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The nature of the passive film on cathodically modified stainless steels

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This paper discusses the effect of additions of platinum group metals (PGMs) on the composition of the passive surface layer formed on stainless steels in reducing acid media. It has been shown that there is an accumulation of these noble metals on the surface of the alloy during the period of active dissolution. The morphology and factors influencing this accumulation of PGMs on the surface are discussed. It was also found that there are differences between passive films formed spontaneously and those formed under potentiostatic control. An interesting fact emerging from the investigations is that different PGMs form different types of oxides on the passivated surfaces. Areas for possible future research are mentioned.

1. Introduction

There are various ways in which the corrosion resistance of an alloy can be improved. The formation of stable oxide layers constitute one such method. Stainless steels owe their corrosion resistance largely to the formation of passivating oxide layers on the surface of the alloys. Another way in which the corrosion of stainless steels can be retarded, is by the addition of small amounts of platinum group metals (PGMs) to the alloy. This technique is known as cathodic modification. The mechanism and electrochemistry of cathodic modification have recently been reviewed in this journal [1]. An extensive description of various alloy systems that had been cathodically modified was also featured [2]. However, the effect of PGMs and/or incorporation in stainless steels on the composition of the passive surface layer has not yet received much attention. The purpose of this paper is, therefore, to investigate the nature of the passive film on cathodically modified stainless steels.

Initially, there is an atmospheric oxide film present on the surface of the cathodically modified alloy [3]. Auger analyses have indicated that the composition and structure of the passive film on some cathodically modified alloys are similar to those on other stainless steels [4]. It is accepted that the less noble components of stainless steel, for example chromium and iron, oxidize the fastest during the initial stage of active dissolution, thus leaving the noble metal atoms originally present in solid solution as adatoms on the surface of the alloy. Since the noble metal atoms do not oxidize at the low potentials normally encountered during active dissolution, they accumulate on the surface of the alloy. Once a sufficient quantity has accumulated, it can cause spontaneous passivation of the alloy to occur. Although there is ample evidence from various sources [3, 5–10] that there is an accumulation of the cathodic component, present in solid solution in the alloy, on the surface of the alloy during the first few minutes of active dissolution, before the passive state is established, very little is known about the nature of the passive film itself, and only a few investigations have been carried out.

2. Russian studies

Tomashov *et al.* [11] concluded that, in the absence of preliminary etching, palladium which is originally present in solid solution in the alloy, is incorporated into the passive film formed on a Fe–25%Cr–6%Ni–3%Mo–N–0.2%Pd alloy after exposure in HCl, but that in the case of preliminary etching in the active region, palladium accumulates on the surface of the alloy in the form of an independent phase. Furthermore, it seems that palladium increases the stability of the passive film. It was also found that the simultaneous presence of palladium and molybdenum in an Fe–25%Cr–2%Mo–0.3%Pd alloy in non-oxidizing acids promotes more stable passivity than do either palladium or molybdenum alone [12]. This is attributed to the direct influence of molybdenum on the anodic process, as well as the assumption that molybdenum was incorporated in the passivating film on the steel.

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Table 1. Composition and morphology of spontaneously passive surfaces [10]

	0.2% Ru	0.1% Ru
0.5 M H_2SO_4	Solid, planar surface; 200 monolayers dissolved; Ru not detected (< la/o).	Smooth, loosely adherent layer 3.6×10^3 monolayers dissolve Max. Ru conc. 7.5 a/o; Ru distrib. 30 nm round particles.
0.5 M HCl	Solid, planar surface; 220 monolayers dissolved; Max. Ru concn. 4 a/o; Ru distrib. probably sub nm.	Rough, thick, loosely adhered layer; 1.12×10^4 monolayers dissolved Max. Ru concn. 16.7 a/o (main metallic comp.); Ru distrib. μm particles; heterogeneous (high S and P).

Tomashov *et al.* [9] also determined that an Fe–25%Cr alloy to which ruthenium is added passivated easier in 5% to 50% H_2SO_4 and 1% to 5% HCl at 50° C to 100° C than did a similar alloy with an equal palladium content.

Electron microscopy indicated that the surface layer on the Fe–25%Cr–2%Pd alloy consisted mainly of a chromic oxide (Cr_2O_3) film with metallic palladium precipitates, while no metallic ruthenium particles were detected in the chromic oxide film on the surface of the Fe–25%Cr–2%Ru alloy. On this basis it was concluded that one of the reasons for the better resistance of the Ru-containing alloy as compared to the Pd-containing one, was due to the fact that a large fraction of the accumulated ruthenium was not present in the form of an independent phase, but was included in the composition of hydroxide and oxide layers that had formed on the surface of the alloy, thereby increasing the resistance of these layers.

