Additive manufacturing – a general corrosion perspective

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ABSTRACT
Metallic additive manufacturing will replace some materials produced by conventional fabrication methods in the nearest future. However, corrosion will remain an important aspect needed to be prevented. The corrosion behaviour of additively manufactured alloys has been sparsely studied and very little work has been published so far. In this article, a general discussion about materials produced by additive manufacturing will be provided.

Introduction
Additive manufacturing (AM), rapid prototyping, sequential layer printing, or 3D printing refers to a process used to create a three-dimensional object in which material is deposited layer-by-layer to produce complex shapes, which may not be possible otherwise. Digital, 3D-design data are used to build up a component by a direct printing procedure, with no other fabricating step involved, in which the material, in the form of powder or wire, is melted by using a laser or an electron beam, followed by subsequent solidification [1,2].

The microstructure produced by AM is akin to that of sintered materials, but it has a distinctive and complex nature, which may not be forecastable. AM has characteristics, which makes the material to be clearly distinguishable from conventionally formed bulk alloys. Little changes in process parameters, such as heat exposure conditions or manufacturing speed, can largely alter the microstructure. The method used, i.e. whether laser or electron beam is used for powder melting, can further lead to different microstructures, thereby affecting corrosion properties.

There are more unknowns than knowns in materials produced by AM, and therefore further research in terms of microstructure characterisation and corrosion testing is required. There is a rapid solidification nature of printed alloys during the selective (laser) melting process, producing quenched microstructures with largely varying structural inhomogeneities. From a macroscopic point of view, in contrast, porosity and inhomogeneous surface roughness are characteristic of AM-materials. Both the surface morphology and structural inhomogeneities promote an inherent sensitivity of AM-materials to localised corrosion and galvanic coupling in different scales.

The corrosive environments were chosen for corrosion testing of additively manufactured alloys in the majority of most published works were seen to be too aggressive, and therefore, the reported data are less representative for an application and little useful to understand the mechanism of corrosion. Understanding corrosion requires an application-relevant selection of a few corrosive conditions representative to the corrosive medium as well as the different corrosion mechanisms that can occur. The temperature, pH, concentration and so on need to be conceptualised thoroughly to study and understand both macroscopic failure of the material and microscopic initiation of corrosion.

Characteristics of additively manufactured materials

General microstructure
The microstructure of AM-materials is usually dendritic due to the rapid solidification nature during processing which has detrimental effects on both mechanical and electrochemical properties. The dendritic solidification structure can only be eliminated by homogenisation which, however, can cause grain coarsening and nucleation of secondary phases. Very good understanding of various stages of the evolution of the microstructure, in general, in conventionally produced alloys exists which, however, does not hold true for AM. Microstructure control seems to be a lasting problem, contrasted to conventionally fabricated materials at least. The processing conditions used for AM can vary largely from those produced via conventional methods, resulting in non-uniform, highly anisotropic physical as well as electrochemical properties. For example, retained austenite in martensitic stainless steels is desired in controlled volume fractions only, which, however, seems to be rather difficult in alloys fabricated via AM. Several factors have been stated as the reason for the weak control of the transformation of austenite to martensite causing it to retain in the microstructure, all associated with the fabrication procedure of AM [3]: (1) the residual strain at high-angle grain boundaries which impede the transformation of austenite to martensite, (2) high dislocation density produced during fabrication, (3) supersaturation of carbon with other phase stabilising elements due to rapid quenching, (4) small grain sizes and interdendritic spacing due to direct solidification with no post-processing.
involved, and (5) the powder manufacturing environment [3]. Post-heat treatments, especially for martensitic steels, seem to be necessary which can reduce the cost-efficiency of AM and, hence, question the fabrication technique. The microstructure of AM-materials contains usually large fractions of secondary phases, such as carbides, nitrides, and sigma and chi phase, which, for example, in stainless steel, typically promote localised corrosion [4]. Secondary phases can be removed by post-heat treatments but the material geometry and dimensions may be affected, which can impose constraints on the motivation to implement AM since such treatments are associated with high costs [4]. The general difficulty of materials or products produced by AM is that a proper characterisation of the microstructure, to represent the entire bulk structure by a sample cut-out from the object in larger scale, is virtually impossible. The microstructure will vary at any point in all directions, and, therefore, conventional metallography cannot be applied, not at least to derive conclusions to describe the entire microstructure. The microstructure of AM-produced alloys is, furthermore, unpredictable due to difficulties in achieving the same component with identical physical properties which certainly can also influence electrochemical properties. Hence, localised corrosion is inevitable and may cause a problem for AM-produced mild steels whose corrosion resistance is typically described by general corrosion rates, expressed by a unit of metal thinning per year. The testing procedure of AM-produced materials needs to be attuned, which may make currently existing, well-established standards out of the question. Testing for stress corrosion cracking (SCC), for example, is typically done by a cut-out of a piece from the bulk material, which still represents the entire body of it. However, since the microstructure is largely heterogeneous at any point in AM-produced materials, representative SCC specimens cannot be manufactured, and if, the results can be misleading and totally irrelevant.

