Corrosion Behaviour of the Fe-Cr-V-Ru System in Reducing Acid Solution

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The corrosion behaviours of Fe-24Cr-6V alloys containing 0.12, 0.24, and 0.35 wt% Ru additions in non-oxidizing acid solutions were studied by means of the electrochemical and Auger electron spectroscopic techniques. The weight-loss measurements show that the addition of Ru to the Fe-24Cr-6V alloy in the composition range 0.12 to 0.35 % is very effective in increasing the corrosion resistance of this alloy in a 5 % H₂SO₄ acid solution at 70 and 98°C, respectively. Also, the addition of Ru to the Fe-24Cr-6V alloy is found to be beneficial in the concentration range 0.24 to 0.35 % range when the alloy is exposed to 5 % HCl solution at 70 and 98°C, respectively. AES results reveal that the spontaneously passivated films formed on the Fe-24Cr-6V-Ru alloy system in 5 % HCl solution at 25°C are enriched in chromium and vanadium but depleted in ruthenium.

KEY WORDS: cathodic modified alloy; non-oxidizing acid; spontaneous passivation; vanadium; potentiodynamic scan; weight-loss; Auger electron spectroscopy; depth-profile.

1. Introduction

The ferritic stainless steels have certain attractive applications in chloride-containing environments. They exhibit superior resistance to stress corrosion cracking and good resistance to pitting and crevice corrosion. The localized corrosion resistance of the stainless steels is generally known to derive from high chromium contents, and substantial amounts of molybdenum. However, the ductility and toughness of the ferritic stainless steels depend significantly on the Cr content, and also on carbon and nitrogen interstitials,¹⁾ as C and N impurities tend to promote the precipitation of chromium carbonitride during the welding process. Thus conventional ferritic stainless steels such as AISI 430 have found little application because of low ductility and sensitization problems. With the introduction of advanced melting techniques such as argon-oxygen decarburization (AOD) or vacuum-oxygen decarburization (VOD), it has been possible to reduce the amounts of C and N, respectively.

It is well known that addition of Mo to the ferritic stainless steels increases their corrosion resistance in chloride solutions. The addition of Mo results in a substantial decrease of the critical current density for passivation, and an increase of the pitting potential thereby extending the passive potential range.²⁾ The beneficial effect of Mo depends on the Cr content and hence Mo interacts synergistically with Cr. However, the role of Mo by which it exerts its beneficial effect remains obscure.³⁾ On the other hand, V has been considered as a potential substitute for Mo because Mo is not widely distributed around the world. Vanadium has also been reported to exhibit beneficial effect on the pitting resistance of austenitic and ferritic stainless steels,⁴⁻⁶⁾ and this element has been added in the conventional stainless steel designated as SCR-3.⁷⁾

Davies and Robinson indicated that V is not as effective alloying element as Mo in improving the pitting resistance of low interstitial ferritic stainless steels.⁸⁾ In non-oxidizing acid solutions, Bieffer reported that the addition of V up to 2 % leads to a decrease in the critical current density for passivation of the ferritic 430 stainless steel in 5 % sulphuric acid solution.⁹⁾ Recently, Goetz *et al.* suggested that the beneficial influence of addition of V on passivation and pitting resistance of the ferritic Fe-Cr alloys in 1M HCl solution was attributed to a decrease in the iron activity of the alloys.⁹⁾

It has been shown that combining Fe-Cr based alloys with platinum group metal (PGM) additions is very effective for increasing the corrosion resistance of these alloys in non-oxidizing acid environments.^{10,11)} The improved corrosion resistance results from the accumulation of PGM on the alloy surface during the initial period of an active dissolution and a subsequent potential shift from an active to the passive region. The beneficial effect of PGM alloying depends on the concentration added, and also on the hydrogen over-voltage characteristics of each of the PGMs. The effect of the addition of various PGMs on the corrosion resistance of ferritic Fe-Cr-Mo alloys was studied by Streicher.^{12,13)} He reported that Fe-28Cr-4Mo alloys become passivated in boiling sulphuric acid solution when PGMs were present in the alloy in excess of a certain minimum concentration. From the economic point of view, Ru costs about one seventh as much as Pt, and half as much as Pd.¹⁴⁾ Hence Ru appears to be more cost effective alloying element than the other PGMs. Furthermore, combining Fe-Cr based alloys with Ru has been shown to be more effective than Pd in enhancing the corrosion resistance of these alloys in non-oxidizing acid solutions.^{15,16)}