A detailed electron microscopy study, by Tomashov *et al.* [8] of the accumulation of palladium on the surface of an Fe–25%Cr steel during active corrosion in H_2SO_4 revealed that the particle size of the accumulated palladium depends on the temperature at which dissolution took place, as well as on the palladium concentration in the steel. This was confirmed by Higginson *et al.* [10], who also found that the concentrations of ruthenium were higher on the passive surfaces of Fe–40%Cr–0.1%Ru alloys than on the passive surfaces of Fe–40%Cr–0.2%Ru. He furthermore established that the accumulation of ruthenium on the surfaces of Fe–40%Cr–(0.1% to 0.2%)Ru also depended on the kind of acid in which corrosion took place.

The composition and morphology of the passive surfaces of the cathodically modified alloys studied by Higginson *et al.* are summarized in Table 1.

The type of morphology summarized in Table 1 is that predicted by Pickering [13] in his review of selective dissolution for alloys containing low concentrations of the noble metal. These results in addition confirm that the chloride ion tends to produce a coarser distribution, thus supporting the suggestion that the chloride ion increases the rate of surface diffusion of ruthenium during selective dissolution.

3. The Fe–40%–PGM system

Although Higginson *et al.* detected ruthenium with Auger analysis in the Fe–40%Cr–(0.1–0.2%)Ru alloy after spontaneous passivation in 0.5 M HCl and in the Fe–40%Cr–0.1%Ru alloy after spontaneous passivation in 0.5 M H_2SO_4, they only conclude that the enrichment in ruthenium occurred at the metal oxide film interface, without elaborating on the possible inclusion of the ruthenium in the passive film. Finer detail about the precise nature of the passive film on Fe–40%Cr–Ru alloys was obtained in a study by Tjong [14]. Tjong confirmed observations by Higginson *et al.* [10] that more ruthenium is present on the surface of the Fe–40%Cr–0.1%Ru alloy after spontaneous passivation in 0.5 M HCl than in the case of the alloy containing 0.2%Ru and ascribes this to the fact that active dissolution preceding passivation of the 0.1%Ru alloy in 0.5 M HCl is faster than that of the Fe–40%Cr–0.2%Ru alloy. As a result, larger amounts of ruthenium adatoms are accumulated on the surface of the alloy containing 0.1%Ru than on that of the alloy containing 0.2%Ru. In both alloys passivating spontaneously in 0.5 M HCl, considerable enrichment of chromium as well as ruthenium occurs in the passive films. Tjong estimated that the thickness of the passive film on the Fe–40%Cr–0.2%Ru alloy, after spontaneous passivation in 0.5 M HCl, was approximately 3.2 nm.

Tjong also agrees with Higginson *et al.* that ruthenium is only incorporated in the passive film of the Fe–40%Cr–0.1%Ru alloy after spontaneous passivation in 0.5 M H_2SO_4 and could not be detected for the Fe–40%Cr–0.2%Ru under similar conditions. However, when X-ray photoelectron spectroscopy (XPS) was used, the presence of Ru in the passive film on Fe–40%Cr–0.2%Ru after passivation in 0.5 M H_2SO_4 was detected in the form of Ru^{4+} as shown in Fig. 1. Tjong concluded that it is likely that both ruthenium hydroxide as well as RuO_2 may be present in the passive film. It was pointed out earlier by Tomashov *et al.* [9] that in chromium steel containing ruthenium the ruthenium tends to be incorporated into the hydroxide or oxide layers formed on the chromium steel. The presence of Ru^{4+} was also detected in the passive films formed on Fe–40%Cr–0.1%Ru after exposure to 0.5 M H_2SO_4 and both Fe–40%Cr–0.1%Ru and 0.2%Ru after spontaneous passivation in 0.5 M HCl. Tjong thus proved that chromium and ruthenium are incorporated in the passive films formed spontaneously on the Fe–40%Cr–0.1%Ru and Fe–40%Cr–0.2%Ru alloys in

