mechanical properties, the specimens were subjected to distinct heat treatment processes.

For the forged samples, this process consisted of a one-hour solution treatment at 820 °C, followed by rapid cooling in ambient air, followed by aging for 5 hours and 30 minutes at 490 °C. Conversely, for the AM samples, only an aging treatment was carried out, holding the sample at 490 °C for 4 hours to promote the formation of precipitates. These samples derive from a previous work where additional data can be found (Tonolini *et al.*, 2022). Furthermore, samples of more conventional die tool steel H11 were also machined and included in the testing. The chemical composition of all investigated samples is reported in **Table 2-4**.

The actual samples for the hot-corrosion test were machined by wire EDM (Electrical Discharge Machining) from their cylindrical shape to obtain 20x10x5 mm samples with a through-hole on the larger face. Prior to the immersion tests, the microstructural characterization was carried out on mirror-polished samples etched with Nital 2% by using a DMI 5000M optical microscope (Leica, Wetzlar, Germany) provided with an image analysis software (Las 4.12). By analyzing 10 images at 500x magnification collected from each sample, the pores fraction area was measured as the ratio of the total area of porosities to the area of the samples that were subjected to analysis.

Table 2-4. Samples mean chemical composition: maraging steel additively manufactured (AM) and forged (F); H11 tool steel.

El. (wt%)	C	Si	Mn	Cr	Mo	Ni	Co	V	Ti	Fe
AM	0.01	0.2	0.3	0.1	5	17.9	13.4	-	-	Bal.
F	0.004	0.02	0.03	0.1	4.95	18.3	9.75	-	1.13	Bal.
H11	0.37	1	0.4	5.3	1.3	-	-	0.4	-	

The static immersion test apparatus, schematized in **Fig. 2-14** involves the use of an electric furnace equipped with a graphite crucible. The Al alloy used was a primary low iron AlSi7Mg (B356.2). Approximately 1 kg (1020 ± 20 g) of Al alloy was molted

for each test and held at 740 ± 3 °C. The quantity of molten Al was defined to guarantee a sufficient volume to cover the sample and to be far from a possible Fe saturation condition for the melt. The temperature was chosen considering that the AlSi7 alloy has a higher melting temperature than conventional AlSi10 alloys typically used for HPDC applications.

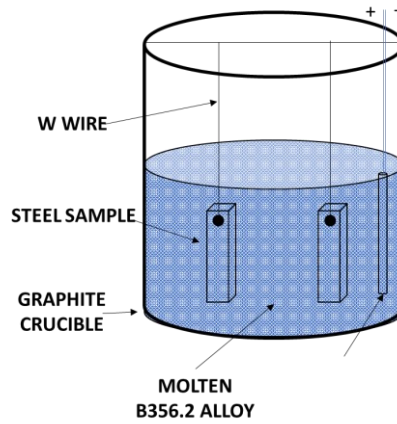


Fig. 2-14. Schematization of the static immersion test apparatus

2.3.4. Results and discussion

Figure 2-15b shows the horizontal cross-section (SD) microstructure of the AM sample. Despite the aging heat treatment, the superimposed elongated scan paths, characteristic of as-fabricated AM components, are still visible. Additionally, the vertical cross-section (BD) of **Figure 2-15a** reveals semi-elliptical molten pools, with dimensions that are consistent with the laser scan parameters and construction strategy employed. Importantly, the porosity detection with optical microscope images analysis resulted in a 99.82 ± 0.08 % dense material. Unetched regions are observable at the boundaries and inside the melt pools in both vertical (**Figure 2-15a**) and horizontal cross-section section (not depicted in **Figure 2-15b**). **Figure 2-15c** shows the microstructure of F samples after solution treatment and aging. Nital 2% samples reveal blocks or packets of lath-type martensite with extremely fine unetched boundaries. On the other hand, the structure of the H11 tool steel consists of a fine dispersion of small spheroidal carbide particles in a matrix of ferrite (**Figure 2-15d**).

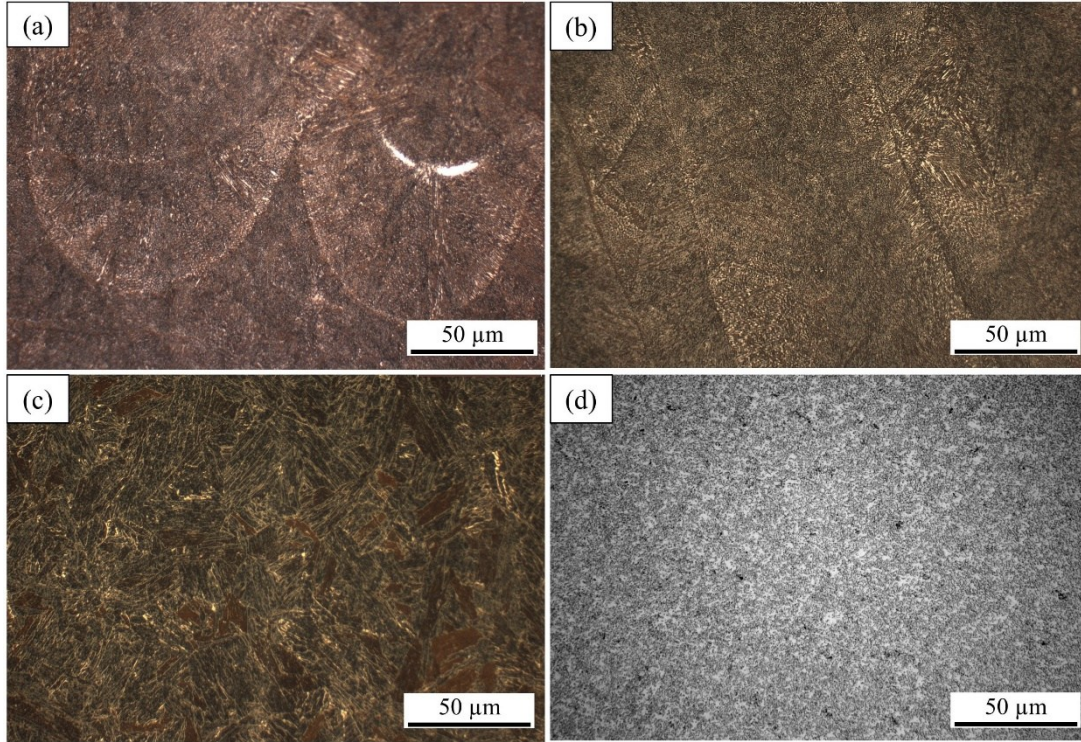


Figure 2-15. All the images were taken after etching the samples with Nital 2%; (a) AMed sample, the presence of the melt pools indicates the section perpendicular to the building direction (BD); (b) AMed sample, the presence of the scant tracks indicates the section perpendicular to the scanning direction (SD); (c) Forged sample; (d) H11 sample.

The plot in **Figure 2-16a** shows the thickness loss of different samples versus the immersion time. It is evident that the AM maraging steel exhibits a superior corrosion resistance compared to the forged one. In fact, in case of forged material, it was not possible to evaluate the thickness loss after 4 hours of immersion due to the strong dissolution of these samples in the Al bath. On the other hand, as expected, the more conventional H11 steel exhibits the best corrosion resistance.

Figure 2-16b shows the same thickness loss data plotted against the square root of immersion time. The data fitting with the parabolic relationship $x=kt^{0.5}$ (where “k” is growth constant, “ Δx ” is the loss of thickness and “t” is the time) is quite good. This confirms that the consumption of steel samples was controlled by diffusion processes, which is reasonable considering the relative long exposure times (Dangi *et al.*, 2018).

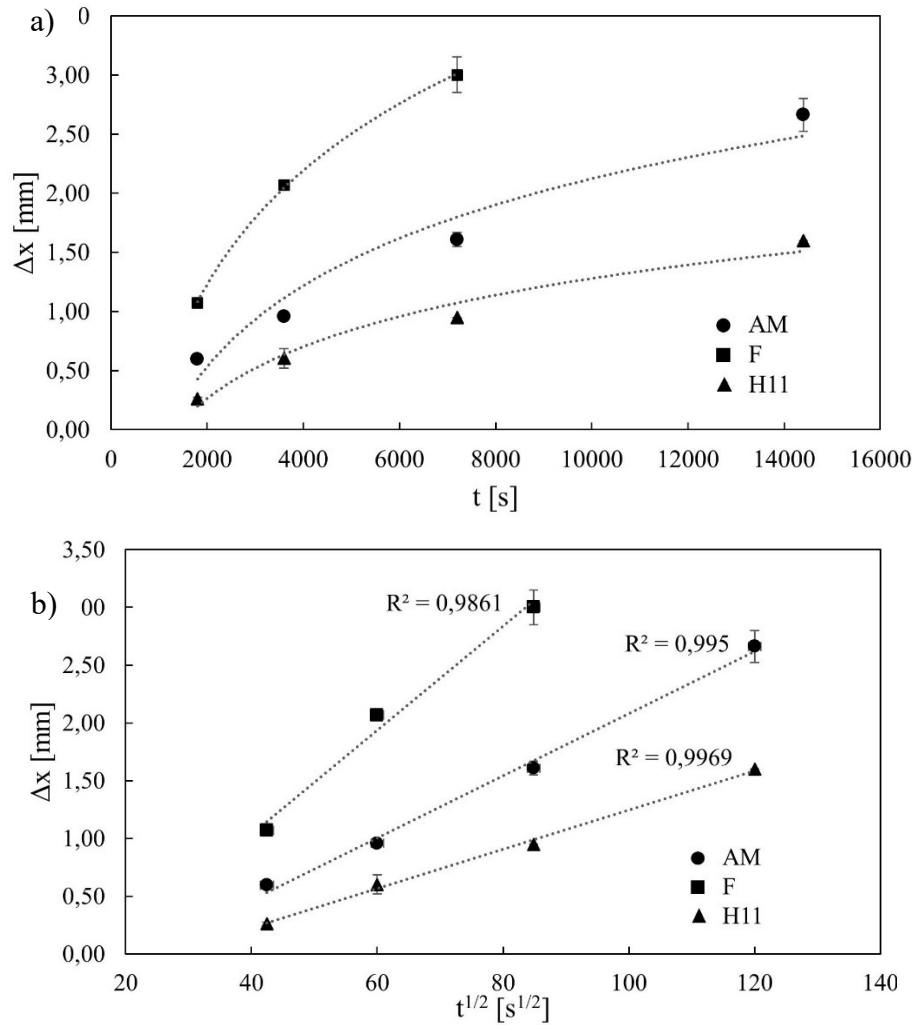


Figure 2-16. (a) Thickness loss Vs the immersion time and (b) thickness loss Vs the square root of immersion time

Despite the samples exhibit similar parabolic dissolution-time relationship, the AM maraging steel one displays a dissolution pattern that is notably more homogeneous in comparison with the forged counterpart (**Fig. 2-17**). This difference may be the consequence of the different corrosion kinetics of the samples in contact with molten Al. However, it is also plausible that the irregular corrosion pattern observed on forged samples is related to their characteristic segregation bands, as highlight in Figure 4c, compared to the more uniform and finer microstructure characteristic of AM samples.

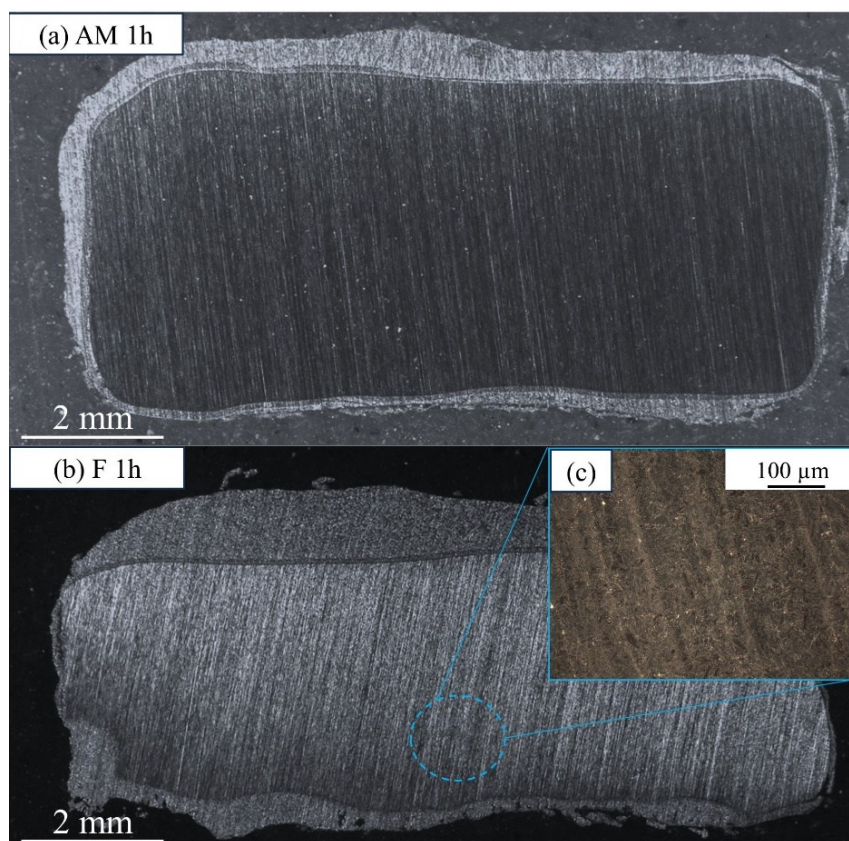


Fig. 2-17 – Digital microscope image of a) AM and b) F samples after 1h of immersion; c) microstructure of F sample segregation bands.

The interaction layers formed on AM and F maraging steel samples after 30-minute of immersion test were analyzed in cross-section by SEM-EDS (**Fig. 2-18**, **Table 2-5**, **Table 2-6**). At this initial stage, EDS analysis confirms the presence of an Al_5Fe_2 intermetallic layer, also called η phase, on both the samples (**Fig. 2-18a-b**). The intermetallic layer has a thickness of about $10\ \mu\text{m}$, but it is difficult to define, as several intermetallic particles detach from the intermetallic/Al interface and progressively dissolve into the molten Al. On the other hand, the steel/intermetallic interface is more continuous (except for few cracks developed upon cooling due to different thermal expansion coefficients), suggesting that the diffusion of Al towards steel is faster than the opposite diffusion of elements from steel to molten Al.

The analysis carried out on the H11 sample reveals the formation of a layer of Al_3Fe , with embedded several unreacted chromium carbide particles. Notably, the thickness of this layer is nearly half that of the maraging steel samples. The formation of these intermetallic compounds aligns with the existing literature (Nazari and Shabestari,

2009). Specifically, it has been reported that when the Si content in the aluminum melt ranged between 5 and 8 wt.%, the growth of the η phase was influenced by both interfacial reactions and diffusion processes. Moreover, it was observed that the apparent activation energy of the η phase decreased with increasing Si content (Zou *et al.*, 2021).

The SEM images presented in **Fig. 2-18d-f** show the interaction layer formed on different samples after 2 hours of immersion. It is evident that the intermetallic layer on the F sample has a thickness approximately double that of the AM sample. Furthermore, as suggested by the EDS analysis, the intermetallic layer of AM sample consists predominantly of two distinct layers, namely η in the inner part, and $\text{Al}_8\text{Fe}_2\text{Si} - \tau_5$ phase (also identified as $\text{Al}_{7.4}\text{Fe}_2\text{Si}$) in the outer part, in contact with molten Al. Conversely, in the case of the forged sample, the intermetallic layer is primarily composed of the η phase. Probably, in case of the AM sample, the formation of a τ_5 intermetallic layer, contributed to reduce its corrosion kinetics. Actually, it was reported in literature that the presence of such Si-containing intermetallic layers may mitigate the interdiffusion of Fe and Al atoms, thereby enhancing corrosion resistance (Dangi *et al.*, 2018). These ternary phases have the potential to hinder the diffusion of atoms by serving as diffusion barriers and/or as inhibitors of the interfacial reaction that forms the η phase (Springer *et al.*, 2011; Zou *et al.*, 2021). However, the precise impact of Al-Si-Fe ternary phases remains a subject of debate, given the intricate interplay between interfacial and diffusional processes.

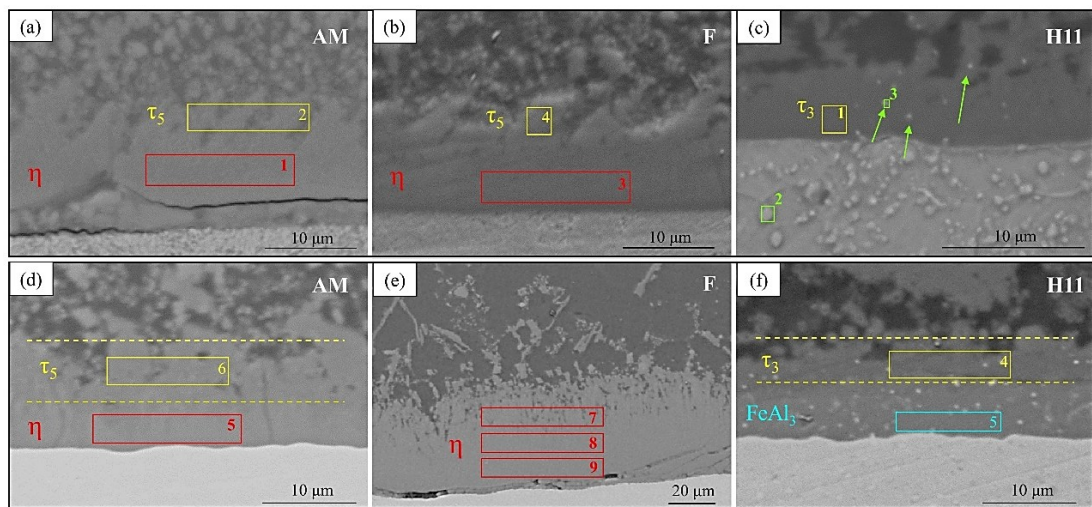


Fig. 2-18 – SEM-EDS analysis of the samples after 30 min (a-b-c) and 2 h (d-e-f) of immersion time.

Table 2-5 – EDS analysis of the AM and forged sample after 30 min (a-b) and 2 h (d-e) of immersion time

<i>Spectrum (a-b-d-e)</i>	Al	Si	Ti	Fe	Co	Ni	Mo
1	74.71	4.13	-	14.57	2.68	2.86	1.05
2	72.02	11.52	-	10.61	2.80	2.24	0.82
3	75.03	4.18	-	15.81	2.00	2.14	0.84
4	73.62	11.19	-	10.79	1.75	1.86	0.78
5	76.71	3.90	-	14.56	2.94	1.90	-
6	74.46	10.08	-	9.85	3.21	2.40	-
7	75.79	4.08	-	15.26	1.82	2.11	0.94
8	75.64	3.29	0.48	14.50	2.06	2.81	1.21
9	75.58	3.47	0.45	14.82	2.15	3.53	-

Table 2-6 - EDS analysis of the H11 sample after 30 min (a-b) and 2 h (d-e) immersion time

<i>Spectrum (c-f)</i>	Al	Si	V	Cr	Fe
1	68.53	15.07	-	1.20	15.20
2	-	-	3.15	22.96	73.88
3	60.55	15.24	1.12	10.19	12.90
4	70.70	13.74	0.15	0.71	14.70
5	71.31	3.58	0.02	1.93	23.15

Moreover, the thickness of the intermetallic layers growing on the AM surface remains relatively constant, at approximately 10 μm , in the period from 30 minutes to 2 hours. In contrast, the η phase layer on the F sample exhibited a notable increase of thickness (about 50 μm) within the same testing period. The relation existing between thin intermetallic layers and reduced interdiffusion rates is confirmed by the data obtained for H11 samples, where the layer thickness remained very small also after 2 hours of immersion test, in the range of 5 - 10 μm (**Fig. 2-18f**). As for the AM maraging steel, the intermetallic layer formed on H11 comprises two distinct layers. However, in this instance, Al_3Fe is the inner layer, while a ternary $\text{Al}_{4.5}\text{FeSi} - \tau_3$ phase is the outer one facing the molten Al alloy. Notably, chromium carbide particles from the steel matrix are embedded in the intermetallic layer as already observed in the H11 sample after 30 minutes. In agreement with the existing literature, such carbides serve as a physical barrier to the interdiffusion of Al and Fe atoms, significantly increasing the corrosion resistance of H11 steel (Xu *et al.*, 2021). Al_3Fe represents the second most prevalent Al-Fe intermetallic compound after Al_5Fe_2 , possibly due to its lower negative enthalpy of mixing and slower growth kinetics (Dangi). It is established that Al_3Fe intermetallic

primarily forms through precipitation within aluminum melt regions that are supersaturated with Fe atoms during cooling from relatively high temperatures, or alternatively, it forms at the steel interface via diffusion mechanisms (Chen *et al.*, 2016). Nevertheless, the presence of this intermetallic compound, contrary to Al_5Fe_2 , may slow down the diffusion process. In fact, the growth of Al_5Fe_2 intermetallic layer proceeds rapidly when contact is maintained between Al/ Al_5Fe_2 and $\text{Al}_5\text{Al}_5/\text{Fe}$ interfaces.

Furthermore, another reason for the superior corrosion resistance of the H11 steel could be linked to higher C content. In fact, as Si, the enrichment of this element at the reaction interface with the melt can inhibit the interdiffusion of Fe and Al atoms.

2.3.5. Conclusion

In this study, a comparative analysis of the hot-corrosion resistance in a molten low-iron AlSi7Mg alloy have been carried out by comparing the 1.2709 maraging steel produced via additive manufacturing with the conventional forging process. Additionally, a well-established H11 tool steel was examined as reference material. The results showed that the primary mechanism governing the hot corrosion of steel samples is the diffusion of elements across the intermetallic layers formed at the surface due to the prolonged static immersion.

The higher material loss was observed in case of forged maraging samples, particularly in comparison with the parent AM sample. Using the best performing H11 tool steel as a reference point, the forged samples exhibited a 2.5 times higher thickness loss compared to the 1.7 times greater loss observed in the AM samples (after 2 h of immersion time). Furthermore, both maraging samples displayed non-uniform corrosion, especially in the case of the forged samples. This non-uniformity could be attributed to the segregation of alloy elements within the forged components, characterized by the typical microstructural banding. However, further analyses are necessary to gain a more comprehensive understanding of this behavior.

SEM-EDS analysis revealed that the AM samples were able to form a more stable intermetallic layer rich in silicon compared to the forged counterparts, which dissolves completely for testing times above 2 hours. Considering that literature states that the

Al-Fe-Si phases hinder the growth of intermetallic compounds, this may be one of the primary reasons for the slower diffusion-related material loss observed in the AM sample. On the other hand, the analysis of H11 samples showed the formation of slightly different intermetallic compounds, with embedded chromium carbides. The extremely thin interaction layer formed over the H11 steel surface is indicative of a low diffusion rate and can be attributed to the inhibitory effects of chromium and carbon, which impede the diffusion of Fe and Al atoms.

Chemical analysis of the AlSi7Mg alloy post-testing revealed the selective diffusion and dissolution of Ni from the maraging steels into the molten alloy. This observation may suggest a greater hindrance to Ni diffusion imposed by the intermetallic Al-Fe-Si layer formed over the AM sample.

The presence of slight differences in the alloying elements of these maraging steels complicates the interpretation of their corrosion behavior. Indeed, as evidenced, small differences in the quantities of alloying elements within the intermetallic layers can have some influence on diffusion coefficients and, consequently, on the dissolution rate of steel into the molten Al alloy. Consequently, it becomes challenging to determine the role of the differential microstructures in the corrosion behavior in liquid Al. Therefore, further analysis is needed to ascertain how the observed differences are related to the respective microstructures or are influenced predominantly by chemical factors.

2.3.6. References

- Brooks, H.; Brigden, K. Design of conformal cooling layers with self-supporting lattices for additively manufactured tooling. *Additive Manufacturing*, 2016.
- Cecchel, S. et al. Lightweighting in light commercial vehicles: cradle-to-grave life cycle assessment of a safety-relevant component. *International Journal of Life Cycle Assessment*, v. 23, n. 10, p. 2043-2054, 2018.
- Chen, S. et al. Interaction Between the Growth and Dissolution of Intermetallic Compounds in the Interfacial Reaction Between Solid Iron and Liquid Aluminum. *Metallurgical and Materials Transactions A: Physical Metallurgy and Materials Science*, v. 47, n. 10, p. 5088-5100, 2016.
- Dangi, B.; Brown, T. W.; Kulkarni, K. N. Effect of silicon, manganese and nickel present in iron on the intermetallic growth at iron - aluminum alloy interface. *Journal of Alloys and Compounds*, v. 769, p. 777-787, 2018.
- European, C. et al. Study on the critical raw materials for the EU 2023 – Final report. Publications Office of the European Union, 2023.
- Nazari, K. A.; Shabestari, S. G. Effect of micro alloying elements on the interfacial reactions between molten aluminum alloy and tool steel. *Journal of Alloys and Compounds*, v. 478, n. 1-2, p. 523-530, 2009.
- Piekło, J.; Garbacz-Klempka, A. Use of Maraging Steel 1.2709 for Implementing Parts of Pressure Mold Devices with Conformal Cooling System. *Materials*. 2020.
- Springer, H. et al. On the formation and growth of intermetallic phases during interdiffusion between low-carbon steel and aluminum alloys. *Acta Materialia*, v. 59, n. 4, p. 1586-1600, 2011.
- Tonolini, P. et al. Wear and corrosion behavior of 18Ni-300 maraging steel produced by laser-based powder bed fusion and conventional route. *Procedia Structural Integrity*, 2022. p.821-829.
- Venkatesh, G.; Ravi Kumar, Y.; Raghavendra, G. Comparison of Straight Line to Conformal Cooling Channel in Injection Molding. *Materials Today: Proceedings*, v. 4, n. 2, Part A, p. 1167-1173, 2017.
- Xu, G. et al. Review on corrosion resistance of mild steels in liquid aluminum. *Journal of Materials Science & Technology*, v. 71, p. 12-22, 2021.
- Zou, T.-P. et al. Effect of Si content on interfacial reaction and properties between solid steel and liquid aluminum. *Transactions of Nonferrous Metals Society of China*, v. 31, n. 9, p. 2570-2584, 2021.

2.4. Corrosion resistance of 3D-printed and conventional die steels in contact with molten aluminum alloys

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2.4.1. Abstract

This study investigates the corrosion resistance of maraging steel produced via additive manufacturing and conventional forging when exposed to molten aluminum alloys used in high-pressure die casting (HPDC). The H11 tool steel, typically used in such applications, was also studied for comparison. Static immersion tests were conducted in three different aluminum alloys for HPDC (AlSi7Mg, AlSi10Mg, AlSi10MgFe). SEM-EDS analysis revealed differences in the formation of intermetallic layers on the metallic surfaces, mainly depending on the material considered. The laser-power bed fused maraging steel, often used for conformal cooling inserts, exhibited the formation of a stable high Fe intermetallic layer without a liquid phase, contributing to superior corrosion resistance compared to the forged maraging steel. The H11 tool steel demonstrated the highest corrosion resistance, especially due to its composition free from Ni and the presence of Cr and Cr-carbide. Thermo-Calc equilibrium simulations identified the phases present in the intermetallic layers at the test temperature, highlighting the effects of different steel compositions on interfacial intermetallic layers. These findings underline the critical role of manufacturing processes and alloy composition on the performance of steels in contact with molten aluminum alloys, with implications for die casting applications.

2.4.2. Introduction

The durability of metals when exposed to molten aluminum is a significant concern in engineering applications such as die casting ^{1,2}. The primary mechanisms of failure in molten aluminum are chemical corrosion and physical erosion ³. Physical erosion involves material loss from the die surface due to contact and rapid motion between the molten alloy and stationary mold walls ⁴. Chemical corrosion occurs when molten

aluminum infiltrates a solid metal, forming intermetallic compound (IMC) layers at the interface ⁵. These layers can comprise either single or multiple phases, depending on the substrate composition and reaction conditions. When multiple phases are present, the region consists of consecutive strata of intermetallic compounds ⁶.

This damaging mechanism commonly results in the so-called “die soldering” phenomenon, which occurs when molten aluminum adheres to the surface of the die, forming a bond that can lead to operational problems and reduced die lifespan ⁷⁻⁹. This issue is nowadays exacerbated by the production of increasingly complex and large high-performance components, which require larger, more expensive molds and potentially higher process temperatures ¹⁰. Under continuous exposure to molten aluminum, ferrous alloys experience high degradation rates due to iron dissolution and IMC loss ¹¹. IMC layers that form at the mold/melt interface vary in morphology, porosity, and thickness depending on the alloys used and the melt flow conditions.

Dies and tooling inserts are conventionally manufactured in hot-working tool steels, which contain alloying elements such as Ni, Si, W, Cr, V, etc. Prior studies have shown that Ni is highly reactive with aluminum, with a solubility at least three times greater than that of Fe across a wide temperature range ¹². Silicon affects the morphology of Fe-Al intermetallic compounds ¹³ and can inhibit the growth of Fe₂Al₅ ¹⁴. The carbon concentration in steel significantly impacts the development of intermetallic compounds (IMCs). Carbon influences IMC formation by reducing layer thickness and improving interfacial uniformity, thereby lowering diffusion and dissolution rates ¹⁵. Cr contributes to corrosion resistance by forming dense Al-Fe-Cr IMCs that act as diffusion barriers ¹⁶.

While H11 (and H13) tool steels remain the standard for HPDC die manufacturing ^{1,2, 17, 18}, maraging steel is increasingly used for inserts featuring conformal cooling channels (CCC), which enhance solidification control ¹⁹. These geometrically complex features can only be fabricated through additive manufacturing (AM), specifically laser powder bed fusion (L-PBF). AM offers precision and customization, and prior research has shown that it significantly influences the microstructure and properties of maraging steel ²⁰.

Efforts in Europe aim to reduce reliance on critical raw materials in HPDC ²¹, promoting the use of low-Si aluminum alloys like AlSi7Mg. These alloys require

higher process temperatures, increasing the risk of die degradation. Despite the growing use of maraging steels in HPDC, little is known about their corrosion behavior in molten aluminum. A preliminary study was done by the authors on maraging steels in contact with molten AlSi7Mg low-iron alloy, suggesting a potential benefit in the use of additive-manufactured maraging components ²². In this context, the primary objective of this study is to evaluate and compare the resistance of maraging steel specimens, manufactured using different technologies, when immersed in three different molten aluminum alloys: EN 43500 (AlSi10Mg) and EN 43400 (AlSi10MgFe), which are commonly used in HPDC, and the unconventional EN 42400 (AlSi7Mg). These alloys differ in their Si and/or Fe content. One maraging steel was manufactured by conventional a forging process, and it is equivalent to AISI 18Ni300–EN 1.2709 grades, called Cryodur®2709. The second one, Printdur® Powderfort, was developed from conventional steel for the production via L-PBF, with the goal of achieving the same post-heat treatment hardness as Cryodur®2709. This led to changes in chemical composition, which exclude the Printdur® Powderfort from the 18Ni300–EN 1.2709 grades. Both F and AM steels were selected in this study for their industrial relevance as die materials in HPDC applications. The Printdur® Powderfort steel was specifically designed with an increased Co content to achieve equivalent mechanical properties when processed by L-PBF, which justifies the comparison for the specific application, despite compositional differences. For comparison, H11 (EN 1.2343) tool steel was also investigated under the same experimental conditions to obtain benchmark data. Although the AM and conventional maraging steels differ in composition, particularly in Co content, they were selected for their direct relevance to industrial applications in HPDC. The Printdur® Powderfort alloy was specifically designed to replicate the mechanical performance of Cryodur®2709 in L-PBF processes, justifying their comparison under realistic and commercially meaningful conditions.