Surface analytical techniques such as Auger electron spectroscopy (AES) and electron spectroscopy for chemical analysis (ESCA) have been used extensively to study the surface chemistry and chemical bonding of the elemental constituents in the passive film formed on the Fe–Cr and Fe–Cr–Mo alloys.^{17–19)} However, little information is available on the application of these techniques to the self-passivation of Fe–Cr alloys containing PGM additions. The present work attempts to reduce the Cr content in the Fe–Cr alloy by partial substitution of Cr with V, as a high Cr content is detrimental to the toughness of the alloy.¹⁾ This paper is a first report on an investigation of the corrosion behaviours of the Fe–24Cr–6V alloy system containing Ru additions in non-oxidizing acid solutions by means of the electrochemical and the AES techniques.

2. Experimental Procedure

2.1. Preparation of the Alloys

The Fe–24Cr–6V(0–0.3)Ru alloys were melted in a vacuum induction furnace under an Ar protective atmosphere. The cast ingots were subsequently hot-rolled into plates of about 8 mm thickness. The chemical compositions of the alloys investigated are listed in Table 1. For the purpose of comparison, the Fe–24Cr alloy containing no V and Ru was also prepared.

2.2. Weight-loss Measurements

Specimen coupons of $\sim 20 \text{ mm} \times 20 \text{ mm} \times 6 \text{ mm}$ were cut from the plates for immersion weight-loss tests. The coupons were heat-treated at 1200°C for 2 h followed by quenching in water. They were wet ground with SiC paper down to 800 grit, rinsed with distilled water, isopropanol, and weighed. Immersion weight-loss tests were performed in 5 % sulphuric and 5 % hydrochloric acid solutions at temperatures of 70 and 98°C , respectively. The test solutions were deaerated with N_2 during the immersion tests at 70°C . Duplicate coupons were placed in a glass cradle immersed in a 2 l Erlenmeyer flask containing about 1.6 l of solution. The flask was fitted with an Allihn condenser. Tests were run for a period of 4 h in 5 % H_2SO_4 solutions at 70°C . However, the test period was reduced to 30 min in the above solution at 98°C . On the other hand, the immersion time of the coupons in 5 % HCl solution at 70 and 98°C were 45 and 30 min, respectively, due to the aggressiveness

of the solutions. After the immersion tests, the coupons were cleaned with a nylon brush, rinsed with distilled water and weighed.

2.3. Potentiodynamic Measurements

Polarization tests were carried out in a deaerated 5 % HCl acid solution at 25 and 70°C , respectively by using a Princeton Applied Research (PAR) model 273 potentiostat. The test specimens were cut from the solution-treated coupons in the form of a disc with 11 mm diameter and 4 mm thickness. They were wet ground with SiC paper down to 800 grit, cleaned ultrasonically in distilled water, and then immersed immediately in the test solutions. Before each measurement, the sample was cathodically reduced at -800 mV for 5 min in order to remove the air-formed oxide on the sample. The potentiodynamic scan was then initiated at this cathodic potential and scanned continuously to 1300 mV at 1 mV/s . All the potentials cited in this paper are referred to a saturated calomel electrode (SCE).

2.4. Potential–Time Response Measurements

Potential–time response measurements were carried out in a 5 % HCl solution at 25°C . The working electrode was reduced cathodically at -800 mV for 5 min. After cathodic reduction, the specimen was allowed to passivate spontaneously. The variation of the potential with time was recorded. The spontaneously passivated surfaces were subsequently analysed in the AES spectrometer.