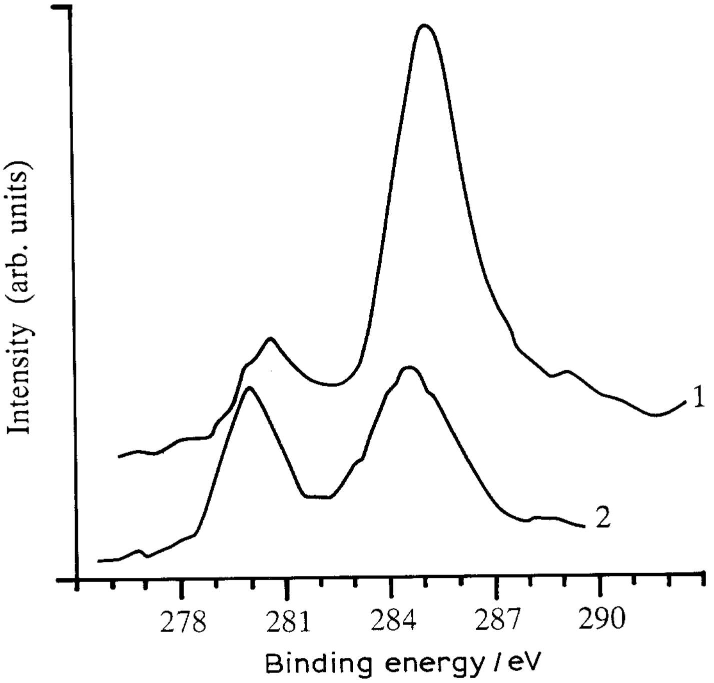

Fig. 1. Ru3d spectra recorded from the Fe–40Cr–0.2Ru alloy passivated spontaneously in 0.5 M H_2SO_4 solution at 25° C. (1) Before sputtering, (2) after 2 min of sputtering. (Redrawn after Tjong [14]).

both hydrochloric and sulphuric acid solutions as Ru^{4+} and Cr^{3+} species.

In another study of the Fe–40%Cr alloy system, Tjong [15] found a remarkable difference in the nature of the passive films formed on an Fe–40%Cr–0.2%Pd alloy that passivated spontaneously and under potentiostatic control in 0.5 M HCl at 25° C. A comparison of the AES composition depth profiles (Figs 2 and 3) as well as in the [Cr]/[Cr] + [Fe] concentration ratios with sputtering time (Figs 4 and 5) reveals that there is a marked difference in the composition of the passive films formed under different conditions. The passive film on the Fe–40%Cr–0.2%Pd alloy that underwent spontaneous passivation in 0.5 M HCl was estimated to be 2.4 nm thick and was enriched in palladium relative to chromium. The enrichment of palladium was responsible for the occurrence of spontaneous passivation. In the passive film formed on this same alloy under potentiostatic control at 220 mV for 40 min, strong enrichment in chromium was found. No palladium was incorporated into this passive film (see Fig. 3). XPS measurements on both passive surfaces indicated that the palladium is present in the spontaneously passivated film as Pd^{2+}, whereas chromium is present as Cr^{3+}. This is a significant finding which indicates that there is a difference in the type of oxide formed by different PGMs when spontaneous passivation of Fe–40%Cr–0.2% PGM alloys occur in 0.5 M HCl.

In a recent investigation [16] of the passivation of Fe–40%Cr–(0.1 to 0.2)% Pt alloy in 0.5 M HCl at 25° C, Tjong found that the passive film that formed on these alloys is extremely thin, i.e. approximately 1.6 nm. Although Auger spectra did not detect the presence of platinum in the passive surfaces of the Fe–40Cr–Pt system, XPS measurements revealed the existence of the Pt—passivating species. Figure 6 indicates that the surface film contains two platinum species, i.e. Pt^{2+} and Pt^0 (metallic platinum).

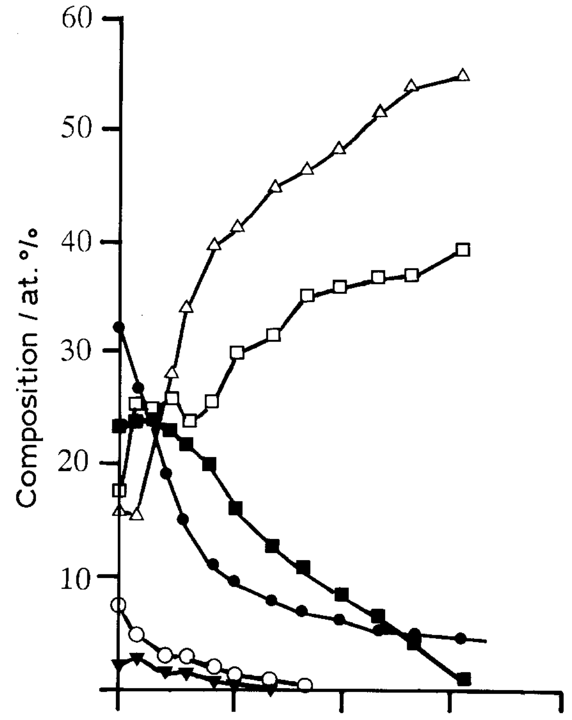

Fig. 2. AES composition depth profile for the Fe–40Cr–0.2Pd alloy passivated in 0.5 M HCl solution at 25° C: (△) iron, (■) palladium, (□) chromium, (●) oxygen, (▼) chlorine, (○) sulphur. (Redrawn after Tjong 15).