2.4.3. Materials and Methods

The maraging steels considered in this study were manufactured by Deutsche Edelstahlwerke Specialty Steel GmbH & Co. KG with two distinct processes, i.e., Additive Manufacturing (AM) and Forging (F).

The forged alloy underwent a sequence of manufacturing steps, including electric arc furnace melting, ladle furnace refinement, vacuum arc remelting, and final forging. The F samples were machined from a forged rounded bar made in the commercial alloy Cryodur®2709, whose chemical composition range fits the AISI 18Ni300 – EN 1.2709 grade, with an original diameter of 60 mm. Distinct heat treatment processes were applied to achieve their ultimate mechanical properties. This involved a one-hour solution treatment at 820 °C, rapid cooling in ambient air, followed by aging for 5 hours and 30 minutes at 490 °C, reaching the target hardness of 54 HRC.

For the AM samples, Printdur® Powderfort, a commercial powder with a modified chemical composition developed from the Cryodur®2709 steel, was used. This powder with a larger content of Co and Ti-free was specifically formulated for the fabrication of AM components, for die casting inserts, which must ensure a definite post-heat treatment hardness, equal to the conventionally manufactured Cryodur®2709 component. Although the AM and F steels have differing Co contents, both alloys were selected based on their commercial availability and industrial relevance for HPDC applications. The AM steel (Printdur® Powderfort) was specifically designed for L-PBF manufacturing to match the final hardness of Cryodur®2709, justifying their comparison under realistic operational scenarios. The specifications for the AM feedstock material are as follows: approximately 3.4 vol.% of particles had a diameter smaller than 20 µm, while 45.6 vol.% were smaller than 38 µm, and 98.2 vol.% were smaller than 53 µm. The powder exhibited a flow rate of 15.6 s/50 g and an apparent density of 3.99 g/cm³. The AM samples were fabricated by using a laser-based bed fusion (L-PBF) system with classified process parameters. The resulting cylindrical AM samples measured 57 mm in diameter and 12 mm in height, with their axis oriented parallel to the building direction (BD). Subsequently, they underwent a direct aging treatment, being held at 490 °C for 4 hours to promote precipitation, reaching the target hardness of 54 HRC.

Forged samples made with the conventional die tool steel H11 (EN 1.2343) were also machined and included in the testing for comparison issues. The H11 samples underwent quenching from 1000 °C by pressurized argon and tempering at 550 °C to reach a hardness of 45 HRC.

The chemical composition of all investigated samples is detailed in **Table 2-7**.

For the immersion test, samples were machined by wire electrical discharge machining (EDM) from their cylindrical shape to obtain 20x10x5 mm samples with a through-hole on the larger face (Figure 2.19b). The average weight of the samples is: 7.70 ± 0.01 g (AM), 7.72 ± 0.02 g (F) and 7.46 ± 0.02 g (H11). The samples' real density, measured with the buoyancy method, resulted as follows: 7.76 ± 0.01 g/cm³ (AM), 7.80 ± 0.01 g/cm³ (F) and 7.40 ± 0.01 g/cm³ (H11). The AM samples exhibited a density of 99.97%, as determined by optical microscopy porosity analysis using LAS 4 image analysis software (Leica). The analysis was based on ten images acquired at 100× magnification.

Before and after immersion tests, microstructural characterization was conducted on mirror-polished samples etched with Nital 5, by using a DMI 5000M optical microscope (Leica, Wetzlar, Germany) equipped with an image analysis software (Las 4.12). Low magnification images, obtained through a DSM300 digital microscope (Leica, Wetzlar, Germany), were used to analyze the surface of the sample after the immersion tests.

Table 2-7. Steels mean chemical composition: maraging steels produced by additive manufacturing (AM) and forging (F), and H11 tool steel.

El. (wt.%)	C	Si	Mn	Cr	Mo	Ni	Co	V	Ti	Fe
AM	0.01	0.2	0.3	0.1	5	17.9	13.4	-	-	Bal.
F	0.004	0.02	0.03	0.1	4.95	18.3	9.75	-	1.13	Bal.
H11	0.37	1	0.4	5.3	1.3	-	-	0.4	-	Bal.

The static immersion test setup includes an electric-heated laboratory furnace equipped with a graphite crucible and a thermocouple (**Figure 2-19a**). The aluminum alloys selected for testing were EN 42400 (AlSi7Mg), EN 43500 (AlSi10Mg), and EN 43400 (AlSi10Mg-Fe), as detailed in **Table 2-8**. The primary difference between the first two

alloys is the silicon content, while the second and third alloys differ in their iron content. The selection of these materials allowed evaluation of the possible effect of these alloying elements on steels corrosion. In fact, AlSi10Mg-Fe alloy is a typical alloy used in HPDC to produce automotive components. The recent demand for high-performance structural die cast parts has moved the attention towards low Fe-content alloys²³, highlighting the need to evaluate their effect on die lifespan. Simultaneously, the growing concern for environmental issues is fueling interest in alloys that reduce dependence on critical raw materials, like Si²¹, thus promoting the use of AlSi7Mg alloys also in die casting. However, few studies address whether different silicon contents in aluminum alloys influence the melt-matrix interaction²⁴ and/or the effect on steel inserts manufactured with different techniques. In. In addition, while it is well-documented that Fe can enhance die longevity in high-pressure die casting (HPDC)²³,²⁵, its beneficial effects may diminish as the process temperature increases⁶.

Table 2-8. Aluminum alloys mean chemical composition.

El. (wt.%)	Al	Si	Mg	Mn	Fe
EN42400 (AlSi7Mg)	90.81	8.11	0.27	0.69	0.12
EN43500 (AlSi10Mg)	89.28	9.74	0.33	0.49	0.16
EN43400 (AlSi10MgFe)	88.60	10.3	0.24	0.25	0.61

Approximately 1 kg (1000 ± 10 g) of aluminum alloy was melted for each test to guarantee adequate coverage of the sample and to prevent a possible iron saturation within the melt, even with the complete dissolution of the tested sample pair. The test temperature was fixed at 730 ± 5 °C, which is a suitable process temperature for AlSi7Mg alloys, and represents an extreme condition for AlSi10Mg alloys, exceeding their standard processing temperatures²⁶. However, the same temperature was applied to all tests to ensure the comparability of results.

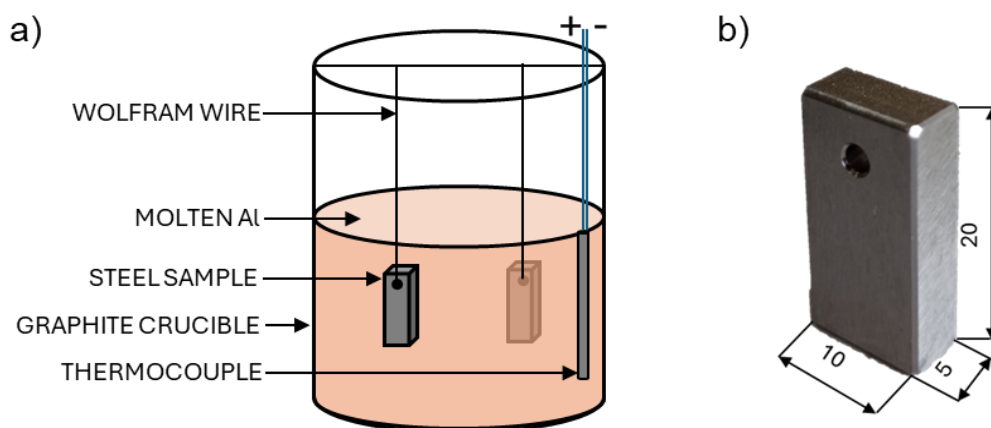


Figure 2-19. (a) Schematization of the static immersion test set-up; (b) Samples dimensions (mm).

Under each test condition (i.e., type of molten alloy, type of steel, and time of exposure), two equivalent samples were simultaneously immersed. Before performing a new set of tests, the alloy was replaced for reasons previously reported. Four exposure time intervals to the liquid alloy were selected: one pair of samples was immersed for 3 minutes, another pair for 30 minutes, one pair for 60 minutes, and one pair for 120 minutes. This procedure was repeated twice with new couples of samples, resulting in a total of four samples for each test condition. One sample from each test condition was left untouched for SEM-EDS analysis, performed by using a Zeiss Sigma 360 scanning electron microscope (Carl Zeiss AG, Milan, Italy) to study the intermetallic layers. For the SEM-EDS analysis, all samples were transversely sectioned approximately 10 mm from the base (**Figure 2-19b**) to ensure consistent sampling. The other three samples for each test condition were prepared for mass loss measurements. To this aim, after removal from the bath and cooling to room temperature, these samples were repeatedly washed with a 10% sodium hydroxide (NaOH) solution at $80^{\circ}\text{C} \pm 10^{\circ}\text{C}$ to remove the aluminum stuck to the surface. When aluminum reacts with dilute sodium hydroxide, it dissolves and forms a sodium aluminate (NaAlO_2) residue, which appears as a black salt covering the sample's surface. This reaction product was mechanically removed by brushing with stainless-steel wool made of a ferritic steel with a hardness of about 20 HRC, which was sufficiently hard to eliminate surface residues but not to scratch the underlying steel

substrate. The absence of surface damage was confirmed by optical microscope analysis.

Thermodynamic equilibrium simulations were carried out with different purposes by using Thermo-Calc (2024a) software. Firstly, these simulations aimed to estimate the solubility of the main steel elements in the Al-Si liquid. Simulations of different combinations of the major steel alloy elements in the ternary phase diagram (Al-Si-X) were performed at 730°C, applying the TCAL8 (v8.2) database with the "Isothermal section" calculation module. Secondly, the chemical compositions of different intermetallic layers collected by EDS analysis were used as inputs for equilibrium simulations at a temperature of 730°C and a pressure of 0.1MPa to determine the stable phases volume fraction in the intermetallic layer under examination.

2.5. Results

2.5.1. *Optical and digital microscopy analysis*

Figure 2-20 presents the metallographic analysis of the tested steels. The microstructure of the AM samples after direct aging treatment is shown in **Figure 2-20a**, revealing the characteristic fine cellular structure produced by the L-PBF process. This cellular-martensitic microstructure results from the rapid solidification inherent to L-PBF, which suppresses coarse grain formation ²⁰. Notably, this microstructure remains intact even after aging heat treatment. The melt pool boundaries, from which the solidification structure grows, are also still visible.

Figure 2-20b and **Figure 2-20c** depict the microstructure of the F samples after solution treatment and aging. At lower magnification, a pronounced banded structure is observed, attributed to microsegregation of alloying elements such as Ni and Mo during solidification, a common feature in forged maraging steels ^{27, 28}. At higher magnification, a martensitic microstructure appears, bounded by a lighter etched zone that corresponds to the prior austenite grain boundaries. These unetched boundaries are indicative of retained or reversed austenite, which is known to persist in this alloy class at levels up to 20% following heat treatment ²⁹. This retained austenite is stabilized by the alloy's high Ni content, which depresses the martensite start (Ms) temperature and promotes partial austenite retention upon cooling.

The microstructure of the H11 steel is shown in **Figure 2-20d**, consisting of fully tempered martensite.

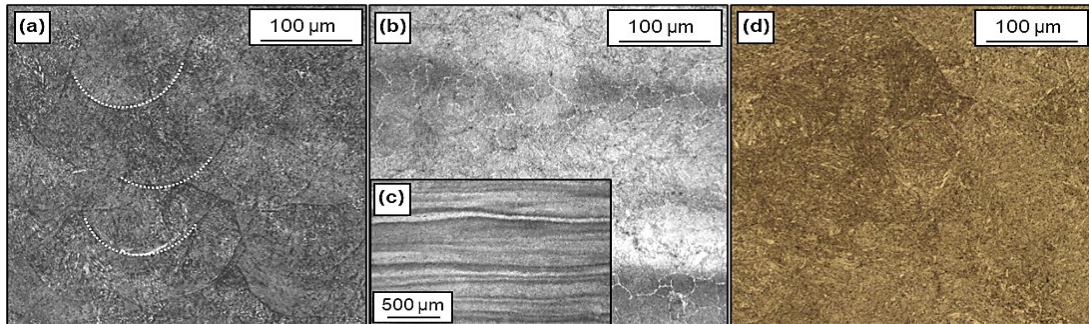


Figure 2-20. (a) Microstructures of the maraging AM sample, the dotted curves highlight the melt pools border; (b-c) maraging forged sample viewed at different magnification; (d) H11 sample; all the samples were etched by Nital 5.

Figure 2-21 illustrates the effects of exposure to molten aluminum at 730 °C using digital and optical microscopy, highlighting both macro- and microstructural differences in steel degradation. Metallographic analysis of the sample cross-sections, with the aluminum coating still intact, reveals that after 60 minutes of immersion, the steel's martensitic microstructure begins to fade near the interface. This change is particularly evident in the maraging steels due to their high Ni content, which enlarges the austenitic field and lowers the austenitization temperature.

The AM sample (**Figure 2-21a**) shows a relatively uniform interaction layer along the cross-section. In contrast, the F sample (**Figure 2-21b**) exhibits non-uniform corrosion, characterized by a wavy and irregular interface in the optical microscopy image. Macroscopic images of the sample faces, taken after NaOH washing to remove aluminum residues, provide further insight. The AM sample shows signs of generalized corrosion, with shallow, evenly distributed grooves. In contrast, the F sample displays more severe, localized corrosion, evident from deeper grooves and more irregular surface degradation.

The H11 sample (**Figure 2-21c**) experienced the least corrosion; degradation was mainly confined to the edges, with the central geometry largely preserved. These degradation patterns were consistent across all test conditions and became more pronounced with increasing immersion time.

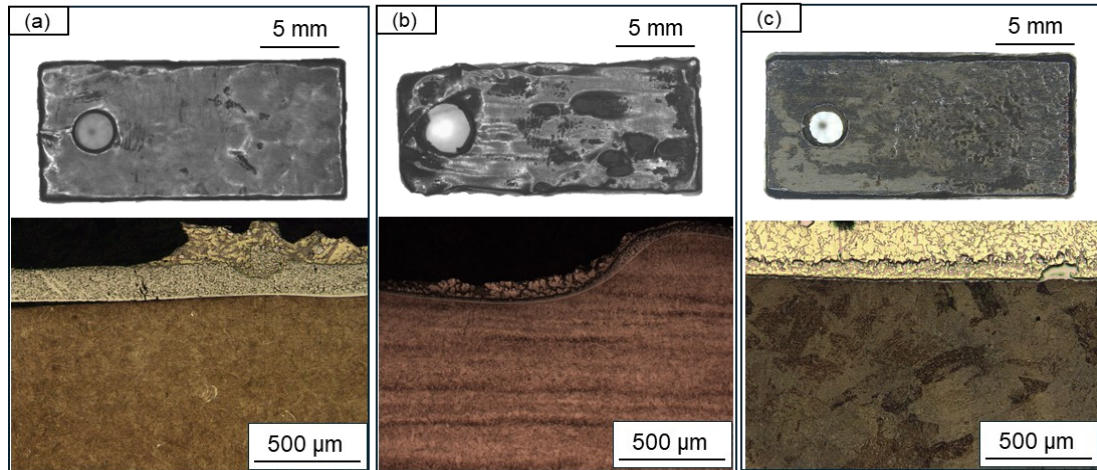


Figure 2-21. Digital (above) and optical (below) microscopy analysis of the tested sample after 60 minutes of testing in the EN 43400 alloy. The optical microscopy analysis referred to samples etched by Nital 5. The low magnification images were taken after the cleaning procedure of the samples from the aluminum coating. (a) F; (b) AM; (c) H11.

2.5.2. Mass loss evaluation

Figure 2-22 illustrates the relationship between mean mass loss and immersion test duration under various conditions. Specifically, **Figure 2-22a** compares the behavior of the three steels (AM, F, and H11) over time when tested in the same aluminum alloy (EN 42400-AlSi7Mg, EN 43500-AlSi10Mg, or EN 43400-AlSi10MgFe). The data were fitted using the “polyfit” function in MATLAB, yielding a good match with a second-degree polynomial. This is consistent with literature findings, which report that the thickness loss of materials in contact with molten aluminum typically follows a parabolic trend with negative concavity. Such parabolic behavior is generally attributed to diffusion-controlled processes, which dominate over interfacial reactions during prolonged exposure¹. An exception to this trend is the AM steel tested in EN 43500, which shows an almost linear mass loss over time, suggesting that other factors may have interfered with the establishment of a stable, diffusion-driven corrosion regime.

When comparing the two maraging steels, the forged variant exhibits higher mass loss under all conditions. In the early stages (30 minutes), the differences between the F and AM samples are relatively small, particularly in the EN 42400 and EN 43500 alloys. However, after 120 minutes of immersion, the differences become more pronounced across all test conditions. These results confirm the superior corrosion

resistance of the AM maraging steel compared to its forged counterpart across all aluminum alloys tested.

The H11 steel shows the best overall corrosion resistance. Notably, the AM steel displays degradation behavior comparable to H11 during the initial immersion period, up to 30 minutes, especially in the EN 42400 and EN 43500 environments. Even at 60 minutes, the differences in mass loss remain relatively modest.

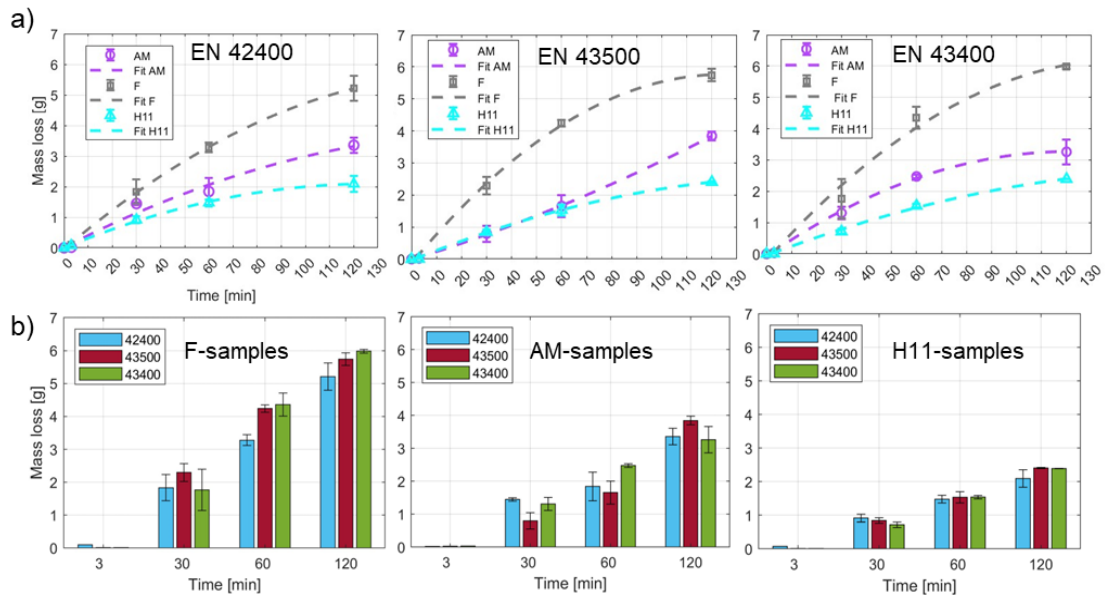


Figure 2-22. Loss of mass of the tested samples as a function of the testing time; (a) Trend of mass loss in the different aluminum alloys: EN42400, EN43500 and EN43400; (b) Bar graph showing the loss of mass for the same steel but with different aluminum alloy testing.

Figure 2-22b illustrates the effect of different aluminum alloys on the corrosion rate of the tested steels by replotting the same experimental data. In this case, each graph shows the mass loss of a single steel over time when exposed to the three different aluminum alloys. For the forged maraging steel (F), EN 42400 appears to be the least aggressive alloy, particularly at longer immersion times, where the mass loss difference becomes more pronounced. Interestingly, the anticipated mitigating effect of Fe, expected to make EN 43400 less corrosive, was not confirmed by the results. No clear trend is discernible from the corrosion data of AM and H11 steels, where the standard deviations of the measurements encompass the differences. Based on these results, it can be concluded that, in general, the different compositions of the aluminum alloys appear to have a limited influence on the corrosion rate of steels.

2.5.3. SEM-EDS analysis

The SEM-EDS analysis provides crucial insights into the microstructural changes and chemical compositions of the intermetallic layers formed on the steel samples after immersion in molten aluminum alloys. **Figure 2-23, Figure 2-24** and **Figure 2-25** display SEM micrographs of the tested samples, while **Table 2-9, Table 2-10** and **Table 2-11** show the corresponding EDS analyses. The EDS analysis revealed the formation of one to three intermetallic compound (IMC) layers under every testing condition. Moving the EDS analysis outward from the steel surface, the chemical composition of the interaction layers at the interface evolves consistently. Moreover, the EDS analysis for the same steel in the different testing conditions gave repeatable compositions. This permitted the identification of four distinct IMC layers, with specific compositional ranges defined for each element:

- **AlFe**: layer rich in Fe, likely mainly composed of a binary Al-Fe intermetallic.
- **AlFeSi**: layer with similar contents of Fe and Si, likely mainly composed of an Al-Fe-Si intermetallic.
- **AlFe-Cr**: AlFe layer formed on H11 steel surface, characterized by the presence of Cr in the composition.
- **AlFeSi-Cr**: AlFeSi layer formed on H11 steel surface, characterized by the presence of Cr in the composition.

Since the analysis of the samples immersed for 3 minutes was equivalent to that of the samples immersed for 30 minutes, the results for the 3-minute immersion are not presented to avoid redundancy.

2.5.3.1. *EN 42400 (AlSi7Mg) immersion tests*

Figure 2-23 shows the SEM images of the steels cross-sections after testing with the EN 42400-aluminum alloy. The corresponding EDS analysis are summarized in **Table 2-9**. The variation in chemical composition moving outward from the maraging steels surface suggests the formation of different intermetallic compounds, which form distinct layers. A high Al/Si ratio encourages the formation of binary AlFe intermetallic. While, when the Si content equals the Fe content, the composition

promotes the formation of AlFeSi compounds. Additionally, the formation of IMCs involving aluminum with cobalt and nickel cannot be excluded.

At the steel–aluminum interfaces of both F and AM maraging samples (**Figure 2-23a,b**), an initial Fe-rich AlFe layer forms adjacent to the steel, followed by a Si-rich AlFeSi layer farther out. In the F sample, the AlFe layer disappears after 120 minutes, leaving only the AlFeSi phase. In contrast, the AM sample consistently retains the AlFe layer at all immersion times.

The thickness of the IMC layers in the maraging steels ranges from 20 to 30 μm , decreasing to approximately 10 μm in the F sample after 120 minutes. In some micrographs, the IMC layers appear detached or fractured, likely due to thermal shock during sample extraction from the crucible.

The H11 surface also forms a double intermetallic layer (**Figure 2-23c**), although with a different chemical composition, being richer in Fe and Cr. At 30 minutes, the H11 IMCs layer breaks into blocks moving towards the Al-rich area. As the testing time increases, its morphology starts to resemble that of maraging IMCs, while a compact layer of approximately 15 μm stabilizes.

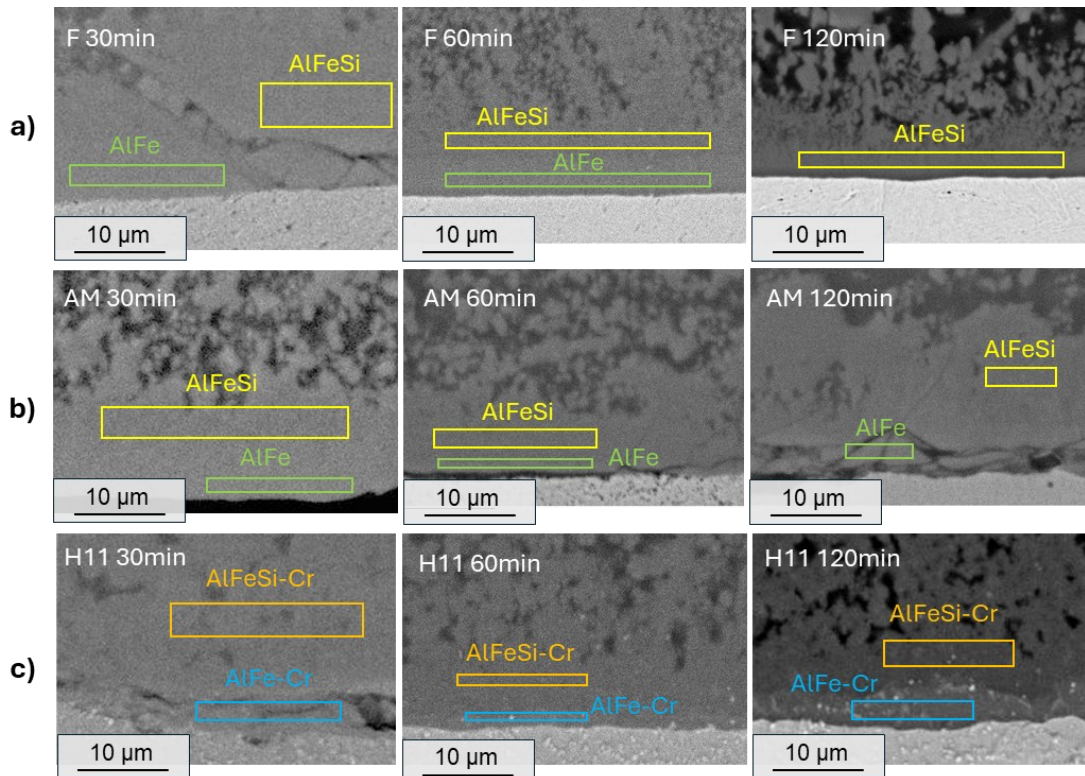


Figure 2-23. SEM-EDS cross-sectional images of the interaction layers formed on different steel grades, Forged (F), Additive Manufactured (AM), and H11, after immersion in molten EN 42400 aluminum alloy for 30, 60, and 120 minutes. The steel substrate is shown at the bottom of each picture, with intermetallic compounds growing upward. Identified different IMC layers are highlighted by colored boxes. Corresponding EDS compositional data are reported in Table 2-9.

Table 2-9. Chemical composition (at. %) of interaction layers detected by EDS analysis for the immersion in molten EN42400 alloy.

Spectrum (at. %)	Al	Si	Mn	Fe	Co	Ni	Cr
AlFe	73-75	3.7-5.3	0.5-0.7	15-19	2.3-3.3	2.3-3.8	
AlFeSi	70-75	9.5-13.1	0.5-1.3	10-13	1.2-3.4	1.6-3.2	
AlFe-Cr	65-69	5.5-8.3		24-25			1.1-1.9
AlFeSi-Cr	68-72	9.9-13	0.57-2.1	12-17			0.93-2.0

2.5.3.2. EN 43500 (AlSi10Mg) immersion tests

Figure 2-24 depicts the SEM images for samples exposed to molten EN 43500 alloy, with the EDS results provided in Table 2.10. The IMC layers in both maraging samples were unstable over time and inhomogeneous along the sample's surfaces. Specifically, the AlFeSi layer stabilized on a large part of the steels' surface after 30 minutes, whereas the AlFe layer formed only in some spots at the interface, as can be seen at 60 min for the AM sample (Figure 2-24a) and 120 min test time for the F sample (Figure 2-24b). By 120 minutes, the AlFe layer on the AM sample surface had mostly disappeared. In contrast, the H11 sample surface was covered by a single, stable IMC layer identified as AlFeSi-Cr across all exposure times (Figure 2-24c). The thickness of the IMC layers for all analyzed steel samples ranged between 10 and 15 μm over time, with no significant differences observed between the different steel types.

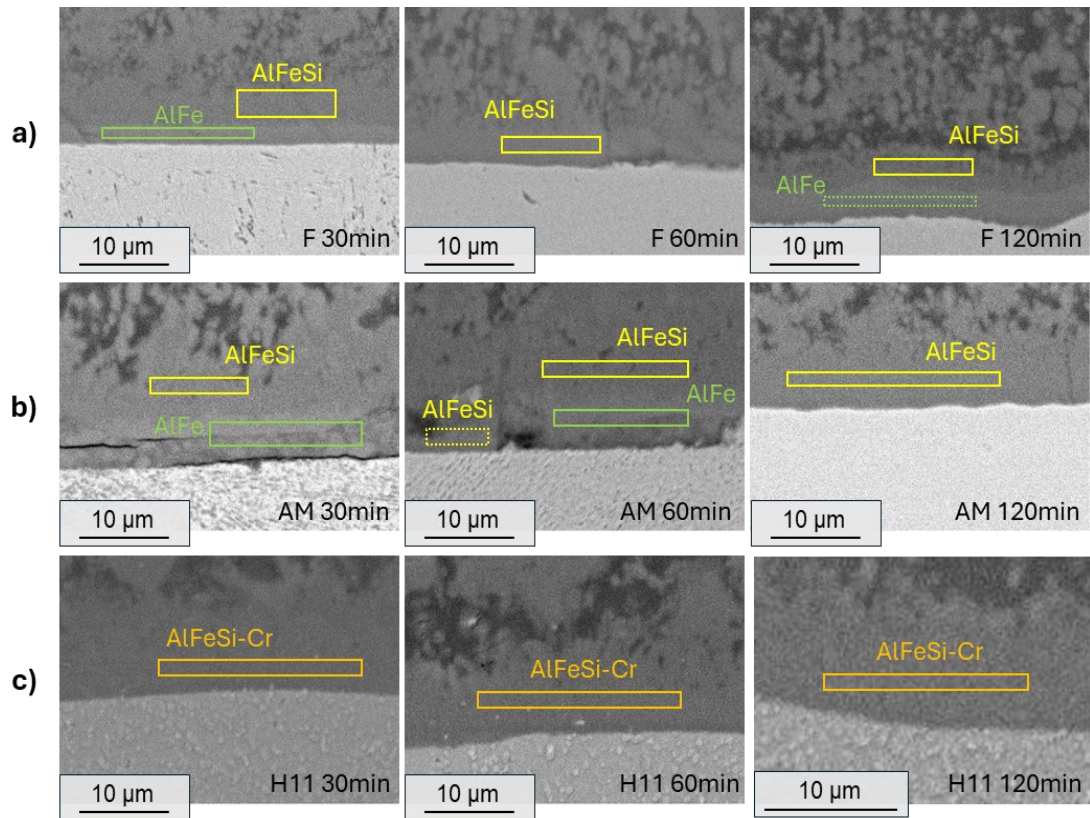


Figure 2-24. SEM-EDS cross-sectional images of the interaction layers formed on different steel grades, Forged (F), Additive Manufactured (AM), and H11, after immersion in molten EN 43500 aluminum alloy for 30, 60, and 120 minutes. The steel substrate is shown at the bottom of each picture, with intermetallic compounds growing upward. Identified different IMC layers are highlighted by colored boxes. Corresponding EDS compositional data are reported in Table 2-10.

