

Oxide formation and anodic polarization behavior of thin films of amorphous and crystalline Fe–Cr–P alloys prepared by ion beam mixing

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An experimental program has been conducted to determine the effect of phosphorus on the corrosion and passivation behavior of Fe–Cr–P alloys. Chemically homogeneous 60 nm films of Fe–10Cr– x P (x from 0 to 35 at.%) were prepared by multilayer evaporation followed by ion beam mixing with Kr⁺ ions. Films with a phosphorus content of at least 25 at.% were found to be entirely amorphous, while films with 15 at.% P consisted of both amorphous and bcc phases. Recrystallization of the amorphous phase was accomplished by heating the samples to 450°C in a purified argon flow furnace.

Electrochemical polarization tests in an acid solution have shown the Fe–10Cr– x P films to be more corrosion resistant than Fe–10Cr, with the corrosion resistance increasing with the amount of P present. The corrosion resistance is not significantly affected when the amorphous films are recrystallized, indicating that the behavior is chemically controlled and not a result of the amorphous structure. When examined by XPS, the phosphorus appears to enhance passivation by encouraging Cr enrichment in the oxide and by incorporating in the oxide as phosphate.

1. Introduction

The remarkable aqueous corrosion resistance of amorphous alloys was first noted by Hashimoto and coworkers in the early 1970s [1]. Since that time, many researchers have investigated this phenomenon in a variety of glassy alloys, considering both metal–metal and metal–metalloid systems [2]. The mechanism by which these alloys remain passive even in highly corrosive environments is a matter of controversy. The objective of this study is to determine whether the passivity of amorphous Fe–10Cr– x P films ($0 < x < 35$ at.%) in acid solutions is a result of the non-metallic surface chemistry or the amorphous structure per se.

Amorphous alloys are most commonly produced by rapid quenching from a melt, but can also be produced by other non-equilibrium techniques such as ion implantation and ion beam mixing. Studies of the corrosion behavior of P-implanted stainless steels and Fe–Cr alloys have been performed [3–5], but because of the distribution of the implanted species under the metal surface there is a good deal of uncertainty about the actual metalloid concentration at the surface during corrosion. For this reason, ion beam mixing techniques were employed in this study to produce chemically and structurally homogeneous 60 nm thick films on a variety

of substrates, which were fully characterized and subjected to standard electrochemical tests.

2. Experimental procedure

Fe–10Cr– x P films were prepared by ion beam mixing 18 alternating layers of Fe/FeP/Cr, produced by sequential e-gun evaporation of Fe, Cr, and Fe₃P sources in a vacuum evaporator (base vacuum = 5×10^{-8} Torr), with a total thickness of 60 nm and P concentrations from 0 to 35 at.% (adjusted by varying the Fe/FeP thickness ratio). These films were evaporated onto glass microscope slides, freshly cleaved NaCl crystals, and mirror-polished Fe–10Cr coupons. The films were irradiated with 300 keV Kr⁺ ions in a Varian 400 ion implanter, to a total dose of 1×10^{16} ions/cm². The samples were cooled to temperatures below –100°C during irradiation to prevent the formation of equilibrium phases. Samples of each film composition were heat treated at 450°C for two hours in an argon flow furnace to recrystallize the amorphous phase.

The films were characterized by 2 MeV He⁺ RBS, using a General Ionex Tandemtron accelerator, to be certain that the films were chemically homogeneous throughout their thickness. The films on NaCl crystals

were floated off in distilled water onto Cu TEM grids, and examined in a JEOL 2000FX analytical electron microscope to ascertain the microstructure.

The corrosion behavior of the films deposited onto glass slides and Fe-10Cr was examined in 0.1N sulfuric acid. All solutions were prepared with deionized water and were not deaerated. Potentiodynamic scans were performed at a rate of 1 mV/s, beginning at a potential at least 250 mV below the open circuit potential and were preceded by a 2 min cathodic polarization to

remove the air-formed oxide if the sample did not spontaneously exhibit a typical active potential.