**Porosity**

The structure of additively manufactured materials is usually porous, which can be quantitatively characterised with a porosity level, typically expressed as volume fraction. Porosities can be considered as 'indigenous' stress concentrators in both macron and micron scale and can lead to material failure, restricting the use of AM-alloys in high performance-requiring applications. From a corrosion point of view, pores can be considered as 'ready pits' to grow. The corrosive within such cavities can easily build up distinct and more severe electrolytic conditions, leading to earlier pitting and perhaps to faster transition to stable pit growth, and in the presence of residual or applied stresses SCC can occur. The situation can be more critical if conglomerated pores with intricate and semi-occluded occurrence exist since the corrosive chemistries can become more severe due to quicker oxygen depletion and faster build-up of critical metal ion concentration, which can enhance the oxidation power of the electrolyte and enhance corrosion initiation and growth. The critical metal ion concentration, the decisive parameter describing the stability of a pit, can be faster reached, causing earlier pitting and hence lowering of the local breakdown potential [5,6]. 'Classic' pitting/crevice test results may largely scatter which may cause difficulties in conducting parametric analysis, such as the effect of pH or chloride concentration and so on, and, therefore, the determined corrosion rate may not be a reliable quantity, especially for critical materials with a fixed life-time expectation.

Micro-pores usually exist due to an uneven distribution of heat delivered by the moving laser or electron beam during AM. The porosity is mainly set by the energy level (temperature) of the depositing beam and the wettability of the powder or wire. The porosity level can vary depending on the processing parameters. For example, a porosity level of 0.48% with a mean pore size of 40 nm has been reported [2]. There is a selective porosity concentrated mainly at the boundaries of the metal pool intersections, which may promote intergranular corrosion or even, in support of acting stress, the transition to intergranular stress corrosion cracking [7]. Porosities can reduce the threshold stresses needed for pit-to-crack transition and further complicate the SCC scenario. Knowledge existing on conventional bulk alloys may not be directly transferable to assess the SCC behaviour of AM-materials. This requires a totally new literature database to be established.

**Structural gradients across the surface**

The surface of a substrate is usually different than its bulk, and there is a distinctive border line (interface) between the surface and the material interior, leading to gradient distributions of strain and stress as well as possible chemical heterogeneities. Large thermal and or mechanical stress variations across the microstructure in macro, meso, and micro scale are common for AM-materials. The structure seems to be always heterogeneous, a clear distinctive drawback of AM-alloys as contrasted with conventionally fabricated bulk materials [1]. A microhardness variation across the surface towards the bulk, measured in cross-section on a laser-fused cladding stainless steel, has been reported [2]. The microhardness dropped by up to 50% over a distance of 2 mm, clearly indicating a surface-hardened nature associated with AM [2]. The hardness of wire-fed electron beam additively manufactured structures have been demonstrated to vary locally throughout the microstructure, with the hardness map being useful in understanding the local variations [8]. The hardness varied between 150-300 HV1, with the surface and the bulk showing alternating hardness values, with no clear position attributable to low or high hardness [8]. Little modifications in the AM process, such as energy input or wire-feeding speed or angle, had a large influence on the hardness, also affecting the hardness 'pattern' in the material [8]. Hardness is associated with stress and, therefore, the corrosion growth or SCC behaviour of a material with a 'patterned' hardness (locally varying hardness gradients) may be manifested in an unprecedented form. There may be no classical pits, such as shallow or deep, and the corrosion front may follow regions with higher flaws (hardness) towards the bulk interior and simply hole the microstructure. SCC cracks may be odd directed within the bulk material and lead to difficulties in understanding the mechanism of cracking. The surface roughness can vary highly, which can promote localised corrosion and/or galvanic coupling over a larger scale.