Table 2-10. Chemical composition (at. %) of interaction layers detected by EDS analysis for the immersion in molten 43500 alloy.

Spectrum (at. %)	Al	Si	Mn	Fe	Co	Ni	Cr
AlFe	70-73	4.3-6.2		16-18	2.3-3.5	2.5-4.1	
AlFeSi	69-72	9-15		11-16	0.7-3.1	1.5-3.2	
AlFeSi-Cr	65-70	13-16	0.34-1.8	13-18			0.71-1.9

2.5.3.3. EN 43400 (AlSi10MgFe) immersion tests

Figure 2-25 shows SEM images of the tested steels after exposure to the EN 43400 aluminum alloy, with corresponding EDS data summarized in Table 2-11. Similar to the EN 43500 test, the IMC layers on the F samples appear inhomogeneous along the surface, alternating between AlFe and AlSiFe phases, particularly in the 60–120 minute exposure intervals (Figure 2-25a). In contrast, under the same conditions, the

AM sample forms a double-layer IMC structure. However, the AlFe layer appears more irregular and discontinuous compared to the other test conditions, especially after 120 minutes (**Figure 2-25b**).

The IMC layer thickness for the F steel samples remains relatively stable at around 10 μm throughout the exposure period. Conversely, the IMC layer on the AM sample is generally thicker, ranging between 10 and 15 μm .

For the H11 steel, EDS analysis suggests the formation of at least three distinct intermetallic phases. The first layer consists of a matrix corresponding to AlFeSi-Cr, interspersed with regions of AlFe-Cr and bright white particles likely corresponding to Cr carbides (**Figure 2-25c**). This layer grows from approximately 4 μm to 8 μm by the 120-minute mark and is overlain by a tongue-shaped AlSiFe layer with an average thickness of about 7 μm .

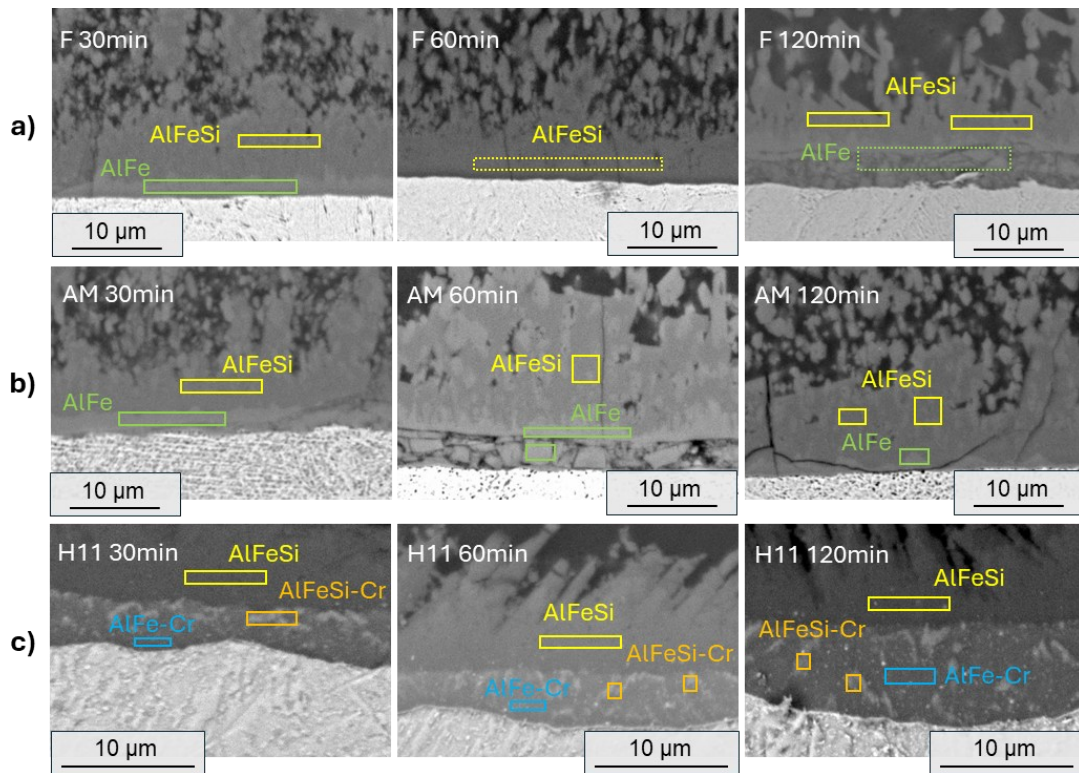


Figure 2-25. SEM-EDS cross-sectional images of the interaction layers formed on different steel grades, Forged (F), Additive Manufactured (AM), and H11, after immersion in molten EN 43400 aluminum alloy for 30, 60, and 120 minutes. The steel substrate is shown at the bottom of each picture, with intermetallic compounds growing upward. Identified different IMC layers are highlighted by colored boxes. Corresponding EDS compositional data are reported in Table 2-11.

Table 2-11. Chemical composition (at. %) of interaction layers detected by EDS analysis for the immersion in molten 43400 alloy. *Mn was detected in the F and AM intermetallic only; ** Cr was detected in the H11 intermetallic only.

Spectrum (at. %)	Al	Si	Mn	Fe	Co	Ni	Cr
AlFe	72-74	4.8-6.0		14-17	2.1-3.0	2.4-3.6	
AlFeSi	68-75	9.9-19	0.31-0.72*	11-15	2.2-2.6*	1.1-2.5	0.8-0.9**
AlFe-Cr	69-70	4.8-6.5		23-24			1.2-1.9
AlFeSi-Cr	56-62	14-18		21-25			1.4-2.2

The measured thicknesses of the IMC layers for each steel–aluminum alloy combination and immersion time are summarized in **Table 2-12**. These values are representative but approximate, as IMC layer morphology and uniformity varied across the sample surfaces, with an estimated measurement uncertainty of $\pm 1 \mu\text{m}$.

Table 2-12. Approximate thickness of intermetallic compound (IMC) layers formed at the steel–aluminum interface in the different test conditions. Values are representative averages based on SEM-EDS cross-sectional analysis. Variability may occur due to local inhomogeneity or detachment of the IMC layers. *Inhomogeneous formation along the analyzed section.

Al alloy	Steel	Time [min]	IMC Layer Thickness (μm)				
			AlFe	AlFeSi	AlFe-Cr	AlFeSi-Cr	Total
EN42400	F	30	10	20			30
		60	5	15			20
		120	5	5			10
	AM	30	5	15			20
		60	3	7			10
		120	5	10			15
	H11	30			5	15	20
		60			5	10	15
		120			5	10	15
EN43500	F	30	2	8			10
		60		8			8
		120	4*	4			8
	AM	30	5	10			15
		60	5	10			15
		120		10			10
	H11	30				10	10
		60				10	10
		120				10	10

EN43400	<i>F</i>	30	2	8			10
		60		8			8
		120	5*	5			10
	<i>AM</i>	30	3	7			10
		60	5	10			15
		120	1-2	10-11			12
	<i>H11</i>	30		6	4	n.a	10
		60		8	4	n.a	12
		120		6	8	n.a	14

2.5.4. Thermo-Calc simulations

It is known that steel corrosion is driven by interfacial reactions and diffusion-controlled processes³⁰. Concentration gradients act as the driving force for diffusion. Greater solubility leads to a steeper concentration gradient, leading to an accelerated diffusion rate in accordance with Fick's laws. Thus, Thermo-Calc equilibrium simulation software was used initially to assess the solubility of the primary alloy elements in the Al-Si-X systems of the tested steels to evaluate the sensitivity to the diffusion of elements when in contact with the different molten alloys. This approach helped clarify how different chemical compositions influence corrosion behavior through dissolution mechanisms. The solubility of Fe, Co, and Ni in the Al-Si-X system and the stable intermetallic compounds at the test temperature are presented in **Figure 2-26**. It is worth noting that Ni has a higher solubility than Fe in the ternary system, as indicated by the comparison of red striped fields in Figures 8a and 8c. Conversely, as illustrated in **Figure 2-26b**, cobalt, one of the principal alloying elements in maraging steel, has lower solubility than Fe, a feature that is rarely discussed in literature. The liquid phase is suppressed for cobalt contents lower than 2.5 wt. % in favor of the formation of the Al₉Co₂ intermetallic compound. In the Al-Si-Fe system³¹, the Al₁₃Fe₄(θ phase) binary intermetallic is more prone to forming at a lower Si content³². As Si increases, more complex ternary intermetallic compounds form, that is, Al₈Fe₂Si (α phase) and AlFeSi (τ_2 phase).

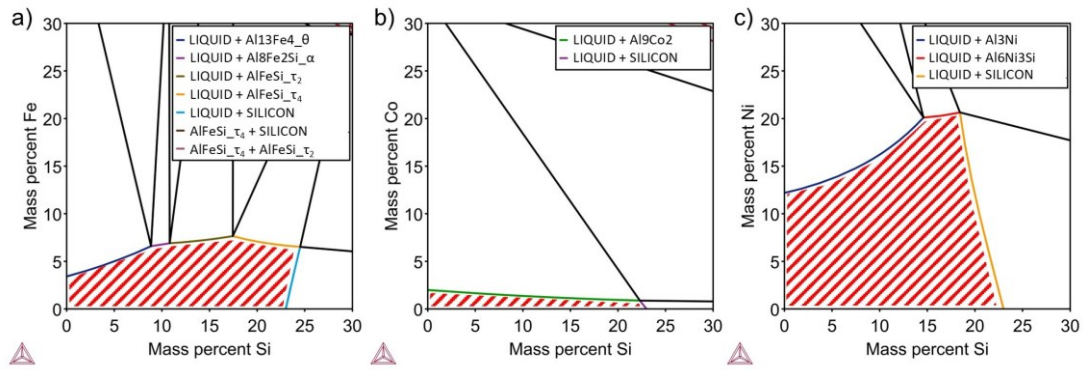


Figure 2-26. Isothermal section of ternary equilibrium calculation at the test temperature (730 °C) of a) Al-Si-Fe, b) Al-Si-Co, and c) Al-Si-Ni systems focusing on the liquid area.

Secondly, equilibrium simulations were performed by using the representative EDS chemical composition data of the various IMC layers depicted in **Table 2-9**, **Table 2-10** and **Table 2-11** to identify the more probable phases formed at the test temperature, which cannot be assessed simply by combining the elements detected by EDS analysis. Since the immersion tests were conducted under static conditions and relatively long exposure times, it is reasonable to assume that local thermodynamic equilibrium was approached at the steel–aluminum interface.

Combining the EDS analysis with the data from literature, for example, for the Al-Fe-Si system ³³, it is possible to predict the IMCs formed at the samples interface. However, in this analysis, it is extremely difficult to identify the exact IMCs due to the numerous steels and aluminum alloy elements. In addition, as shown in Figure 2-26, aluminum forms IMCs with most of the maraging steels alloying elements. To address this issue, four representative chemical compositions of the IMC layer from EDS were selected, based on the average values of the compositional ranges presented in **Table 2-9**, **Table 2-10** and **Table 2-11**. These compositions, expressed as weight percentage, were used to perform equilibrium simulations to identify the stable phases at the test temperature:

- AlFe: 60 Al, 4 Si, 28 Fe, 4 Co, 4 Ni (wt. %)
- AlFeSi: 62 Al, 8 Si, 23 Fe, 4 Co, 3 Ni (wt. %)
- AlFe-Cr: 51Al, 7 Si, 40 Fe, 2 Cr (wt. %)
- AlFeSi-Cr: 54 Al, 14 Si, 30 Fe, 2 Cr (wt. %)

The results of the equilibrium simulation are presented in **Figure 2-27a** as Phase Volume Fraction (y-axis) in equilibrium in a range of temperature 730 ± 10 °C (x-axis), to consider a small variation of temperature around the tested one. The AlFe composition shows that $\text{Al}_{13}\text{Fe}_4$ is the main IMC, followed by AlFeSi_{τ_2} and Al_9Co_2 compounds, and a residual 3% of liquid phase. On the other hand, in the layer with a higher Si content (AlFeSi layer), the liquid phase is still abundant, with a content that is 10 times larger compared to the AlFe layer, as better evidenced in **Figure 2-27b**, where the volume fraction of the stable phases at 730 °C is visualized as a bar with the percentage value.

Instead, the intermetallic layers formed on H11 steel were characterized by high Cr contents and consequently were named AlFe-Cr (low-Si) and AlFeSi-Cr (high-Si). The AlFe-Cr layer predominantly consists of $\text{Al}_{13}\text{Fe}_4$ (**Figure 2-27a**), up to 26% more than in the AlFe, reasonably due to higher Fe content in H11 steel, and in a smaller part of AlFeSi_{τ_9} and CrSi_2 (**Figure 2-27b**). The liquid phase is absent. Even the high-Si layer AlFeSi-Cr has almost no liquid phase, forming complex ternary compounds such as AlFeSi_{τ_2} and $\text{Al}_{15}\text{Si}_2\text{Fe}_4$.

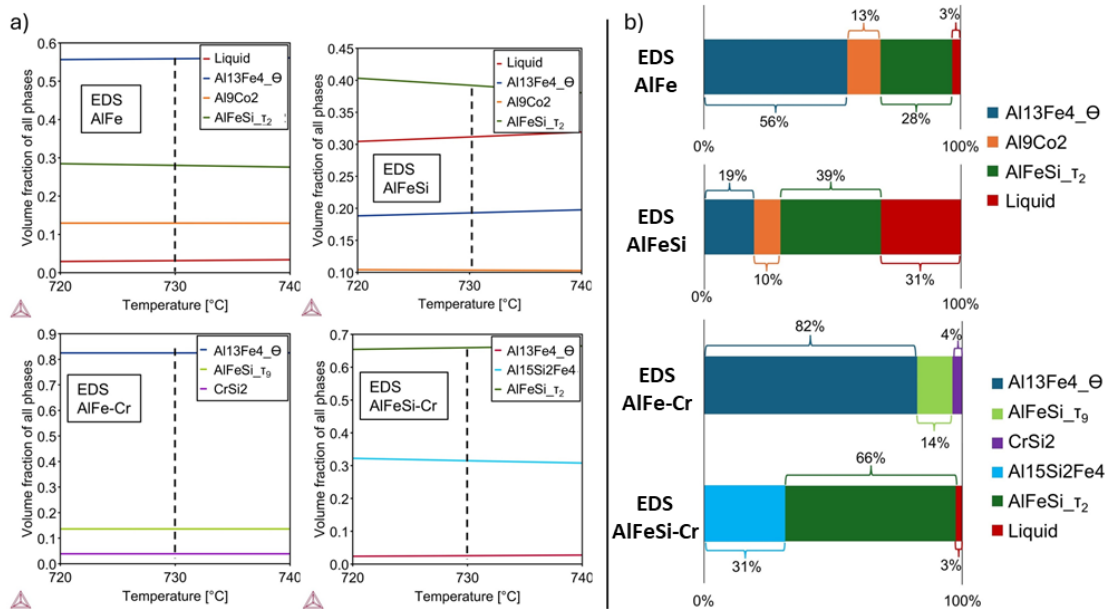


Figure 2-27. (a) Volume fraction of the stable phases that are present in the interaction layers in the range of 720 - 740 °C, from ThermoCalc equilibrium simulation (b) Volume fraction percentages of the stable phases calculated at 730 °C.

2.5.5. Discussion

2.5.5.1. Factors contributing to the corrosion of different steels

Comparing the chemical compositions (**Table 2-7**) and the Thermo-Calc equilibrium simulation results (**Figure 2-26**), the solubility of the main alloying elements in the Al-Si-X system appears to significantly affect steel dissolution. The AM maraging steel contains 3.65 wt.% more Co than the forged variant, and Co is far less soluble in Al-Si than Fe. H11 lacks Ni, the most soluble alloying element in the Al-Si-X system. These differences help explain the superior corrosion resistance of H11, followed by AM maraging steel, and then the forged one. Additional factors, however, must be considered to explain the significantly greater mass loss of F samples and the similar corrosion performance between AM and H11 steels for exposure times under 60 minutes, particularly in EN 42400 and EN 43500.

At the steel–aluminum interface, IMCs such as $\text{Al}_{13}\text{Fe}_4$, Al_5Fe_2 and AlFe_3 form and influence steel degradation^{2, 33, 34}. While the majority of studies concentrate on steel–pure aluminum systems, ternary Al-Fe-Si intermetallic compounds are suggested to provide superior diffusion barriers¹⁴.

The SEM-EDS analysis performed at the steel–aluminum interfaces revealed the formation of various intermetallic compound layers, whose compositions, expressed in terms of phase fractions, were assessed by Thermo-Calc equilibrium simulations. When the Si content ranged between 4–6 at.% ("AlFe" composition), the IMC layer closest to the steel substrate mainly consisted of $\text{Al}_{13}\text{Fe}_4$, with the liquid phase almost completely suppressed (Figure 2.27b). In contrast, when the Si content increased to 9–19 at.% ("AlFeSi" composition), a second IMC layer formed, characterized by a higher fraction of AlFeSi_{τ_2} and a significantly larger liquid phase volume—approximately ten times greater than in the AlFe layer. In both cases, a small amount of Al_9Co_2 was detected, with a volume fraction variation of only ~3%, considered negligible in its impact. Mn was only occasionally detected in the intermetallic layers and was therefore not included in the Thermo-Calc simulations. However, it could replace for Fe in IMC phases such as $\text{Al}_{19}(\text{Fe},\text{Mn})_4$ and $\text{Al}_3(\text{Fe},\text{Mn})$, potentially altering the morphology or formation temperature of Al-Fe IMCs during solidification.

A comparison of SEM-EDS results with mass loss data over time revealed that the discontinuity or absence of the Fe-rich $\text{Al}_{13}\text{Fe}_4$ layer, replaced by the AlFeSi layer, correlated with increased sample mass loss. This was particularly evident in the F samples after 60 minutes of immersion across all aluminum alloys (**Figure 2-22b**). For instance, in the EN 42400 alloy, the AlFe layer remained stable up to 120 minutes, and mass loss at 60 minutes was roughly one-third lower than for samples tested in EN 43500 and EN 43400. In these latter alloys, the AlFe layer became discontinuous over time, favoring the formation of AlSiFe -rich layers associated with a higher liquid phase content, thus promoting faster steel dissolution. This correlation was further confirmed in the AM samples tested for 120 minutes in the EN 43500 alloy (**Figure 2-22b**), where the absence of the AlFe layer corresponded to the highest mass loss observed. Therefore, when the protective $\text{Al}_{13}\text{Fe}_4$ layer was missing or unstable, the development of a Si-rich IMC with greater liquid phase fraction led to accelerated corrosion due to the enhanced solubility of alloying elements into the melt. The formation of a stable Fe-rich IMC layer, coupled with liquid phase suppression, appears critical in mitigating steel degradation. The instability of the $\text{Al}_{13}\text{Fe}_4$ -rich layer observed in AM samples immersed in EN 43500 between 60–120 minutes could explain the anomalously high mass loss recorded. The localized reappearance of AlFe IMCs, such as after 120 minutes of immersion in EN 43500, may be attributed to two mechanisms. First, local mechanical instability or cracking of the brittle AlFeSi_{τ_2} -rich layer could expose fresh steel substrate to the molten aluminum, enabling renewed nucleation and growth of Fe-rich $\text{Al}_{13}\text{Fe}_4$ intermetallic at specific sites. Second, microstructural or compositional inhomogeneities at the steel surface, such as segregation bands or small surface irregularities, could promote heterogeneous diffusion kinetics and localized depletion of silicon activity, further facilitating the formation of $\text{Al}_{13}\text{Fe}_4$ phases. These combined effects likely explain the sporadic appearance of AlFe layers after prolonged exposure. Furthermore, the segregated banded microstructure characteristic of the forged maraging steel likely contributed to IMC layer instability due to local compositional fluctuations, promoting the formation of less protective intermetallic phases. This hypothesis is supported by the corroded surface profiles, where the AM and H11 samples maintained smoother surfaces compared to the more irregular corrosion observed in the F samples (**Figure 2-21**).

Regarding the H11 steel, distinct behavior was observed due to its specific chemical composition promoting the formation of Cr-rich AlFe and AlFeSi layers. These layers were devoid of liquid phase, making them inherently more protective of the substrate. In the AlFe-Cr layer, $\text{Al}_{13}\text{Fe}_4$ reached a volume fraction of up to 82% with no detectable liquid phase, while the AlFeSi-Cr layer corresponded mainly to AlFeSi_{τ_2} and $\text{Al}_{15}\text{Si}_2\text{Fe}_4$, again without significant liquid phase formation, unlike the Si-rich IMC layers seen in maraging steels.

Additionally, the initial IMC layer adjacent to the H11 steel showed increased Cr concentrations, present either in solid solution within the intermetallic matrix or as undissolved chromium carbides (**Figure 2-28**). From the SEM-EDS data discussed in Section 3.3, Cr was detected at around 1–2 at.%. The Cr enrichment peaks seen in Figure 10 suggest that steel carbides could remain intact within the first IMC layer. Cr present in solid solution is known to inhibit aluminum–iron interdiffusion, thereby slowing IMC layer growth ³⁵. Similarly, undissolved or partially undissolved chromium carbides reduce steel dissolution in molten aluminum ³⁶. Thus, in both conditions, Cr enhances the corrosion resistance of H11 steel in molten aluminum environments.

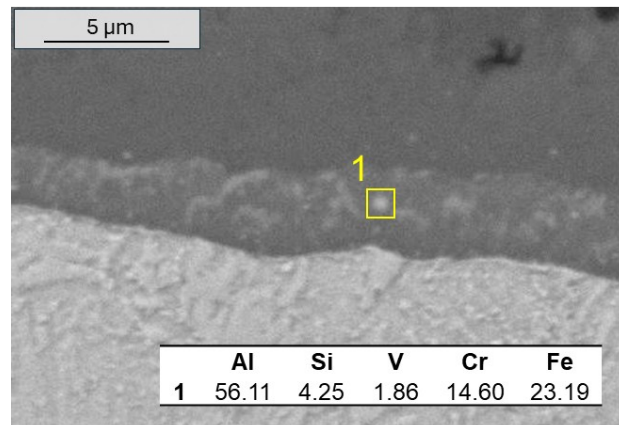


Figure 2-28. Detail of the SEM-EDS analysis of the H11 tool steel and EN 43400 interface after 120 min immersion. Light-grey particles exhibit extremely high Cr content (at. %). Carbon microanalysis data is not presented due to the inherent inaccuracy of its measurement.

Therefore, the absence of a liquid phase within the intermetallic layers, combined with the beneficial effect of Cr and the favorable overall chemical composition, explains

the superior corrosion resistance of the H11 steel compared to the maraging steels. These factors consistently resulted in lower mass losses under all testing conditions. **Table 2-12** summarizes the approximate IMC layer thicknesses under different test conditions. A general trend was observed in which the total thickness of the IMC layer tended to decrease over time when only a single layer stabilized, particularly in the absence of a distinct double-layer structure. Importantly, layer thickness, whether greater or smaller, did not systematically correlate with corrosion resistance. Instead, improved performance was associated with the formation of a protective double-layer structure, especially when a continuous Fe-rich layer was maintained at the steel interface. This trend was evident in the F sample tested in EN 42400, where the AlFe layer remained stable throughout the exposure period, contributing to lower mass loss. In contrast, the AM samples generally showed more consistent AlFe layer stability across all aluminum alloys, reinforcing their enhanced resistance. Although H11 formed compositionally distinct IMCs, specifically Cr-containing AlFe-Cr and AlFeSi-Cr phases, these variations had minimal impact on corrosion performance. As previously discussed, all IMC layers at the H11 interface lacked a liquid phase, which was a dominant factor in limiting steel dissolution. Overall, these findings emphasize that the stability, continuity, and phase composition of the interfacial layer are more decisive for corrosion resistance than its thickness alone.

2.5.5.2. *The effect of Al alloys chemical composition*

The composition of the molten aluminum alloy may affect the mass loss rate, with results indicating that the EN 42400 alloy is the least aggressive towards forged maraging steel (**Figure 2-22b**). This suggests that the Si content may have an influence on the corrosion process. Although the presence of silicon in the ferritic matrix or the aluminum bath can alter the diffusion dynamics of aluminum and the formation of intermetallic compounds, its effect on corrosion rates remains uncertain. Some studies suggest that silicon contributes to the formation of stable intermetallic layers, potentially preventing the development of IMC such as FeAl_2 and Fe_2Al_5 , which are associated with reduced corrosion resistance ¹⁴. Conversely, higher Si content in the melt has been shown to increase the solubility of Fe in the aluminum melt. In one case,

this correlated with increased consumption of a low-carbon steel, while a tool steel showed no significant effect from varying Si content in the aluminum melt ³⁶. This is consistent with the mass loss results observed for the AM and H11 samples, where little to no effect from Si variation was discernible (**Figure 2-22b**).

The potential inhibitory effect of silicon on binary Al-Fe IMCs may be diminished by the presence of Ni or Cr in solid solution within the IMC layers, as the dissolution of these elements at the steel/aluminum interface can favor the formation of $\text{Al}_{13}\text{Fe}_4$ ¹¹. Other influencing factors include process parameters: long exposure times and elevated temperatures promote thermal contributions to the growth kinetics of the interfacial layers, reducing the observable effect of small differences in alloy composition ³⁷.

Regarding the effect of iron content, comparison of the two AlSi10Mg alloys (**Figure 2-22b**), which differ primarily in Fe concentration, revealed no clear trend. Iron did not significantly influence the dissolution behavior of the tested steels. This aligns with the findings of Q. Han et al. ⁶, who reported that while Fe is often added to aluminum alloys to discourage die soldering in HPDC, its protective effect diminishes at processing temperatures exceeding 700 °C unless its concentration exceeds 5 wt.%. Thus, while the chemical composition of the aluminum alloys had a negligible direct effect on steel dissolution, the relative abundances of Si and Fe in the melt indirectly influenced the formation and stability of the interfacial IMC layers, as discussed in Section 2.5.5.1.

2.5.6. Conclusions

This study has examined the corrosion resistance of die steels used in high-pressure die casting when exposed to different molten aluminum alloys, with a focus on the influence of manufacturing processes and alloy compositions of the steels.

The results showed that maraging steel produced through laser-powder bed fusion has significantly better corrosion resistance than its forged counterpart. According to experimental results and Thermo-Calc equilibrium simulations, this improvement can be mainly attributed to the formation of a stable Fe-rich intermetallic layer, which is correlated with the suppression of the liquid phase, thereby reducing the dissolution of

the steel. Other factors contributing to the lower corrosion rate include the more uniform microstructure of the AM maraging steel, which helps prevent localized corrosive attacks, and the higher Co content due to its extremely low solubility in the aluminum alloy.

The H11 tool steel demonstrated the highest overall corrosion resistance, due to its favorable Ni-free chemical composition and its Cr content, which enhances the stability of protective intermetallic layers. This is further supported by the formation of stable intermetallic compound layers with minimal or no liquid phase formation.

While limited to a specific temperature (i.e., 730°C) and three aluminum alloys, the results suggest that the influence of alloy composition on corrosion is minimal. Thus, when the alloy is significantly overheated, as can occur to promote the filling of complex and thin cavities, even using Al alloys with a higher Fe content may not prevent the steel die-liquid aluminum alloy interaction. However, broader studies involving other alloys compositions are necessary to generalize these conclusions.

The static immersion tests performed in this study may not fully replicate the dynamic conditions typical of real HPDC operations, where thermal cycling and erosion also contribute significantly to die degradation. However, they provide valuable insights into fundamental aspects related to the contact between liquid aluminum and steel dies, allowing specific mechanisms like intermetallic formation, wetting behavior, and diffusion phenomena to be isolated and deeper understood. Given this, expanding the testing framework to simulate and quantify these dynamic effects will provide more reliable and transferable results for improving the performance of steels in HPDC applications.

2.5.7. References

1. G. Xu, K. Wang, X. Dong, L. Yang, M. Ebrahimi, H. Jiang, Q. Wang and W. Ding: *J. Mater. Sci. Technol.*, 2021, vol. 71, pp. 12-22.
2. D. Balloy, J.-C. Tissier, M.-L. Giorgi and M. Briant: *Metall. Trans. A*, 2010, vol. 41, pp. 2366-76.
3. P. F. Tortorelli and S. J. Pawel: in *Corrosion: Fundamentals, Testing, and Protection*, ASM International, 2003.
4. M. Yan and Z. Fan: *J. Mater. Sci.*, 2000, vol. 35, pp. 1661-67.
5. César A.C. Sequeira: *High Temperature Corrosion: Fundamentals and Engineering*, John Wiley & Sons, 2019, pp. 325-339.
6. Q. Han and S. Viswanathan: *Metall. Trans. A*, 2003, vol. 34, pp. 139-46.
7. S. Shankar and D. Apelian: *Metall. Trans. B*, 2002, vol. 33, pp. 465-76.
8. Z. W. Chen: *Mater. Sci. Eng. A*, 2005, vol. 397, pp. 356-69.
9. E. K. Tentardini, A. O. Kunrath, C. Aguzzoli, M. Castro, J. J. Moore and I. J. R. Baumvol: *Surf. Coat. Technol.*, 2008, vol. 202, pp. 3764-71.
10. Z. Niu, G. Liu, T. Li and S. Ji: *J. Mater. Process. Technol.*, 2022, vol. 303, 117525.
11. H. He, L. Zhang, Z. Liu and W. Zhao: *Mater. Charact.*, 2023, vol. 203, 113062.
12. A. Školáková, J. Körberová, P. Kratochvíl, P. Salvetr, D. Deduytsche and P. Novák: *Mater. Chem. Phys.*, 2021, vol. 271, 124941.
13. N. Takata, M. Nishimoto, S. Kobayashi and M. Takeyama: *Intermetallics*, 2014, vol. 54, pp. 136-42.
14. B. Dangi, T. W. Brown and K. N. Kulkarni: *J. Alloys Compd.*, 2018, vol. 769, pp. 777-87.
15. S.-H. Hwang, J.-H. Song and Y.-S. Kim: *Mater. Sci. Eng. A*, 2005, vol. 390, pp. 437-43.
16. S. Chen, D. Yang, M. Zhang, J. Huang and X. Zhao: *Metall. Trans. A*, 2016, vol. 47, pp. 5088-100.
17. V. I. Dybkov: *J. Mater. Sci.*, 1990, vol. 25, pp. 3615-33.
18. X. Zhang, X. Li and W. Chen: *Surf. Interface Anal.*, 2015, vol. 47, pp. 648-56.
19. K. A. Nazari and S. G. Shabestari: *J. Alloys Compd.*, 2009, vol. 478, pp. 523-30.
20. R. Casati, J. N. Lemke, A. Tuissi and M. Vedani: in *Metals*, 2016.
21. C. European, I. E. a. S. Directorate-General for Internal Market, M. Grohol and C. Veeh: *Study on the Critical Raw Materials for the EU 2023 – Final Report*, Publications Office of the European Union, 2023.
22. L. Marchini, P. Tonolini, L. Montesano, M. Gelfi and A. Pola: in *Procedia Struct. Integr.*, 2024, pp. 203-11.
23. G. K. Sigworth and R. J. Donahue: *Int. J. Metalcast.*, 2021, vol. 15, pp. 1031-46.
24. H. Springer, A. Kostka, E. J. Payton, D. Raabe, A. Kaysser-Pyzalla and G. Eggeler: *Acta Mater.*, 2011, vol. 59, pp. 1586-600.
25. X. Fang, G. Shao, Y. Q. Liu and Z. Fan: *Mater. Sci. Eng. A*, 2007, vol. 445-46, pp. 65-72.
26. D. S. Cantú-Fernández, J. J. Taha-Tijerina, A. González, P. G. Hernández and B. Quinn: in *Metals*, 2024.
27. M. V. Maisuradze and O. A. Surnaeva: *Metallurgist*, 2017, vol. 61, pp. 558-64.
28. F. D'Errico: *J. Fail. Anal. Prev.*, 2010, vol. 10, pp. 351-57.
29. P. Tonolini, L. Marchini, L. Montesano, M. Gelfi and A. Pola: *Procedia Struct. Integr.*, 2022, vol. 42, pp. 821-29.
30. J. Rong, Z. Kang, S. Chen, D. Yang, J. Huang and J. Yang: *Mater. Charact.*, 2017, vol. 132, pp. 413-21.
31. M. C. J. Marker, B. Skolyszewska-Kühberger, H. S. Effenberger, C. Schmetterer and K. W. Richter: *Intermetallics*, 2011, vol. 19, pp. 1919-29.
32. C. M. Fang, Z. P. Que, A. Dinsdale and Z. Fan: *Intermetallics*, 2020, vol. 126, 106939.
33. Z. Que, Y. Wang, C. L. Mendis, C. Fang, J. Xia, X. Zhou and Z. Fan: in *Metals*, 2022.
34. V. Joshi, A. Srivastava and R. Shivpuri: *Wear*, 2004, vol. 256, pp. 1232-35.
35. W.-J. Cheng and C.-J. Wang: *Appl. Surf. Sci.*, 2013, vol. 277, pp. 139-45.
36. I. Goto, R. Ohyama and K. Kurosawa: *Int. J. Metalcast.*, 2024, vol. 18, pp. 2872-81.
37. T.-p. Zou, G.-y. Yu, S.-h. Chen, J.-h. Huang, J. Yang, Z.-y. Zhao, J.-p. Rong and J. Yang: *Trans. Nonferrous Met. Soc. China*, 2021, vol. 31, pp. 2570-84.