Following ion beam mixing, heat treatment, and potentiostatic polarization, all of the films were examined by XPS using a PHI 5400 system with an argon ion beam to sputter depth-profile the surface oxide and the underlying metallic film. The sputter rate was approximately 0.3 nm/min in the metallic film, as measured by completely sputtering through a film of known thickness. Since oxides generally have 20–30% of the

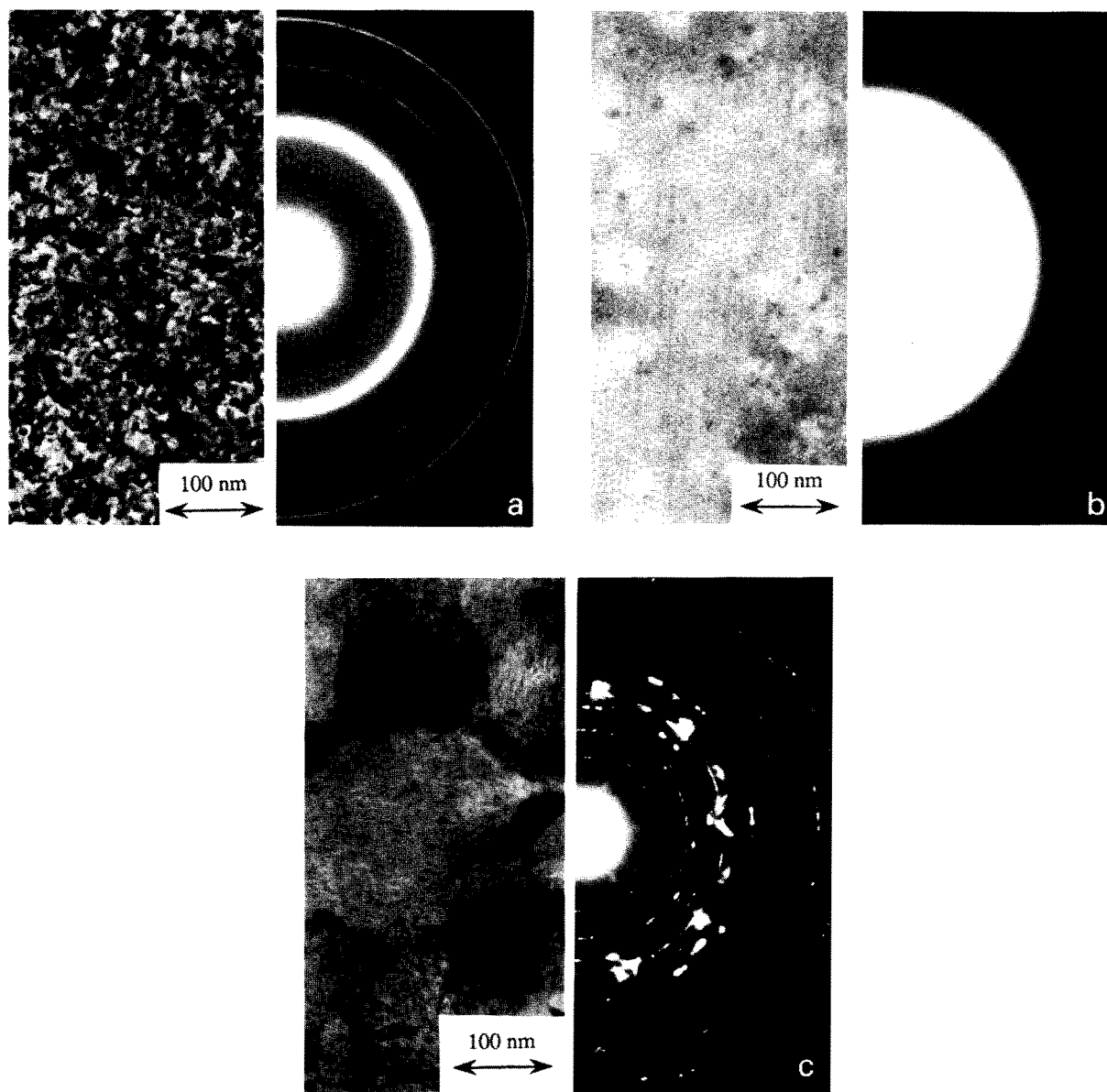


Fig. 1. Bright field TEM and selected area diffraction patterns for Fe-10Cr-25P film, (a) as-evaporated, (b) after ion beam mixing, and (c) after recrystallization by heat treatment.

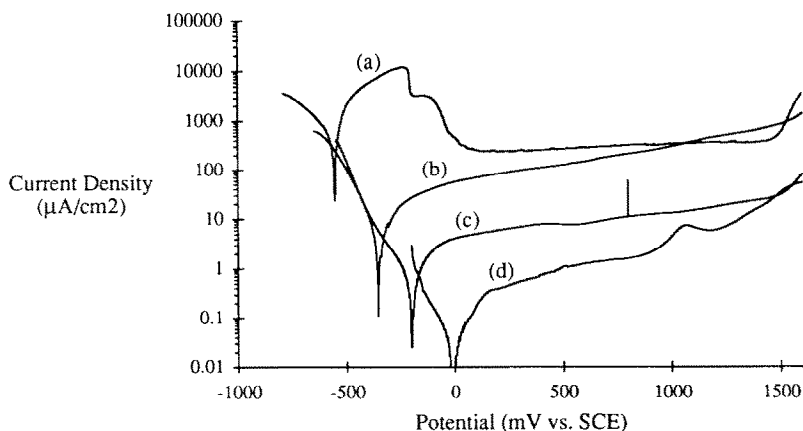


Fig. 2. Potentiodynamic polarization of Fe-10Cr-xP in 0.1N sulfuric acid, scanned at +1 mV/s. (a) $x = 0\%$, (b) $x = 15\%$, (c) $x = 25\%$, and (d) $x = 35\%$.