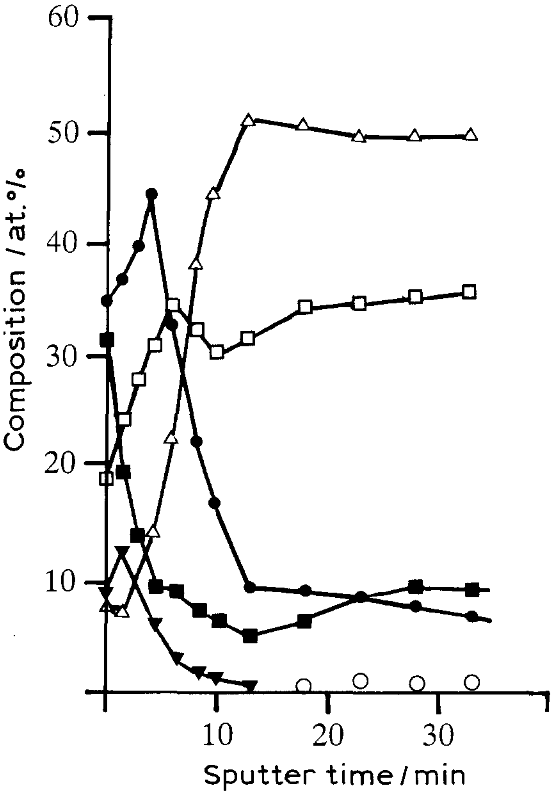

Fig. 3. AES composition depth profile for the anodic oxide film formed on the Fe–40Cr–0.2Pd alloy in 0.5 M HCl solution at 220 mV: (△) iron, (■) carbon, (□) chromium, (●) oxygen, (▼) chlorine, (○) palladium. (Redrawn after Tjong [15]).

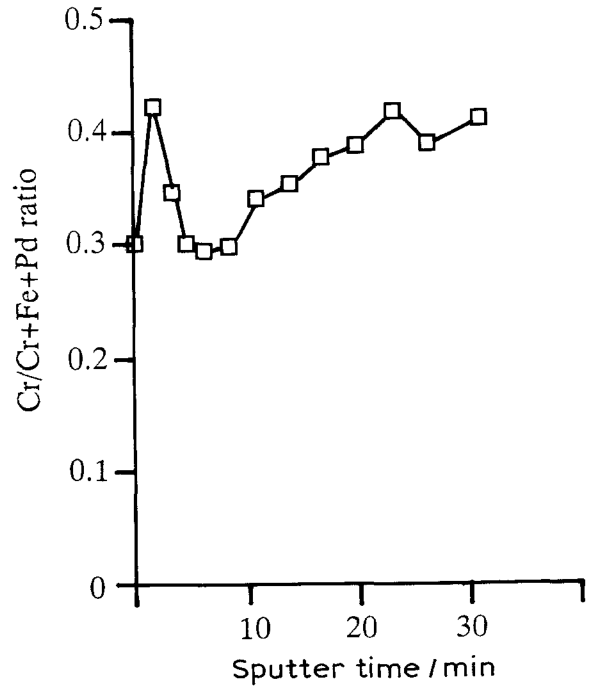

Fig. 4. Variation in [Cr]/([Cr] + [Fe] + [Pd]) concentration ratio with sputtering time for the spontaneous passivated film formed on the Fe–40Cr–0.2Pd alloy in 0.5 M HCl solution at 25° C. (Redrawn after Tjong [15]).

