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Optical and electrochemical studies of passive film formation in amorphous Ni-Cr-P-C alloys

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to be caused by formation of an amorphous layer at grain boundaries. Thermal annealing after ion irradiation causes irreversible compositional changes near the film surface.[14,15] We do not observe such severe segregation in our films even though our doses and annealing temperatures are relatively high. White *et al.*[16] found that the damage due to the films is greater when they are implanted below 90 K. Our films may have escaped this level of damage because they were implanted at room temperature.

The above results show that a Y-Ba-Cu-O film can be compensated for a Cu deficiency by ion implantation with a significant improvement in zero-resistance temperature. Better results may result with closer approach to the stoichiometric composition.

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Optical and electrochemical studies of passive film formation in amorphous Ni-Cr-P-C alloys

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The investigation of passivation of an amorphous Ni-14Cr-17P-0.5C alloy in 1*N* H_2SO_4 through anodic polarization and near-normal optical reflectance is reported. It was found that the alloy passivates with a current density of 10^{-1} A/m^2 extending to 1.0 V with current density dependent upon surface morphology. In the transpassive region under constant current density conditions the reflectance of the film exhibits strong interference phenomena and overall exponential decay in intensity. The behavior of the system in this region is described with a single thin-film optical model consistent with the formation of a chromium phosphate deposit layer which increases in thickness at a rate of 7 nm/s at a 1.67 mV/s sweep rate.

Amorphous nickel based alloys have been of interest for their mechanical, magnetic, and corrosion properties.[1-5] In particular, they display enhanced corrosion resistance and passivity relative to crystalline alloys of the same composition and passivity enhancement as a function of increased concentration of certain metals, notably Cr and Mo. In the Ni-Cr-type alloys the corrosion enhancement is due to the formation of a passivating chromium oxyhydroxide film.[6,7]

In this communication we performed simultaneous potentiodynamic polarization and monochromatic reflectance measurements on an amorphous Ni-14Cr-17P-0.5C alloy in order to obtain real time information on passive film formation and surface morphology of this system.

The samples used (Mfr. Id. No. MBF65, provided by Allied Corporation Metglas Products Division[8]) have a nominal composition Ni-14Cr-17P-0.5C. They are produced in ribbons, 5.0 cm wide and 35 μm thick, and cut for use in circular form with a 0.79 cm^2 exposed area. The sam-

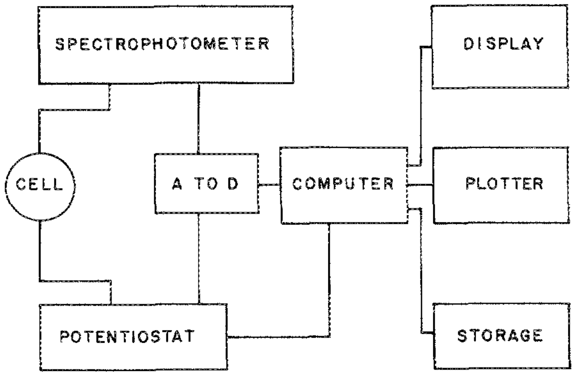

FIG. 1. The block diagram of the instrument.

ples, as supplied, had one shiny side and the other side somewhat duller in appearance. The foils were analyzed by x-ray diffraction and found to be uniformly amorphous. This study was carried out with a computer-controlled instrument which allows simultaneous *in situ* measurements of near-normal monochromatic reflectance for wavelengths from 300 to 800 nm and several electrochemical processes. A block diagram of the instrument is shown in Fig.1. Electrochemical measurements have been carried out with a three-electrode potentiostat and cell which is an expansion of the instrument which has been reported[9] with enhanced computer capabilities. A standard Ag/AgCl reference electrode was used. The potentiodynamic polarization was performed at a sweep rate of 1.67 mV/s through the corrosion potential up to 1.8 V in 1*N* H_2SO_4. The current limit imposed on the system is 13.65 mA or a current density of 171 A/m^2 with the 0.79 cm^2 sample area. The optical reflectance was measured through a bifurcated fiber optics tube fitted in the electrochemical cell in a manner suggested by Puyn and Park[10] and by Reed and Hawkridge.[11]

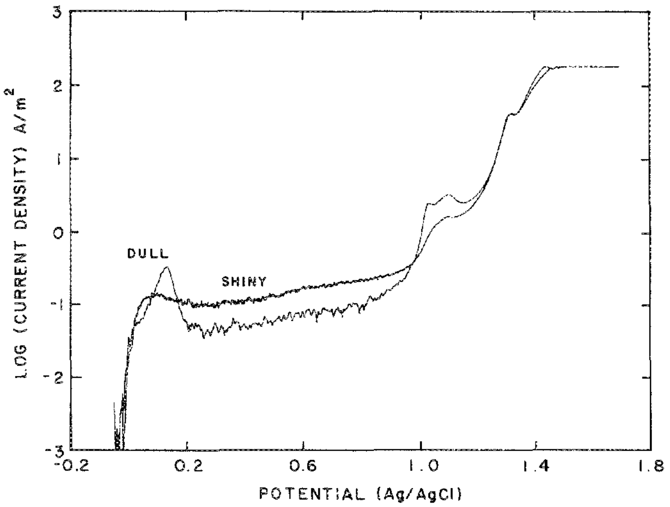

FIG. 2. Potentiodynamic polarization of the dull and shiny sides of MBF65 in 1*N* H_2SO_4 at a sweep rate of 1.67 mV/s.