sputter yield of metals, it is assumed that the sputter rate in the oxide portion of the profiles is roughly 0.1 nm/min.

3. Results and discussion

RBS analysis showed that the ion dose used for mixing was sufficient to completely homogenize the evaporated layers. The technique was able to resolve the P-containing layers in an unmixed sample, and show that the P concentration was uniform throughout the thickness of the film after mixing. The ion beam irradiation also provided the stimulus for the crystalline-to-amorphous phase transition in samples with sufficient P to stabilize that phase. Fig. 1a shows a phosphorus bearing film in bright field TEM, along with its selected

area diffraction pattern, after multilayer evaporation. The film is microcrystalline, with grain size less than 5 nm, and shows only a supersaturated solution of P in bcc-Fe/Cr. After ion beam mixing, the film is nearly featureless in bright field, and the diffraction pattern is a halo characteristic of amorphous metals (fig. 1b). In this study, only the 0% P film was entirely crystalline, the 15% P film was almost entirely amorphous, with some evidence of bcc grains in the film, and the 25% and 35% P films showed no crystallinity whatsoever. The amorphous phase can be recrystallized by heat treating, leading to equilibrium phosphide phases with somewhat larger grains (fig. 1c).

Potentiodynamic polarization data for the ion beam mixed alloys is shown in fig. 2. The presence of P has a strong effect on the anodic current density of the samples, reducing the passive current density by more than

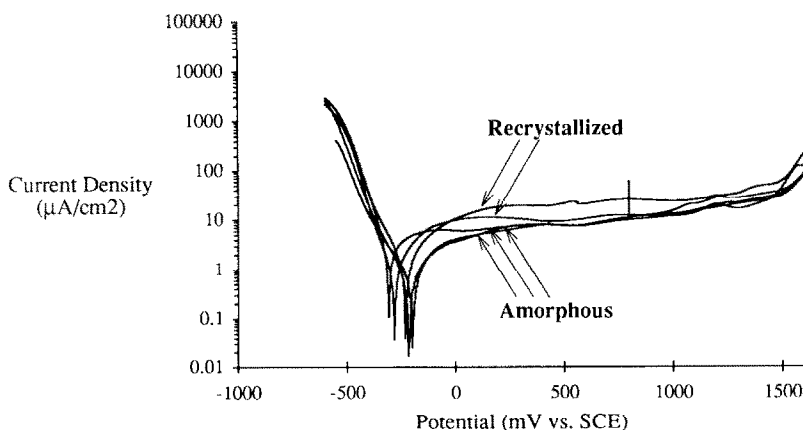


Fig. 3. Potentiodynamic polarization of Fe-10Cr-25P in 0.1N sulfuric acid, scanned at +1 mV/s. in amorphous phase and after recrystallization by heat treatment.

two orders of magnitude and eliminating the prominent active peak altogether. The 0% P alloy on a glass substrate dissolved so rapidly that it was impossible to record a potentiodynamic scan, even at 10 mV/s (the curve shown for 0% P in fig. 2 is that of the 0% P evaporated film on a polished Fe–10Cr substrate – all of the other data are from samples on glass substrates). Note that the cathodic portion of the scans seems relatively unaffected by the presence of P, but the suppression of the anodic reaction progressively moves the corrosion potential to more positive values.

It is generally thought that the oxide on an amorphous metal is inherently more uniform and protective than that on a crystalline metal, since it is not weakened by underlying grain boundaries or other crystal defects. Hence, one would expect the corrosion resistance of the amorphous films to be degraded by recrystallization, as has been reported in the case of melt-spun alloys [6]. In this study, recrystallization was found to have little effect on the corrosion resistance. Fig. 3 shows several potentiodynamic scans for the Fe–10Cr–25P alloy before and after recrystallization. The difference between crystalline and amorphous alloys of the same chemical composition is negligible, indicating that the corrosion resistance of the alloy is due to chemical, not structural, effects.