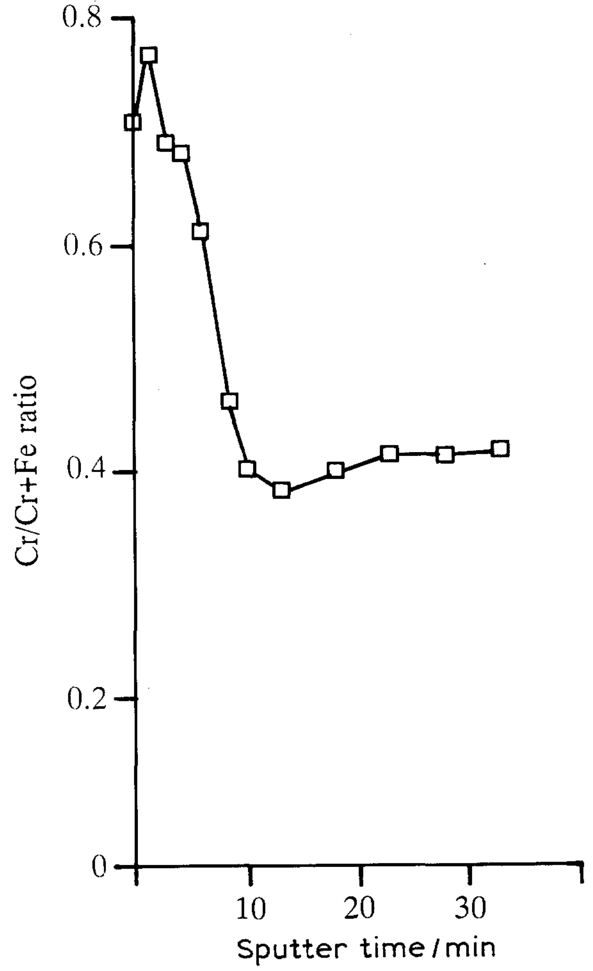

Fig. 5. Variation in [Cr]/([Cr] + [Fe]) concentration ratio with sputtering time for the anodic oxide film formed on the Fe–40Cr–0.2Pd alloy in 0.5 M HCl solution at 220 mV. (Redrawn after Tjong [15]).

4. Other quaternary and ternary Fe–Cr alloys with PGMs

Tjong also investigated the passivation characteristics of an FeCrNiMoRu ferritic stainless steel containing 22%Cr, 5%Ni, 3%Mo and 0 to 0.3%Ru in 0.5 M HCl at 25° C [17]. XPS analysis of the passive film on the FeCrNiMo alloy containing 0.3%Ru after spontaneous passivation in 0.5 M HCl showed the presence of three molybdenum species, namely Mo^0, Mo^{4+} and Mo^{6+}, in the passive film, as is indicated in Fig. 7. The presence of molybdenum in the spontaneously formed passive film indicated that the film is thin enough to allow escape of photoelectrons ejected from the substrate alloy through the film. It was also found that nickel and ruthenium were absent and did not accumulate in the passive film.

Olefjord and Elfstrom [18] have reported that the beneficial effect of nickel is not connected with the occurrence of this metal in the passive film. Instead the accumulation of nickel in the underlying alloy surface decreases the dissolution rate in the active condition and thereby enhances the formation of the anodic passive film [19]. It has been pointed out previously by Tomashov *et al.* [20] that ruthenium blocks lattice point defects during active dissolution and thereby

