Corrosion properties of Fe–24Cr stainless alloy modified by plasma immersion ion implantation in 0.5 M sulfuric acid solution

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Abstract

Ruthenium (Ru) and mixed Ru–Ti ions were implanted respectively into ferritic Fe–24Cr alloy using the plasma immersion ion implantation (PI3) technique. Potentiodynamic and potential-time response measurements were used to characterize the corrosion behavior of Fe–24Cr alloy exposed to a deaerated sulfuric acid solution. The results showed that the ferritic alloy does not passivate in dilute sulfuric acid. However, plasma-implanted Ru ions can induce spontaneous passivation of the alloy exposed to a sulfuric acid solution. X-ray photoelectron spectroscopy (XPS) analysis showed that Ru is incorporated as Ru4+ species in the hydrated chromium oxyhydroxide passive film formed on the Ru-implanted Fe–24Cr alloy.

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1. Introduction

In the past two decades there has been much interest in the modification of the corrosion and mechanical properties of metals by ion implantation. Ion beams can be used to create a highly nonequilibrium surface alloy layer without any change in the bulk properties. Ion implantation involves bombarding the surface layer of solids with specific energetic ions typically in the 40 to 500 keV range. This technique has been recognized of yielding beneficial effects on improving the corrosion resistance and mechanical property of metallic alloys [1–4]. However, conventional ion implantation has several disadvantages, including high equipment cost, line-of-sight feature and extremely shallow depth of the implanted layer. To overcome these shortcomings, plasma immersion ion implantation (PI3) can be used since it is a high-rate deposition, non-line-of-sight process and capable of modifying the structure of surface layer with a thickness larger than 1 μm [5]. The corrosion and mechanical properties of Fe-based alloys modified by PI3 have been widely reported in the literature [6–8]. Fe–Cr stainless alloys are known to suffer from high-rate active dissolution on exposure to the hydrochloric and sulfuric acids. However, these alloys can be easily transformed from an active dissolution into the passive regime by alloying them with small amounts of platinum group metals (PGMs) such as ruthenium [9,10]. The usefulness of the PI3 in the materials design is that small quantities of scarce and expensive alloying elements can be implanted in the alloy surface for corrosion protection.

2. Experimental

The Fe–Cr alloy was prepared in a vacuum induction furnace. Disc specimens of 11 mm were cut from the ingot and polished with diamond paste down to 1 μm. Ru ions were generated from the metal vacuum arc plasma sources of a PI3 chamber. High-voltage pulses of −25 kV were applied to the target specimens for 140 min to yield a total dose of ~1.0 × 1018 ions cm–2. For mixed Ru–Ti implantations, Ti plasma were subsequently implanted into the Ru-treated specimens to a dose of ~5.0 × 1017 ions cm–2 under a negative bias of 20 kV for 70 min at ~100 °C. It is considered that Ru or mixed Ru–Ti ions are implanted into the surfaces of the substrates using the above
processing conditions. Thin films of Ru or mixed Ru–Ti would not form as higher implanting doses are needed.

Electrochemical measurements were performed in a 0.5 M H₂SO₄ acid solution using a Princeton Applied Research potentiostat (model 273A) equipped with corrosion measurement computer software. The cell consisted of the working electrode, saturated calomel electrode (SCE) and graphite counter electrode. Each specimen was immersed in the nitrogen purged electrolyte (23 °C) and then held cathodically at −800 mV (SCE) for 5 min for removing the air-formed oxide. After this treatment, the applied potential was removed, and the potential-time response curves were recorded. The plasma-implanted specimens were passivated spontaneously accordingly. XPS analysis of spontaneously formed passive films formed in the Ru-implanted Fe–24Cr alloy in the 0.5 M H₂SO₄ solution was performed with a Perkin-Elmer PHI 5902 system (AlKα). A Gaussian–Lorentzian peak profile was used to fit the O 1s spectrum. In potentiodynamic tests, the specimen was also cathodically reduced at −800 mV (SCE) for 5 min. The scan was then initiated from this potential to the noble direction at a rate of 1 mV/s.

3. Results and discussion

Fig. 1 shows the potentiodynamic curves of both the unimplanted and implanted Fe–24Cr alloy specimens exposed to a 0.5 M H₂SO₄ solution. The corrosion behavior of the unimplanted alloy is of typical active–passive type with large critical current density for passivation. Ru implantation is beneficial to improving the corrosion resistance of the alloy by eliminating the active–passive transition peak. The corrosion potential of the implanted alloy is shifted towards a more noble potential, i.e. −10 mV (SCE), thereby promoting spontaneous passivation. This is attributed to the hydrogen evolution reaction that has a large exchange current density on the Ru surface. For mixed Ru–Ti implantation, the active–passive transition peak is also eliminated but the corrosion potential is shifted to a less positive value of −260 mV (SCE), thereby promoting spontaneous passivation. This is attributed to the hydrogen evolution reaction that has a large exchange current density on the Ru surface. For mixed Ru–Ti implantation, the active–passive transition peak is also eliminated but the corrosion potential is shifted to a less positive value of −260 mV (SCE). The less noble corrosion potential of the Ru–Ti alloy can be explained in terms of the mixed potential effect as the standard electrode potential of Ti (−1.63 V; with respect to standard hydrogen electrode (SHE)) is more active than that of Ru. Tomashov et al. [11] explained the spontaneous passivation of PGM-containing alloys in terms of the surface diffusion of the PGMs to the kinks and ledges, and then accumulated on these surface sites. Accumulation of PGMs on the surface defect sites that could induce a large exchange current density for the hydrogen evolution reaction and the resultant galvanic effect facilitates spontaneous passivation [11]. From Fig. 1, the corrosion current density for the unimplanted Fe–24Cr alloy is rather large, i.e. $\sim 3 \times 10^{-4} \text{A/cm}^2$. However, the corrosion current densities for the Ru–Ti and Ru-implanted Fe–24Cr specimens are reduced...
to $\sim 10^{-6}$ and $2 \times 10^{-7}$ A/cm$^2$, respectively. The anodic current density of the unimplanted Fe–24Cr alloy ($\sim 5 \times 10^{-5}$ A/cm$^2$) is also larger than those of the Ru–Ti- and Ru-implanted alloy specimens, i.e. $\sim 2 \times 10^{-5}$ A/cm$^2$.