2.6. Root-Cause Analysis of a Failed LPBF Conformal Cooling Insert for die-casting

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2.6.1. Abstract

This study investigates the failure of a 1.2709 (18Ni300) maraging steel insert used in high-pressure die casting applications. The insert was manufactured by laser powder bed fusion technology. The component, featuring conformal cooling channels, was decommissioned due to coolant leakage. A comprehensive failure analysis was conducted through optical and scanning electron microscopy, energy-dispersive X-ray spectroscopy. Results revealed a combination of failure mechanisms, namely, corrosion fatigue and stress corrosion cracking, exacerbated by die thermal cycling and contact with aggressive aqueous environments. The channel geometry also acted as an intrinsic stress concentrator for cracks nucleation. The presence of oxidized cracks, corrosion product buildup, and copper deposits is consistent with environmental conditions that significantly contributed to the failure. A basic finite element analysis was also performed to verify that the points of maximum stress concentration on the component corresponded to the crack nucleation sites. These findings underscore the importance of coolant water quality control and channel design in improving the durability of LPBF maraging steel tooling for HPDC applications.

2.6.2. Introduction

Additive manufacturing, particularly laser powder bed fusion (LPBF), has reshaped the design of tooling for high-pressure die casting (HPDC)¹. By enabling conformal cooling channels (CCCs), LPBF improves heat extraction and temperature uniformity, supporting higher casting quality^{2,3}.

EN 1.2709 (18Ni300) maraging steel is widely adopted for LPBF tooling owing to weldability; rapid solidification yields a martensitic microstructure that is strengthened by direct aging⁴⁻⁷. Nevertheless, LPBF can introduce defects (porosity, lack of fusion)

that threaten internal features such as cooling channels; external die surfaces are often polished, whereas internal CCC surfaces typically remain as-built due to access limitations^{8,9}.

Compared with straight-drilled channels, CCCs track the cavity contour at smaller diameters and with frequent directional changes and close spacing, introducing design/fabrication, thermal and durability challenges; these geometric features act as stress concentrators near the melt–die interface¹⁰. Despite these concerns, CCCs (**Figure 2-29**) are increasingly used in HPDC tooling for their thermal benefits, with process-level gains already demonstrated in production¹⁰. Beyond the documented cycle-time and porosity gains, CCCs can also reduce die soldering by keeping the steel surface below critical Al–Fe intermetallic growth temperatures and, by reducing spray demand, limit lubricant pyrolysis and surface contamination. Independently controlled cooling loops further allow on-press tuning of flow and temperature to balance productivity with surface finish on a part-specific basis, provided coolant quality and channel placement are tightly controlled¹¹.

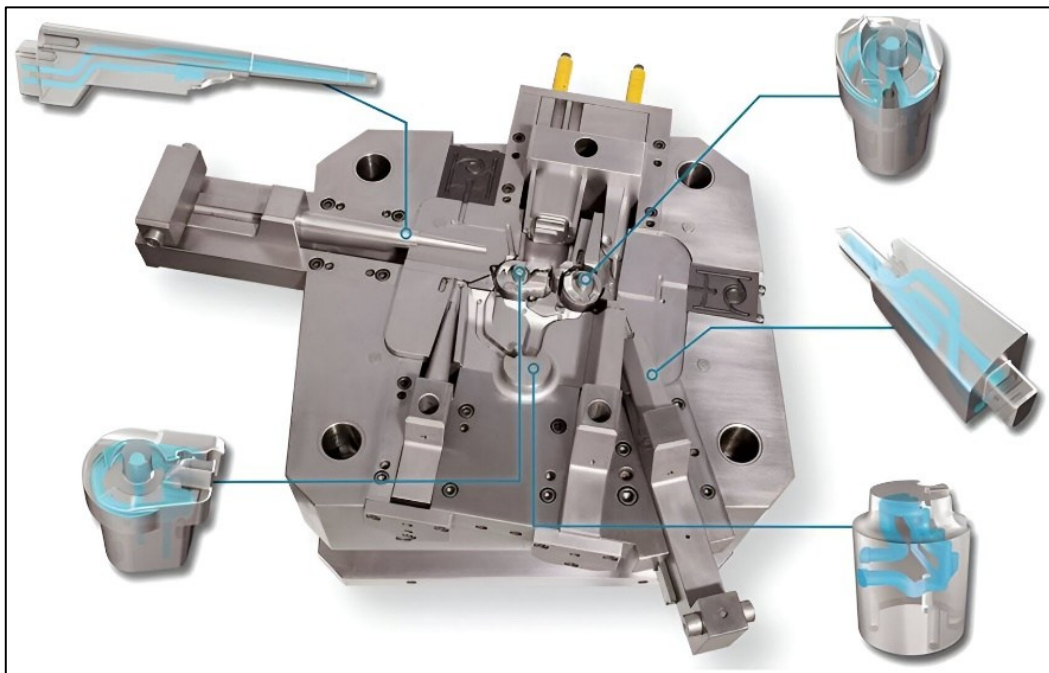


Figure 2-29 Example of an L-PBF-fabricated insert featuring conformal cooling channels (CCCs) within a die for high-pressure die casting (HPDC) of aluminium. Image reprinted from ¹⁰ under CC BY 4.0.

The mechanical reliability of LPBF 18Ni300 maraging steel largely depends on the effectiveness of aging treatment, which triggers the precipitation of Ni_3Ti and Fe_2Mo and raises hardness from ~ 350 HV in the as-built state to > 550 HV after aging at $480\text{--}500^\circ\text{C}$ ^{12,13}. Owing to the refined cellular substructure and segregation inherited from rapid solidification, precipitation kinetics are accelerated compared with wrought material, but the over-aging window is narrower, leading to rapid softening if temperature exposure is prolonged^{4,6}. Direct aging, without prior solution treatment, typically achieves ~ 54 HRC and tensile strengths above $1900\text{--}2000$ MPa while maintaining $3\text{--}5\%$ ductility^{14,15}. Thus, LPBF maraging steels can attain mechanical strength comparable to conventional counterparts, although anisotropy, residual stress, and melt-pool boundaries may locally reduce toughness and favor crack deflection. Under cyclic loading, LPBF 1.2709 maraging steel exhibits a fatigue limit near 730 MPa at 10^7 cycles in the optimally aged condition, with failures typically initiating at surface or near-surface lack-of-fusion defects¹⁶. Heat treatment markedly improves high-cycle fatigue life compared to the as-built state by reducing retained austenite and homogenizing the microstructure, although surface quality and defect orientation remain dominant factors.

These aspects underline that, while LPBF enables highly efficient thermal management through conformal cooling, the material's service performance ultimately depends on aging parameters, microstructural uniformity, and the aggressiveness of the cooling environment, factors examined in the following analysis.

Environmental conditions inside cooling circuits further influence durability. Maraging steels can exhibit cracking susceptibility in alkaline, aerated water, especially at elevated conductivity and in the presence of contaminants; higher crack growth in water versus oil and branching in low-inhibitor solutions have been reported¹⁷. Environmentally assisted mechanisms in related systems involve anodic dissolution and/or hydrogen embrittlement¹⁸; aggressive ions (e.g., Cl^- , S^{2-}) and turbulent flow can disrupt passive films and accelerate damage, whereas corrosion inhibitors are routinely used to form protective layers and limit electrochemical reactions^{19,20}.

During the HPDC cycle, inserts undergo steep transient thermal gradients and rapid temperature fluctuations that superimpose mechanical restraint and residual stresses; in CCC-equipped regions these effects localize at directional changes and thin ligaments, creating pronounced stress concentrations^{21,22}. A plasticity-loss criterion has recently been shown to predict crack onset at CCC surfaces under such loading²³ yet catastrophic failures originating within conformal cooling networks remain insufficiently documented.

Given typical life targets on the order of 10^5 cycles under well-controlled conditions, premature failures have significant economic implications and warrant focused analysis^{11,24}. The present study examines a die insert in which fracture initiated from within the conformal cooling channels, relating channel geometry, thermo-mechanical loading, and cooling-water chemistry to the observed damage, with the goal of providing actionable guidance for CCC design and coolant management in HPDC practice.

2.6.3. Materials and Methods

The present study investigates the failure of an LPBF-fabricated die insert with conformal cooling channels produced by Texer Design S.r.l. using 1.2709 (18Ni300) maraging steel, age-hardened with proprietary heat treatment parameters by the supplier to achieve a hardness of 48 HRC (**Figure 2-30**). The insert was used for HPDC production of AlSi9Cu3(Fe) alloy components, with the molten metal injected at a specific pressure of 1200 bar. The component head, which directly contacts the melt, connects to a guiding body that positions the insert within the die. The internal cooling system operated in a closed loop with water at 150 °C and 5.25 bar. Water enters through a central channel in the head, flows through the upper section, and exits via the bottom return channel. After only a brief time in service, water leakage compromised the thermal-regulation system, leading to the component's decommissioning. The number of cycles recorded before failure was approximately 15,000, which is very low considering the theoretical lifespan of about 100,000 cycles expected for these components operating under optimal conditions, corresponding to a service life reduction of about 85%.

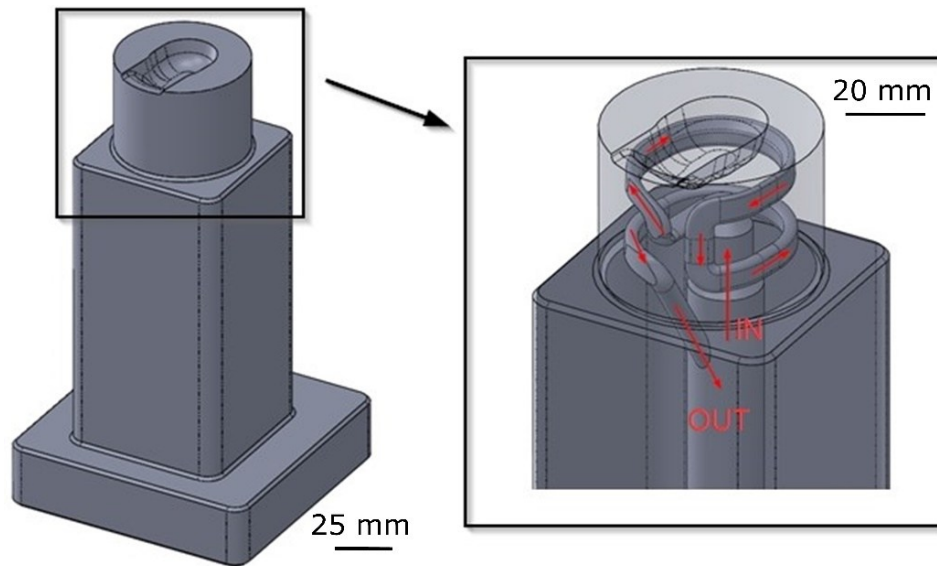


Figure 2-30. Reconstructed model of the HPDC insert highlighting the internal conformal cooling channels (transparent view). Red arrows indicate the direction of water flow through the system. *Courtesy of Texer Design S.r.l.*

A sample of the damaged tooling insert shown in **Figure 2-30** was collected from the head region, where the water leakage was more evident, in order to investigate the failure mechanisms affecting the water-cooling system. As illustrated in **Figure 2-31a**, the image of this sample has been superimposed on a longitudinal cross-sectional sketch of the insert to highlight the intersection with the internal cooling channels. The sketch shows geometric differences between the upper and bottom channel sections. While the bottom channel exhibits a simple stadium-like cross-section, the upper channel presents a more complex profile adapted to follow the component's top surface contour. Comparison of the schematic and actual cross-sections clearly demonstrates that localized erosion significantly modified the geometry of the internal channel. This degradation has led to an irregular channel profile and the partial loss of the original shape. Moreover, numerous cracks propagate from various regions of the cooling system, including both the upper and bottom channel sections, as well as the top region of the supply channel. Notably, the cracks appear to initiate preferentially from the channel edges. To further assess the extent of the damage, higher magnification images of the upper and bottom channel sections are provided in **Figure 2-31b** and **Figure 2-31c**, respectively. The upper channel section exhibits more severe erosion, as indicated

by yellow arrowheads, along with a prominent branched crack at the top right, with the propagation direction marked by a red arrow. In contrast, although the bottom channel section appears less affected by erosion, multiple cracks are still visible along the upper and lower boundaries. Notably, a critical through-thickness crack connects the right side of the bottom channel with the adjacent supply channel.

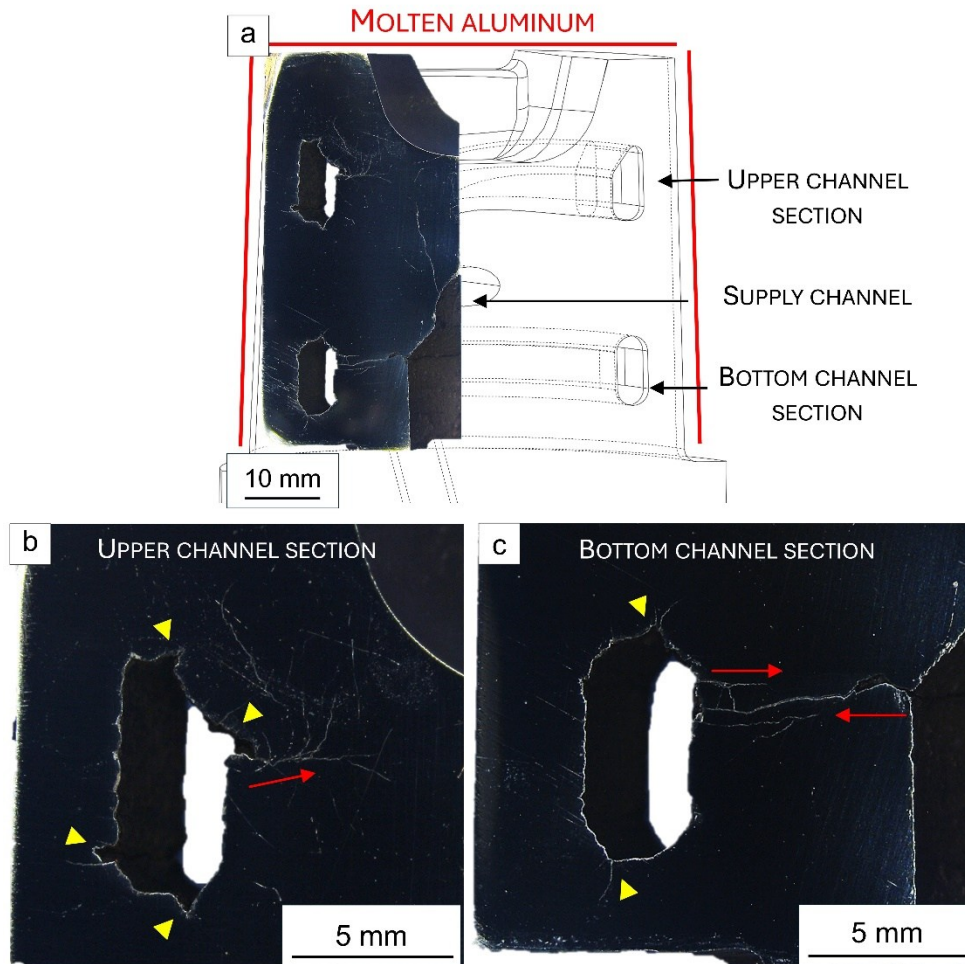


Figure 2-31. (a) Cross-sectional view of the insert head showing the analyzed region superimposed on a schematic of the internal cooling channels. (b) Upper channel section with severe erosion (yellow arrowheads) and a branched crack (red arrow). (c) Bottom channel region with multiple cracks, including a through-thickness crack extending toward the adjacent supply channel (red arrows). The sample pictures appear dark because polarized light and high contrast were used to enable clearer visualization of the cracks.

The chemical composition of the water typically used in this thermoregulation system was assessed using ion chromatography, following the DIN EN ISO 10304-1 standard for dissolved anions. Photometric determination was also applied where required, as

indicated in **Table 2-13** and **2-14**. The results show that the water is softened to an extremely low hardness level (0.26 °dH) and treated with corrosion-inhibiting additives. Among these, molybdates (MoO_4^{2-}) are used as the primary inhibitors for protecting steel surfaces, with a concentration of 272 mg/l. The detection of elevated levels of PO_4 (31.9 mg/l) and total phosphorus (10.4 mg/l) suggests the presence of phosphate-based compounds, such as polyphosphates and orthophosphates, although their specific chemical forms cannot be definitively confirmed.

Despite being a closed-loop system, the water exhibits a relatively high electrical conductivity (841 $\mu\text{S}/\text{cm}$), which is expected to increase further at the operating temperature of 150 °C. This elevated conductivity, in conjunction with the presence of aggressive ions such as Cl^- (5.9 mg/l) and NO_2^- (12.5 mg/l), can promote localized corrosion and increase the susceptibility of metallic parts to corrosion-assisted cracking phenomena. The water also contains measurable concentrations of other metallic ions, such as Fe (3.2 mg/l), Zn (1.8 mg/l), and Cu (0.28 mg/l), which may originate from corrosion or leaching within the cooling system. The measured pH is 8.46, i.e. mildly alkaline; this level is likely maintained by periodic addition of calcium bicarbonate, $\text{Ca}(\text{HCO}_3)_2$, which functions as a buffer and mild hardness conditioner²⁵.

Table 2-13. Chemical composition of the process water used in the cooling system. Dissolved anions were determined by ion chromatography in accordance with DIN EN ISO 10304-1.

Elements (mg/l)														
Mg	Ca	Na	K	Cu	Fe	Zn	Al	B	Si	P	Mn	Ni	Cr	Mo
0.16	1.60	195	0.28	0.28	3.2	1.8	0.22	0.13	2.0	10.4	0.14	0.18	0.02	148

Ions (mg/l)							
Cl^-	SO_4^{2-}	NO_3^-	NO_2^-	Br	PO_4^{3-}	MoO_4^{2-}	
2.1	3.4	12.5	<0.5	5.9	20.9	272	

Table 2-14. Additional physicochemical properties of the cooling water, including hardness, conductivity, and buffering constituents. Values marked with * were obtained by photometric analysis.

Alkaline earth	Hardness	CO_2	HCO_3	PO_4	SiO_2	Polyacrylate*	Conductivity	pH
0.05 mmol/l	0.26 °dH	3.6 mg/l	407 mg/l	31.9 mg/l	4.3 mg/l	35.2	841 $\mu\text{S}/\text{cm}$	8.46

The hardness of the failed insert was measured using a Rupac 500 Mra hardness tester. To document the macroscopic condition of the component, a Leica DSM300 digital

microscope was used at low magnification to acquire a complete image of the cross-sectioned sample. A preliminary metallographic analysis of the damaged cross section shown in Figure 3b was conducted by means of a Leica DMI 5000M optical microscope. For this observation, the sample was mirror-polished using a 1 μm diamond paste on a cloth and etched with Nital 5 (5% HNO_3 in ethanol) for 10 seconds to reveal the maraging steel microstructure.

To assess internal porosity, image analysis was carried out using LAS4 software (Leica). Ten micrographs (100 $\times$ magnification) covering a total area of 3.29 mm^2 were processed to identify pores and calculate the area fraction as the ratio between the pores area and the total picture area (A_p/A_t).

Scanning electron microscopy (SEM) combined with energy-dispersive X-ray spectroscopy (EDS) was performed using a Leo Evo 40XVP microscope equipped with an Oxford EDS detector. The internal surfaces of the cooling channels as well as the fracture cross-sections were examined to evaluate the presence of corrosion products and determine their chemical composition. Additionally, the principal cracks originating from both the upper and lower cooling channels were mechanically opened to allow the inspection of the fracture surfaces.

A simple finite element analysis (FEA) was conducted using a CAD reconstruction of the insert to estimate thermal-stress distributions under steady-state conditions and to verify that the cracks observed on the channel originated from the most highly stressed regions. In detail, the component was partially reconstructed in SolidWorks®, and its structural response to thermal and pressure loads was evaluated using the Simulation® module. The complex, non-classical stress state around the channels required a finite element approach to estimate the local stress increase near critical areas.

The analyses were performed in two subsequent steps. In the first phase, thermal analyses were carried out to evaluate the temperature distribution within the insert, considering both the temperature of the molten aluminum and that of the cooling water. In the second phase, structural analyses were performed by applying the temperature field obtained from the thermal simulation to estimate the resulting stress distribution. The mechanical analysis was conducted in the elastic regime, assuming linear elastic behavior, and the consistency of this assumption was verified by the fact that the simulated stress values remained below the estimated material's yield strength. The

model employed symmetrical quadratic tetrahedral elements, with approximately 190,000 nodes and 32,000 elements. The minimum element size in the regions of maximum stress was 0.02 mm, ensuring adequate spatial resolution. The following material properties were used as input parameters for the simulation:

- Young's modulus at 100 °C: 190 GPa, reduced of 5 GPa per 100 °C increment, as reported by Hameed et al.²⁶;
- UTS (Ultimate Tensile Stress) and yield strength: retrieved from MatWebTM ²⁷;
- thermal expansion coefficient: 10.1 K⁻¹;
- thermal conductivity: 27 W/mK;
- Poisson's ratio: 0.3.

Although this approach neglects the transient and cyclic nature of temperature variations during HPDC, it was intentionally adopted to conservatively identify the most critical stress-concentration zones under peak thermal gradients. These results are not intended to reflect actual stress amplitudes at service temperatures but rather to highlight geometrical vulnerabilities under extreme scenarios.

During each HPDC cycle, the die surface experiences sharp thermal fluctuations, rising rapidly to 400–500 °C upon molten aluminum injection, and then cooling to 150–200 °C shortly thereafter due to lubricant spraying^{22,28,29}. To assess the resulting thermal stresses induced by these fluctuations, the simulation was conducted by evaluating representative steady-state temperature distributions corresponding to distinct stages of the thermal cycle. Among these, only the most critical condition, corresponding to a peak surface temperature of approximately 500 °C, is reported in detail. This approach provides a conservative estimate of the stress field and allows the identification of the most critical geometrical features, which represents the main objective of this auxiliary analysis.

2.6.4. Results and Discussion

2.6.4.1. Steel chemical composition assessment

The chemical composition of the sample was verified by combining the data collected from a Thermo Scientific Niton XL2-100G used to determine the alloy elements and

a Thermo Scientific ARL 4460 high-performance OES spectrometer used for the impurity (i.e., S and P). The results reported in **Table 2-15** confirm that the sample is made with a 1.2709 maraging steel. However, slight deviations from the standard composition were detected, specifically a higher chromium content (0.24 wt.%), a slightly elevated sulfur level (0.012 wt.%), and a lower titanium concentration (0.69 wt.%). These small deviations remain within or close to the typical specifications of gas-atomized powders and may reflect minor variability or contamination introduced during atomization.

Table 2-15. Measured chemical composition of the LPBF-fabricated insert, compared with standard specifications for 1.2709 (EN 10027-2:2015) maraging steel.

El. (wt.%)	C	Si	Mn	Cr	Mo	Ni	Co	Ti	S	P	Fe
Sample	0.02	0.05	0.07	0.24	5.14	18.12	8.76	0.69	0.012	0.006	Bal.
1.2709	< 0.03	< 0.10	< 0.15	<0.025	4.50- 5.20	17.0- 19.0	8.50- 10.0	0.80- 1.20	< 0.010	< 0.010	Bal.

The hardness measured in the sample (48 HRC) meets the requirements for this type of product and is consistent with the typical values obtained after aging treatment³⁰. The porosity analysis revealed a total pore area fraction of less than 0.01%, a very low value that unlikely play a significant role in the observed failure mechanism, thereby confirming the proper manufacturing quality of the insert. This finding rules out porosity as a critical defect, unlike in previous failure analyses of similar LPBF components where aligned pores facilitated crack propagation³¹.

2.6.4.2. Optical microscopy analysis

The optical microscope analysis provided a comprehensive assessment of the damage within the cooling channels, focusing on both the general distribution of cracks and the finer details of their morphology, as illustrated in **Figures 2-32** and **2-33**.

Figure 2-32a shows a section of the insert head where a very long crack propagated starting from the internal surface of the upper cooling channel. This crack, corresponding to that highlighted in **Figure 2-31b**, grew initially approximately

normal to the channel wall and subsequently branched. The channel's internal surface is covered by a thick, dark corrosion layer that is cracked at multiple points, forming loose fragments.

Figure 2-32b is a higher-magnification view of the most damaged region highlighted in **Figure 2-31c**. This area is characterized by the presence of a main crack that traverses the ligament separating the bottom and supply channels. It is interesting to note that, in this case, the crack initiated at the supply channel, and propagated leftward until reached the bottom channel. This is evident from the propagation direction of the secondary branches. Conversely, a shorter crack propagated from the bottom channel and interconnected with the main crack, promoting the detachment of material fragments.

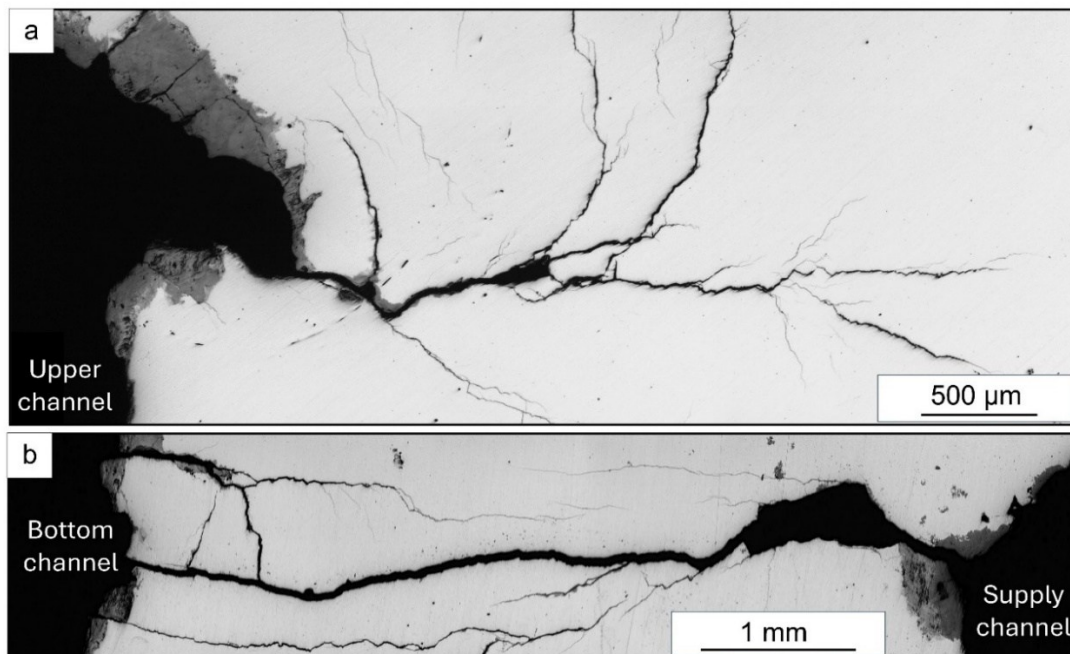


Figure 2-32. (a) Upper channel section showing multiple cracks originating from corroded inner surfaces. (b) Bottom channel section with a major through-crack connecting to the supply channel.

Notably, crack initiation was often observed at channel edges, where thermal-mechanical stress is geometrically amplified. This is consistent with the presence of repeated directional changes and reduced cross-sections in conformal cooling geometries, which act as intrinsic stress concentrators during HPDC operation. The observed features point toward a mutually reinforcing degradation between localized corrosion and mechanically driven crack propagation.

In **Figure 2-33a**, the lower portion of the bottom-channel section shows several straight cracks, minimally branched, propagating approximately normal to the channel wall. These cracks often nucleate at the bottoms of corrosion pits and then traverse the oxide layer, which becomes fragmented and readily spalls, exposing fresh metal and promoting further corrosion. This behavior points to a synergistic corrosion–cracking mechanism in which each process accelerates the other.

The higher-magnification images in **Figures 2-33b-c** support the interpretation of corrosion-assisted damage. **Figure 2-33b** reveals that corrosion is active at the crack tip. **Figure 2-33c** shows a magnified view of the heavily oxidized channel surface (cf. **Fig. 2-32a**). The crack propagates within the surface-oxide without cutting into the substrate. Under repeated thermal cycling, cyclic strain can break this brittle oxide; small fragments may spall and be removed by the coolant, exposing fresh metal and promoting further attack.

