



Review

The influence of nanocrystalline structure and processing route on corrosion of stainless steel: A review

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ABSTRACT

Nanocrystalline materials with a grain size <100 nm have attracted significant attention over the past two decades. Various attempts have been made to prepare nanocrystalline stainless steel using various routes, along with the study of attendant corrosion properties. A nanocrystalline structure imparts an improvement in mechanical properties, coupled with distinct corrosion behaviour, not always leading to better corrosion resistance. This paper reviews the relevant works to date which have studied corrosion behaviour of nanocrystalline stainless steels, relating the performance to processing, along with attention given to mechanistic aspects which dictate corrosion of nanocrystalline stainless steel.

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1. Introduction

Stainless steel (SS), owing to its passivation ability and resistance to environmental degradation, has found wide applications ranging from kitchenware to critical components in nuclear reactors [1–6]. Many types of SS have been developed to meet various industrial demands, with the main alloying elements being chromium and nickel. Stainless steels are divided in four main groups based on their microstructure which is composition and processing dependent: ferritic, austenitic, duplex, and martensitic [4–6]. Corrosion behaviour of the various types of SS is well documented, along with the underlying mechanisms as discussed in the related monographs and journal literature [7–13].

Although stainless steels possess a higher density in comparison to the light metals (Al, Mg, Ti), their specific strength can be very high, which is in addition to high stiffness, fracture toughness, and excellent corrosion resistance [14–16]. Therefore, SS with improved strength and corrosion resistance could be next generation of metallic materials (due to high specific strength and durability) for the aerospace and several niche industries. Various strategies, e.g., thermochemical processing, nitriding, carburizing, alloying, etc. have been proved to be effective means of enhancing the surface as well as bulk strength [4,6,17–21]. Grain refinement

has great influence on the mechanical strength and corrosion behaviour of SS [6,22–25]. Initial investigations have shown that grain refinement can improve both the corrosion and mechanical properties; however, grain refinement was limited to a few microns [6,21–32].

The finding that grain refinement to <100 nm induces distinctive properties [33–37] stimulated research in developing SS with a nanocrystalline structure. Various nanocrystalline SS have been prepared in recent years via various processing routes and their properties have been investigated. A nanocrystalline structure in SS has been reported to impart significantly higher oxidation resistance (owing to greater Cr diffusion and ease of formation of compact Cr-oxide layer) [38–43] and mechanical properties than [44–49] conventional coarse grain counterparts of the same chemical composition.

The unique properties of nanocrystalline materials are associated with a very fine grain size and a large number of structural defects, i.e., grain boundaries and triple points [33–35,50,51]. Such a high fraction of structural defects in nanocrystalline materials can lead to a significant increase in stored energy which may increase reactivity. This phenomenon is expected to have a dual effect on corrosion behaviour which depends upon material/environment system as reviewed in [52,53]. In passivating electrolytes (i.e., stainless steel in many aqueous environments) a nanocrystalline structure has been reported to lead to an improvement in corrosion resistance, whilst in depassivating electrolytes a decrease in corrosion resistance is reported [52,53].

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Diffusivity of alloying/impurity elements in nanocrystalline materials are reported to be significantly higher than that in conventional coarse grained materials due to considerably higher volume fraction of grain boundaries [54–58]. Detailed discussion of the diffusion processes in the nanocrystalline material is reported elsewhere [59–62]. The increase in the diffusivities of solute/impurity atoms in nanocrystalline alloys (i.e., P in Ni-P and Co-P alloys [63–67], and Cr in SS [53,68]) was reported to influence corrosion behaviour. However, recently it was proposed that the diffusion coefficient of Cr in SS at room temperature, even in nanocrystalline alloys, was too low to cause any significant influence on corrosion behaviour of SS [48,62]. These contradicting views related to the influence of diffusion on corrosion at room temperature require further investigations.

The unique structure of nanocrystalline alloys, which is concomitant with increased free energy, alloying element diffusivity and chemical homogeneity, is expected to induce significantly distinct electrochemical/corrosion properties [62]. Initially, it was believed that nanocrystalline materials (including SS), owing to a high surface energy, may have displayed inferior corrosion resistance [69]. However, in recent years, the corrosion resistance of nanocrystalline SS produced by various routes has been investigated and the reported data presents a range of differing corrosion behaviour. Inconsistency in the reported data may be attributed to be a result of the various processing routes and processing parameters used to fabricate a nanocrystalline structure; in addition to the influence of the various electrolytes in which testing has been executed. Processing route used to fabricate nanocrystalline alloys will not only influence the grain size, but also several other metallurgical parameters, i.e., chemical homogeneity, dislocation density, phase transformations (i.e., resolutionising), and morphology of inclusions (size range and distribution), etc. The influence of all these parameters on corrosion behaviour is as important as grain size. The aim of the present review is to investigate works performed on the corrosion of nanocrystalline SS, as fabricated by various processing routes, leading to a timely discussion of the critical factors influencing the resultant corrosion as presently understood.