**Chemical inhomogeneities**

The microstructure of conventionally fabricated alloys can be optimised by hot/cold rolling and heat treatments, in which
chemical segregation and any inhomogeneities can be removed, preventing or minimising galvanic corrosion. In contrast, additively manufactured microstructures assume their morphology during the printing process, and usually, no quenching, heat treatment, or mechanical deformation is involved. However, stress relaxation treatments can be possible to remove stresses which may have developed during the printing process, but are not desired due to the intention to keep the production costs at a minimum. Such a treatment would, however, not remove chemical inhomogeneities which play key role in corrosion reaction. Therefore, additively manufactured alloys are usually heterogeneous in varying scales and lengths and, hence, are a priori vulnerable to galvanic corrosion and localised attack. The classic chemical segregation problem, often observed in direct-cast materials, seems to re-manifest itself in AM-materials. Higher melting point elements solidify first and concentrate in the centre of dendrites or grains which form a gradient towards the interdendritic or grain boundaries, in which elements with lower melting points can be enriched [9]. The alloys are highly susceptible to micro-segregation, a non-uniform composition in micrometre scale produced by non-equilibrium solidification. Micro-segregation (interdendritic segregation and coring) usually occurs over short distances between dendrite arms or produces grains with chemically varying composition and, hence, resulting in properties differing from one region to the next, leading to poorer properties as a whole [9].

**Microstructural heterogeneities**

The microstructure of additively manufactured alloys is in non-equilibrium. Dendritic and interdendritic structures with nanometre-sized precipitates and oxide compounds can usually be seen. Intermetallic compounds or any other products, such as oxides, which are not or may not be possible to be formed in conventionally produced microstructures, may become likely in additively fabricated microstructures. Carbides, nitrides, and even inclusions are very likely to nucleate in large fractions, which can impose the material additional risk to a low corrosion resistance. Such heterogeneities are known to be detrimental to the material. Widmannstätten microstructures were also observed, not often wanted as reference microstructures [10]. Local nobility variations in the corrosion point of view are highly detrimental since micro-galvanic interactivities can be promoted. Oxides either partially covering the surface or in the microstructure as an inclusion can severely affect corrosion properties since these can be ‘loosely’ bound to the material and can lead to enhanced corrosion activities [11]. Oxides can be semi- or incoherent to the matrix and, therefore, crevices at the oxide-matrix interfaces can be easily formed, often leading to a disintegration and fall-out of the inclusion from the bulk, resulting in an aggressive ‘ready’ pit to grow [11]. The oxide formed on the surface is different than the naturally grown, protective oxide on metals.

**Defective Passive film nature**

The microstructure, as well as the surface oxide of additively manufactured alloys, is usually defective [2,3,12]. It cannot be worse than having a partially covered oxide scale on the surface which can act as promoters for crevice corrosion. Moreover, the question remained whether the surface oxide can be called ‘native’ since its appearance resembles more a scale rather than the protective oxide forming on corrosion-passive metals. The oxide layer is thick and non-native which emanates from the melting process. The thickness of the oxide scale can be very thick, being further trapped as oxide inclusions in the microstructure [12]. Perhaps one can introduce the parameter ‘oxide-to-bulk ratio’ to characterise the quality of AM-materials. The oxide is, furthermore, chemically and most-likely structurally different from the usual native oxide. The oxide is protective if it is dense and well-structured without any defects or with low defect density, sustaining also low in ionic as well as electronic conductivity [13,14]. However, the ‘rapid’ manufacturing (quenched melted surface) is associated with a large in-built dislocation density which may be similar to highly deformed microstructures. There has been no systematic study performed on additively manufactured alloys to characterise and quantify surface defects, not published at least. Subtracting procedures, e.g. descaling, can be performed to remove thick oxide scales to improve the corrosion resistance of the material. However, the new oxide film formed on the metal would nevertheless highly differ compositionally and possibly also structurally over the material surface as well as through its thickness due to chemical and structural inhomogeneities. This makes difficult to characterise the oxide films of passive-film-forming AM-materials.

**Texture**

There is an inherent epitaxial solidification nature of printed alloys leading to textured microstructures with columnar or non-regular grain shapes, often observed for AM-materials [10,12,15]. Texture can be a serious matter in terms of stress corrosion cracking. Textured materials can be both more susceptible to corrosion and environmentally assisted cracking. The microstructure of AM-materials produced by wire-feeding, for example, is anisotropic and is more affected than AM-materials produced in a powder bed [8]. Solidification texture, in general, depends on the direction of the local heat flow and competitive grain growth occurring during printing [15]. However, texture seems to be controllable using a so-called point heat source strategy in which the printing area in an electron beam melting process is patterned in ‘points’ with some space leaving between the points and then filling these points to reach a homogeneous-like melting/solidification as contrasted to traditional rasterised printing (serpentine) in which solidification follows the printing path [16]. Texture may impose a corrosion problem as such that crystallographic pitting can be favoured, producing numerous localised corrosion sites [17].

