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Corrosion and passivation mechanism of chromium diboride coatings on stainless steel

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Abstract

The corrosion resistance of fully crystalline CrB_2 coatings magnetron sputtered onto AISI 316L stainless steel was tested in acidic solutions. CrB_2 coatings showed excellent corrosion protection, but suffered a breakdown when an anodic potential of greater than about +1 V (SHE) was applied to the surface in a 1 M HCl electrolyte. The coating failure at high potentials is attributed to transpassive dissolution of the coating at volume defects, enabling the electrolyte to reach the underlying 316L substrate, resulting in its rapid corrosion and subsequent fracturing of the coating. Electrochemical data and potential–pH (Pourbaix) diagrams, constructed from thermodynamic data, indicate that the corrosion resistance of CrB_2 is due to the formation of a Cr(III) oxide passive film in the absence of activation corrosion.

Keywords: A. Acid solutions; A. Sputtered films; C. Passive films; C. Pourbaix diagram

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1. Introduction

Austenitic stainless steels possess high toughness which makes them a more commonly used class of corrosion resistant alloy compared with other varieties of

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stainless steels such as ferritic, martensitic and precipitation hardened stainless steels [1]. However, given that the toughness in a material is generally achieved at the expense of hardness, performance of austenitic stainless steels are not as satisfactory in applications in which wear may be responsible for material degradation [2].

Hard, corrosion resistant coatings on austenitic stainless steels are desired in engineering applications where corrosion and wear act simultaneously, such as during processing in corrosive media and possibly in some biomedical situations. For such applications, chromium borides are promising coating materials because of their high hardness and reported resistance to corrosion in both acids and bases [3,4]. These materials are examples of transition metal–metalloid alloys which are known to exhibit superior corrosion resistance to that displayed by pure chromium. For example in 6.5 N HCl at 50 °C, an amorphous chromium boride coating, $Cr_{80}B_{20}$, produced on a glass substrate, was found to corrode at a much lower rate of <1 mm per year compared with 1600 mm per year for pure chromium [5].

In another immersion test study conducted in 12 N HCl at room temperature, amorphous films of composition $Cr_{60}B_{40}$ and $Cr_{80}B_{20}$ were found to display no measurable loss in thickness even after three months exposure. In contrast pure crystalline chromium corroded in this medium at a rate of 700 μm/day which is more even than AISI type 304 stainless steel which corroded at a lower rate of 218 μm/y [6].

Many metal–metalloid binary alloys, sometimes in a glassy or amorphous state, display superior corrosion characteristics to that of pure crystalline chromium. Such alloys are based on a number of combinations of Ni, Fe, Co, Mo and Cr together with Si, C, P and B [7]. Whilst it has been found that in $Fe_{80}B_{20}$ and $Fe_{80}P_{20}$ the metalloids (B, P) degraded the passive properties of the alloy (and hence enhanced corrosion rates) the chromium analogues exhibited the opposite behaviour. Thus the key to understanding the corrosion performance characteristics of amorphous Cr–B (and Cr–P) alloys lies in the synergistic relationship between chromium and boron (or phosphorus) in promotion of passivity.

Although the corrosion resistance of the chromium borides is much higher compared with that of pure chromium, the mechanism of corrosion protection in oxidising acids is suggested to be the same in both the cases, i.e., formation of a laterally homogeneous chromium oxy-hydroxide or Cr_2O_3 passive film [3].

The electrochemical mechanisms of chromium corrosion phenomena in acidic conditions are associated firstly with activation corrosion, in which chromium metal is oxidised to Cr^{2+}, at low potentials (near the corrosion potential) before the surface potential is high enough for passive film formation to occur. As the potential of the metal is increased in the more noble direction an active/passive transition is typically seen with a subsequent decrease in corrosion rate, followed by a passive region. At high potentials transpassive dissolution via the formation of Cr(VI) occurs.

The current due to passive film formation on Cr in H_2SO_4 solutions has been demonstrated to be mainly due to film formation, while 5–10% is consumed in the production of soluble Cr(III) ions [8]. The film thickness has been shown to be a linear function of applied potential. Resistance measurements during passive film growth showed the film growth to be associated with an exponential increase in the film resistance which was attributed to formation of Cr(III) from Cr(II) via a solid state