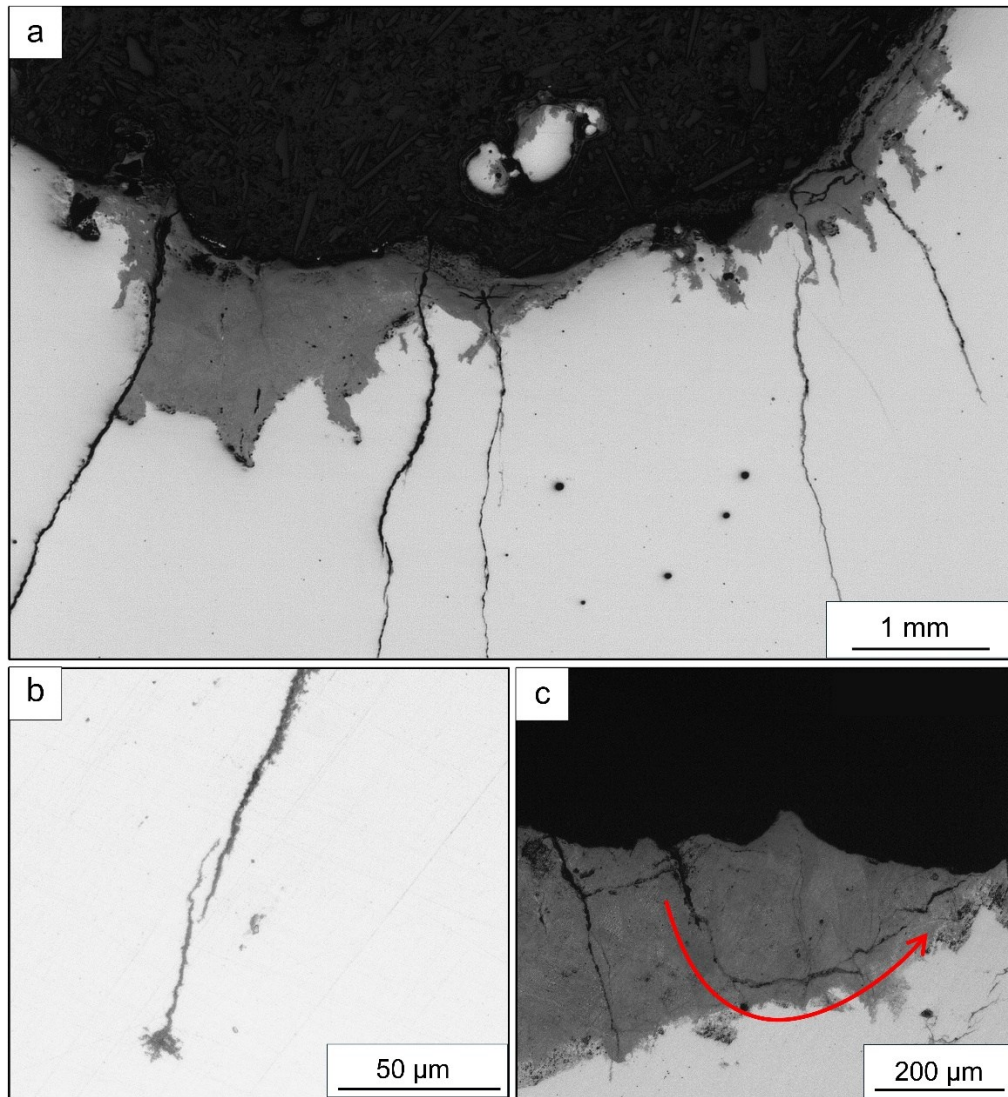


Figure 2-33. (a) High magnification image of orthogonal crack propagation through a thick, uneven oxide layer. (b) Crack tip showing active corrosion. (c) Crack development is limited to the surface oxide near the channel edge.

Additional insights were obtained from the Nital 5 etched section shown in **Figure 2-34**. The characteristic martensitic lath microstructure was revealed (**Fig. 2-34a**), and remnants of melt-pool boundaries were faintly visible in regions where the laths changed orientation. In **Figure 2-34b**, a crack deviates along a melt-pool boundary, indicating that the thermal history of the LPBF process may locally influence crack paths through microstructural gradients or segregation. Such deflection behavior is consistent with previous observations in additively manufactured alloys such as Inconel 625 and stainless steels, where fusion boundaries, due to segregation or

residual stresses, can exhibit locally reduced corrosion resistance and mechanical integrity^{32,33}. However, most cracks propagate along straight paths, limiting the influence of melt-pool boundaries on crack progression to sporadic, localized events, consistent with their faint appearance after etching. The presence of oxide-rich zones at crack sites confirms the contribution of corrosion processes. Taken together, the prevalence of straight cracks with occasional branched morphologies indicates that corrosion-fatigue (CF) was the primary damage mechanism. The branched features, often associated with stress corrosion cracking (SCC), may also arise from thermally driven fatigue processes under high cyclic gradients, as reported in similar studies^{34,35}. Hence, any contribution from SCC is considered local and secondary, possibly occurring under quasi-static stress conditions where crack growth is less influenced by cyclic loading^{36,37}.

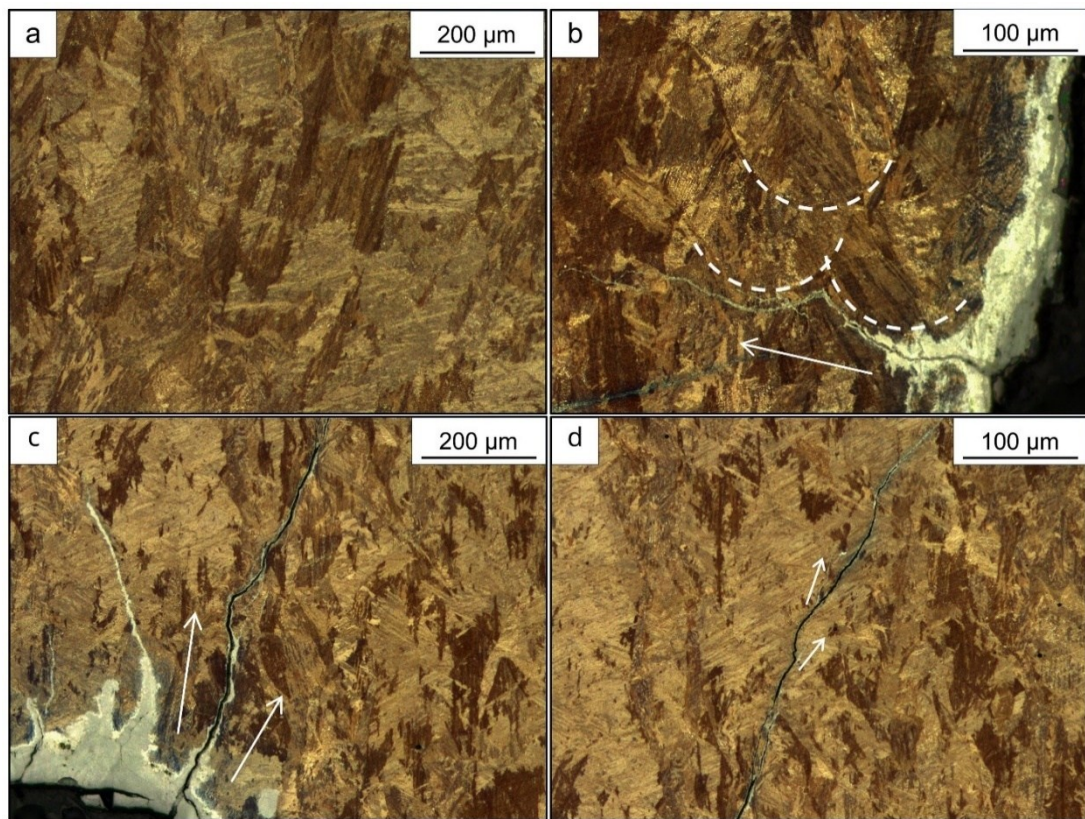
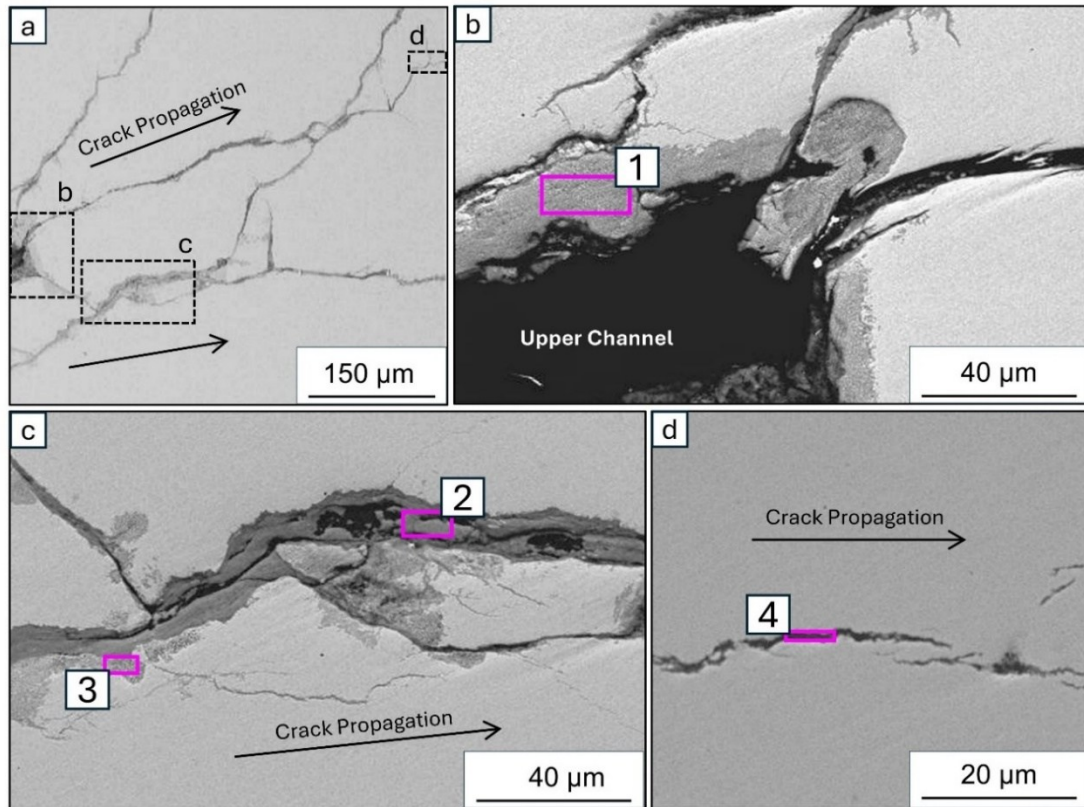


Figure 2-34. (a) Etched cross-section revealing a lath-martensite microstructure. (b) Crack whose path appears to follow faint melt-pool boundaries (dashed arcs). (c–d) Predominantly straight, transgranular cracks with limited branching, consistent with corrosion-fatigue damage. White arrows indicate crack-propagation direction.

2.6.4.3. SEM-EDS analysis

To characterize the corrosion products inside the cracks, BSE imaging and spot-EDS analyses were performed on a representative region of the upper cooling channel, in the same area highlighted in **Figures 2-31b** and **2-32a**. **Figure 2-35a** shows an overview of the propagated crack pattern in this region; the dashed boxes mark the areas magnified in **Figure 2-35b–d**. Magenta boxes indicate the EDS spots (1–4), with compositions reported in the table below. Along the crack, from the oxidized channel surface to the interior, the oxide does not show substantial compositional changes: it mirrors the Fe–Ni matrix (with minor Co and Mo), indicating in-situ oxidation. Occasional S, Si, and Ca are present as coolant-borne impurities, whereas C is mainly attributed to sample-preparation residues. Taken together with the morphologies documented in **Figures 2-32 – 2-34** (pit/edge-rooted initiation, straight vs. branched paths, oxide-lined crack flanks), the uniform Fe–Ni oxide along the crack length confirms in-situ oxidation during service and is consistent with a corrosion-assisted mechanism at channel surfaces.



wt. %	C	O	Si	S	Ca	Ti	Cr	Fe	Co	Ni	Mo
1	3.73	18.91	0.29	0.66		1.04	0.30	42.54	5.54	20.55	6.54
2	2.63	31.34	2.35	0.72				48.81	7.15	5.80	1.12
3	2.49	31.65		0.77		1.03		48.51	6.37	21.17	6.52
4	4.69	17.13			0.20	0.52	0.23	55.10	7.44	11.35	3.33

Figure 2-35. BSE micrographs of upper channel crack morphology and oxide chemistry. (a) Overview of the propagated crack network; dashed boxes locate the regions magnified in (b–d). Magenta boxes indicate EDS acquisition spots (1–4), with corresponding compositions reported in the table below.

Quantitative EDS results from corrosion products observed in cracks and near-surface regions SEM-EDS analysis of the mechanically opened crack offers complementary information on the channel wall (**Figure 2-36a–b**) and the adjacent fracture surface (**Figure 2-36c–d**).

On the channel wall (**Figure 2-36a–b**), spectrum 2, acquired from the greyish corrosion film, shows a composition that still reflects the base material, with iron and nickel from the maraging substrate, but also reveals a notable enrichment in copper (~8 wt.%) and zinc (~6 wt.%), accompanied by traces of magnesium and silicon. This chemical signature points to the deposition of brass-derived corrosion products, plausibly indicating contamination by corroding brass fittings or deteriorated

heat-exchanger elements in the cooling circuit. Spectrum 1, taken from one of the bright, cauliflower-like agglomerates, confirms this interpretation: it contains ~63 wt.% copper with only minor oxygen and iron, indicating the presence of metallic Cu debris. However, this feature becomes clearly distinguishable only at higher magnification, as detailed in **Figure 2-37**.

The fracture morphology is masked by a thick oxide scale. Spectrum 3, taken from a darker region, contains more than 40 wt.% oxygen, along with iron, nickel, and minor amounts of magnesium and silicon, indicating a thick Fe–Ni oxide layer. Spectrum 4, sampled from a brighter patch, shows a similar oxygen content but also includes ~7 wt.% copper and a measurable amount of zinc, confirming that the Cu/Zn-rich debris identified on the channel surface had also infiltrated the interior of the crack. At the transition between the crack and the channel surface, spectrum 5 reveals a calcium content as high as ~30 wt.% and oxygen exceeding 50 wt.%, with virtually no other elements present, this supports the presence of calcium carbonate (CaCO_3) precipitated from thermal decomposition of $\text{Ca}(\text{HCO}_3)_2$, following the reaction $\text{Ca}(\text{HCO}_3)_2 \rightarrow \text{CaCO}_3 \downarrow + \text{CO}_2 + \text{H}_2\text{O}$ ³⁸. Precipitation of CaCO_3 is plausible on the hot channel walls where water pH rises³⁹. Inside the narrow crack, however, oxygen ingress is limited, so differential-aeration cells are unlikely. Instead, the crystalline carbonate acts as an electrolyte-soaked wedge that preserves solution continuity along the crack path.

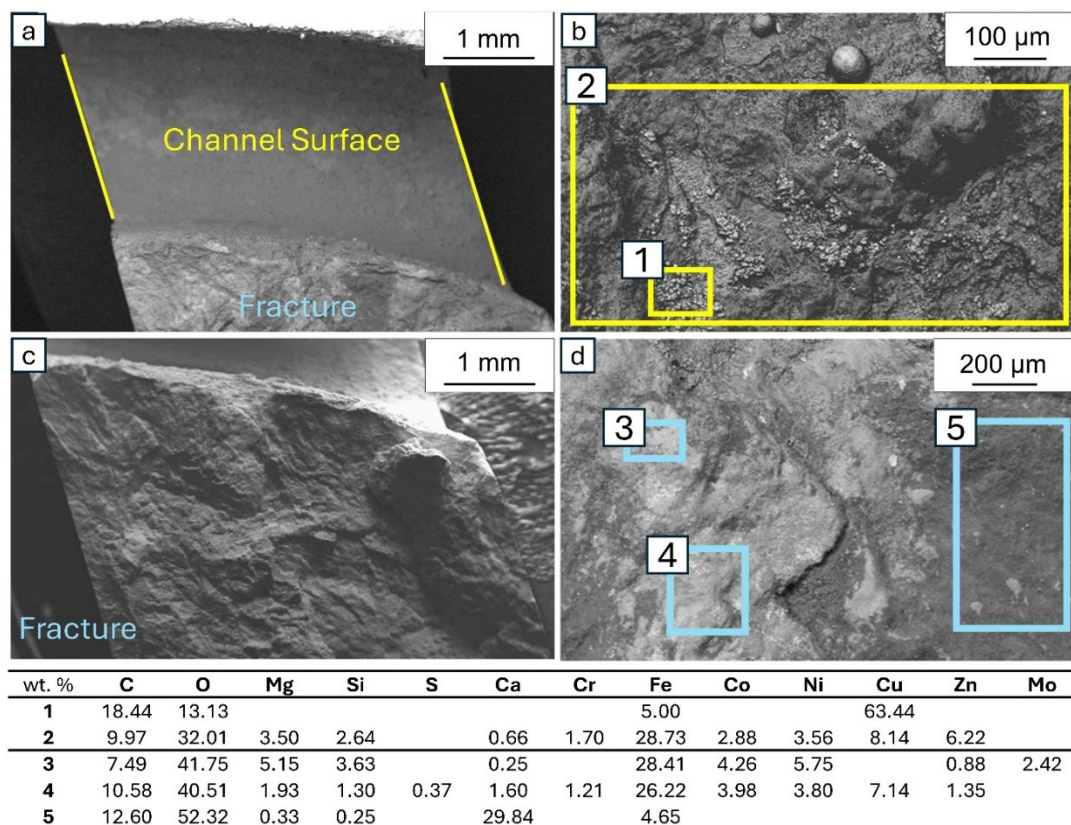


Figure 2-36. SEM analysis of upper channel mechanically opened crack. (a) Cross-sectional view showing the channel wall (upper band) and adjacent fracture surface. (b) Higher magnification of the inner surface, with metallic copper debris (Spectrum 1) and a Cu/Zn-rich corrosion film (Spectrum 2). (c) Overview of the oxidized fracture surface. (d) Close-up highlighting Fe-Ni oxides (Spectra 3-4) and a calcium carbonate deposit (Spectrum 5). Quantitative EDS data are reported in the accompanying table.

These results confirm that the crack flanks and tips were not only oxidized but also coated with Cu/Zn-rich corrosion products and substantial calcareous deposits, raising doubts about whether the true water hardness reflected the declared calcium levels. In particular, the metallic copper and zinc debris in direct contact with the steel matrix can establish strong micro-galvanic cells that favor anodic dissolution of the maraging steel and simultaneously provide cathodic sites for hydrogen evolution. The resulting acidification and hydrogen ingress create favorable conditions for SCC, while the repeated thermal cycling typical of die-casting service promotes CF. These combined effects not only intensified the observed localized damage but also reinforced the coexistence of CF and SCC mechanisms already proposed earlier in the analysis.

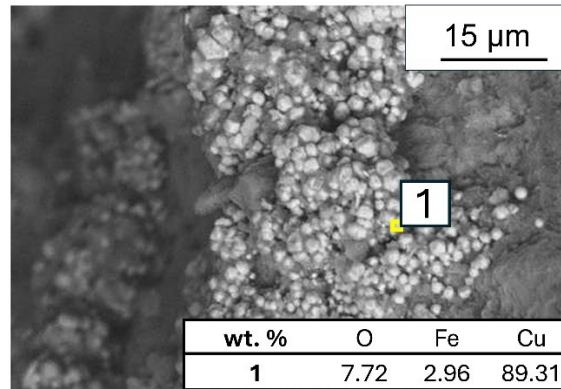


Figure 2-37. SEM–BSE image of the inner channel surface showing cauliflower-like bright particles. EDS spot analysis (Spectrum 1) identifies them as metallic copper (~89 wt %) with minor oxygen and iron.

Finally, the potential contribution of the cooling water chemistry cannot be overlooked. Molybdate-based inhibitors, although effective under stable conditions, can lose their protective function when diluted or stripped away by turbulent flow. If not regularly monitored, their concentration may fall below the protective threshold⁴⁰. In closed-loop systems relying on anodic inhibitors, such dilution is especially dangerous, as it increases the anode-to-cathode area ratio and fosters pitting initiation⁴¹. Given that maraging steels form only a weak passive layer under alkaline conditions⁴², the combination of inhibitor failure, cyclic loading, and occluded-cell chemistry creates a highly aggressive environment, fully consistent with the observed damage.

2.6.4.4. Auxiliary FEA

Finite element analysis (FEA) was used to map the location and relative severity of stress concentrations within the insert. Thermal stresses were evaluated under steady-state boundary conditions, assuming peak temperature gradients representative of HPDC service. As shown in **Figure 2-38**, the stadium-like channel geometry produces a markedly asymmetric maximum principal stress field⁴³, with local maxima at directional changes and sharp corners. These hot-spots (A, B) coincide with the experimentally observed crack-initiation sites (**Figures 2-31, 2-32**). The temperature field (**Figure 2-38b**) highlights the steep wall-normal thermal gradient, especially on surfaces closer to the molten aluminium.

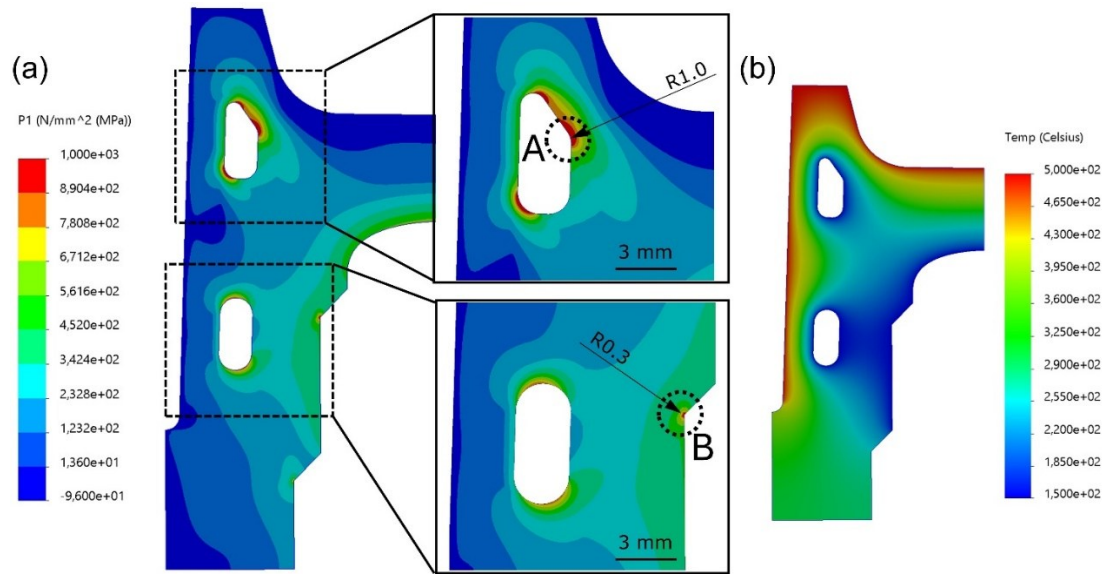


Figure 2-38. (a) Principal stress distribution over the reconstructed insert cross-section. (b) Simulated temperature field during steady-state thermal loading.

Two stress regimes can be distinguished in the simulated field. At location A, the calculated thermal stresses reach their highest magnitudes over a broad region around the channel perimeter and exhibit the steepest spatial gradients, indicating an area prone to crack initiation and accelerated corrosion-fatigue damage. The corresponding experimental observations of branched or interconnected cracks are consistent with thermally driven corrosion-fatigue under high stress gradients. At location B, the high stress level is confined to the sharp corner; here, cracks tend to propagate in a more stable and rectilinear manner, reflecting the localized nature of the stress field.

Overall, these results underscore the coupled role of geometric stress concentration and thermally induced loading in the observed failure. Given model and input limitations, the present FEA is intentionally trend-based: rather than quantifying absolute stress magnitudes, which are highly sensitive to boundary conditions, it identifies spatial patterns of stress localization that closely match the regions where cracking was observed. In particular, the analysis supports a sequence in which the through-crack in **Figure 2-32** is nucleated from the supply channel and subsequently linked with secondary cracks originating from the bottom channel.

2.6.5. Conclusions

The premature failure of the LPBF-fabricated 1.2709 (18Ni300) maraging steel die-casting insert primarily resulted from thermally assisted corrosion-fatigue, promoted by cyclic thermal loading, an aggressive cooling medium, and pronounced stress concentrations. Localized evidence of stress-corrosion cracking was also observed in limited regions where the loading conditions were more compatible with this mechanism, that is, where the cyclic component of the stress was less dominant.

SEM–EDS and metallographic examinations showed that the interior of the cracks was fully oxidized and contained mixed corrosion products together with metallic copper originating from the contaminated cooling water. Crack paths, predominantly straight but locally branched, were transgranular and characteristic of environmentally assisted fatigue growth.

A simplified finite-element analysis was performed to qualitatively identify the regions of highest thermal stress. The predicted stress hot-spots correspond well with the experimentally observed crack-initiation sites, supporting the interpretation that channel geometry and cyclic thermal loading were the primary contributors to failure, while corrosion acted as an accelerating factor once cracking had initiated.

Overall, the premature failure resulted from the combined effects of thermal–mechanical stresses, aggressive coolant chemistry, and limited corrosion protection, rather than from intrinsic material deficiencies of the LPBF maraging steel. This case doesn't mean LPBF maraging steels are intrinsically unfit for HPDC dies; rather, it underscores the need for targeted mitigation measures, as detailed below:

- optimizing cooling-channel geometry to avoid sharp corners and reduce peak cyclic stresses;
- maintaining coolant chemistry (inhibitor dosage, hardness, pH, and conductivity) within specification to suppress corrosion and deposit formation;
- scheduling regular coolant monitoring to prevent inhibitor depletion and contamination.

Alternatively, a more corrosion-resistant alloy, such as stainless steel, may be considered when continuous water-quality control cannot be ensured. In rare cases,

heat-transfer oils can replace water, although this option is generally avoided in HPDC tooling due to flammability and environmental concerns.

2.6.6. References

1. Feng S, Kamat A M, Pei Y, *Design and fabrication of conformal cooling channels in molds: review and progress updates. Int. J. Heat Mass Transf.* **171**, 121082 (2021). <https://doi.org/10.1016/j.ijheatmasstransfer.2021.121082>
2. Karakoc C, Dizdar K C, Dispinar D, *Investigation of effect of conformal cooling inserts in high-pressure die-casting of AlSi9Cu3. Int. J. Adv. Manuf. Technol.* **121**, 7311–7323 (2022). <https://doi.org/10.1007/s00170-022-09808-7>
3. Andronov V, Pitrmuc Z, Zajíc J, Šotka P, Beránek L, Bock M, *Conformal cooling as a support tool for eliminating local defects in high-pressure die-casting series production. Prog. Addit. Manuf.* (2024). <https://doi.org/10.1007/s40964-024-00721-x>
4. Oliveira A R, Diaz J A A, Nizes A D C, Jardini A L, Del Conte E G, *Investigation of building orientation and aging on strength–stiffness performance of additively manufactured maraging steel. J. Mater. Eng. Perform.* **30**, 1479–1489 (2021). <https://doi.org/10.1007/s11665-020-05414-4>
5. Allam T, Pradeep K G, Köhnen P, Marshal A, Schleifenbaum J H, Haase C, *Tailoring the nanostructure of laser powder bed fusion additively manufactured maraging steel. Addit. Manuf.* **36**, 101561 (2020). <https://doi.org/10.1016/j.addma.2020.101561>
6. Conde F F, Escobar J D, Rodriguez J, Afonso C R M, Oliveira M F, Avila J A, *Effect of combined tempering and aging in the austenite reversion, precipitation, and tensile properties of an additively manufactured maraging 300 steel. J. Mater. Eng. Perform.* **30**, 4925–4936 (2021). <https://doi.org/10.1007/s11665-021-05553-2>
7. Chadha K, Tian Y, Bocher P, Spray J G, Aranas C, *Microstructure evolution, mechanical properties and deformation behavior of an additively manufactured maraging steel. Materials* **13**, 2380 (2020). <https://doi.org/10.3390/ma13102380>
8. Poudel A, Yasin M S, Ye J, Liu J, Vinel A, Shao S, Shamsaei N, *Feature-based volumetric defect classification in metal additive manufacturing. Nat. Commun.* **13**, 6369 (2022). <https://doi.org/10.1038/s41467-022-34122-x>
9. Bidare P, Jiménez A, Hassanin H, Essa K, *Porosity, cracks, and mechanical properties of additively manufactured tooling alloys: a review. Adv. Manuf.* **10**, 175–204 (2022). <https://doi.org/10.1007/s40436-021-00365-y>
10. Asnafi N, *Tool and die making, surface treatment, and repair by laser-based additive processes. BHM Berg- Hüttenmänn. Mon.* **166**, 225–236 (2021). <https://doi.org/10.1007/s00501-021-01113-2>

11. Armillotta A, Baraggi R, Fasoli S, *SLM tooling for die-casting with conformal cooling channels*. *Int. J. Adv. Manuf. Technol.* **71**, 573–583 (2014). <https://doi.org/10.1007/s00170-013-5523-7>
12. Tan C, Zhou K, Kuang M, Ma W, Kuang T, *Microstructural evolution, nanoprecipitation behaviour and mechanical properties of maraging steel produced by selective laser melting*. *Sci. Technol. Adv. Mater.* **19**, 746–758 (2018). <https://doi.org/10.1080/14686996.2018.1522625>
13. Mugwagwa L, Yadroitsev I, Matope S, *Effect of process parameters on residual stresses, distortions, and porosity in selective laser melting of maraging steel 300*. *Metals* **9**, 1042 (2019). <https://doi.org/10.3390/met9101042>
14. Tan C, *Microstructural evolution, nanoprecipitation behavior and mechanical properties of selective laser melted high-performance grade 300 maraging steel*. *Mater. Des.* (2017). <https://doi.org/10.1016/j.matdes.2017.08.026>
15. Xu X, Ganguly S, Ding J, Guo S, Williams S, Martina F, *Microstructural evolution and mechanical properties of maraging steel produced by wire + arc additive manufacturing*. *Mater. Charact.* **143**, 152–162 (2018). <https://doi.org/10.1016/j.matchar.2018.04.006>
16. Félix-Martínez C, Cruz-González C E, Sánchez-Santana U, Salgado-López J M, Gomez-Ortega A, *High and low cycle fatigue characterization for 1.2709 maraging steel at different additively manufacturing conditions*. *Int. J. Adv. Manuf. Technol.* **133**, 1519–1530 (2024). <https://doi.org/10.1007/s00170-024-13870-8>
17. Diwakar V, Arumugam S, Lakshmanan T S, Sarkar B K, *Environmental stress intensity for maraging steel*. *J. Mater. Sci.* **21**, 1927–1931 (1986). <https://doi.org/10.1007/BF00547927>
18. Bagchi A, Gope D K, Chattopadhyaya S, Wuriti G, *A critical review on susceptibility of stress corrosion cracking in maraging steel weldments*. *Mater. Today Proc.* **27**, 2303–2307 (2020). <https://doi.org/10.1016/j.matpr.2019.09.117>
19. Kritzer P, *Corrosion in high-temperature and supercritical water and aqueous solutions: a review*. *J. Supercrit. Fluids* **29**, 1–29 (2004). [https://doi.org/10.1016/S0896-8446\(03\)00031-7](https://doi.org/10.1016/S0896-8446(03)00031-7)
20. Ma I A W, Ammar S, Kumar S S A, Ramesh K, Ramesh S, *A concise review on corrosion inhibitors: types, mechanisms and electrochemical evaluation studies*. *J. Coat. Technol. Res.* **19**, 241–268 (2022). <https://doi.org/10.1007/s11998-021-00547-0>
21. Klobčar D, Tušek J, *Thermal stresses in aluminium alloy die-casting dies*. *Comput. Mater. Sci.* **43**, 1147–1154 (2008). <https://doi.org/10.1016/j.commatsci.2008.03.009>
22. Long A, Thornhill D, Armstrong C, Watson D, *Predicting die life from die temperature for high-pressure die-casting aluminium alloy*. *Appl. Therm. Eng.* **44**, 100–107 (2012). <https://doi.org/10.1016/j.applthermaleng.2012.03.045>
23. Piekło J, Garbacz-Klempka A, *Analysis of phenomenon of plasticity loss of steel core made by selective laser melting method in zone of pressure mould conformal cooling channel*. *Materials* **16**, 4205 (2023). <https://doi.org/10.3390/ma16124205>

