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Microstructure–mechanical and chemical behavior relationships in passive thin films

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ABSTRACT

The passive films play an important role in corrosion and stress corrosion cracking of austenitic stainless steels. The current research investigates the relationship between alloy chemistry, microstructure, and mechanical behavior of passive films formed on 316, 304, and 904L stainless steels (SS). X-ray photoelectron spectroscopy and transmission electron microscopy were used to investigate the effect of alloy chemistry and microstructure constituents on the thin film fracture properties determined by nanoindentation tests. The analyses showed that fracture loads are directly related to the crystallography of the thin films. It was found that decreasing the ratio of iron to other metallic elements in the film led to an increase in the load required to fracture the film. It was also found that films grown on 304, 316, and 904L stainless steels were the cubic polymorph of Cr_2O_3, rather than the lower energy rhombohedral form. In the case of 904L SS the film formed as an epitaxial layer. In the other two cases it consisted of small crystalline islands in an amorphous matrix. A dichromate treatment of 316 SS decreased the iron content in the oxide film and increased the hardness. It also resulted in an epitaxial film.

1. Introduction

It is well established that passive films formed on austenitic stainless steels play an important role in corrosion and stress corrosion cracking. Breakdown of the passive film on the metal surface results in localized corrosion such as pitting of the metal itself. The passive film on austenitic stainless steel (SS) has been described as consisting of distinct bilayers. The inner layer is enriched in chromium oxide while the outer layer is a mixture of iron oxide and a hydroxide film [1–3].

The presence of the passive film affects the surface mechanical properties of the alloy. Li et al. recently studied the influence of passive film formation on the yield stress of the 321 alloys [4]. The film was formed by immersion in an $MgCl_2$ solution at 115 °C for 1 h. Due to the generation of additive stresses that increased dislocation multiplication and motion, the presence of the passive film decreased the yield stress. Other researchers have performed bulk experiments that enable measurements of passive film strength, but these usually couple both the bulk metallic alloy as well as the very thin passive film [5–7].

Nanoindentation is a popular and powerful technique by which the mechanical properties of very small volumes such as thin films can be evaluated [8]. A load discontinuity may be considered as the event by which the loading portion is divided into elastic and plastic deformation. Load discontinuities, “pop-in” events, are indicative of either dislocation nucleation and multiplication or a through-thickness fracture of a film [8,9].

Pang et al. studied the mechanical properties of a titanium oxide film anodically formed on polycrystalline titanium in 0.1 M H_2SO_4 at different anodization rates using nanoindentation [10]. It was found that the strength of the oxide film depended on the applied potential. Mudali and Katada used electrochemical atomic force microscopy to study passive films formed on nitrogen-bearing austenitic SS and demonstrated that the stiffness of passive films decreased with an increase of applied potential [11]. Rodriguez-Marek et al. investigated the mechanical response of the passive film anodically formed on 304 SS in 0.1 M H_2SO_4 with different chloride concentration using nanoindentation [12]. It was found that the load required to fracture the film decreased with increasing chloride concentration in the electrolyte. In our previous studies [13,14], the load needed to break the passive films formed on different stainless steel alloys, 304 SS, 316 SS, and 904L SS in two different potential regions was determined. The loads required to fracture the films increased as a function of increasing chromium concentration at a stable passive potential [13].

One widely used chemical treatment to improve the corrosion resistance of stainless steels by stabilizing the passive film is a chromate or dichromate treatment [15]. Chiba *et al.* [16] used nanoindentation to study the effects of the dichromate treatment on the mechanical properties of passivated surfaces formed on single crystal iron. The dichromate treatment increased the hardness and the ratio of elastic work to plastic work of these surfaces at depths > 30 nm. Seo and Chiba investigated the effect of the dichromate treatment on the load-displacement curves for iron (100) and (110) surfaces [17]. A

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