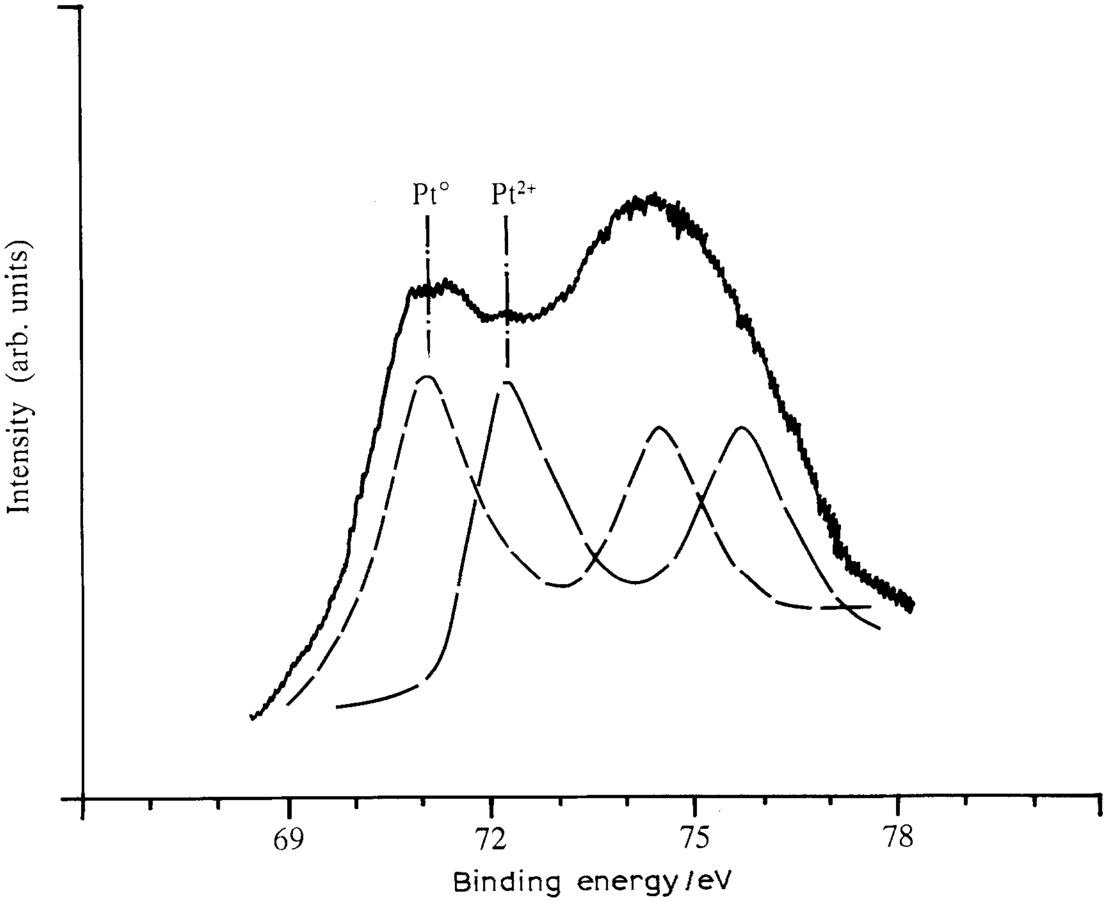

Fig. 6. Pt4f XPS spectrum prior to sputtering for the passive film spontaneously formed on the Fe–40Cr–0.1Pt alloy in 0.5 M HCl at 25° C. (Redrawn after Tjong [16]).

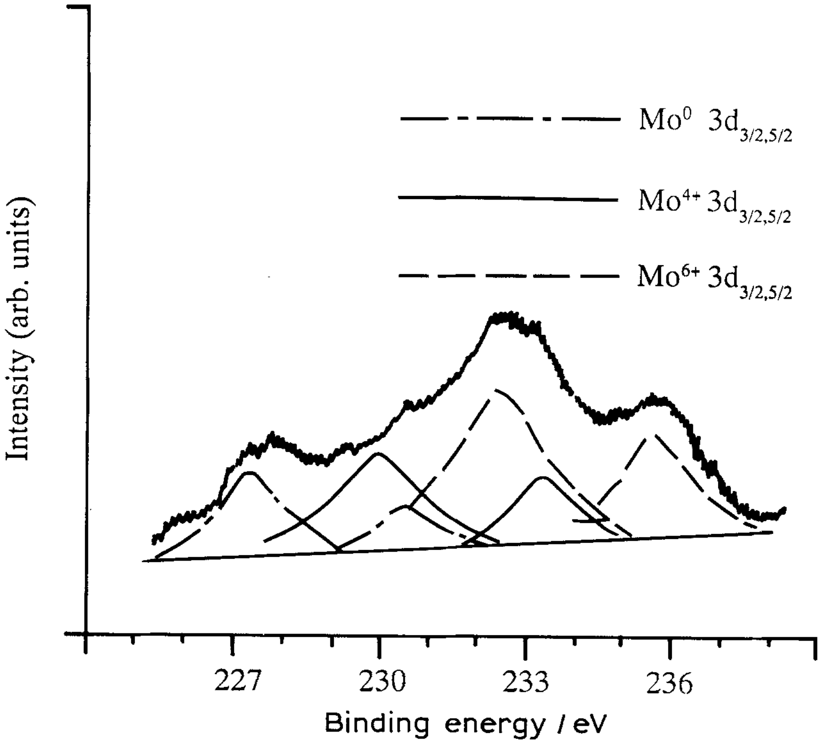

Fig. 7. Mo3d XPS spectrum of Fe–22Cr–3Mo–5Ni–0.3Ru alloy spontaneously passivated in 0.5 M HCl solution before sputtering. (Redrawn after Tjong [17]).

decreases the dissolution rate of chromium from the active sites. It is believed that molybdenum exhibits similar blocking characteristics. It is therefore clear that Mo, Ni and Ru are competing species in promoting self-passivation. The absence of ruthenium from the XPS spectra, while molybdenum is evidently present in the spectra, can be explained by taking into account the fact that the molybdenum concentration is approximately 10 times higher than that of the ruthenium. Therefore, the molybdenum adatoms presumably blocked the majority of the active surface sites prior to passivation, while only a small number of defect sites is blocked by ruthenium adatoms. After spontaneous passivation the molybdenum adatoms were incorporated into the film as Mo^{4+} and Mo^{6+} species. The XPS measurements also showed that the outermost zone of the passive film that formed on the spontaneously passivated FeCrNiMo alloy with 0.3%Ru consists of chromium and molybdenum hydroxides.