2.5. AES Measurements

AES was carried out in a Varian ultra-high vacuum chamber equipped with a Physical Electronic Industries model 15–110 A cylindrical mirror analyser. The spectrometer was operated at a primary electron beam of 5 keV and a current of $2 \mu\text{A}$ with a peak-to-peak modulation of 3 eV. Sputtering was performed using an argon ion gun at 2 keV with a current density of $7 \mu\text{A}/\text{cm}^2$ and at a pressure of $3.5 \times 10^{-5} \text{ Torr}$. A sputter rate of about $4 \text{ \AA}/\text{min}$ was obtained under these conditions by using a Ta_2O_5 sample of known thickness. Auger depth profiles were obtained by measuring peak-to-peak heights (pph) of the constituent elements in the spontaneously passivated film, with the exception of the Cr peak. This is because the O (510 eV) peak interferes with the Cr (529 eV) peak. It has been reported that the background to negative excursion for the Cr (529 eV) peak gives a corrected Cr content in the Fe–Cr alloys.^{20,21)} Hence the background to negative excursion for Cr (529 eV) peak was measured for depth profiling purpose.

3. Results and Discussion

3.1. Immersion Weight-loss Results

The results of the weight-loss measurements in 5 % H_2SO_4 and 5 % HCl acid solutions are listed in Tables 2 and 3, respectively. It can be seen in Table 2 that the alloys investigated containing Ru additions exhibit satisfactory performances in sulphuric acid

Table 1. Chemical compositions of the alloys investigated. (%)

Alloys	Elements						
	C	N	O	Cr	V	Ru	Fe
1	0.010	0.001	0.07	24.00	—	—	Balance
2	0.012	0.003	0.10	24.00	6.08	—	Balance
3	0.011	0.003	0.10	24.30	6.20	0.12	Balance
4	0.011	0.002	0.11	24.00	6.30	0.24	Balance
5	0.011	0.002	0.11	23.80	6.50	0.35	Balance

Table 2. Corrosion rates (mm/year) of the alloys investigated immersed in 5 % H_2SO_4 solution at boiling temperature (98°C) and at 70°C, respectively.

Corrosion rates	Alloy				
	1	2	3	4	5
Boiling solution	3 292	3 218	W.G.	W.G.	W.G.
70°C solution	1 225	W.G.	W.G.	W.G.	W.G.

Note: W.G. implies the samples passivated in the test solutions and showed net weight-gains after the immersion tests.

Table 3. Corrosion rates (mm/year) of the alloys investigated immersed in 5 % HCl solution at boiling temperature (98°C) and at 70°C, respectively.

Corrosion rates	Alloy				
	1	2	3	4	5
Boiling solution	5 247	4 830	6 656	532	166
70°C solution	1 667	1 077	317	44	19

solution at both test temperatures. These samples passivated in the sulphuric acid solutions upon immersion and shows no evidence of active dissolution during the test periods. The alloy 2 containing no Ru exhibits corrosion resistance to 5 % H_2SO_4 solution only at a lower test temperature (70°C) whereas the alloy 1 shows the greatest dissolution in sulphuric acid solution at both test temperatures as expected. On the other hand, the addition of Ru to the Fe-24Cr-6V alloy system was found to be beneficial at concentration levels of 0.24 and 0.35 %, respectively in boiling 5 % HCl solution. Addition of 0.12 % Ru was observed to exhibit a slightly beneficial effect in 5 % HCl solution only at a test temperature of 70°C. On the basis of these results, it appears that additions of 0.24 and 0.35 % Ru to the Fe-24Cr-6V based alloy are very effective to promote spontaneous passivation in non-oxidizing sulphuric and hydrochloric acid solutions. Because the Fe-24Cr-6V alloy system exhibits higher weight-loss in HCl solution than that in H_2SO_4 solution, attention is focussed on the corrosion behaviour of this system in HCl solution.

3.2. Effect of Ru on the Corrosion Potentials of the Fe-24Cr-6V Based Alloys

Fig. 1 shows typical potential-time response curves for the alloys investigated in 5 % HCl solution at 25°C. For the Fe-24Cr-6V alloy containing no Ru, the initial potential was located at -560 mV and it then shifted slightly to -552 mV after immersion for 100 s. After this period, the potential gradually shifted to original value and remained in this vicinity region for extended period of time. However, addition of 0.12 % Ru resulted in a displacement of the corrosion potential of the Fe-24Cr-6V alloy in the noble direction as a function of time. This implies that small amount of Ru alloying element causes spontaneous passivation to occur in the Fe-24Cr-6V alloy. The transition time for spontaneous passiva-

Fig. 1. Potential-time responses for the Fe-24Cr-6V-Ru alloy system in 5 % HCl solution at 25°C.

tion for this sample is about 14 s. Increasing Ru contents to 0.24 and 0.35 % leads to a substantial decrease in the transition time for spontaneous passivation.

