

Beneficial Aspects of Anodic Segregation

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Abstract

XPS has contributed greatly to our knowledge of the nature of the passive film formed on metals from early stage formation through to the well aged structure (1). This is because the depth of analysis of XPS is often comparable to that of the passive film thickness and therefore enables nondestructive variable angle analysis to be performed incrementally throughout the depth of the of the passive film and, more important to this paper, the passive film-alloy interface. During anodic dissolution of alloys local atomic bonding differences can lead to non-uniform dissolution rates for alloy constituents. As a result the composition of the alloy surface may be quite different from the bulk composition. Marcus was the first to coin the term *anodic segregation* in studies of the surfaces segregation of S in Ni containing 50ppm S (2). In this paper we review briefly the detrimental effect on passivity of sulphur impurities in Ni resulting from anodic segregation of S on the metal surface. Then we consider the beneficial effect of the anodic segregation of phosphorus on Ni amorphous alloys and nitrogen in austenitic stainless steels. In the latter case we shall discuss attempts to simulate surface segregation of nitrogen by solution doping with nitrate ions, which provided insight into the synergistic role of nitrogen and molybdenum in beneficially influencing the passivity of ferrous alloys.

Rapidly solidified amorphous alloys of the type Ni-20P (0, 3,6 and 10 at% Cr) potentiostatically polarized at a passive potential in deaerated 0.2M HCl were shown to generate high surface enrichments of P (3-5). Variable angle XPS analysis determined the P to be in the form of black phosphorus a metallic allotrope which dominated the electrochemical behavior of Ni20P and generating a unique passive film, devoid of Ni, but comprised of a univalent P compound, namely hypophosphite. Cr alloying resulted in passive films also devoid of Nickel as well as metal oxides, usually the back bone of passive films, but in stead containing phosphites, phosphates and hydroxyphosphates of Cr, depending on polarization potential, having remarkable resistance to localized corrosion. Even more unique this entire range of alloys exhibited almost identical D.C. polarization behavior in deaerated 0.2M HCl and 0.2M H₂SO₄. This unique anion independent behavior was seen from XPS analysis to coincide with the absence of anion uptake from the test electrolyte and the formation of passive films exhibiting essentially identical composition and thickness. Clearly, these alloys exhibited beneficial corrosion characteristics in part due to the anodic segregation of P to the alloy surface during the active stage of passivation.

In studies of the influence of Nitrogen content on the electrochemical behavior and the composition of the passive film formed by high and low nitrogen content stainless steels in deaerated acidic chloride solutions, variable angle XPS analysis provided an atomistic interpretation of the electrochemical behavior. This enabled the function of Nitrogen in altering corrosion behavior to be explained in terms of anodic segregation of

nitrogen as a mixed nitride phase at the alloy-passive film interface (6,7), and the resulting pH buffering affect of the nitride (8) due to reaction with acidified solution to form ammonium ions rendering a locally higher pH environment. This self-buffering action in turn supported the formation and retention of the corrosion inhibiting molybdate ion in the outer region of the passive film as a ferrous molybdate salt layer. In previous work we had shown that molybdate acted to produce an ionically rectifying bilayer on the stainless steels consisting of a cation selective layer in the outer region of a predominantly anion selective inner oxide layer (9). The general concept of bipolarity in thick anodic films has been proposed by Sato and Sakashita (10).

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