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# CORROSION BEHAVIOUR OF ADDITIVELY MANUFACTURED METALLIC MATERIALS

## KOROZIJSKO OBNAŠANJE KOVINSKIH MATERIALOV IZDELANIH Z DODAJNO TEHNOLOGIJO

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Additive manufacturing (AM) represents a technological advancement over traditional manufacturing methods, offering cost-effective production of high-quality, geometrically complex components for various applications. With its ability to rapidly manufacture metallic parts and a capability to better customise products due to the possible recycling of used powder materials, AM facilitates customized product development. On the other hand, the technology raises questions regarding microstructure, residual stresses, porosity and surface roughness. All these aspects need to be evaluated to achieve the quality of the end products. This paper reviews the corrosion behaviour of AM-produced metallic materials, examining how various factors, including porosity, microstructure, melt-pool boundaries, residual stresses, and surface roughness, influence the end-product quality.

Keywords: additive manufacturing, corrosion, steel, Inconel 625, FeMn alloy

Dodajna tehnologija (AM) predstavlja dodano vrednost h konvencionalnim proizvodnim tehnologijam in ponuja proizvodnjo visokokakovostnih, geometrijsko kompleksnih komponent za različne aplikacije, s sorazmerno nizkimi stroški izdelave. AM omogoča boljšo prilagoditev izdelkov ter struktur, hkrati pa omogoča proizvodnjo z manj odpadnega materiala, saj lahko uporabljene prahove recikliramo. Po drugi strani pa tehnologija odpira vprašanja glede mikrostrukture, zaostalih napetosti, poroznosti in hrapavosti površine. Vse te vidike je potrebno ovrednotiti, da bi dosegli večjo kakovost končnih izdelkov. Ta članek obravnava korozijsko obnašanje kovinskih materialov, proizvedenih z AM, in preučuje, kako različni dejavniki, vključno s poroznostjo, mikrostrukturo, mejami talilnega bazena, preostalimi napetostmi in površinsko hrapavostjo, vplivajo na kakovost končnega izdelka.

Ključne besede: dodajna tehnologija, korozija, jeklo, Inconel 625, zlitina FeMn

## 1 INTRODUCTION

Additive manufacturing (AM) has emerged as a promising manufacturing tool, revolutionizing traditional manufacturing methods with its layer-by-layer addition of powders or liquids to build geometrically complex components.[1] Various metallic materials can now be effectively printed, with AM technologies categorized into powder-fed[2–5] or powder-bed[1,6–8] systems. Within these categories, two techniques have gained a lot of attention. One of the most promising AM technologies utilizing a focused laser beam is Selective Laser Melting (SLM), which offers many advantages in metallic material production, boasting high accuracy and superior mechanical properties (**Figure** 1).[9] The second most commonly used AM technology is Directed Energy Deposition (DED), which is known for its faster printing times, although, at the expense of lower resolution, leading to decreased dimensional accuracy in printed parts.2 Nevertheless, AM stands out as a rapid manufacturing process offering the freedom of shape and design, high performance, cost effectiveness, and reduced material waste compared to conventional methods.[10–12] Notably, AM facilitates almost 100 % recycling of unconsumed powders, enhancing its cost-effectiveness and environmental friendliness.[13]

In the recent years, the advances in the printing equipment have allowed the fabrication of various metallic materials, such as AlSi10Mg,[14] Ti6Al4V,[15] CoCr,[16] Fe-based[17] and Ni-based alloys.[18] However, ensuring the quality of printed parts remains a significant challenge, attributed to factors such as rapid cooling rates leading to non-equilibrium phase formation and structural imperfections prone to corrosion.[19] The unique thermal features of AM technology, such as rapid melting and resolidification have a strong impact on the microstructure, corrosion and mechanical properties of printed alloys.[1] The optimization of AM process parameters is therefore crucial. An additional heat treatment is necessary to improve the ductility, reduce the thermal stresses and achieve superior mechanical properties.[20] Surface-treatment techniques, such as plasma nitriding, are generally employed to improve their surface properties.[21–27]