3.3. Potentiodynamic Results

Figs. 2(a) and 2(b) show the potentiodynamic curves for the alloys investigated in 5 % HCl solution at 25 and 70°C, respectively. From Fig. 2(a), one can see that the alloy 2 exhibits typical active-passive transition characteristics with a high critical current density for passivation ($\sim 5 \times 10^4 \mu\text{A}/\text{cm}^2$). The addition of up to 0.35 % Ru decreased the critical current density for passivation dramatically to a value of $3 \times 10^2 \mu\text{A}/\text{cm}^2$. On the other hand, the active-passive transition in the polarization curves tends to diminish for the Fe-24Cr-6V alloys containing Ru additions tested in 5 % HCl solution at 70°C. Furthermore, the corrosion potentials of Ru containing alloys were shifted to a more positive value of ~ -250 mV; the current densities in the passive region for Ru containing alloys are about two orders of magnitude smaller than those of Ru-free Fe-24Cr-6V alloy. Hence Ru is very effective in promoting spontaneous passivation of the Fe-24Cr-6V alloy, thereby reducing the anodic dissolution of this alloy in hydrochloric solution.

3.4. AES Spectra and Composition Depth-profiles

Figs. 3(a) and 3(b) show the AES spectra of the spontaneously formed film on the alloy 5 in 5 % HCl solution at 25°C before sputtering and after sputtering for 6 min, respectively. The Auger spectrum of the film before sputtering shows the presence of alloying elements V and Cr, but does not show Ru. It is known that the spectrum of pure V shows three principal Auger peaks located at 437, 473 and 509 eV.²²⁾

Fig. 2. Potentiodynamic curves for the alloys 2, 3, and 5 in 5% HCl solution at (a) 25°C and (b) 70°C.

(a) Before sputtering

(b) After sputtering for 6 min

Fig. 3. Auger spectra for the Fe-24Cr-6V-0.3Ru alloy passivated spontaneously in 5% HCl solution at 25°C.

The strongest V peak at 473 eV tends to interfere with the O peak located at 468 eV, whereas the smallest principal V peak at 509 eV tends to interfere

Fig. 4. Auger spectrum for the Fe-40Cr-0.2Ru alloy passivated spontaneously in 0.5M HCl solution at 25°C before sputtering.

with the strongest O peak located at 510 eV. Hence the V peak at 473 eV is used for the depth profiling measurements. On the other hand, the spectrum of pure Ru shows 4 strong principal Auger peaks located at 150, 200, 231, and 273 eV, respectively.²²⁾ The strongest Ru peak at 273 eV interferes with the principal peak for C located at 272 eV, and the Ru 150 eV tends to interfere with the S peak located at 152 eV. It is interesting to see that Ru is not detected in the spontaneously passivated film formed on the Alloy 5. For the purpose of comparison, the AES spectrum of the spontaneously passivated film formed on the Fe-40Cr-0.2Ru alloy in 0.5M HCl solution at 25°C before sputtering is shown in Fig. 4. It can be seen that Ru was present in the spontaneously passivated film formed on the Fe-40Cr-0.2Ru alloy.

Tomashov *et al.* reported that the initial dissolution of Cr into solution from Cr alloys containing PGM additions resulted in the formation of PGM adatoms since the PGM atoms lose their bond to adjacent Cr atoms. The PGM adatoms were then diffused to the surface defect sites of the lattice, *e.g.*, kinks, and subsequently blocked and accumulated in these sites. Hence the active dissolution of Cr from the Cr alloy becomes lower. The blocking PGM atoms led to the spontaneous passivation of the Cr alloys due to their low overvoltage for hydrogen evolution.²³⁾ For this reason, Ru was detected in the film formed on

the Fe-40Cr-0.2Ru alloy.