**Grain size**

The grain size can be varied by the size of the metal powder which is usually in the order of ~50 µm. However, the grain size distribution of additively manufactured alloys is usually higher with more difficulties in controlling the ‘balance’ [3,10,12]. The grain size is not a big problem in terms of corrosion resistance. However, the grain size in a microstructure should be optimised, and the grain size distribution should not vary largely since clusters of small grains usually contain higher strains and can promote localised corrosion or micro-galvanic coupling between larger grains [18,19]. The grain
size, however, can be a major problem in hydrogen exposed environments or conditions where hydrogen can be generated by cathodic reactions [20–22]. Super duplex stainless steels are known to suffer from severe hydrogen-related cracking in corrosive media with microstructures having large austenite spacing (>30 µm) [20–22].

**Strain and Stress**

A major drawback of AM is that it causes both macro and micro strain development and, hence, stresses in the material. Residual stresses are generated during the printing process due to high temperature gradients and re-iterative rapid melting-cooling events, with the surface of AM-produced alloys showing high tensile stresses [23,24]. The residual stresses in AM-materials are more complicated than those evolved in conventionally fabricated materials since steep residual stress gradients are generated all over the surface as well as the interior of the material which can cause distortion, ultimately resulting in deterioration of the functionality of the produced component [23,24]. Stress relaxation treatments, such as heat treatments or surface machining, may be needed to remove the stresses formed during printing; however, this can lead to secondary phase formation and impose other kinds of strains/stresses. Strain and stress typically accelerate corrosion and stress corrosion cracking [18,25,26]. Compressive surface stresses may impede corrosion for ‘a while’, but would be enhanced when the compressive stress/strain layer is removed since there is always a balancing tensile region underneath. However, the stress may vary over the surface and alternate locally with tensile/compressive stresses, further complicating the matter. The measurement of ‘local’ strains/stresses may not be possible, which requires modelling work [24,27]. Finite element modelling of residual stress formation in AM-alloys revealed that residual stresses can alternate by re-iteratively changing from tensile to compressive throughout the printed layers [27]. Corrosion and/or SCC of such components may not be straight forward to understand since a delamination of the printed layers similar to brittle/failed coatings would be expected to occur, which may further be complicated to be modelled. The residual stress was shown to change with larger magnitudes along the printing direction than towards the depth (opposite side of the building direction) [24]. Hence, corrosion growth as well SCC propagation may be favoured along underneath the surface, leading to layer delamination. The associated corrosion/SCC crack growth rates may largely vary over time, requiring a thorough thinking of data interpretation. The residual stress state of highly porous structures may be further complicated, and the SCC behaviour may be unforeseeable. SCC and corrosion may occur ‘under’ the surface, if large and interconnected pores exist, with the residual stress playing a vital role. The residual stress state can further be complicated in the microstructure of multi-phase alloys, such as duplex stainless steel, due to different physical and mechanical properties of ferrite and austenite phases, which will lead in most cases to varying stresses [18,26,28]. Information about the location, nature, and magnitude of stress has utmost importance for assessing the SCC resistance or propensity to hydrogen embrittlement (HE).

**Final remarks**

In a nutshell, the entire microstructure of additively manufactured alloys are incomparable to conventionally fabricated materials, but a comparison of multi-pass welded structures or directly casted materials may be useful. The comparison, however, is not simple since AM-alloys with no post-treatment are heat-affected at any point and can contain residual stresses varying locally in high gradients. The grains can be textured with sizes, shapes, and orientations varying from top to bottom (building direction) and across the printing direction. Microstructure characterisation of multi-pass welded structures, however, may be promising in optimising the AM procedure since a controlled microstructure can be useful in obtaining reproducible properties. Additive manufacturing of materials with simple microstructures is by far more promising than those sensitive to composition and/or manufacturing technology. Bi- or multi-phase alloys, such as duplex stainless steels, can be critical unless the microstructure can be controlled with no inclusions or sensitised microstructures. AM-materials with low-wall thickness can be critical due to accelerated loss of life-time caused by corrosion or stress corrosion cracking, which is the most deleterious form of damage. The microstructure performance of AM-alloys may be of similar quality to cast alloys but not necessarily to conventional forged materials [7]. The question remained whether the duplex stainless steel produced by AM has a real duplex microstructure? More systematic research is needed to understand the microstructure performance and associated corrosion resistance of additively manufactured alloys. Research on the development of AM-materials should be made in parallel to optimise corrosion properties.

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