In spite of the large global annual financial losses due to corrosion, the corrosion behaviour and durability of SLM parts have yet to receive substantial attention.1 This paper provides a concise review of various metallic

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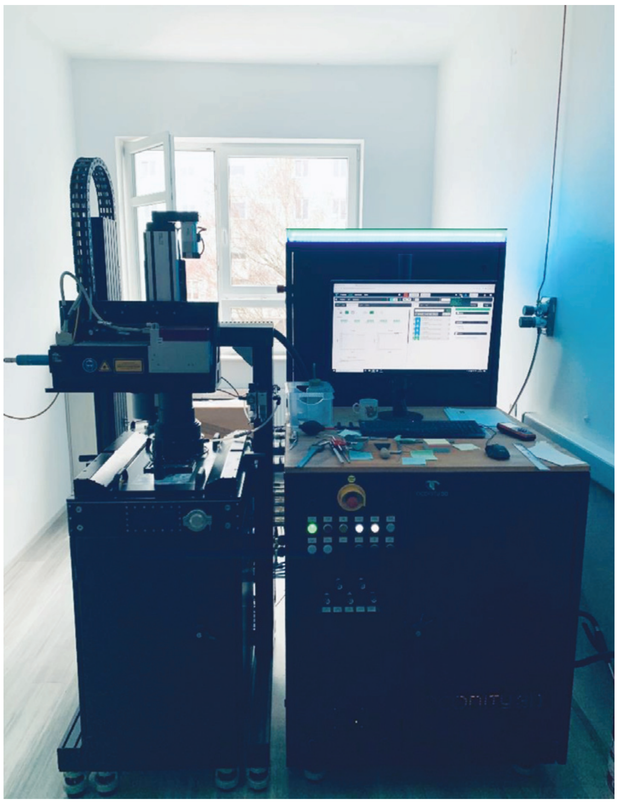

**Figure 1:** SLM Aconity3D MINI instrument equipped with 800 °C preheating option, installed at the Institute of Metals and Technology

materials fabricated via AM technology, along with recent research findings, aiming to elucidate the differences in corrosion behaviour between traditional manufacturing and the AM approach.

## 2 FACTORS INFLUENCING THE CORROSION BEHAVIOUR OF AM METALLIC MATERIALS

Several factors influence the corrosion behaviour of AM metallic materials, including porosity, microstructure, melt-pool boundaries, residual stress and surface roughness.[1]

Porosity, which initially occurs in powder metallurgy processes and also manifest in AM parts, can significantly impact the corrosion behaviour of components.[28] Typically, pores in AM parts exist in two forms: around un-melted powders and due to trapped gas during gas atomization.[1] Optimizing printing conditions, such as laser energy and scanning parameters, can mitigate porosity to some extent.

Microstructure has an important influence on the corrosion of metallic materials, taking into consideration the formation of different phases during AM or post-processing, inclusions, grain size and shape, alloying elements, elemental segregation as well as the presence of oxygen in the feedstock powder.[29]

Melt-pool boundaries are common in AM alloys, often exhibiting elemental segregation, thermal stress, and non-equilibrium phases.[1] These boundaries can negatively impact the mechanical properties, particularly plasticity.

Anisotropic residual stress in AM parts arises from differential solidification rates and heat conductivity in different directions.[1,30] This microstructural anisotropy leads to variations in the mechanical and corrosion properties across different planes.

Surface roughness in AM parts is generally higher compared to other manufacturing routes, primarily due to evaporation.[1,23] This can be attributed to factors such as improper powder melting and the balling phenomenon. Surface conditions play a crucial role in material corrosion properties, with increased roughness correlating with susceptibility to pitting and general corrosion rates.

Overall, addressing these corrosion issues is crucial for ensuring the reliability and durability of AM components in various applications.

