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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 (PI^3) 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 Ru^{4+} species in the hydrated chromium oxyhydroxide passive film formed on the Ru-implanted Fe–24Cr alloy.

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Keywords: Plasma immersion ion implantation; Ferritic alloy; Ruthenium; Spontaneous passivation

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 (PI^3) 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 PI^3 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 PI^3 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 PI^3 chamber. High-voltage pulses of −25 kV were applied to the target specimens for 140 min to yield a total dose of $\sim 1.0 \times 10^{18}$ ions cm^{-2}. For mixed Ru–Ti implantations, Ti plasma were subsequently implanted into the Ru-treated specimens to a dose of $\sim 5.0 \times 10^{17}$ 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

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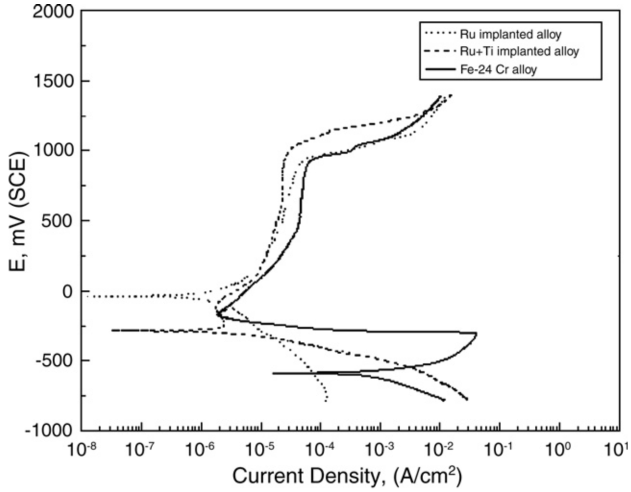

Fig. 1. Potentiodynamic curves for PI^3-treated and -untreated Fe–24Cr alloy specimens exposed in a 0.5 M H_2SO_4 acid solution.

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 H_2SO_4 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 H_2SO_4 solution was performed with a Perkin-Elmer PHI 5902 system (AlK_α). 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.

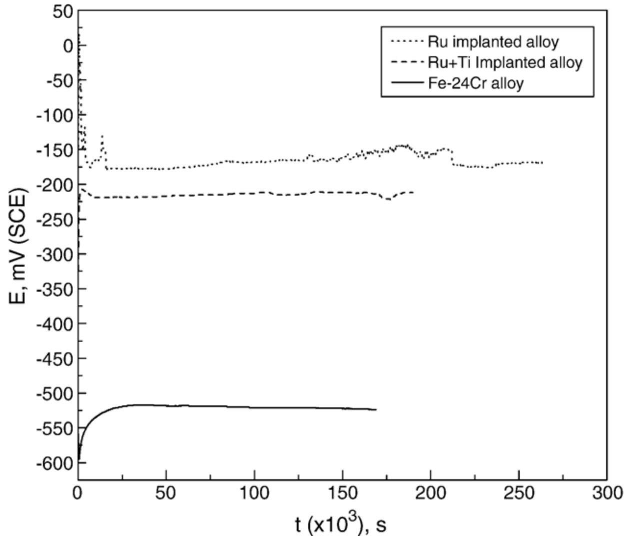

Fig. 2. Potential-time response curves for PI^3-treated and -untreated Fe–24Cr alloy specimens exposed in a 0.5 M H_2SO_4 acid solution.

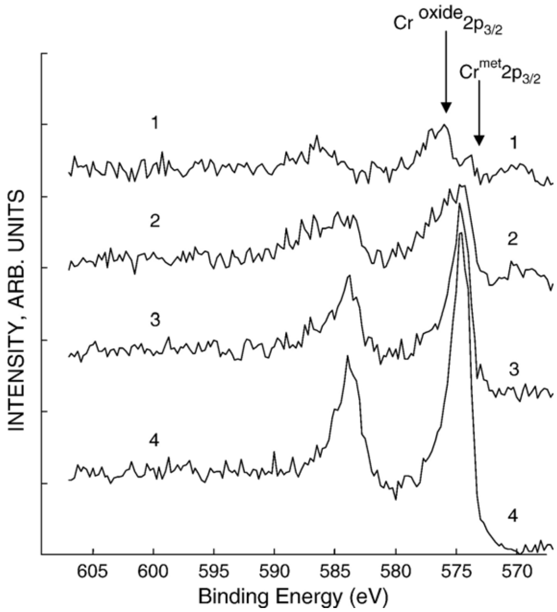

Fig. 3. Cr (2p) spectra for the passive film formed on Ru-implanted Fe–24Cr alloy in a 0.5 M H_2SO_4 solution. (1) Before sputtering; (2) after sputtering for 1 min, (3) 2 min, and (4) 10 min.

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 H_2SO_4 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). 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. $\sim 3\times 10^{-4}$ A/cm^2. However, the corrosion current densities for the Ru–Ti and Ru-implanted Fe–24Cr specimens are reduced