In a recent investigation on the corrosion behaviour of an Fe–24%Cr–6%V alloy containing various amounts of Ru (0.12 to 0.35%), Tjong [21] concluded from the Auger spectrum (shown in Fig. 8) that ruthenium was absent in the passive film on the alloy that passivated spontaneously in 5% HCl solution at 25° C. This was in contrast to what was found for a spontaneously passivated Fe–40%Cr–0.2%Ru alloy in 0.5 M HCl, where ruthenium was detected in the passive film. However, the Auger spectrum in Fig. 8 does show the presence of both chromium and vanadium in the spontaneously formed passive film. It therefore seems that the presence of ruthenium in the passive film not only depends on experimental conditions, but also on the alloy composition and the presence of other alloying elements.

According to Tjong, the absence of ruthenium in the spontaneously formed passive film on the Fe–25%Cr–6%V–0.35%Ru alloy can be explained in terms of the competition between vandium and ruthenium in blocking the surface-defect sites of the lattice. Because the concentration of vanadium is about 20 times greater than that of ruthenium, most of the surface defect sites are blocked by vanadium rather than ruthenium. It was also found that both chromium and vanadium were enriched in the passive film formed on this alloy. The thickness of the passive film was estimated to be approximately 1.8 nm.

Peled and Itzhak [22] investigated the nature of the passive films on hot pressed and sintered 316 stainless steel containing Cu, Au, Pd and Pt additions of various concentrations after spontaneous passivation occurred in 0.5 M H_2SO_4. Auger spectroscopy indicated a maximum in the molybdenum concentration at a depth of about 0.6 nm in all the passive steel samples, regardless of the composition. These observations mean that molybdenum is accumulated in the passive film. Furthermore, it was found that the oxide-film thickness of passive samples containing Au, Pd and Pt was about 12–15 nm as compared to about 2–3 nm for passive sintered 316 stainless steel. This was ascribed to the low cathodic overpotential of gold, palladium and platinum which enhances hydrogen evolution in the cathodic areas and promotes the creation of a passive oxide layer in the anodic areas, thus resulting in a thicker oxide film. However, marked enrichment of copper was found on the surface of the passive, Cu-containing, sintered stainless steels samples after exposure to H_2SO_4, while only a slight surface enrichment of the noble alloying elements was observed in the passive samples containing gold, palladium and platinum.

5. Conclusions

The following conclusions can be made concerning passive films formed in reducing acid media.

(i) Accumulation of PGMs originally present in solid solution in the alloy occur on the surface of the alloy during the initial dissolution period.

(ii) Other alloying elements such as Mo, V, and Ni can compete with the PGMs in blocking active surface sites during the initial stage of the corrosion process. This might result in the PGMs not being detected in the formed passive film, especially if the concentration of the other alloying elements is significantly higher ($> 10\times$) than that of the PGMs.

(iii) The amount, particle size, and morphology of the accumulated PGM on the surface of the alloy depend on the temperature at which the dissolution occurs as well as the medium in which it is taking place. A greater amount of PGMs are found on surfaces of alloys that corroded in HCl than on those that were placed in H_2SO_4. This is attributed to increased surface-diffusion rates of the PGM adatoms in the presence of Cl^- ions. Another factor that influences the accumulation of PGMs on the alloy surface is its initial concentration in the alloy. In alloys with lower PGM concentrations, active dissolution occurs faster and results in more adatoms accumulated on the final passive surface.

(iv) There is a difference in the passive films formed spontaneously and those formed under potentiostatic control. In the former case the PGM is incorporated in the passive film as an oxide, while in the latter case it is not, and is only present in an accumulated metallic form.

(v) Different PGMs form different types of oxides on passivated surfaces. Ruthenium occurs as Ru^{4+} in the passive film after spontaneous passivation in H_2SO_4 and HCl, while palladium is incorporated into the passive film as Pd^{2+} after spontaneous passivation of the same base alloy in HCl. Platinum occurs in both the Pt^{2+} and Pt^0 states the passive film.