## 3. CORROSION BEHAVIOUR OF DIFFERENT AM ALLOYS

### *3.1 Corrosion behaviour of AM AISI 316 L*

Austenitic stainless steels are particularly suitable for AM technology due to their lack of martensitic phase transformation and precipitation during rapid solidification, making them extensively studied materials in this field.[21]

The comparison of AM and conventionally produced AISI 316L stainless steel in a chloride-rich environment shows that AM material exhibits good corrosion properties despite the high dislocation density and chemical nano-segregations.[21,31,32] A solution treatment induces the grain growth, resulting in decreased corrosion stability (**Figure** 2).[21] Generalizing the influence of grain size on corrosion resistance is challenging, as it is affected by factors like grain refinement, surface-reactivity changes, and environmental conditions.[33] While grain refinement typically enhances corrosion resistance by promoting passive layer formation, variations in chemical composition, environment, and processing can alter the corrosion process. In our study, a slight increase in corrosion rate is observed in samples with larger grain sizes after solution treatment.[21] On the other hand, nitriding is expected to improve the corrosion characteristics, but instead applied independently has a negative effect on corrosion stability due to the formation of chromium nitrides (CrN).[34] Our findings suggest that a combination of solution treatment and nitriding optimizes the mechanical and corrosion properties, owing to stress release during solution treatment, which hinders CrN formation.[21] Carbon content affects the corrosion performance by stabilizing the austenitic phase, but can also form chromium carbides,[21] although levels below 0.03 *w*/% typically do not detrimentally impact the corrosion resistance, as confirmed in our study. Conventionally processed 316 L stainless steel

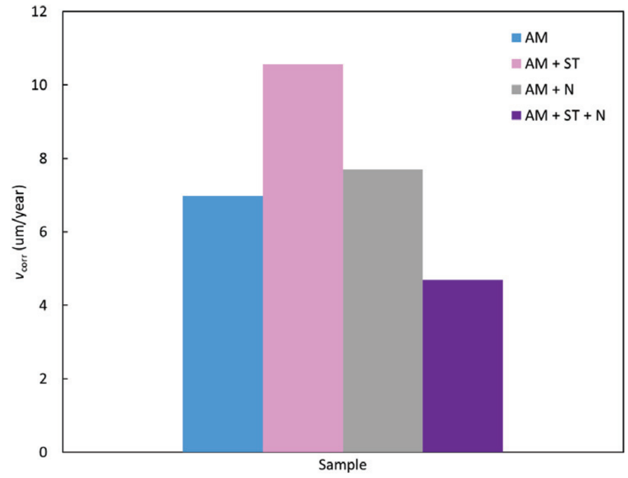


**Figure 2:** Corrosion rates calculated from potentiodynamic measurements for AM 316 L as-built (AM), nitrided at 430 °C for 15 h (AM + N), solution treated at 1060 °C for 30 min) (AM + ST) and solution treated and nitrided (AM + ST + N) in 3.5 % NaCl

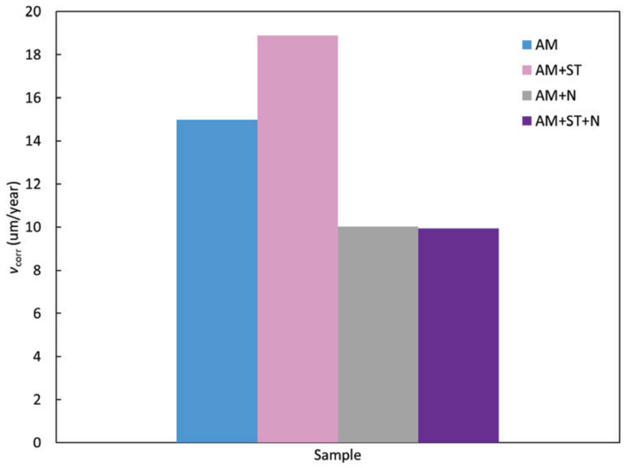


**Figure 3:** Corrosion rates calculated from potentiodynamic measurements for AM as-built 18Ni-300 maraging steel (AM), after aging treatment at 520 °C for 6 h (AM + ST), after nitriding at 520 °C for 6 h (AM + N) and after aging treatment at 520 °C for 6 h and nitriding (AM + ST + N)

shows the highest corrosion rate, likely due to the presence of MnS and accompanying Cr depletion.[35] Improved barrier characteristics are observed after nitriding.[21]