24. Vicario I, Idoiaga J K, Arratibel E, Erauskin I, Plaza L M, Crespo I, Caballero P, *Development of HPDC advanced dies by casting with reinforced tool steels. Int. J. Manuf. Eng.* **2015**, 287986 (2015). <https://doi.org/10.1155/2015/287986>
25. Bhatia A, *Cooling water problems and solutions*. Continuing Education and Development, Inc., Forest Hills, NY (2012).
26. Hameed M Z, Wölfle C H, Robl T, Obermayer T, Rappl S, Osterminski K, Krempaszky C, Werner E, *Parameter identification for thermo-mechanical constitutive modeling to describe process-induced residual stresses and phase transformations in low-carbon steels. Appl. Sci.* **11**, 550 (2021). <https://doi.org/10.3390/app11020550>
27. AISI grade 18Ni (300) maraging steel. <https://www.matweb.com/search/DataSheet.aspx?MatGUID=7d7084dfb36f4446afb1adade67d5767&ckck=1>. Accessed 23 Oct 2025
28. Kan M, *Determination of the casting–mold interface heat transfer coefficient for numerically die-casting process depending on different mold temperatures. J. Mech. Sci. Technol.* **37**, 427–433 (2023). <https://doi.org/10.1007/s12206-022-1240-1>
29. Kan M, Ipek O, Koru M, *An investigation into the effect of vacuum conditions on the filling analysis of the pressure casting process. Int. J. Metalcast.* **17**, 430–446 (2023). <https://doi.org/10.1007/s40962-022-00770-4>
30. Małyśza M, Żuczek R, Wilk-Kołodziejczyk D, Jaśkowiec K, Bitka A, Głowacki M, Zięba Ł, Pysz S, *Application of a 3D-printed part with conformal cooling in high-pressure die-casting mould and evaluation of stress state during exploitation. Materials* **17**, 5988 (2024). <https://doi.org/10.3390/ma17235988>
31. He X, Vian C, Wang X, *Line distributed pores in laser powder bed fusion manufactured dies: a critical factor in die failure for high-pressure die-casting. J. Mater. Process. Technol.* **330**, 118480 (2024). <https://doi.org/10.1016/j.jmatprotec.2024.118480>
32. Zhu J, Kokawa H, Feng K, Li Z, *Unexpectedly high corrosion susceptibility near fusion boundaries of Inconel 625 manufactured by laser powder bed fusion. Corros. Sci.* **223**, 111432 (2023). <https://doi.org/10.1016/j.corsci.2023.111432>
33. Hemmasian Ettefagh A, Guo S, Raush J, *Corrosion performance of additively manufactured stainless steel parts: a review. Addit. Manuf.* **37**, 101689 (2021). <https://doi.org/10.1016/j.addma.2020.101689>
34. Li C-D, Yang H-Y, Dong B-X, Chen D-L, Shu S-L, Qiu F, Jiang Q-C, Zhang L-C, *Thermal fatigue failure mechanisms and enhancement strategies of die steel. J. Mater. Res. Technol.* **38**, 4567–4599 (2025). <https://doi.org/10.1016/j.jmrt.2025.08.198>
35. Srivastava A, Joshi V, Shivpuri R, *Computer modeling and prediction of thermal fatigue cracking in die-casting tooling. Wear* **256**, 38–43 (2004). [https://doi.org/10.1016/S0043-1648\(03\)00281-3](https://doi.org/10.1016/S0043-1648(03)00281-3)

36. Donahue J R, Lass A B, Burns J T, *The interaction of corrosion fatigue and stress-corrosion cracking in a precipitation-hardened martensitic stainless steel*. *npj Mater. Degrad.* **1**, 11 (2017). <https://doi.org/10.1038/s41529-017-0013-2>
37. Hussain I, Khan R H, *Corrosion-fatigue and stress-corrosion cracking behavior of maraging steel 350 grade*. In: *Proc. Int. Symp. Adv. Mater.*, Islamabad, Pakistan (1993).
38. Chirkunov A, Kuznetsov Y, *Corrosion inhibitors in cooling water systems*. In: Amjad Z, Demadis K D (eds), *Mineral Scales and Deposits*. Elsevier, Amsterdam, pp. 85–105 (2015). <https://doi.org/10.1016/B978-0-444-63228-9.00004-8>
39. Pedferri P, *Corrosion in waters*. In: Pedferri P (ed), *Corrosion Science and Engineering*. Springer, Cham, pp. 423–445 (2018). https://doi.org/10.1007/978-3-319-97625-9_20
40. Saremi M, Dehghanian C, Sabet M M, *The effect of molybdate concentration and hydrodynamic effect on mild steel corrosion inhibition in simulated cooling water*. *Corros. Sci.* **48**, 1404–1412 (2006). <https://doi.org/10.1016/j.corsci.2005.06.009>
41. Amjad Z, *The science and technology of industrial water treatment*. 1st edn. (CRC Press, Boca Raton, FL, 2010). <https://doi.org/10.1201/9781420071450>
42. Zhao Z, Dong C, Kong D, Wang L, Ni X, Zhang L, Wu W, Zhu L, Li X, *Influence of pore defects on the mechanical property and corrosion behavior of SLM 18Ni300 maraging steel*. *Mater. Charact.* **182**, 111514 (2021). <https://doi.org/10.1016/j.matchar.2021.111514>
43. Xu X, Sachs E, Allen S, *The design of conformal cooling channels in injection molding tooling*. *Polym. Eng. Sci.* **41**, 1265–1279 (2001). <https://doi.org/10.1002/pen.10827>

2.7. Additional electrochemical polarization corrosion testing

2.7.1. Introduction

While the preceding sections have focused on corrosion–fatigue interactions in service and under accelerated laboratory conditions, additional electrochemical testing was performed to better isolate the intrinsic corrosion response of the investigated steels. In particular, potentiodynamic polarization was conducted in a mildly alkaline chloride–borate medium, chosen to approximate the buffered conditions of industrial cooling water. This complementary analysis provides a comparative baseline for maraging steel (both AM and forged) and H11 tool steel, allowing their passive behavior and susceptibility to localized attack to be evaluated independently from mechanical or thermal loads.

2.7.2. Methods

Potential dynamic polarization measurements were used to detect the corrosion resistance of 18Ni300 maraging steel and H11 tool steel (details on the tested materials can be found in Section 2.2.2) in an alkaline environment that simulates the pH condition of an industrial cooling system. AM maraging samples were cut along the building and scanning direction plane. The samples were mounted on a sample holder to expose a circular area of 5 mm diameter. The surface of the working electrodes (samples) was ground to P1200 grit with SiC paper, then cleaned with the distilled water and absolute alcohol. The test solution in this study was a 0.1 M NaCl+0.1 M borate buffer solution (pH = 9.0) prepared with analytical-grade reagents and distilled water. The electrochemical experiment was conducted on an Amel 2551 workstation with three electrodes system at 25 °C. The reference electrode was a saturated calomel electrode (SCE), and the counter electrode was two short-circuited platinum rods. The scanning rate of potentiodynamic polarization was 0.160mV/s.

2.7.3. Results and Discussion

In the borate-buffered chloride medium, all specimens remained globally passive; damage was localized as discrete pits (plan-view area $\approx 0.01\text{--}0.10\text{ mm}^2$) rather than generalized attack. The three maraging-steel conditions exhibited essentially overlapping polarization curves with $E_{\text{corr}} \approx -0.66$ to -0.67 V and $j_{\text{corr}} \approx (3\text{--}4) \times 10^{-8}\text{ A cm}^{-2}$, and an anodic response characterized by a long, low-current passive plateau without a pronounced active peak up to the onset of transpassivity. By contrast, H11 displayed a nobler mixed potential ($E_{\text{corr}} \approx -0.41\text{ V}$) and a broader active-to-passive transition yet did not sustain a lower passive current nor exhibit a wider passive window than maraging. Taken together, these features indicate that maraging, although electrochemically more active at open circuit, develops a more extended and protective passive state than H11, which is consistent with the observed propensity for localized attack.

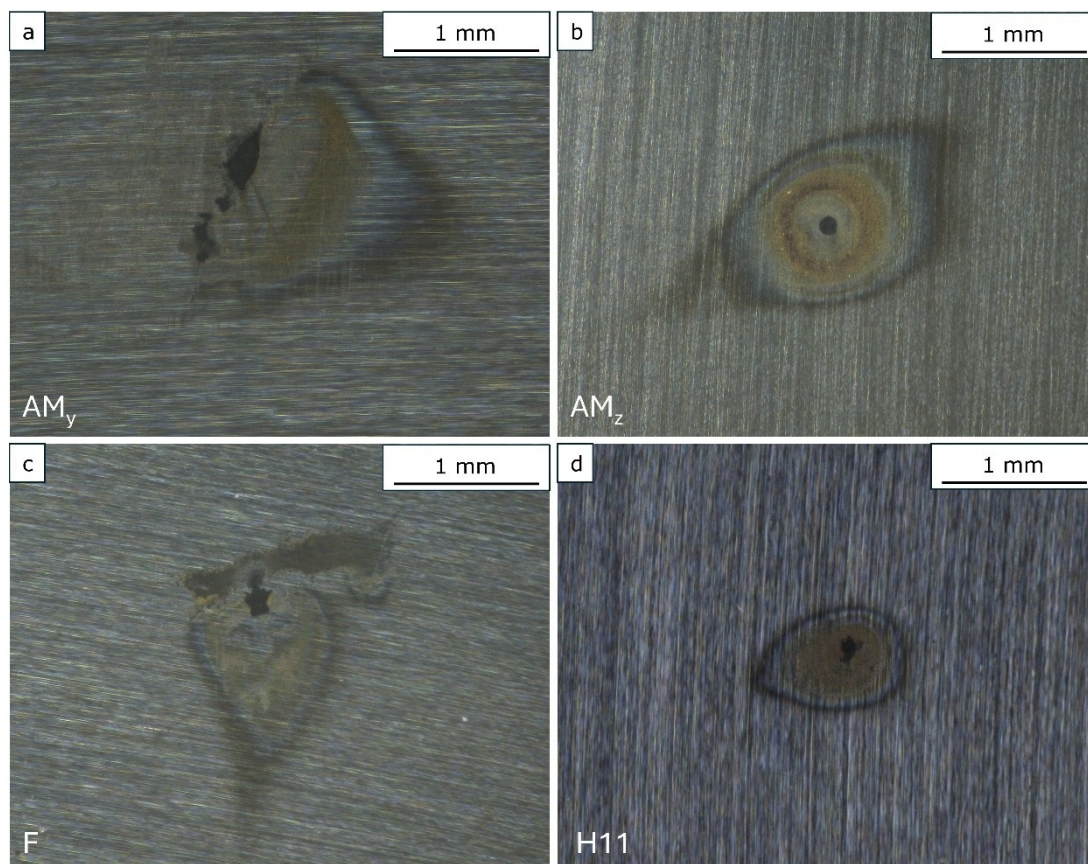


Figure 2-39. Picture of the pit formed after the electrochemical testing on the samples surface. a) AM_y, b) AM_z, c) F and d) H11.

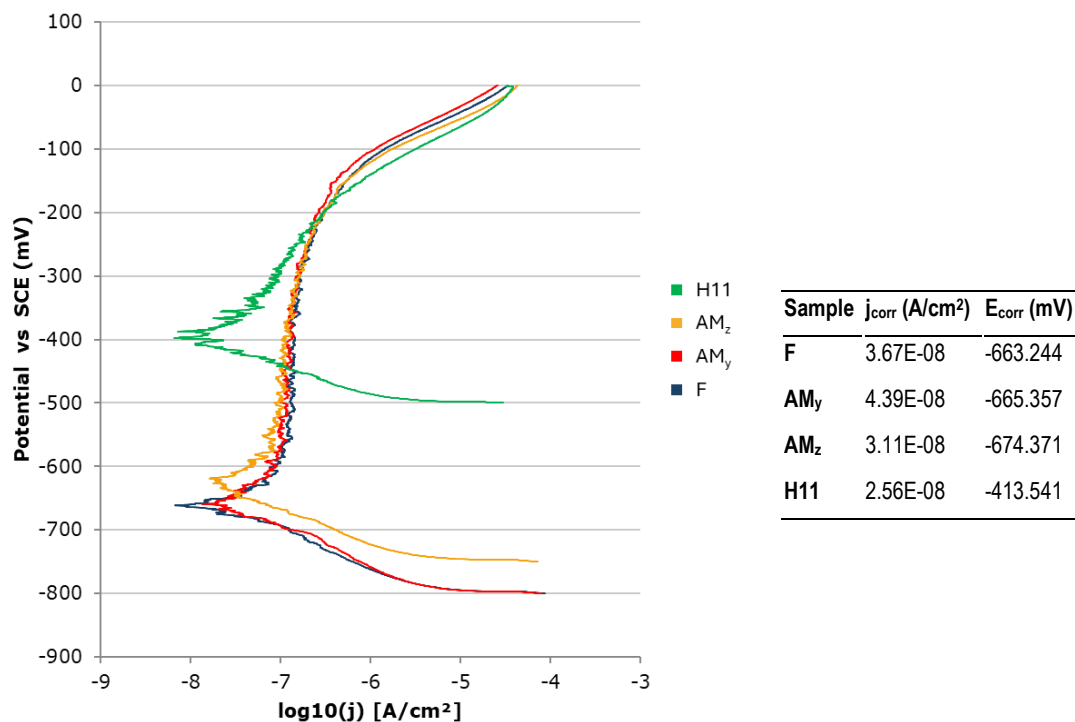


Figure 2-40. Potentiodynamic polarization in 0.1 M NaCl + 0.1 M boric acid/borate for maraging steel (F, AM_y, AM_z) and H11.

This trend aligns with a pitting-resistance ranking based on the Pitting Resistance Equivalent Number, $\text{PREN}^1 = \% \text{Cr} + 3.3 \times \% \text{Mo} + 16 \times \% \text{N}$: using nominal compositions yields $\text{PREN} \approx 16.6$ for maraging steel and ≈ 9.6 for H11, reflecting the absence of significant Mo in H11 and supporting its lower resistance to chloride-induced localized breakdown relative to maraging. We note that PREN is formally established for stainless systems; here it is used qualitatively to rationalize the relative susceptibility observed. Overall, the controlling difference in this electrolyte is therefore localized-corrosion propensity rather than uniform corrosion rate: maraging steels behave equivalently across processing/orientation and outperform H11 in passivity robustness and pitting resistance, despite their more negative E_{corr} . However, if the passive film is mechanically disrupted (e.g., by deformation) or eroded as

¹ Pedferri P. Corrosion Science and Engineering. Engineering Materials. Cham: Springer; 2018.

observed in the failure case, the more negative E_{corr} of maraging can render it more susceptible to active dissolution than H11 until repassivation is re-established.

2.7.4. Conclusions and links to failure case

These electrochemical results reinforce the interpretation that maraging steel, although intrinsically capable of sustaining a protective passive state in alkaline chloride solutions, remains vulnerable if the passive film is periodically removed or mechanically damaged. This condition mirrors the failure scenario of the AM insert, where cyclic stresses and coolant impingement disrupt the surface oxide, exposing the underlying metal to localized dissolution.

SECTION 3.

3.L-PBF CuZn42 Characterization

3.1. Cavitation erosion and corrosion behavior of LPBF and conventional produced CuZn42 alloy

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Currently under publication in Progress in Additive Manufacturing.

3.1.1. Abstract

Lead-free biphasic brasses are attractive for fluid-handling components due to their environmental and regulatory advantages. However, the absence of lead reduces machinability, prompting the need for alternative strategies to optimize component design and performance. In this context, additive manufacturing offers new opportunities for geometrical customization and material efficiency. The present study evaluates the corrosion and cavitation-erosion performance of CuZn42 (CW510L) produced by laser powder bed fusion (LPBF), in comparison with conventionally manufactured material. Microstructural characterization reveals a layered, anisotropic architecture with residual porosity and evidence of Zn depletion relative to the wrought bar, features that concentrate stress and influence the stability and distribution of the α and β phases. Under vibratory cavitation, both materials exhibit a similar delay before damage accelerates, yet the additively manufactured alloy transitions more readily to significant material removal, with damage paths guided by interlayer interfaces and pores. In chloride solution, corrosion appears highly localized. The build-direction section is the most electrochemically active condition, whereas the scan-plane section approaches the behavior of the wrought bar. Prolonged exposure promotes pit-centered dezincification and the development of zinc-rich corrosion products at pit peripheries, with a deeper affected layer in the additively processed material. Overall, the performance gap is governed primarily by process-induced heterogeneity rather than an intrinsic shortcoming of the alloy. The results offer guidance for the deployment of LPBF CuZn42 in components exposed to cavitation erosion or corrosion in salt water.

3.1.2. Introduction

Biphase ($\alpha+\beta$) brasses are widely used in fluid-handling hardware, fittings, valves, and marine components, because they offer a favorable balance of strength, corrosion resistance, and machinability [1]. These components are typically produced by hot forming from wrought bar stock, and their functional performance is governed by the morphology and distribution of the α (fcc) and β (bcc) phases [2]. Moreover, leaded grades are particularly advantageous in subtractive manufacturing because lead enhances chip breakability and tool life [3-5].

In service, functional brass components exposed to dynamic fluid environments, such as valves and pump elements, are subject to multiple degradation mechanisms. Cavitation erosion is especially critical, as repeated bubble collapse induces localized high stresses and surface pitting [6]. In aqueous chloride media, mechanical depassivation under cavitation can synergize with corrosion, notably through selective Zn dissolution, thereby accelerating material loss [7, 8]. These phenomena are strongly influenced by phase balance, interface cohesion, and grain boundaries, underscoring the importance of microstructural design strategies to mitigate degradation [2].

Increasingly stringent environmental and health regulations (e.g., EU RoHS/REACH), along with drinking-water quality standards, have driven the transition toward lead-free brass grades for potable-water and related applications. Within this context, CuZn42 (CW510L) has emerged as a prominent alternative to traditional free-cutting leaded brasses [3]. However, the absence of lead compromises machinability, prompting interest in manufacturing approaches that minimize post-processing—such as additive manufacturing (AM) [4, 5].

Among AM routes, Laser Powder Bed Fusion (LPBF) is attractive for copper-alloy components with complex geometries, yet it presents nontrivial challenges for Cu–Zn systems, since high reflectivity and thermal conductivity limit absorptivity, while Zn volatility perturbs melt-pool chemistry [5, 9, 10]. To date, AM research has focused primarily on pure Cu and high-performance Cu alloys (e.g., Cu–Cr–Zr, Cu–Sn), with industrial brasses receiving comparatively less attention. Where explored (e.g., CuZn42), studies have largely emphasized process feasibility and preliminary microstructural characterization, rather than application-relevant properties [4, 5, 9].

Importantly, the rapid solidification and cyclic reheating intrinsic to LPBF reshape brass microstructures, refining α -cell structures, altering β -phase stability, introducing solute segregation and porosity, and imparting crystallographic texture and anisotropy [10]. Because corrosion and wear in brasses are highly sensitive to these microstructural attributes, LPBF-induced features are expected to significantly influence degradation behavior.

Against this backdrop, the present work investigates both cavitation-erosion and corrosion performance of additively manufactured CuZn42 (CW510L) brass, directly comparing it with the conventionally manufactured counterpart. Although these two degradation phenomena are of primary concern for brass components operating in fluid-handling and marine environments, they have never been examined for this alloy in the context of additive manufacturing. By correlating processing-route-dependent microstructural features with electrochemical behavior and cavitation-erosion resistance, the study aims to clarify the factors governing material durability in chloride environments and under cavitation loading.

3.1.3. Materials and Methods

3.1.3.1. Samples Fabrication and Preliminary Characterization

CuZn42 (CW510L) brass specimens were produced using two different manufacturing routes: laser powder bed fusion (LPBF) additive manufacturing and conventional bar drawing. The additively manufactured samples were fabricated using a 3D4Brass system equipped with a 1070 nm nLight fiber laser (1 kW), operating at a laser power of 150 W and a scan speed of 215 mm/s, with a spot size of 35 μm . A layer thickness of 30 μm was employed, and no preheating was applied. The geometrical details of the specimens are described in the corresponding Methods subsections for each test (Sections 3.3.2-3.3.4). Additively manufactured specimens are denoted as AM_y when the scanning-plane (xy) section is tested and as AM_z when the build-direction (z) section is tested. The extruded specimens, referred to as BR samples, were machined from a commercial brass bar ($\varnothing$ 27 mm). The transverse section is labeled BR_T, and the longitudinal section BR_L. Specimens from the longitudinal section were cut with dimensions specific to each test. The bar was produced starting from a billet obtained

through horizontal continuous casting with three strands using an induction furnace. After extrusion, the bars underwent cold drawing at a speed of 60 m/min. Chemical pickling was performed using a sequence of four baths containing sulfuric acid at concentrations ranging from 15% to 20%.

Table 3-1 reports the chemical composition of the studied materials. The composition of the brass sample was determined by XRF using a Malvern Panalytical multi-element analyzer. Regarding the AM powder, its composition is based on supplier-provided data, obtained by ED-XRD analysis, as well as its physical properties, reported in **Table 3-2**. The conventional brass shows a Cu/Zn ratio (60/40) consistent with a typical $\alpha+\beta$ brass [11]. On the other hand, the additively manufactured samples exhibit a notably higher Cu/Zn ratio, suggesting a shift toward the α -phase field in the Cu-Zn phase diagram. This reduction is attributed to selective vaporization of Zn during laser melting, as evidenced by the higher Zn content in the powder.

The last composition, AM ox, corresponds to the analysis of the surface region of the AM samples still covered by oxides from the manufacturing process. Here, the Zn content is higher than in the AM bulk, likely due to selective Zn oxidation, as observable in Figure 1, which shows the as-produced samples with evidence of surface oxidation.

Table 3-1. Chemical composition of the tested sample

wt. %	Cu	Zn	Pb	Fe	Ni	Mn	Sn	Cd	Mg	Ti	Si
BR	58.64	41.06	0.11	0.12	0.025	–	0.15	0.011	0.001	0.003	–
AM	63.2	35.46	0.016	0.355	0.459	0.029	0.303	0.005	–	0.008	–
AM powder	56.1	bal. (~43)	0.05	0.2	0.3	0.1	0.3	–	–	–	0.1
AM ox	58.4	40.48	0.013	0.358	0.446	0.053	0.321	0.01	–	0.016	–

Table 3-2. CuZn42 powder, used to build AM samples, physical analysis.

Characteristic	Method / Standard	Min	Max	Obtained	Unit
d10 [μm] (xc min)	ISO 13322-2	20	30	21	μm
d50 [μm] (xc min)	ISO 13322-2	35	50	39	μm
d90 [μm] (xc min)	ISO 13322-2	50	60	54	μm
Flow ($\varnothing 2,5\text{mm}$, statically)	ISO 4490			28	s/50g
App. Density ($\varnothing 2,5\text{mm}$, stat.)	ISO 3923-1:18-05			4.54	g/cm^3

A preliminary microstructural characterization was carried out on both BR and AM brass. Samples were ground sequentially with P320, P800, P1200, and P2400 SiC papers, followed by polishing with 3 μm and 1 μm diamond suspensions. Porosity analysis was performed on polished samples using a Leica DMI 5000M optical microscope equipped with image analysis software. For the AM specimens, porosity was evaluated on both polished cross-sections (xz plane) and scanning sections (xy plane), covering a total area of 13 mm² for each orientation, to assess the presence of internal defects. The conventionally processed samples were fully dense. Chemical etching was then performed using a solution consisting of 7g FeCl₃, 5ml HCl, 30ml H₂O and 60ml C₂H₆O. The etched specimens were examined with the Leica DMI 5000M optical microscope to reveal their microstructural features.

Hardness testing was performed at two scales. Bulk hardness was measured using Brinell (HRB) testing with a Rupac 500 Mra machine, in order to compare the values with literature data. In addition, microhardness testing was conducted on etched samples with a Mitutoyo HM-200 instrument to determine the hardness of the individual phases and features revealed by etching.

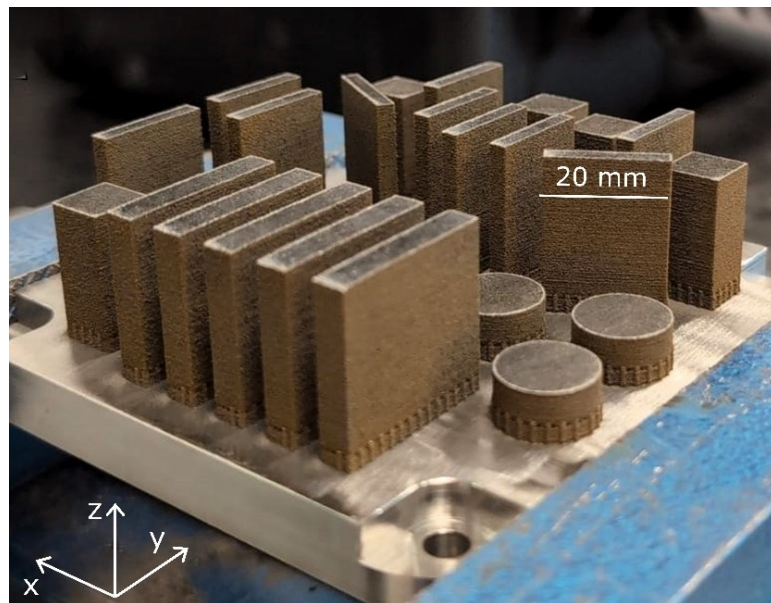


Figure 3-1. Batch of AM samples in as-built condition.

3.1.3.2. Cavitation Erosion Testing

Cavitation erosion resistance was evaluated on both AM and BR samples using the indirect vibratory method indicated in the ASTM G32-16 standard [12]. The objective was to assess the influence of the manufacturing route on the material's resistance to cavitation-induced damage. To this aim, a vibratory apparatus operating at a frequency of 21 ± 0.2 kHz and a peak-to-peak amplitude of 50 μm was employed. Cavitation erosion specimens were 5 mm thick, with exposed surfaces sufficiently large to encompass the erosion area generated by the sonotrode tip ($\varnothing$ 16 mm). The AM specimens were prepared as plates with dimensions of 28×25 mm (**Figure 3-1**), while the BR specimens (BR_T) were machined as disks with a diameter of 27 mm cut from the bar's transverse section.

Based on the microstructural and hardness results (Section 3.4.1), testing was limited to the AM_z and BR_T sections. The AM_z orientation represents the typical layered morphology and defect alignment along the build direction, while showing no significant variation of hardness compared to the scanning-plane section. Conversely, BR_T was selected as the reference for the conventional alloy, as it exhibits slightly lower hardness and larger variability than BR_L due to extrusion-induced edge hardening, thus representing the most critical comparison conditions.

Samples were mounted in a stationary position supported by a sample holder, which guaranteed the parallel positioning of 0.5 mm below the vibrating tip of the sonotrode, and submerged in deionized water maintained at 23 ± 1 °C. A representative schematization of the test set-up is shown in **Figure 3-2**.

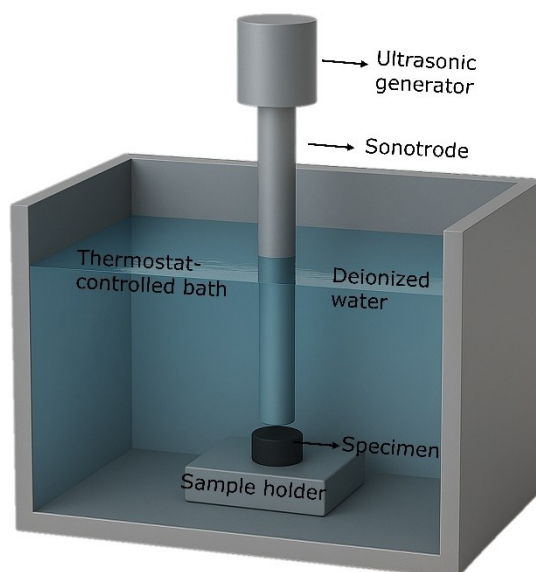


Figure 3-2. Schematic diagram of the ultrasonic cavitation-erosion test rig.

Mass loss was monitored at short exposure intervals (2–4 minutes) during the initial incubation phase to capture early damage mechanisms, followed by longer intervals (up to 30–60 minutes) as the erosion rate stabilized. Each test continued for a total duration of 8 hours. After each interval, specimens were rinsed, dried, and weighed using an analytical balance with an accuracy of 0.001 mg to determine the cumulative mass loss-time curve, thereby determining the incubation period.

Surface degradation was monitored during testing using a Leica di DSM300 digital microscope (Leica Microsystems, Wetzlar, Germany) at low magnification. Post-test analyses were performed using a Leica DMI 5000M optical microscope and a Zeiss Sigma 360 scanning electron microscope (Carl Zeiss AG, Milan, Italy) to characterize surface morphology and damage mechanisms at higher resolution.

3.1.3.3. *Electrochemical corrosion testing*

Electrochemical measurements were carried out to evaluate the corrosion behavior of both AM and BR CuZn42. Samples prepared for corrosion tests had a thickness of 3 mm and lateral dimensions not exceeding 12 mm in order to fit the sample holder. The experiments were conducted in 3.5 wt% sodium chloride (NaCl) aqueous solution using a conventional three-electrode setup. The brass samples acted as working electrodes, with an exposed circular area of 5 mm in diameter defined by the sample holder, while two platinum rods and a saturated calomel electrode (SCE) were

employed as the counter and reference electrodes, respectively. Samples were ground with silicon carbide papers down to P1200 grit, rinsed with deionized water, and dried prior to testing. Open-circuit potential (OCP) was monitored for 90 minutes prior to each electrochemical test to ensure system stabilization. After OCP stabilization, the potential was scanned from -500 mV below OCP to $+500$ mV above OCP at a scan rate of 0.15 mV/s. Corrosion potential (E_{corr}) and corrosion current density (i_{corr}) were determined via Tafel extrapolation.

3.1.3.4. Immersion and Dezincification Testing

Immersion corrosion tests were conducted to evaluate the long-term behavior of the materials in a 3.5 wt.% NaCl aqueous solution. Both AM and BR samples were immersed for 30 days at 50 °C. Three specimens were tested for each condition. The exposed surface area of each specimen was 78.54 mm² (corresponding to a circular opening of 10 mm in diameter), defined by a hollowed insulating tape. The sections tested were the transverse section of the bar (BR_T) and the xy-scanning plane of the LPBF samples (AM_y). At the end of the test, samples were extracted from the corrosion medium, immediately rinsed with distilled water to remove any residual surface salts and dried using warm forced air. A surface characterization was performed using a digital microscope to document the morphology and extent of the corrosion products formed during exposure. Chemical cleaning for measuring mass loss was not possible due to localized corrosion. Again, samples were analyzed by scanning electron microscopy (SEM) to investigate the localized degradation phenomena in greater detail.