Fig. 2 shows the potential-time response curves of the Fe–24Cr and PI3 modified Fe–24Cr specimens exposed in 0.5 M H$_2$SO$_4$ solution. Apparently, the Fe–24Cr alloy does not passivate in this solution. There is no displacement of the corrosion potential from the region of active dissolution to the passive region immediately after cathodic reduction at $-800$ mV (SCE). The corrosion potential shifts from $-800$ mV to $-520$ mV (SCE) for extended periods of time. The corrosion potential of $-520$ mV for the unimplanted Fe–24Cr alloy remains in the active region indicating that no passive film is formed on this sample. On the other hand, the corrosion potential of Ru-implanted specimen shifts towards more noble value of $-10$ mV immediately after cathodic reduction. The corrosion potential then decays to $-170$ mV (SCE) and stabilizes within this potential for extended period of time. This implies that spontaneous passivation occurs for the implanted Fe–24Cr alloy exposed to a sulfuric acid solution. Similarly, the corrosion potential of the Ru–Ti-implanted specimen moves from the active region towards a noble potential of $-205$ mV immediately after cathodic reduction. It then stabilizes at $-220$ mV (SCE). A shift from an active potential of $-800$ mV to $-220$ mV (SCE) is derived from the spontaneous passivation. The surface chemistries of spontaneously passive film formed on the Ru-implanted Fe–24Cr alloy are determined with XPS.

Fig. 3 shows the Cr 2p spectra for the passive film formed spontaneously on the Ru-implanted Fe–24Cr alloy in 0.5 M H$_2$SO$_4$ solution prior to and after sputtering for various periods of time. The spectrum prior to sputtering shows a major peak located at $\sim 576.9$ eV together with a shoulder at $573.9$ eV. The main 2p$_{3/2}$ component at $576.9$ eV represents Cr$^{3+}$ in an oxide or hydroxide environment [12]. The shoulder at $573.9$ eV represents the metallic peak of Cr, i.e. Cr$_{\text{metal}}$ [12,13]. After sputtering for 1 min, the intensity of Cr$_{\text{metal}}$ peak increases considerably whereas that of the hydroxide component decreases. The oxide/hydroxide component is nearly removed after sputtering for 2 min. The sputtering rate is roughly estimated to be $\sim 8$ nm/min using an SiO$_2$ standard under similar sputtering conditions.

Fig. 4(a) shows that the O 1s spectrum for the passive film formed spontaneously on Ru-implanted Fe–24Cr alloy in 0.5 M H$_2$SO$_4$ solution can be deconvoluted into two peaks at 530.0 and 532.2 eV, which are assigned to O$_2^-$ and OH$^-$ respectively [13]. After etching for 1 min, the OH$^-$ component decreases whereas the O$_2^-$ component increases (Fig. 4(b)). As the etching time increases to 10 min, the O 1s peak nearly disappears indicating a complete removal of the passive film layer. On the basis of Cr 2p and O 1s spectra analysis, it is evident that the passive film consists of hydrated chromium oxyhydroxide [12,14]. It is noted that the Ru should incorporate into the
hydrated chromium oxyhydroxide film to promote the spontaneous passivation. Fig. 5 shows the Ru 3d spectra for the passive film formed spontaneously on the Ru-implanted Fe–24Cr alloy in a 0.5 M H₂SO₄ solution. The peak at ~280.7 eV is the oxide part of the Ru 3d₅/₂ signal, which was reported as either RuO₂ (280.7 eV) or hydrated RuO₂ (281.4 eV) [15]. The Ru 3d₃/₂ peak at ~284.8 eV interferes with the C 1s peak of contaminated hydrocarbon at 284.6 eV, leading to a large increase in the intensity of the signal. Thus, a precise determination of the Ru oxide and hydroxide by peak deconvolution is complicated by the interference of the C 1s peak. After sputtering for 1 min, the C contamination is partially removed and the intensity of Ru 3d₅/₂ signal increases. Moreover, the Ru 3d₅/₂ signal shifts from 280.7 eV to 280.2 eV. The peak at 280.2 eV derives from metallic Ru 3d₅/₂ signal [13,16]. From the O 1s spectrum, the passive film is not etched out after 1 min of sputtering, thus the appearance of the metallic Ru may be an effect of ion sputtering because the Ru⁴⁺ species is reduced to Ru°met. Further sputtering to 10 min, the Ru 3d₅/₂ signal decreases dramatically resulting from a nearly complete removal of Ru-implanted atoms.

4. Conclusion

Electrochemical tests revealed that both the Ru-implanted and Ru–Ti-implanted Fe–24Cr alloy specimens passivate spontaneously in a 0.5 M H₂SO₄ solution. However, unimplanted Fe–24Cr alloy was susceptible to an active dissolution in a deaerated sulfuric acid solution. Ru and Ru–Ti implantation improved the corrosion resistance of Fe–24Cr alloy dramatically as demonstrated by its very low current density values after implantation. XPS measurements showed that the incorporation of Ru⁴⁺ species into the hydrated chromium oxyhydroxide film is responsible for spontaneous passivation of the Ru-implanted alloy in dilute sulfuric acid solution.

References