### *3.2 Corrosion behaviour of AM maraging steels*

Maraging steels are extensively employed in AM technology due to their good weldability.[24] The 18Ni-300 steels, belonging to the low-carbon, iron-nickel alloys class and exhibit exceptional strength-to-toughness ratio, ductility and machinability, are extensively used in aircraft and aerospace applications, moulds and tooling.[36] The ultra-high strength is a consequence of a hardening during aging treatment, where intermetallic nanoparticles precipitate within a martensitic microstructure, enhancing microhardness and strength.[36] The main disadvantage of maraging steels is reduced wear and corrosion resistance compared to other tool steels.[24] Plasma nitriding has been employed to mitigate these limitations, by enhancing surface properties without compromising the base material's properties.[23,24] AM-produced maraging steels generally exhibit higher corrosion rates compared to conventionally produced ones due to the inhomogeneity, porosity and the local stresses affected by melt cavities, a dendritic cellular structure and an increased surface roughness.[37] Plasma nitriding improves the corrosion resistance by forming a corrosion-resistant compound layer.[24] Our results show that plasma nitriding even without the prior heat treatment achieves acceptable corrosion rate (**Figure 3**). However, the heat treatment is needed to avoid cracking of the nitride layer due to the internal stresses. While conventional maraging steel successfully combines aging and nitriding, attempts to replicate this process in AM materials resulted in crack formation within the compound layer. Plasma nitriding with prior heat treatment prevents crack formation. Alternatively, a short-term annealing for stress relief may prevent cracking during nitriding while maintaining a high dislocation density, facilitating a compound layer without porosity.[24]

### *3.3 Corrosion behaviour of AM nickel-based superalloys*

Inconel 625, a nickel-based superalloy rich in chromium, exhibits good weldability, corrosion and mechanical properties (high-temperature strength, fatigue and creep resistance).[22,38] It is extensively used in aerospace, marine, petrochemical and nuclear applications.[22,39] However, its hardness limits its workability, particularly for complex geometries, leading to its restricted use in such applications.[38] Here, AM is favourable due to its ability to meet demands for geometrically complexed designs. AM process parameters significantly influence the microstructure and mechanical properties. Heat treatment is often necessary to mitigate the residual stresses, non-equilibrium phases, and micro cracks.[22]

Despite their advantages, nickel-based alloys suffer from poor tribological performance.[40] Surface-engineering techniques are therefore required to enhance the surface properties. Plasma nitriding, although extensively studied for Fe-based alloys, receives less attention for Ni-based alloys due to the nitride-forming elements.[22] While promising results have been observed, several issues require further investigation, including determining the optimal nitriding parameters and understanding the impact of prior heat treatments on the nitriding process.

Regarding the corrosion behaviour of AM Inconel 625, the heat treatment does not significantly alter the corrosion resistance compared to as-built AM samples (**Figure 4**). The polarisation and passivation behaviours are primarily influenced by plasma-nitriding temperatures, with early-stage nitride formation at lower temperatures showing a slight improvement in the corrosion performance. In contrast, higher nitriding temperatures