In addition, a quantitative evaluation of the corrosion resistance of different samples was evaluated by accelerating the dezincification behavior of the different alloy conditions. Dezincification resistance was evaluated following the UNI EN ISO 6509-1:2014 standard [13]. Two sections were considered for both BR and AM brass: for BR, transverse (BR_T) and longitudinal (BR_L) with respect to the extrusion direction; for AM, aligned with the building direction (AM_z) and scanning direction (AM_y). To ensure data consistency and repeatability, each test was performed in triplicate. Each specimen was mounted in phenolic resin, ground to expose an area of approximately 100 mm² and polished using 1200-grit abrasive paper.

Samples were immersed for 24 hours at 75 ± 5 °C in a 1 wt. % solution of copper (II) chloride dihydrate ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$) prepared by dissolving 25.4 g of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ in deionized water to a total volume of 2000 mL. After exposure, samples were rinsed, sectioned perpendicularly to the test surface, and metallographically prepared for optical microscopy. The depth of dezincification was quantified using LAS 4.12 image analysis software by dividing the surface area of the dezincified zone by the corresponding sample width.

3.1.4. Results and Discussion

3.1.4.1. Preliminary Characterization

Fig. 3 displays the optical micrographs of the BR and AM samples analyzed, both in the transversal and longitudinal sections. Significant microstructural differences were observed between BR and AM brass. The BR samples (**Fig. 3-3a–b**) exhibit a dense, biphasic structure with α (light) and β (dark) phases uniformly distributed. Image analysis confirmed a uniform phase distribution, revealing approximately 47% α -phase in the BR_T section and 48% in the BR_L section. In the transverse section (**Fig. 3-3a**), grains appear equiaxed, while in the longitudinal section (**Fig. 3-3b**) they are elongated along the extrusion axis, consistent with hot-working deformation.

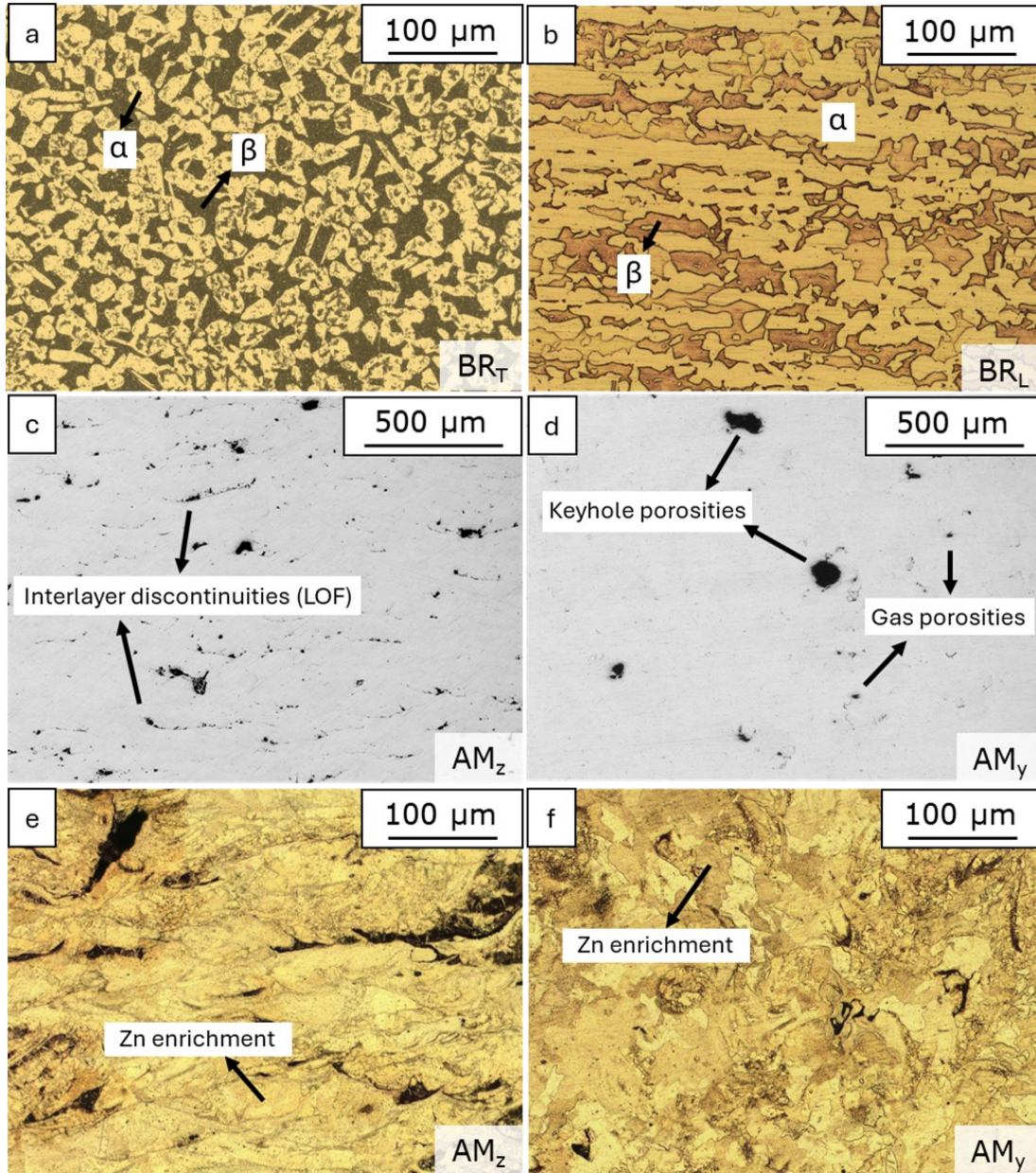


Figure 3-3. Optical micrographs of the samples: (a) etched transversal section of brass bar (BR_T); (b) etched longitudinal section of brass bar (BR_L); (c) unetched LPBF brass, build direction section (AM_z); (d) unetched LPBF brass, laser scan section (AM_y); (e) etched LPBF brass, build direction section (AM_z); (f) etched LPBF brass, laser scan section (AM_y).

While the BR material is fully dense, image analysis revealed residual porosity in the AM specimens, with relative densities of 98% and 97% for the xy and xz sections, respectively. In fact, in unetched AM_z samples (**Fig. 3-3c**), elongated voids aligned with the build direction indicated lack-of-fusion defects arising from incomplete melting during the layer-by-layer process. In un-etched AM_y samples (**Fig. 3-3d**), larger and more spherical pores were detected, consistent with keyhole porosity rather than entrapped gas.

After etching (**Fig. 3-3e,f**), with no clear evidence of a biphasic structure, in accordance with the chemical composition of AM sample after L-PBF reported in Table 1. Some darker regions can be observed. These regions are hypothesized to be locally enriched in Zn, as chemical etching is known to preferentially darken Zn-rich areas, as also seen in BR alloy. This can be attributable to solute segregation under the high cooling rates of LPBF. In AM_y (**Fig. 3-3f**), irregular grains are visible, while AM_z (**Fig. 3-3e**) displayed a layered morphology aligned with the build direction, including partially melted zones associated with interlayer defects and elongated darker areas, likely corresponding to segregated regions.

Microhardness testing showed local variations within the AM samples. Measurements ranged from approximately 110 ± 2 HV in the lighter areas to about 130 ± 9 HV in the darker ones. No sharp boundary was observed between these regions, which is consistent with the absence of a clearly defined microstructural pattern. Notably, the latter value is close to that of the BR sample (135 ± 7 HV). It should be noted that, for the BR alloy, local microhardness measurements on individual α or β phases could not be reliably performed due to the limited spatial extent of these phases relative to the indentation size (**Fig. 3-3a,b**). As a result, the reported microhardness values for the BR alloy should be considered as representative of the combined $\alpha + \beta$ microstructure rather than of single phases. The lower hardness of the lighter AM areas likely corresponds to the α -phase hardness, while the higher values in darker regions suggest localized Zn enrichment [14]. Such enrichment may arise from microsegregation phenomena induced by the rapid solidification conditions inherent to the process, that can eventually result in the local formation of β -phase regions. This interpretation is consistent with the shift toward the α -phase field in the Cu–Zn phase diagram, as previously discussed, indicating that the AM samples are predominantly composed of α phase, with only localized regions exhibiting increased Zn content.

Brinell hardness test results confirmed these trends, with the AM samples, mainly α -phase, showing 68.0 ± 1.0 HRB in the xy section and 69.0 ± 0.5 HRB in the xz section, while the BR samples reached higher values, 77.5 ± 2.0 HRB in the longitudinal section (BR_L) and 74.0 ± 5.0 HRB in the transverse section (BR_T). The localized increase in hardness at the outer regions of the BR material originates from the extrusion process, which induces a deformation gradient across the cross-section: the

surface layers undergo more intense plastic deformation, leading to altered mechanical properties, while the core remains comparatively less affected.

3.1.5. Cavitation Erosion behavior

3.1.5.1. Cumulative Mass Loss

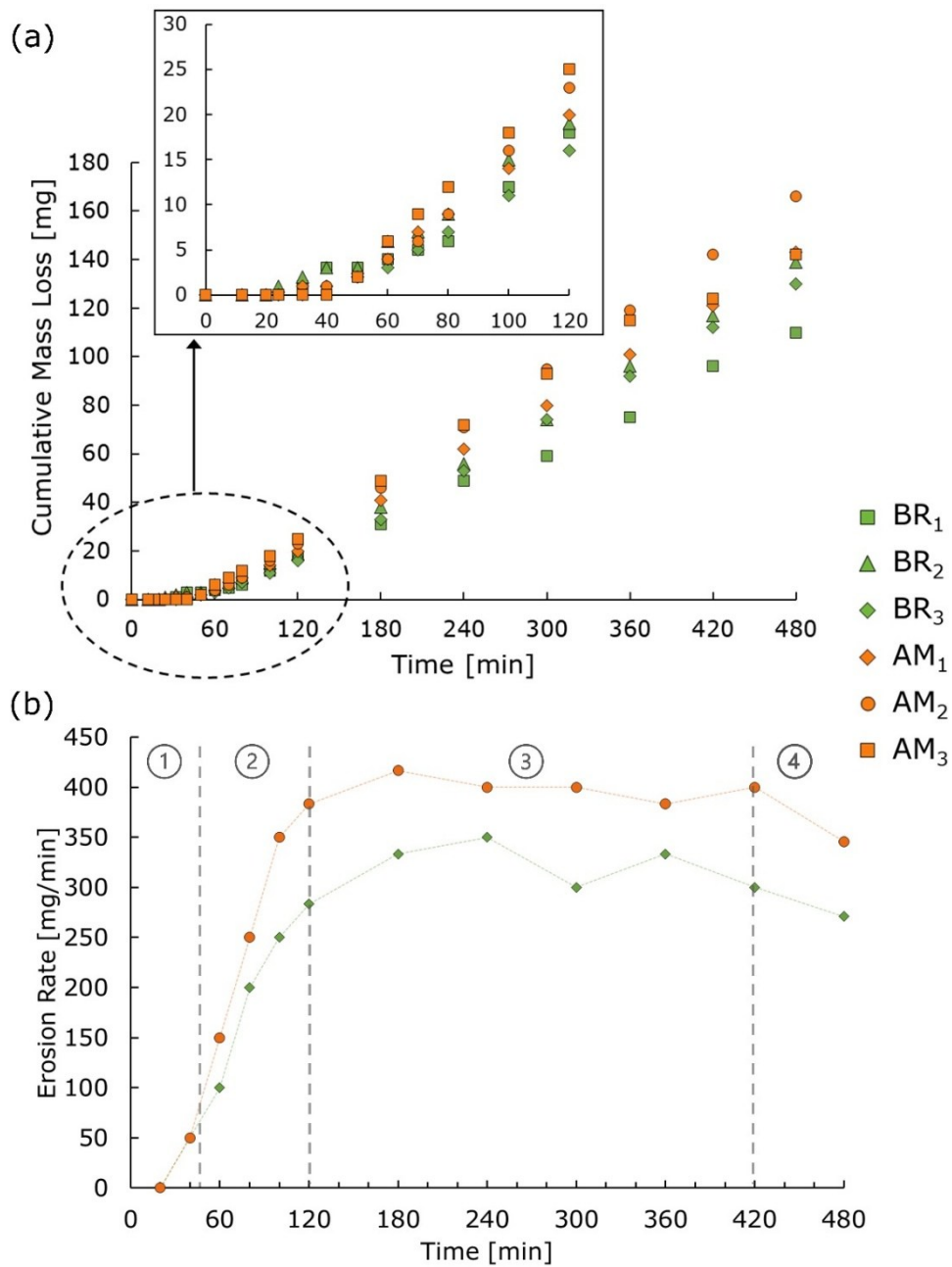


Figure 3-4. (a) Cumulative mass-loss of each BR sample (green symbols) and AM sample (orange symbols) analyzed, together with the insert (0-120 min) highlighting the incubation period. (b) Display of the erosion

rate curves of sample BR₃ and AM₂ showing the typical stages: (1) incubation, (2) acceleration, (3) maximum erosion rate and (4) deceleration.

Figure 3-4a shows the cumulative mass-loss curve for all the analyzed samples, together with a magnification from 0 to 120 min revealing the incubation period. BR specimens seem to exhibit a slightly earlier incubation period than the AM samples, as their curves start to increase at shorter exposure times. However, the calculation of the incubation time as the intercept of the maximum slope line (corresponding to the maximum erosion rate) on the time axis [12] revealed 57 ± 4 min for BR brass and 51 ± 8 for AM brass, indicating comparable onset of the damaging mechanisms.

Once steady-state erosion sets in (around 60 min), the gap widens. In particular, at 240 min the AM samples have already lost on average 70 mg, whereas the BR specimens remain below 60 mg. This divergence continues steadily up to 480 min, with values of mass loss ranging between 140–160 mg for AM and between 115–135 mg for BR. The consistent separation of the green (BR₁, BR₂, BR₃) and orange (AM₁, AM₂, AM₃) symbols also indicate a slightly higher erosion rate for the AM material, i.e. 21 ± 2 mg/h, versus 17 ± 2 mg/h for the BR alloy.

To provide a clearer view of the erosion rate evolution, **Figure 3-4b** reports the data of samples BR₃ and AM₂, which are representative of the two material conditions. Both curves exhibit the typical stages of cavitation erosion: incubation (1), acceleration (2), stabilization within the range of maximum erosion rate (3) and possible deceleration (4).

A summary of the fundamental recorded data is provided in **Table 3-3**. The table reports the volumetric erosion rate and total volume loss, accounting for the different theoretical densities of the materials (BR: 8.11 g/cm³; AM: 8.21 g/cm³), which were calculated based on the ideal mixture of their chemical compositions (**Table 3-1**).

The enhanced cavitation-erosion resistance of the BR specimens correlates directly with their higher surface hardness. Although the BR material shows only a slightly delayed onset of steady-state erosion, it exhibits a lower cumulative mass loss. In contrast, the AM specimens' lower hardness likely facilitated more rapid material removal under cavitation loading. This interplay between hardness and erosion kinetics suggests that the strain-hardening and more homogeneous microstructure achieved in the BR results in higher resistance to the propagation of cavitation erosion

damage. This is consistent with the assumption that the AM samples retained an extremely small fraction of the harder β phase observed in the previous section.

Table 3-3. Average results summary of cavitation erosion tests.

Sample	BR	AM
Incubation time [min]	57 ± 4	51 ± 8
Erosion rate [mg/h]	17 ± 2	21 ± 2
Volumetric Erosion rate [mm ³ /h]	2.10 ± 0.25	2.56 ± 0.24
Total mass loss [mg]	126 ± 12	150 ± 11
Total Volume loss [mm ³]	15.54 ± 1.48	18.28 ± 1.34

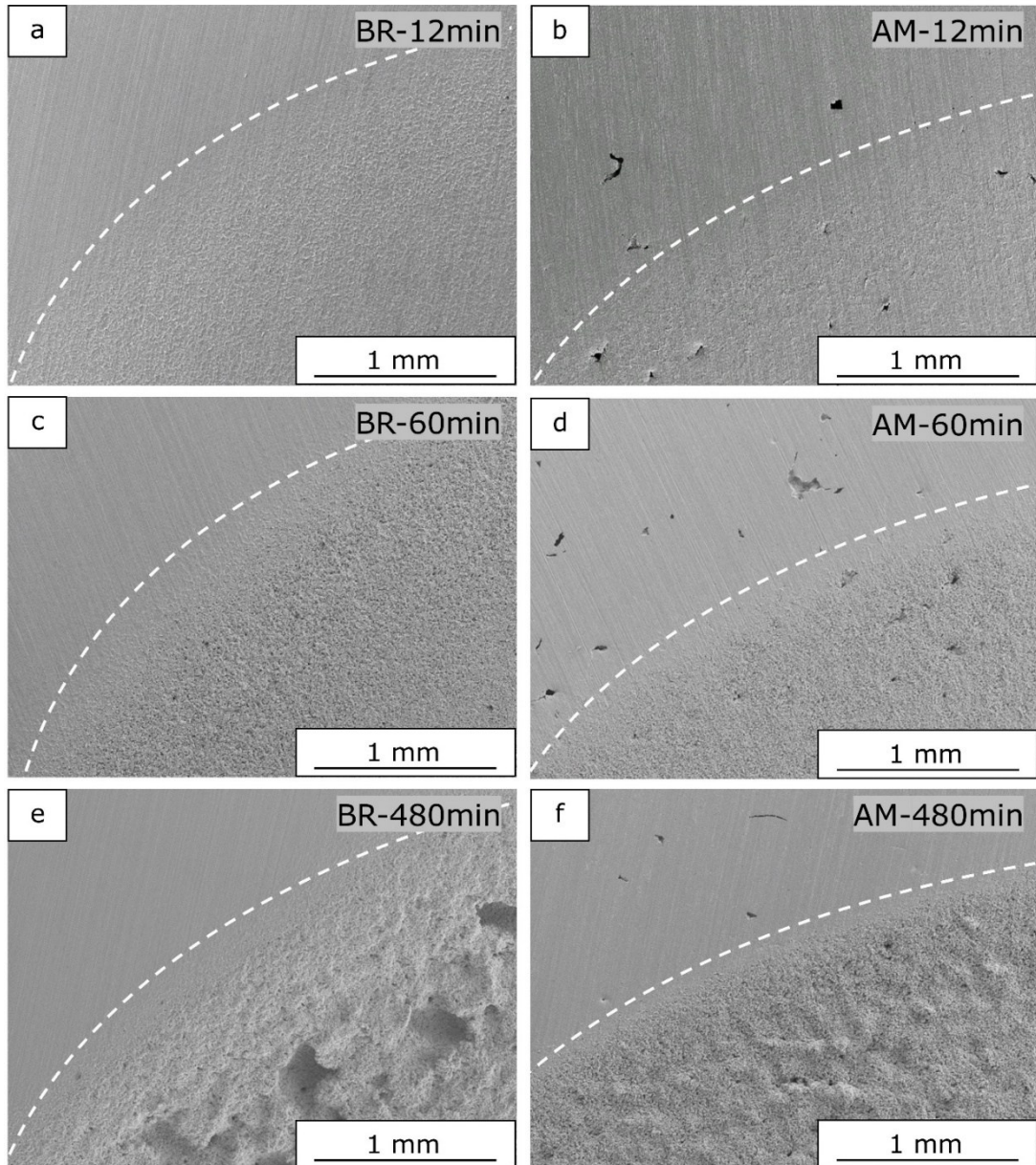


Figure 3-5. SEM shows micrographs of the cavitation zone edge at different times, with dotted lines indicating the boundary between cavitation-exposed and unexposed areas.

At short exposure (12 min, **Fig. 3-5a,b**), both materials exhibit incipient deformation in the form of surface roughening near the edge of the erosion imprint. In BR, a fine and uniform distribution of small pits is already evident, suggesting an early onset of plastic accommodation to cavitation loading. In the AM sample, the affected zone appears less homogeneous owing to the presence of lack-of-fusion voids. These defects, sometimes plastically deformed under cavitation loading, act as preferential sites for early damage accumulation, particularly when polygonal in shape and larger

than $\sim 13\text{ }\mu\text{m}$ [15]. In contrast, narrow slit-like pores tend to close under compressive stress, while small spherical pores do not serve as preferential damage initiation sites. With increasing exposure (60 min, **Fig. 3-5c,d**), the damage becomes more severe and the contrast with the surrounding intact surface becomes more distinct. The BR sample develops a roughened halo characterized by coalescing pits and micro-craters, indicative of progressive fatigue-driven erosion. In comparison, the AM sample shows a wear track with slightly lower roughness, which can be ascribed to its finer microstructure limiting the extent of surface relief development at this stage, coherently with the slightly shifted onset of the incubation time. Small porosities from printing defects remain visible in the AM sample. As discussed earlier, their impact on damage progression is non-uniform. Larger polygonal voids tend to initiate erosion craters, while smaller spherical pores often remain inactive and blend into the eroded surface, as seen in the AM-60min image.

After prolonged exposure (480 min, **Fig. 3-5e-f**), both alloys exhibit advanced degradation, with significant material removal in the cavitated region. In the BR sample, the erosion appears heterogeneous, with deep craters concentrated in specific areas, while the surrounding regions remain comparatively smooth. In contrast, the AM sample displays a more uniformly eroded surface, where the wear track is characterized by a continuous roughened topography without strongly localized features. This distinction suggests that BR undergoes localized but severe material loss, whereas AM develops a more evenly distributed surface degradation.

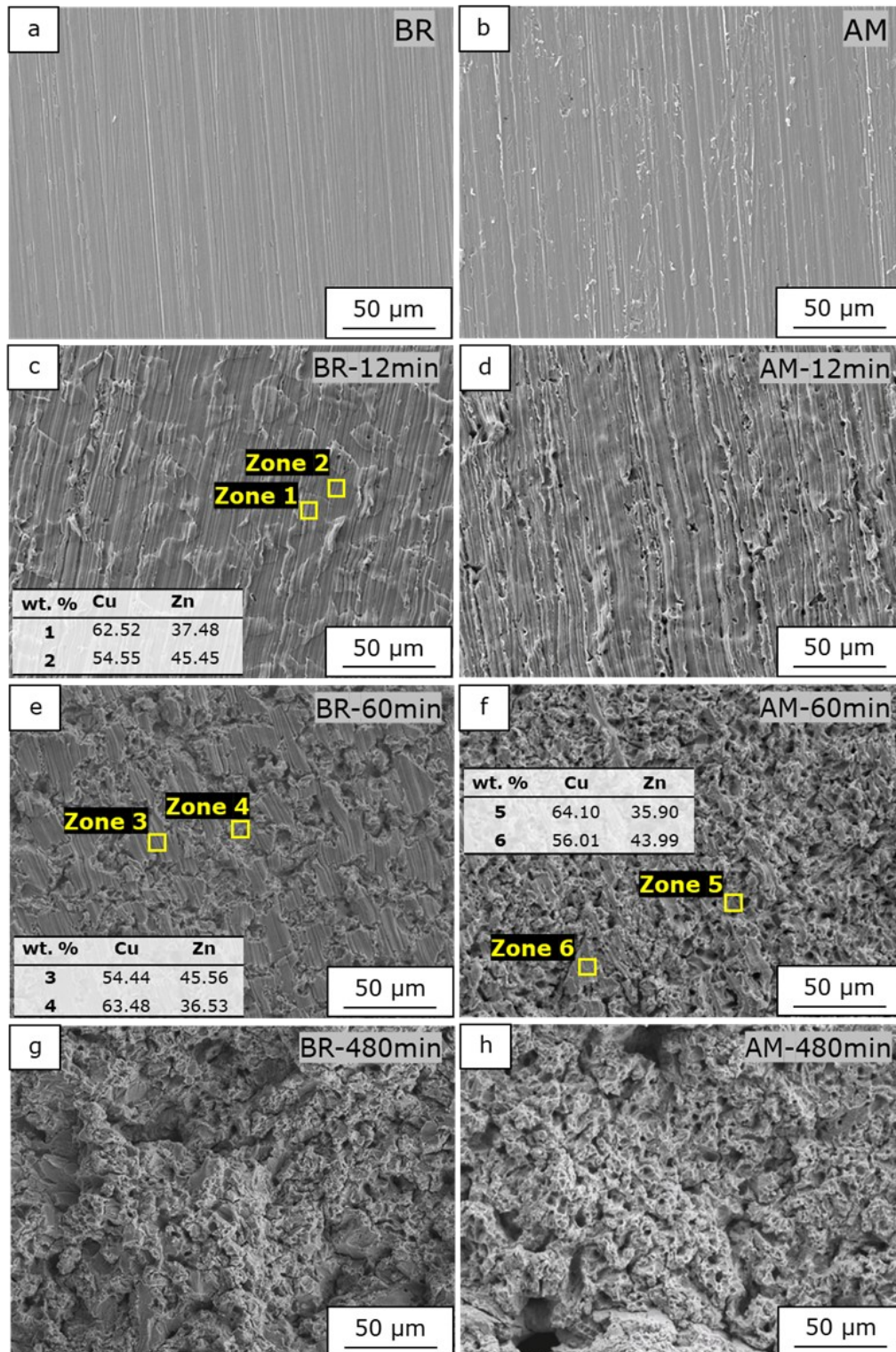


Figure 3-6. SEM micrographs of the CuZn42 brasses sample surface subjected to cavitation erosion for different exposure times. In the left column (a,c,e,g) the conventional sample BR. In the right column (b,d,f,h) the additive manufactured sample AM. (a, b) Initial polished surfaces prior to exposure; (c, d) after 12 minutes, showing the onset of surface damage, shallow grooves and few erosions pit. (e, f) After 60 minutes: the AM surface becomes porous and rough, while the BR sample shows localized degradation. (g, h) After 480 minutes: severe erosion is evident on both surfaces, but the AM sample displays larger craters and material removal. Yellow squares indicate regions selected for EDS analysis. EDS quantitative analysis (wt.%) of selected surface regions were embedded in the relative pictures

The SEM–EDS analysis of cavitation-eroded surfaces (**Figure 3-6**) allows to highlight differences in degradation mechanisms between the AM and BR samples and underscores the influence of microstructural phases on wear initiation and progression. The first two images (**Figure 3-6a, b**) show the surface condition of the samples before the test.

At 12 min of exposure (**Figures 3-6c, d**), just beyond the average incubation time for both materials, the distortion of the initially straight grinding lines reveals the accumulation of plastic deformation. These features may act as stress concentrators from which fatigue cracks initiate under repeated bubble collapse and reflect incubation-stage plasticity [16]. In the BR sample (**Figure 3-6c**), the different responses of the α - and β -phases to cavitation loading become visible (with the α -phase being more affected), allowing their identification based on contrast and morphology. This phase-selective deformation suggests that local mechanical properties strongly influence early-stage erosion

At 60 min (**Figures 3-6e, f**), just beyond the average incubation time for both materials, preferential erosion is evident in regions with lower zinc content, where the softer α -phase is expected to dominate. EDS confirms zinc depletion in the more rugged, heavily damaged zones (table in **Fig. 3-6e**). Consistently, the AM sample appears more severely degraded than the BR, which can be attributed to its overall lower Zn content and the resulting higher fraction of α -phase. In contrast, areas corresponding to the β -phase, particularly in the BR sample, still preserve the original polishing lines, indicating delayed damage [17].

After 480 min (**Figures 3-6g, h**), surface deterioration becomes more extensive in both materials; however, the AM sample shows larger microcraters as well as more pronounced material loss (see **Table 3-3**). This observation supports the hypothesis that the β -phase acts as a load-bearing and protective constituent, offering improved resistance to erosion by distributing stress under repeated bubble collapse and pressure shock waves [18, 19].

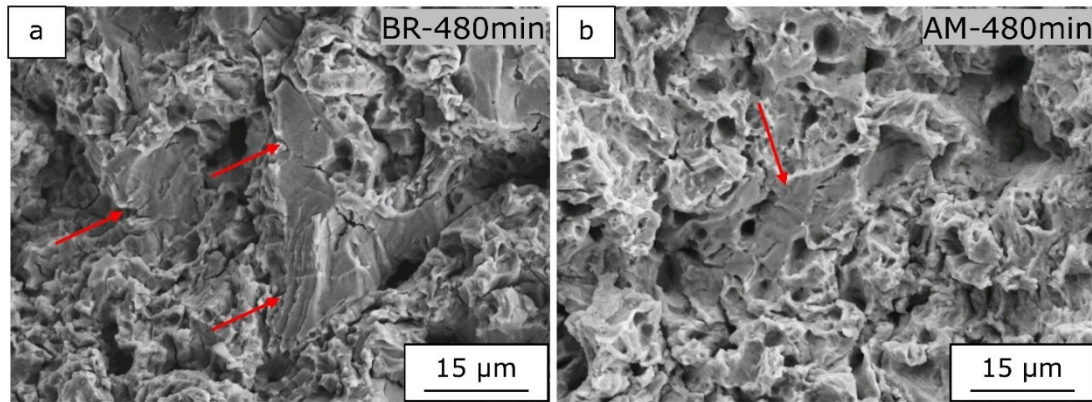


Figure 3-7. High-magnification SEM of cavitation-eroded surfaces after 480 min. (a) BR sample: mixed-mode fracture surface featuring both heavily fragmented regions and flatter zones exhibiting fatigue-like features. The red arrows highlight flat fracture areas with extremely fine striations; characteristic of fatigue crack propagation typically associated with the β -phase. (b) AM sample: highly porous and fragmented morphology with internal voids, indicative of ductile micro-fracture and early material removal.

Moreover, the greater steady-state erosion of AM brass arises from its layered build and inherent porosity, which provide additional sites for fatigue-crack nucleation. As a result, erosion proceeds in a phase-selective manner: α -rich regions degrade first, whereas β domains offer temporary resistance before eventually failing by fatigue [20]. High-magnification SEM images (**Figure 3-7**) clarify the underlying mechanisms. The BR sample (**Figure 3-7a**) shows well-defined flat facets with fine fatigue striations (red arrows) alternating with irregularly eroded areas. In contrast, the AM surface (**Figure 3-7b**) displays a markedly heterogeneous morphology. The combined effect of porosity and finer microstructure blurs the damage pattern: striations appear only locally on isolated flat facets (red arrow), while most of the surface exhibits multifaceted features with cleavage-like characteristics.

Overall, the cavitation morphology is consistent with a fatigue-controlled process. It initiates with early plastic flow, visible as slip-band bundles, followed by crack nucleation at surface discontinuities. Fine striations form on late-stage fracture facets, a classic signature of cavitation fatigue.

Occasionally striated patches in the AM sample indicate β domains that temporarily delay damage before failing by fatigue. These observations support the interpretation of **Figure 3-6**: α degrades earlier due to its lower hardness, producing a rough and porous relief, whereas β offers initial resistance. However, the larger defect population

in AM brass, particularly keyhole porosity, enhances crack-nucleation susceptibility and accelerates steady-state material loss [21, 22].