From the above discussion, the absence of Ru in the spontaneously passivated film formed on the Fe-24Cr-6V-Ru alloy system can be explained in terms of the competition between V and Ru in blocking the surface defect sites of the lattice. The concentration of V in bulk alloy 5 is 20 times greater than that of Ru. Hence most of the surface defect sites are blocked by V rather than Ru atoms. Spontaneous passivation occurs when the surface concentration of Ru reaches a critical value. Ru can be detected by the AES, provided that there is an enrichment of this element in the passive surface similar to that in the Fe-40Cr-0.2Ru alloy.

Fig. 5 shows the Auger depth-profile of the alloy 5 spontaneously passivated in 5 % HCl solution at 25°C. The thickness of the passive film can be estimated from the O profile where the oxygen amplitude has reduced to half its maximum amplitude and the sputter rate was assumed to be correlated with that of Ta₂O₅. In this case, the thickness of the film is estimated to be ~18 Å. In this figure, Cr and V signals are low at the surface of the passive film and they pass through an apparent maximum in the film. The normalized $(Cr/(Fe+Cr+V))$ and $(V/(Fe+Cr+V))$ Auger peak-to-peak heights ratios *vs.* the amount of film removed by sputtering for the spontaneously passivated film formed on the alloy 5 is shown in Fig. 6. It can be seen that both Cr and V are enriched in the spontaneously passivated film. The enrichment of Cr in the passive film is generally known to be responsible for an increase in the corrosion resistance of the Fe-Cr alloys. Thus the beneficial effect of V addition on the corrosion resistance can be explained by the enrichment of this element in the passive film. V and Mo are known to exhibit similarity in corrosion be-

haviour brought about by alloying due to their adjacent positions in the periodic table. Both elements exhibit beneficial effects on pitting corrosion resistance of the ferritic stainless steels, although V was not as effective as Mo.^{6,9)} Furthermore, Mo was enriched in the passive films formed on the Fe-Cr-Mo alloys at low potentials in the active region and at low potentials in the passive region.^{18,24)} Similarly, the concentration of V in the films formed on the Fe-Cr-V alloy at high potentials in the passive region is lower than that formed in the cathodic region.⁹⁾ Fig. 7 shows the normalized $(Cr/(Fe+Cr+V))$ and $(V/(Fe+Cr+V))$ Auger peak-to-peak height ratios *vs.* sputtering time for the spontaneously passivated film formed on the alloy 3. Similar enrichment characteristics are observed in the spontaneously passivated film formed on the alloy 3 in 5 % HCl solution at 25°C.

4. Conclusions

(1) Weight-loss measurements show that Fe-24Cr-6V alloys containing 0.12–0.35 % Ru exhibit good corrosion resistance in boiling 5 % H₂SO₄ solution and also in 5 % H₂SO₄ solution at 70°C. However, the addition of Ru to the above based alloy is only found to be beneficial at concentration levels of 0.24 and 0.35 %, respectively, in 5 % HCl solution at 70°C and at boiling temperature.

(2) Potentiodynamic measurements indicate that addition of Ru to the Fe-24Cr-6V based alloy is effective in decreasing the critical current density for passivation, and in promoting spontaneous passivation in 5 % HCl solution by shifting the corrosion potential towards the noble direction.

(3) AES spectra reveal that the spontaneously passivated films formed on the Fe-24Cr-6V-Ru alloy system are depleted of Ru. However, the composition depth-profiles show that enrichment of Cr and V occurs in the spontaneously passivated films formed on this system.

Fig. 5. Auger depth-profile for the Fe-24Cr-6V-0.3Ru alloy passivated spontaneously in 5 % HCl solution at 25°C.

Fig. 6. Normalized Auger peak height ratios $(Cr/(Fe+Cr+V))$ and $(V/(Fe+Cr+V))$ *vs.* sputtering time for the passivated film spontaneously formed on the Fe-24Cr-6V-0.3Ru alloy in 5 % HCl solution at 25°C.

Fig. 7. Normalized Auger peak height ratios $(Cr/(Fe+Cr+V))$ and $(V/(Fe+Cr+V))$ *vs.* sputtering time for the passivated film spontaneously formed on the Fe-24Cr-6V-0.1Ru alloy in 5 % HCl solution at 25°C.

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