The chemical effect can be identified by XPS depth profiling of the oxides after a long polarization at a passive potential. Fig. 4 shows a typical depth profile of a passive oxide, with Fe, Cr, and P normalized to 100% (i.e., oxygen is omitted). All of the oxides are of similar thicknesses, around 5 to 10 min sputtering time (approximately 0.5 to 1.0 nm), but their compositions vary. Table 1 summarizes the composition of the oxides

Table 1

Average cationic composition (at.%) of oxide films formed by anodic polarization^a

P	Oxidized Fe	Oxidized Cr	Oxidized P
0	65	35	0
15	15	30	35
25	11	29	60
35	15	35	50

^a At +500 mV (SCE) in 0.1N sulfuric acid as measured by XPS depth profiling. Polarization time is 5 s for the 0% P sample, and 1 h for all others.

formed by anodic polarization. The 0% P oxide consists of both Fe and Cr oxide, and is the least protective. The addition of P results in a larger Cr-to-Fe ratio, which perhaps accounts for some of the increasing protective-ness of the oxide. The P itself participates in the oxide as well, primarily as phosphate. In the 15% P film, both oxidized phosphate and metal-bound phosphide are present at the surface (hence, the cationic compositions do not add up to 100%), but at higher bulk concentrations of P, a uniform phosphate film is seen. In both the 25% and 35% P cases, half of the cations in the surface oxide are P cations, and it is likely that they control a large part of the surface chemistry. A Cr phosphate salt would not be expected to be as structurally sound as dehydrated Cr oxide, but the oxidized P could form an effective chemical barrier between the underlying metal and the electrolyte, as was reported for NiP alloys [7]. This phosphate barrier exists on both the amorphous and recrystallized alloys, and seems to be the primary factor in the suppression of anodic dissolution which

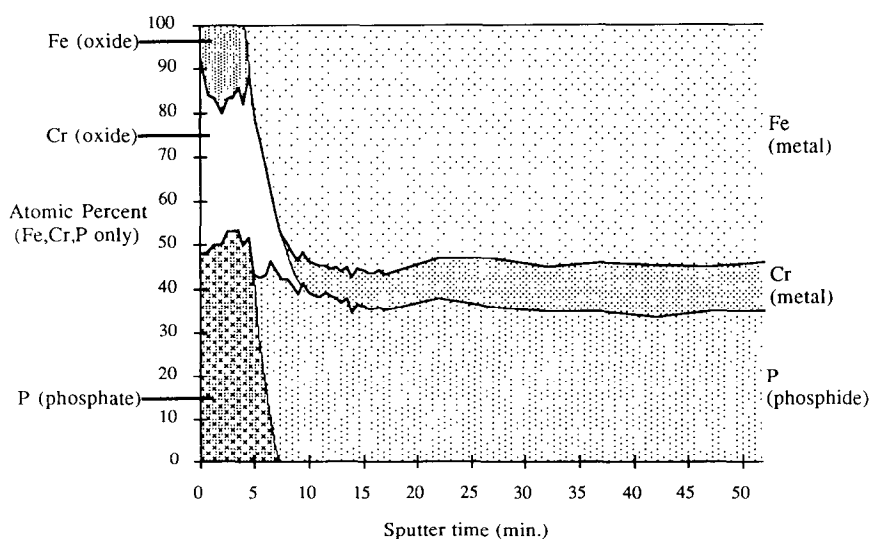


Fig. 4. Schematic of XPS depth profile of Fe–10Cr–35P after anodic polarization at +500 mV (SCE) for 1 h in 0.1N sulfuric acid, neglecting oxygen.

leads to the remarkable corrosion resistance of these alloys in acid solutions.

4. Summary

1) Ion beam mixing techniques can be successfully employed to produce chemically homogeneous thin films of Fe-Cr-P, with the amounts of each element easily controlled during the multilayer evaporation process.

2) Thin films prepared in this way will be amorphous if a sufficient amount of P is present. Films with 15% P were amorphous, with some evidence of embedded crystalline grains. Films with 25% and 35% P were entirely amorphous.

3) The presence of P reduced the active and passive current densities significantly, with the size of the reduction increasing with the amount of P. The reduction is a result of suppression of the anodic dissolution process.

4) Recrystallization of the amorphous phase had little effect on the corrosion behavior, indicating that the corrosion resistance of these alloys is chemically controlled, and not merely a result of the amorphous phase.

5) The presence of P enhanced the amount of Cr present in the passive oxide. Phosphorus, in the form of phosphate, was a major constituent of the oxides formed on the films containing large amounts of P. It is thought that this phosphate may provide a chemical barrier against anodic dissolution, and be the primary factor in the corrosion resistance of the high P alloys.

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