3.1.6. Corrosion behavior

3.1.6.1. Electrochemical tests

Figure 3-8 compares the polarization behavior in aerated 3.5 wt.% NaCl of the conventionally processed brasses (BR_T: transverse section; BR_L: longitudinal section) and LPBF samples (AM_y: scan direction; AM_z: build direction). **Table 3-4** reports the values of corrosion potential and corrosion current density values. All curves show a cathodic branch dominated by oxygen reduction and an anodic rise consistent with the onset of selective Zn dissolution. Across most of the potential range, AM_y overlaps the response of the conventionally processed brasses (both BR_T and BR_L), and differences remain within about 0.05 decades up to -250 mV vs SCE. A mild separation emerges at higher anodic overpotentials, where AM_y currents exceed BR by 0.15–0.20 decades ($\approx$ 40–50%) near 0 mV, while AM_z remains clearly the most active condition throughout. To benchmark the specimens under identical conditions, **Table 3-4** summarizes the mean values and standard deviations for corrosion potential (E_{corr}) and nominal corrosion current density (j_{corr}). These values are intended for relative comparison only.

The corrosion potential confirms the electrochemical ranking inferred from **Fig. 3-8**: AM_z is the most active, while BR_T is the noblest, with AM_y and BR_L in between. The nominal corrosion currents derived from the polarization data show that AM_z exhibits the highest value while AM_y the lowest. The difference between BR_T and BR_L in E_{corr} does not translate into a meaningful separation in j_{corr} , indicating minimal orientation effect for the bar material. Given that (i) the cathodic branch is oxygen-transport-limited, (ii) the anodic fits span only about half decade, and (iii) attack is highly localized so the currents are nominal (geometric-area normalized), these j_{corr} values should be read as preliminary comparative indices of corrosion behavior rather than absolute rates. Within this framework, AM_y is comparable to the BR samples, whereas AM_z remains worse.

The superior response of AM_y over AM_z is best explained by its lower internal porosity (≈ 2 vol.% vs ≈ 3 vol.% in AM_z). Because attacks proceed through isolated spots rather than uniformly, the logarithmic current densities extracted from the curves must be regarded as nominal values, normalized to the geometric area. They do not represent a spatially uniform flux and therefore cannot be converted to penetration rates via Faraday's law. This clarification does not alter the qualitative ranking, but it underscores that porosity control is the primary lever to improve the corrosion performance of LPBF CuZn42 in chloride media.

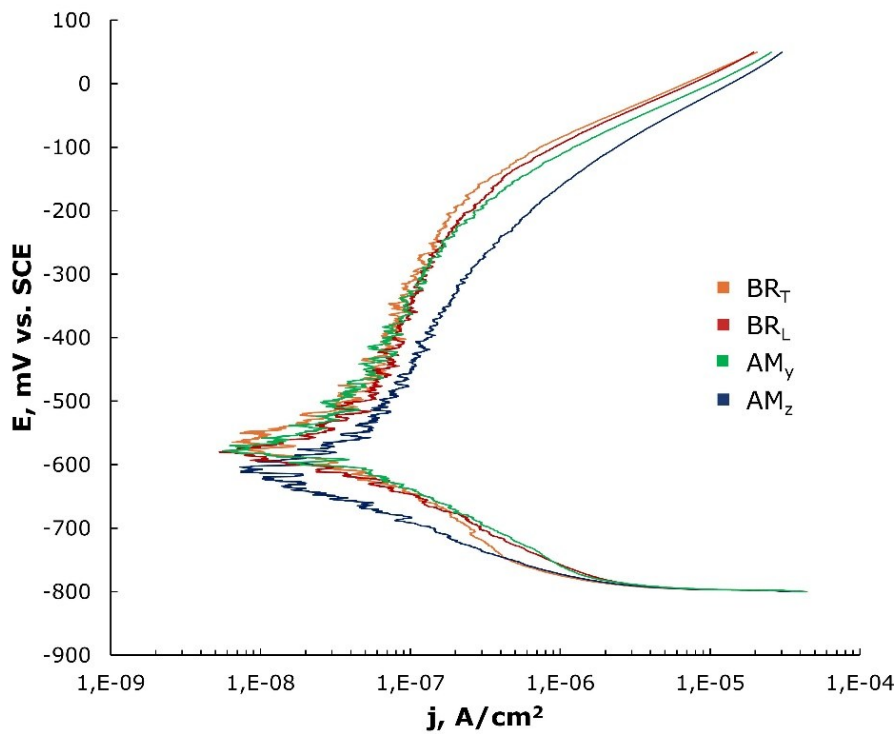


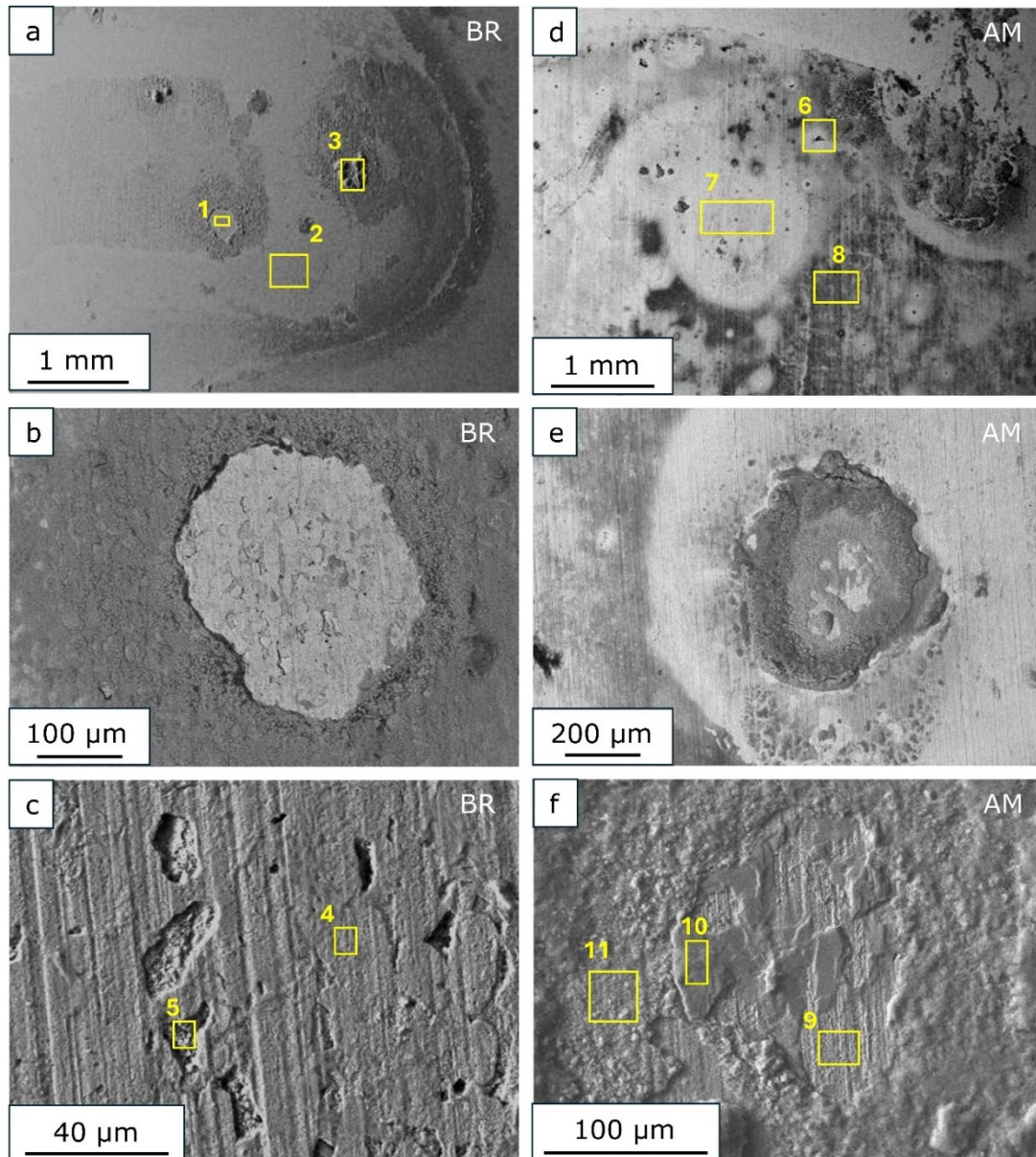
Figure 3-8. Representative potentiodynamic polarization curves of BR_T, BR_L, AM_y and AM_z. Potentials are reported vs SCE and current data were filtered by Savitzky–Golay method.

Table 3-4. E_{corr} (vs SCE) and nominal j_{corr} from LVS in aerated 3.5 wt.% NaCl.

Sample	E_{corr} (mV vs SCE)	j_{corr} (A/cm ²)
BR _T	-537 ± 9	$(2.96 \pm 0.31) \times 10^{-8}$
BR _L	-595 ± 8	$(2.91 \pm 0.33) \times 10^{-8}$
AM _y	-553 ± 11	$(2.22 \pm 0.34) \times 10^{-8}$
AM _z	-643 ± 9	$(3.16 \pm 0.50) \times 10^{-8}$

3.1.6.2. *Immersion tests*

The surfaces of the BR and AM CuZn42 samples observed after 30 days of immersion testing in 3.5 wt.% NaCl are shown in **Figure 3-9**, together with the corresponding EDS analyses results. Corrosion appears localized on both materials. Circular pits with broad halos and granular rim deposits are observed (**Fig. 3-9a, f**), whereas regions far from pits show only light tarnish. On the conventional bar surface, attack concentrated on a few sites (**Fig. 3-9a**). EDS confirms selective Zn dissolution at the pit interior (spectrum 1), while the nearby halo (spectrum 2) retains a Cu/Zn ratio close to the bulk composition. Spectrum 3, acquired on a deposit of the corrosion product, is Zn-rich with minor Fe and Cu, consistent with zinc oxy(hydroxy)chloride precipitates. A higher-magnification view of the pit corresponding to spectrum 1 (**Fig. 3-9b**) reveals the α/β lamellar contrast accentuated by selective Zn removal and the presence of small craters. Further magnification (**Fig. 3-9c**) shows that both phases are Zn-depleted (spectra 4-5), with the most eroded micro-areas exhibiting near-complete Zn loss, i.e., a dealloyed Cu skeleton.



wt. %	O	Mg	Al	Si	S	Cl	Fe	Ni	Cu	Zn
1	16.02					0.31			72.97	10.70
2	18.16		1.63	0.61		0.52			42.78	36.30
3	36.12		0.83	1.38	1.92	0.80	10.18		9.76	39.00
4	9.26								84.59	6.15
5	11.98					0.73			85.73	1.56
6	12.13		0.68	0.78		0.36		0.76	52.53	32.77
7	12.56		1.37	0.86			0.52		53.18	31.51
8	22.55	0.74	3.75	2.07			0.38	0.53	41.69	28.28
9	7.19					0.50	0.60		73.49	18.22
10	38.71				6.08	6.71	1.06		3.02	44.42
11	30.81				0.82	6.70	3.10	0.58	16.96	41.04

Figure 3-9. SEM-EDS of CuZn42 after 30 days in 3.5% NaCl: conventional bar (BR, a-c) vs LPBF (AM, d-f). Corrosion is localized. BR shows fewer, larger pits; AM shows numerous smaller sites with thick granular rims on the layered surface. Pit interiors are Cu-rich/Zn-poor (dezincification; spots 1, 7-9); rim deposits are Zn-/Cl-rich, O-high (spots 3, 10-11). EDS compositions (wt%) in table.

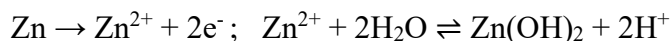
In the AM specimen, surface-connected pores can already be observed (**Fig. 3-9d**), suggesting potential initiation sites for the widespread localized attack described below. Accordingly, the AM surface shows numerous smaller damaged sites distributed across the field of view (**Fig. 3-9d**). At low magnification, no single region exhibits the extreme Zn depletion seen at the BR pit interior. Instead, pits are surrounded by thick, porous deposits that blanket the local topography (**Fig. 3-9d-f**). The site analyzed in **Figs. 3-9e-f** illustrates this morphology: the corrosion product is rich in Zn and Cl with high O (spectra 10–11), consistent with zinc hydroxy-chlorides (e.g., simonkolleite-type) precipitated from Zn^{2+} released during dezincification, whereas exposed metal islands inside the halo remain compositionally close to the substrate but slightly Zn-depleted (spectrum 5-9).

Taken together, the EDS data supports a dezincification-controlled mechanism. Bright, porous regions at scratches or within pit interiors are Cu-rich/Zn-poor (e.g., spots 7–9), indicating a dealloyed copper framework produced by preferential Zn dissolution. Areas remote from pits (e.g., spots 1–6) show moderate oxygen with both Cu and Zn present and only trace Cl, typical of a thin mixed oxide/hydroxide film. The granular rim deposits that ring AM pits (spots 10–11) indicate an under-deposit environment sustained by differential aeration, which favors Zn-salt precipitation and prolongs localization.

3.1.6.3. Corrosion behavior in NaCl solution

The overall degradation behavior observed in polarization and immersion tests can be interpreted in light of established mechanisms for brass corrosion in chloride media. The zinc content and phase constitution strongly condition the response. A higher bulk Zn fraction generally increases susceptibility to dezincification, leaving behind a porous Cu-rich framework layer [23]. In α - β brasses, the seawater behavior is largely governed by the β/β' constituent, since selective Zn dissolution from β preferentially triggers dezincification and compromises structural integrity [24] [25].

Consistent with literature and Pourbaix diagrams, polarization curves of brass typically exhibit limited current densities below about -244 mV vs SCE, a potential region where Cu remains passive while Zn is active [26]. In this range, the anodic current is predominantly due to Zn dissolution:



As Zn is progressively removed, the near-surface becomes Cu-enriched. This dealloyed Cu skeleton, characterized by vacancies and under-coordinated sites, can itself destabilize at higher overpotentials, enabling further Cu dissolution [27, 28]. Beyond this Zn-limited regime, the current rises steeply, indicating mixed Zn–Cu dissolution. For Cu, the thermodynamic pathways include Cu₂O/CuO formation; in chloride-rich media, dissolution often proceeds via CuCl(s) and soluble chloro-complexes (e.g., CuCl₂⁻, CuCl₃²⁻) [29].

This interpretation is linked with the lower bulk Zn content measured for AM (≈35.5 wt. %) compared with BR (≈41.1 wt%), which shifts AM toward the α-rich field (Table 1), and with the phase contrast seen in the etched micrographs (**Figure 3-3**). The AM sample does not show improved corrosion resistance in the polarization test. This is attributed to its layered architecture, characterized by lack-of-fusion defects and residual porosity (≈2 vol.% in AMy and ≈3 vol.% in AMz).

Microstructural and chemical factors further refine this scenario under saltwater immersion. The conventionally extruded alloy (≈50/50 α–β) is intrinsically more susceptible than α-brass in chloride solutions [24], consistent with reports that α-rich compositions display higher polarization resistance and lower dezincification rates [23]. Nevertheless, the AM samples, despite being α-rich, exhibited more severe localization. This apparent paradox arises from manufacturing-induced features, such as near-surface porosity, lack-of-fusion defects that create occluded sites, and melt-pool boundaries, which provide favorable locations for corrosion initiation. In particular, the occluded sites may trap electrolyte and stabilize aggressive local chemistries. Additionally, these sites can supply Zn along segregated paths, promoting persistent dezincification plugs and the deposition of Zn-Cl-O compounds [30]. Inside occluded cells, oxygen depletion and hydrolysis lower pH while Cl⁻ concentrates, accelerating Zn dissolution and sustaining dezincification fronts. These effects outweighed the intrinsic advantage of the α matrix, leading to abundant localized pits in AM, whereas the bar material developed fewer but deeper pits centered on β-rich zones.

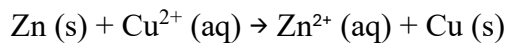
Additional elements may also influence corrosion behavior. Lead, though present only in trace amounts, segregates as discrete cathodic inclusions and can locally perturb

current distribution; higher Pb levels have been associated with increased corrosion rates in certain environments [31]. In the present alloys, Pb is negligible (**Table 3-1**) and unlikely to dominate the response, although minor micro-galvanic effects cannot be excluded.

3.1.6.4. Dezincification tests

Optical micrographs of the cross-sections after dezincification tests reveal significant differences between the BR (**Figure 3-10a, b**) and AM samples (**Figure 3-10c, d**). The dezincified regions appear as a distinct, orange-colored layer near the surface.

The exposure of brass to a copper (II) chloride dihydrate ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$) solution promotes a galvanic displacement reaction that leads to selective zinc dissolution (dezincification). In this redox process, zinc, being the less noble element, is preferentially oxidized to Zn^{2+} , while Cu^{2+} ions in solution are reduced and deposited as metallic copper on the brass surface. The overall reaction can be summarized as:



This reaction results in a porous, copper-enriched surface layer and is often used to simulate aggressive corrosion conditions or to highlight the phase-specific reactivity of α and β' regions in biphasic brass. The deposited copper typically appears as a reddish or brownish film, while zinc remains in solution as a soluble ion. In environments rich in chloride ions, additional complexation reactions may occur, forming species such as CuCl_2^- and ZnCl_4^{2-} . Over time, the accumulation of corrosion products and the depletion of zinc compromise the mechanical integrity of the material, leading to embrittlement and increased surface roughness.

The results concerning the dezincification depth, summarized in **Figure 3-10e**, indicate that the AM samples exhibited markedly higher susceptibility to dezincification compared to BR counterparts. Specifically, the AM_z specimen showed the deepest zinc-depleted layer ($790 \pm 32 \mu\text{m}$), followed by AM_y ($576 \pm 23 \mu\text{m}$). In contrast, conventionally extruded samples displayed shallower penetration depths: $324 \pm 16 \mu\text{m}$ for BR_L and $247 \pm 12 \mu\text{m}$ for BR_T , values consistent with ISO 6509-1 reference benchmarks.

The more severe attack observed in the AM specimens is primarily attributed to their higher defect density, such as lack-of-fusion porosity and interlayer discontinuities.

These volumetric defects serve as preferential paths for electrolyte penetration and zinc dissolution, promoting the initiation of corrosion as well as the rapid advancement of the corrosion front.

In addition to defect-related features, microstructural aspects may also contribute to the propagation of the corrosion front. For AM samples, no clear evidence of phase-selective corrosion was observed, consistent with Fig. 3e-f, where no well-defined biphasic distribution was identified. Dezincification in brasses is in fact often associated with selective attack of the β -phase, known to be more prone to dezincification due to its higher Zn content and more anodic nature. However, the effects of local compositional variations, such as Zn-enriched regions suggested by the microstructural observations in Fig. 3e-f, may locally facilitate corrosion advancement and cannot be completely excluded. Furthermore, the finer microstructure in the AM samples, together with the absence of a preferential orientation of α grains, as instead observed in the BR sample (Fig.3a-b), may reduce the barrier effect.

Although these microstructural features may contribute to promoting the propagation of the corrosion front, defect-related features (such as porosity and interlayer discontinuities) are considered the primary factors governing the corrosion behavior of AM samples.

In this regard, even if conventional brass contains a higher fraction of the β -phase, the superior resistance observed in the BR samples is ascribed to their significantly lower porosity and more consolidated microstructure. In these samples, although the attack appears more localized and consistent with phase-selective dezincification, the overall penetration depth remains significantly lower.

This observation is consistent with the electrochemical corrosion results, where AM brass exhibited slightly inferior performance than BR, indicating that pores play a role, albeit limited, in corrosion initiation under electrochemical testing. Their presence becomes more significant and critical during prolonged exposure in aggressive environments, as in dezincification testing, facilitating deeper penetration of selective corrosion and resulting in significantly higher dezincification depth.

In addition, when comparing the two BR orientations, the BRT specimen exhibited the lowest dezincification depth. This can be linked to the orientation of the α -phase grains and β -phase lamellae: in BRT, the grain structure appears aligned more favorably to

impede corrosion propagation perpendicular to the surface, thereby enhancing the barrier effect.

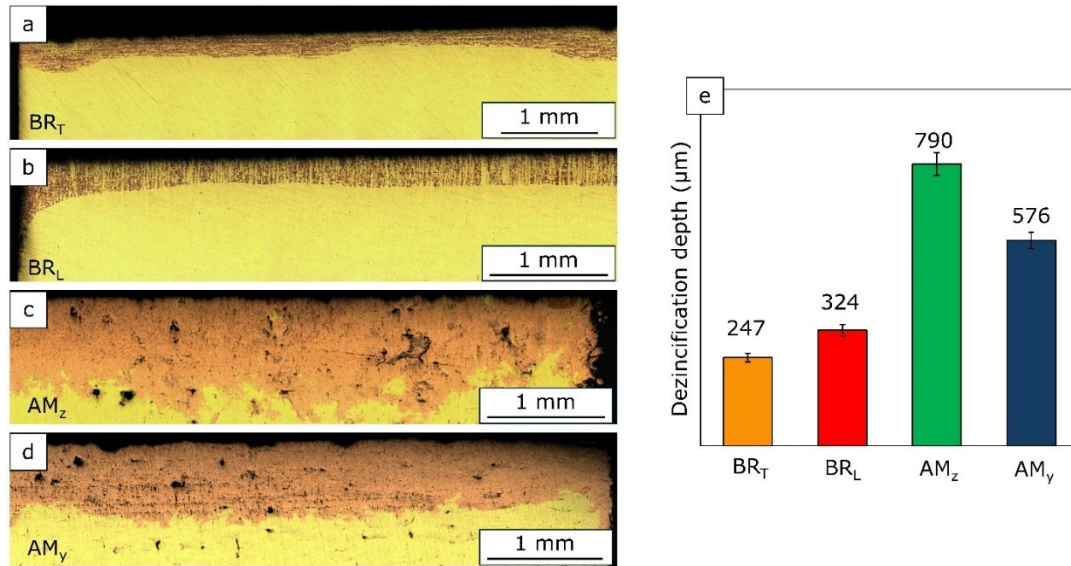


Figure 3-10. Dezincification morphology and depth in CuZn42 brass after corrosion testing. (a–b) Optical micrographs of conventionally processed brass (BR), cut along the longitudinal (BR_L) and transverse (BR_T) directions. (c–d) Additively manufactured brass (AM), observed along the laser scan direction (AM_y) and build direction (AM_z). (e) Bar chart summarizing the measured dezincification depth.

Taken together, these considerations corroborate the experimental ranking derived from polarization and immersion: $BR_T \approx BR_L > AM_y > AM_z$. The immersion morphologies align with the electrochemical data (Table 3-3), and the dezincification depths (Fig. 3-10e) reinforce the same order, indicating that defect topology (porosity, interlayer discontinuities) is the dominant factor controlling the corrosion resistance of AM brass in NaCl solution.

3.1.7. Conclusions

Processing route dictates composition and microstructure and, ultimately, degradation behavior in CuZn42. LPBF yields an α -rich alloy with a layered architecture, interlayer flaws in the building direction, and surface-connected porosity, whereas the conventional bar is fully dense with an $\alpha+\beta$ phase constitution. These features set the boundary conditions for both cavitation erosion and saltwater corrosion.

Under cavitation loading, incubation times are comparable across routes, but the AM condition exhibits higher steady-state loss. SEM surface morphology and high-magnification fractography indicate that interlayer boundaries and porosity in AM may

act as stress concentrators and crack-initiation paths, yielding a more uniformly distributed erosion imprint, whereas BR exhibits fewer but deeper, localized craters. In aerated NaCl, corrosion initiates through selective Zn dissolution and evolves toward mixed Zn–Cu dissolution as the Cu-rich skeleton destabilizes at more positive potentials. Despite its α -rich chemistry, the AM material shows stronger localization because pores and lack-of-fusion features create occluded cells that concentrate Cl^- , acidify locally, and stabilize Zn-salt deposits. Electrochemical trends, immersion morphologies, and dezincification depths are mutually consistent and rank performance as $\text{BRT} \approx \text{BRL} > \text{AM}_y > \text{AM}_z$, underscoring that defects outweigh phase balance in governing corrosion resistance. With reduced defects, achievable through further process optimization or post-processing treatments, phase balance would likely become more relevant in determining corrosion behavior.

Overall, the topology and connectivity of near-surface defects are the primary determinants of durability. Under cavitation loading, the results indicate that process optimization can narrow the performance gap between LPBF and conventional brass. In particular, reducing surface-connected porosity and achieving a more homogeneous microstructure are key factors. The AM condition approaches the bar response despite its substantially lower hardness. In chloride solution, however, both porosity and phase constitution are critical: even when porosity is mitigated, process-induced shifts in the α/β balance can alter corrosion resistance relative to the conventional alloy and must be accounted for in design and qualification.

References

1. Davis JR (2001) Copper and Copper Alloys. Materials Park, ASM International
2. European Copper I. Publication 117 — Section 6: Types of Brass. 2016.
3. World Health O. Guidelines for Drinking-water Quality. 4 ed. Geneva: WHO; 2011.
4. Vilarinho C, Davim JP, Soares D, Castro F, Barbosa J (2005) Influence of the chemical composition on the machinability of brasses. *J Mater Process Technol.* <https://doi.org/10.1016/j.jmatprotec.2005.05.035>
5. Gatto A, Gatto ML, Groppo R, Munteanu D, Mengucci P (2023) Influence of laser powder bed fusion process parameters on the properties of CuZn42 components: case study of the laser surface energy density. *Prog Addit Manuf.* <https://doi.org/10.1007/s40964-022-00361-z>
6. He J, Liu X, Li B, Zhai J, Song J (2022) Cavitation Erosion Characteristics for Different Metal Surface and Influencing Factors in Water Flowing System. *Appl Sci.* <https://doi.org/10.3390/app12125840>
7. Abedini M, Reuter F, Hanke S (2019) Corrosion and material alterations of a CuZn38Pb3 brass under acoustic cavitation. *Ultrason Sonochem.* <https://doi.org/10.1016/j.ultsonch.2019.104628>

8. Liu H, Deng Z, Chen J, Kang C, Li B (2022) Synergetic Effect of Corrosion and Ultrasonic Cavitation Erosion on Lead Brass. *J Mater Eng Perform*. <https://doi.org/10.1007/s11665-021-06435-3>
9. Trapp J, Rubenchik AM, Guss G, Matthews MJ (2017) In situ absorptivity measurements of metallic powders during laser powder-bed fusion additive manufacturing. *Appl Mater Today*. <https://doi.org/10.1016/j.apmt.2017.08.006>
10. Yin J, Zhang W, Ke L, Wei H, Wang D, Yang L, Zhu H, Dong P, Wang G, Zeng X (2021) Vaporization of alloying elements and explosion behavior during laser powder bed fusion of Cu–10Zn alloy. *Int J Mach Tools Manuf*. <https://doi.org/10.1016/j.ijmachtools.2020.103686>
11. F.C. Campbell (2008) *Elements of Metallurgy and Engineering Alloys*, ASM International doi:10.31399/asm.tb.emea.9781627082518
12. ASTM (2016) ASTM G32-16 Standard Test Method for Cavitation Erosion Using Vibratory Apparatus
13. UNI EN ISO 6509-1:2014 Corrosion of metals and alloys – Determination of dezincification resistance of copper alloys with zinc – Part 1: Test method
14. Chen X, Wu C, Zhang Y, Mei J, Guo L, Wang C, Yang S (2024) Achieving exceptional combination of strength and ductility in $\alpha+\beta$ diphasic brass with harmonic structure. *Mater Sci Eng A*. <https://doi.org/10.1016/j.msea.2024.146325>
15. Song Y, Wang Z, Ma B (2025) The Role of Pores in the Cavitation Erosion of Additively Manufactured Metal: An In Situ Study. *Metals*. <https://doi.org/10.3390/met15070787>
16. Ahmed SM, Hokkirigawa K, Oba R (1994) Fatigue failure of SUS 304 caused by vibratory cavitation erosion. *Wear*. [https://doi.org/10.1016/0043-1648\(94\)90238-0](https://doi.org/10.1016/0043-1648(94)90238-0)
17. Abedini M, Lopez de Arcaute y Lozano C, Kostka A, Hanke S (2024) Influence of surface finishing by grinding on the cavitation erosion resistance of 316L and NiAl-bronze. *Wear*. <https://doi.org/10.1016/j.wear.2024.205432>
18. Hanke S, Kaiser SA (2021) Comparison of damage mechanisms: Acoustic cavitation versus series of single laser-induced bubbles. *Wear*. <https://doi.org/10.1016/j.wear.2021.203641>
19. Long J, Eliceiri MH, Wang L, Vangelatos Z, Ouyang Y, Xie X, Zhang Y, Grigoropoulos CP (2021) Capturing the final stage of the collapse of cavitation bubbles generated during nanosecond laser ablation of submerged targets. *Opt Laser Technol*. <https://doi.org/10.1016/j.optlastec.2020.106647>
20. Wang Z, Wang Y (2022) Cavitation erosion and its effect on corrosion resistance of nuclear-grade Z3CN20–09M stainless steel. *Mater Des*. <https://doi.org/10.1016/j.matdes.2022.110978>
21. Du Plessis A, Yadroitsava I, Yadroitsev I (2020) Effects of defects on mechanical properties in metal additive manufacturing: A review focusing on X-ray tomography insights. *Mater Des*. <https://doi.org/10.1016/j.matdes.2019.108385>
22. Tammas-Williams S, Withers PJ, Todd I, Prangnell PB (2017) The Influence of Porosity on Fatigue Crack Initiation in Additively Manufactured Titanium Components. *Sci Rep*. <https://doi.org/10.1038/s41598-017-06504-5>
23. Sugawara H, Ebiko H (1967) Dezincification of brass. *Corros Sci*. [https://doi.org/10.1016/S0010-938X\(67\)80090-8](https://doi.org/10.1016/S0010-938X(67)80090-8)
24. Heidersbach RH Jr, Verink ED Jr (1972) The dezincification of alpha and beta brasses. *Corrosion*. <https://doi.org/10.5006/0010-9312-28.11.397>
25. Selvaraj S (2003) Dezincification of brass and its control – An overview. *Corros Rev*. <https://doi.org/10.1515/CORRREV.2003.21.1.41>
26. Vanleugenhaghe C (1974) *Atlas of electrochemical equilibria in aqueous solutions*, NACE
27. Martín H, Carro P, Hernández Creus A, Morales J, Fernández G, Esparza P, González S, Salvarezza RC, Arvia AJ (2000) Interplay of Surface Diffusion and Surface Tension in the Evolution of Solid/Liquid Interfaces. Dealloying of β -Brass in Aqueous Sodium Chloride. *J Phys Chem B*. <https://doi.org/10.1021/jp001077c>
28. Vu T.N, Mokaddem M, Volovitch P, Ogle K, (2012) The anodic dissolution of zinc and zinc alloys in alkaline solution. II. Al and Zn partial dissolution from 5% Al–Zn coatings, *Electrochim Acta*, <https://doi.org/10.1016/j.electacta.2012.04.037>
29. Al-Kharafi F (2004) Selective dissolution of brass in salt water. *J Appl Electrochem*. <https://doi.org/10.1023/B:JACH.0000005616.41240.d0>
30. Dridi A, Dhoubi L, Hihn JY, Berçot P, Rezrazi EM, Sassi W, Rouge N (2020) Analytical Study of CuZn 30 and CuZn 39 Brass Surfaces in 3% NaCl Solution Under Polarization. *Chem Afr*. doi: 10.1007/s42250-020-00182-z.

31. Wang X, Su H, Xie Y, Wang J, Feng C, Li D, Wu T (2023) Atmospheric corrosion of T2 copper and H62 brass exposed in an urban environment. Mater Chem Phys. <https://doi.org/10.1016/j.matchemphys.2023.127487>