(vi) Determinations of thicknesses of passive films formed on cathodically modified stainless steels were carried out on a limited number of ferritic stainless steels that passivated spontaneously in HCl. Vast

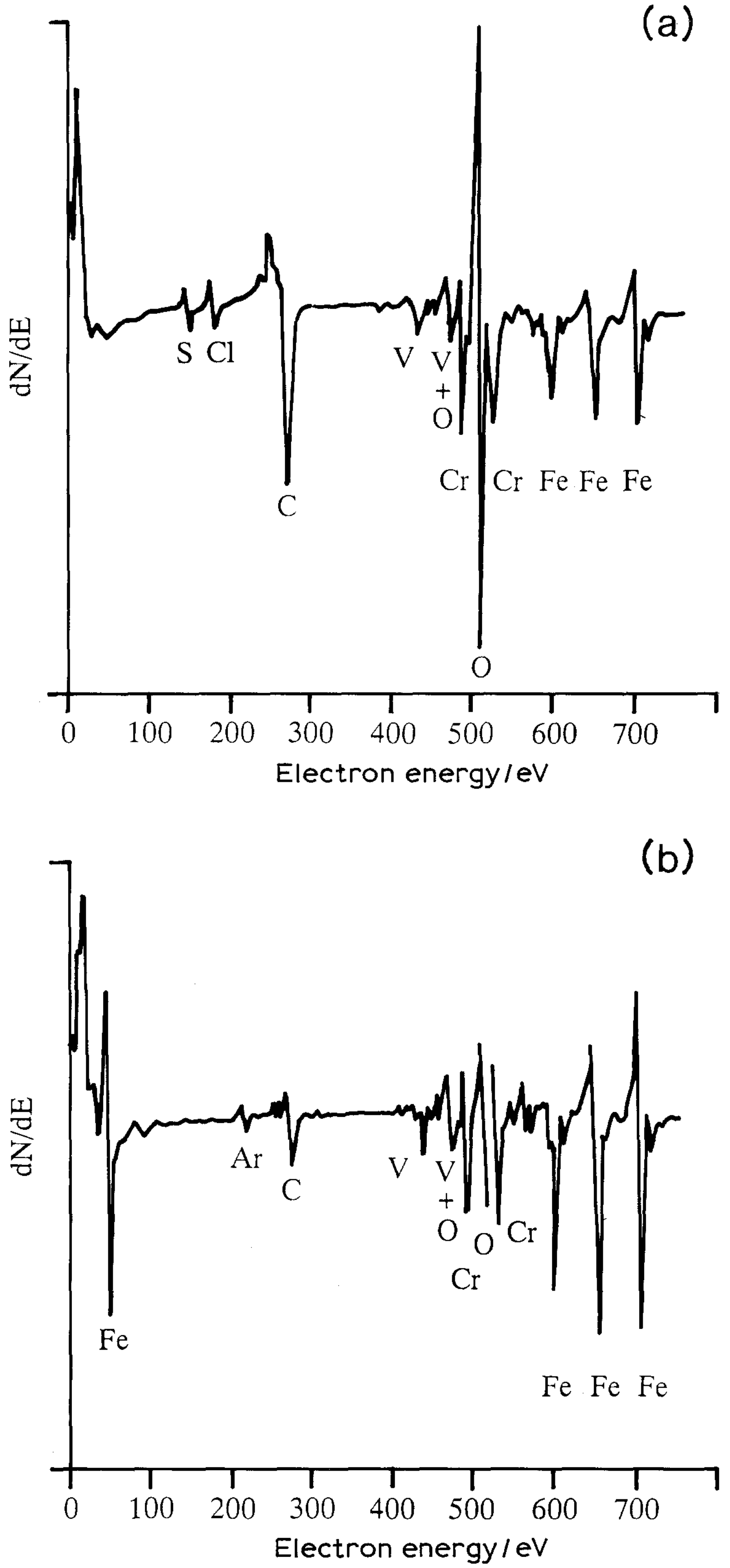

Fig. 8. Auger spectra for the Fe–24Cr–6V–0.3Ru alloy passivated spontaneously in 5% HCl solution at 25° C. (a) Before sputtering, (b) after sputtering for 6 min. (Redrawn after Tjong [21]).

opportunities exist to extend this kind of investigations to other stainless steels in the same or different media (e.g. in H_2SO_4) under a variety of conditions. Such an endeavour would shed more light on the role of PGMs and other alloying elements in enhancing the corrosion resistance of cathodically modified alloys.

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