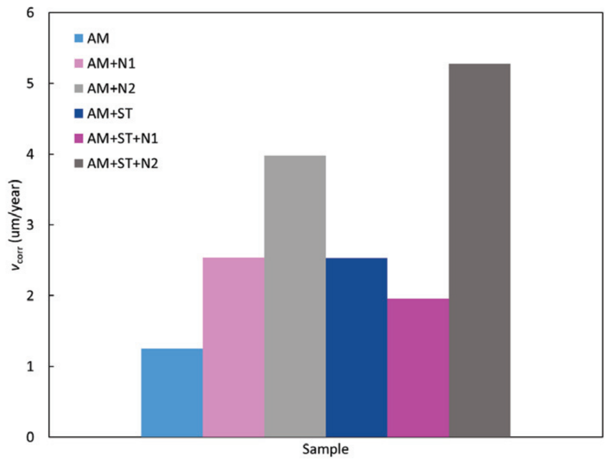


**Figure 4:** Corrosion rates calculated from potentiodynamic measurements for AM as-built (AM), as-built + nitrided at 430 °C/15 h (AM + N1), as-built + nitrided at 500 °C/15 h(AM + N2), as-built + solution treated 1050 °C/1 h (AM + ST), as-built + solution treated 1050 °C/1 h + nitrided at 430 °C/15 h (AM + ST + N1) and as-built + solution treated 1050 °C/1 h + nitrided at 500 °C/15 h (AM + ST + N2)

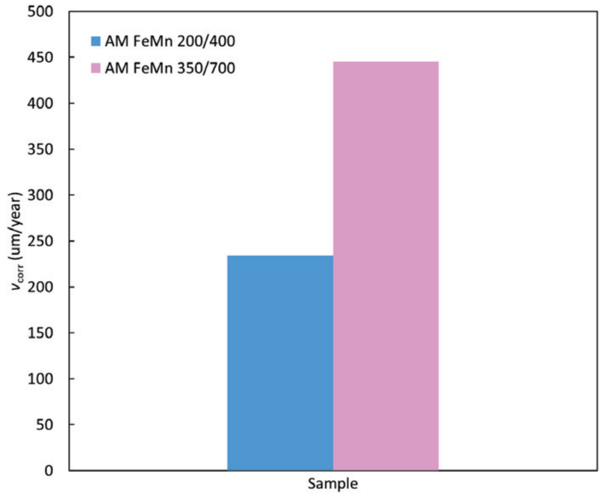


**Figure 5:** Corrosion rates calculated from potentiodynamic measurements for AM FeMn 200/400 sample (laser power 200 W, scanning speed 400 mm/s) and AM FeMn 350/700 sample (laser power 350 W, scanning speed 700 mm/s) measured in Hank's solution

result in poorer passivity attributed to the transformation of expanded austenite and the local depletion of Cr due to the formation of CrxNy phases.[41]

### *3.4 Corrosion behaviour of AM FeMn alloy*

The AM production route for biodegradable metallic implants is a powerful platform for personalized biomedical applications. These implants provide temporary support and gradually degrade *in vivo*, aiming to completely dissolve without implant residues. Our research group extensively studies AM-produced FeMn biodegradable alloys.[42] Their limitation is a slower degradation rate, which can be successfully surpassed by suitable tailoring of the AM process parameters. The mechanical, microstructural, and corrosion properties are strongly correlated with scan-related and temperature-associated AM process parameters. Increased porosity and dual-phase microstructure ($\gamma$-austenite and $\varepsilon$-martensite) are key factors which accelerate the corrosion rate and can be accomplished by modifying the process parameters (**Figure 5**).[42] Significant decrease of corrosion resistance is also observed in samples with more crystal lattice defects, dislocations, grain boundaries, retain stresses and presence of oxides.[43]

## 4 CONCLUSIONS

Additive manufacturing (AM) is an innovative tool in the manufacturing of metallic materials, offering geometrically complex structures, rapid production and reduced waste. Despite its noticeable advantages, challenges such as porosity, microstructure, melt-pool boundaries, residual stress, and surface roughness persist. All these factors influence mechanical properties and corrosion behaviour, requiring optimization of printing conditions and post-processing treatments (heat treatment, plasma nitriding). Some groups of metallic materials are extensively studied by our research team. Austenitic stainless steels, maraging steels and nickel-based alloys demonstrate promising corrosion resistance through suitable post-processing treatments. Additionally, AM offers a potential in biomedical applications with biodegradable metallic implants, though challenges remain in tailoring the process parameters to optimize the degradation rates while maintaining the mechanical integrity. Addressing these challenges is crucial for ensuring the reliability and durability of AM components across various applications.

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