2. Passivation and pitting corrosion of stainless steels

The corrosion resistance of SS results from the presence of a thin “passive film” upon the metal surface that is typically 1–3 nm thick [11–13]. The phenomenon of formation of such a protective surface film is called passivation. Various theories of passivation and passive film growth kinetics have been proposed. One of the early models, known as the High Field Model (HFM) assumed that the rate determining step for film growth was the transfer of cations between adjacent lattice sites within the passive film. This model assumed that driving force for the transport of cations in the passive film was an electric field [70]. The Mott-Cabrera model was later proposed, which assumed that the rate-limiting step for the passive film growth is the emission of metal cations from the metal into film at the metal/passive film interface [71,72]. The Mott-Cabrera model [71,72] was later modified by Fehlner and Mort [73] who proposed that the rate-limiting step in passive film growth was the emission of anions from the environment into the passive film at the passive film/environment interface. Macdonald and co-workers proposed a comprehensive model of the passive film growth [74,75] which has been evolving since the late 1970s. This model, known as point defect model (PDM), accounts for the cation and anion mobility, vacancy mobility, interaction among cations, anions and vacancies, and reactions occurring at the passive film/electrolyte and passive film/metal interfaces. The PDM has been extended to account for the break-

down of the passive film and influence of alloying elements on passive film [76–79]. Various theories of passivity and fundamentals of SS corrosion have been covered in key review articles and monographs [10–13,74–77,80–86].

It is now well documented that the addition of Cr to Fe leads to a dramatic improvement in the corrosion resistance, owing to the replacement of the surface (passive) film from the native Fe-oxide to a stable Cr-oxide [56,87,88]. Whilst it is appreciated that a critical Cr content is essential to impart this phenomenon, understanding the enhanced corrosion resistance caused by the Cr derived passivation, and the precise role of Cr, took several decades. Further, it is generally reported that with the an increase in Cr content, the pH region of stable passivity enlarges, passive current density decreases, re-passivation potential shifts to lower (more negative) potentials, and pitting resistance increases significantly [87–90].

Corrosion behaviour of SS is attributed to depend upon the characteristics of the passive film which is largely influenced by Cr content of the alloy. It is generally believed that selective dissolution of Fe and oxidation of Cr leads to the formation of Cr rich passive layer [91–98]. Characteristics of the passive film and its relationship with the alloy composition have been investigated widely [99–104]. It was suggested that a Cr content >50% in passive film was required for stable passivity [105]. The Cr content of the passive film has been demonstrated to increase with increase in Cr content of the alloy [105–107]. An X-ray photo electron spectroscopy study of a series of Fe–Cr alloys indicated that the Cr content in the passive film formed in 0.5 M H₂SO₄ increased abruptly when Cr content in the alloy was above 13% [106,107]. These reports suggested requirement of the critical Cr content in SS to cause passivity, which was later explained on the basis of percolation model [108–112].

Passive film was proposed to be composed of an outer and inner layer [97,99–104,113]. Cr³⁺ was found to accumulate in the inner layer of passive film [99,100,106] which was suggested to be pure oxide whereas outer layer was reported to be composed of hydroxides [97,99–104,113]. Chemical composition of the passive film was found to depend upon the environment as well as applied potential [99–103]. It was shown that Fe²⁺, Fe³⁺ and Cr³⁺ were present at lower polarisation potentials, Fe³⁺ content was reported to increase with increase in potential [97,99,100,102].

The electronic properties of passive films developed over variety of materials are investigated in the past a few decades [114,115]. It is shown that the passive film behaves like a highly doped semiconductor and characteristics of the passive film depend upon alloying additions and Cr content of the SS [115–120]. Increasing Cr content of the SS alters the electronic properties of the passive film in a manner that improves stability of passive film [115,116]. Details of electronics structure of passive film and its dependency on composition can be found in [114–119,121–125].

The passive film on SS is susceptible to breakdown as a result of aggressive ions (i.e. halides), pH changes, and temperature [126,127]. Local breakdown of the passive film can lead to the localized corrosion known as pitting. Pitting can be characterised in three stages [128–130]:

- (1) Pit initiation or nucleation caused by the breakdown of the passive film. Nucleation events are followed by repassivation.
- (2) Metastable pitting where pit growth stops on the verge of stability. Metastable pits grow for a finite time and size before repassivation. Metastable pitting is proposed to be a measure of pitting susceptibility [130–136].
- (3) Pit growth where pits grow as long as the pit interior can maintain the sufficiently aggressive electrolyte such that repassivation is prevented.

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