Polarization current density and reflectance as a function of potential were measured for dull, shiny, and polished samples of both surfaces for multiple samples of the MBF65 with very good repeatability. Surface structure and morphology were investigated by scanning electron microscopy (SEM) and energy dispersive x-ray dot mapping. X-ray photoemission spectroscopy (XPS) spectra from the surface of treated samples was performed with a Physical Electronics 5100 ESCA system with Mg*K*α excitation. Film thickness was measured on polished samples with a Reichert polarizing interferometer in 590-nm light. An Abbe refractometer was used to determine the index of refraction of the electrolyte at a temperature of 20 °C.

SEM studies of the sample surfaces showed convolutions on the dull side while the shiny side was smooth and

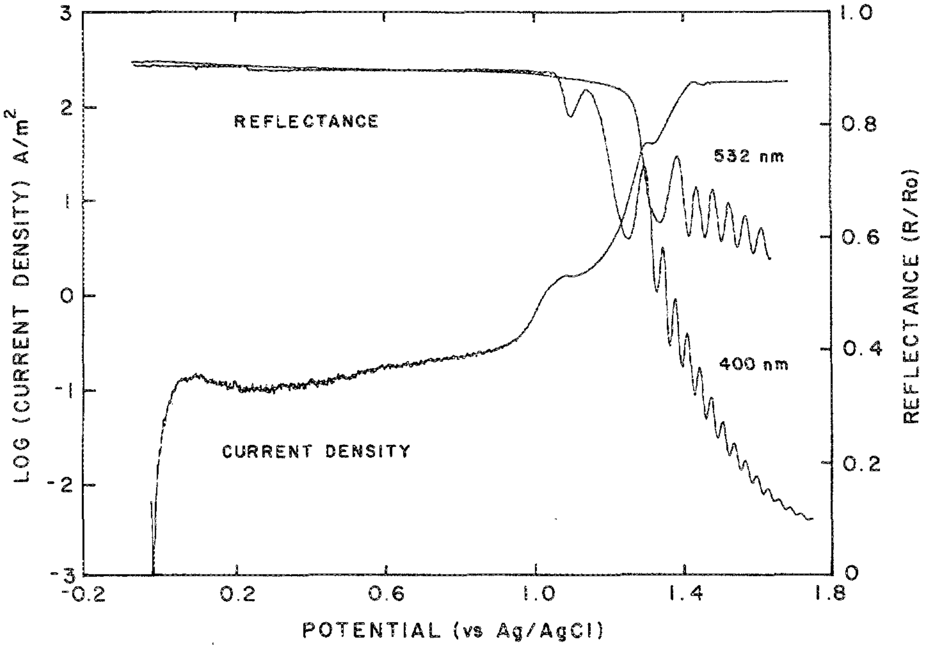

FIG. 3. Potentiodynamic polarization of MBF 65 in 1*N* H_2SO_4 at a sweep rate of 1.67 mV/s with normalized reflectance.

TABLE I. Single thin-film model optical parameters used in Eq. (1).

	nm	n	k	β
Electrolyte	400	1.36[a]	0.01[b]	0.25[c]
	532	1.36[a]	0.01[b]	0.05[c]
Film[d]	400	1.58	0.019	
	532	1.58	0.019	
Metal alloy[e]	400	1.81	3.12	
	532	1.81	3.12	

Values obtained from the following:

[a] Refractometry of fluid at 1.7 V.

[b] Fit to curve.

[c] Absorption spectroscopy 0.245 mm^{-1} at 400, 0.055 mm^{-1} at 532 nm.

[d] Values are for Cr_2PO_4 (Ref. 16).

[e] By ellipsometry.

featureless. Semiquantitative analysis showed no measurable variations in composition of the two sides to within approximately 1 μm depth. This is in contrast to the results reported for a related system of amorphous Fe-Ni-Cr-C,[12,13] where a gradient of composition for chromium was found with higher chromium concentration on the dull side of the film.

The potentiomdynamic polarization measurements (Fig. 2) yielded different characteristics of current density in the region near the corrosion potential depending upon the surface morphology. The dull samples exhibited an active region while the shiny side passivated spontaneously. Since the current density curves for the polished dull and the shiny sides are identical, only the results for the shiny surface are reported.[14]

The current density curve (Fig. 2), exhibited the general chararacteristics as those reported by Kawashima, Asami, and Hashimoto[15] for Ni-9Cr-15P-5B in 2*N* H_2SO_4 with spontaneous passivation and a comparable current density in the passive region.

According to Hashimoto and co-workers,[7] amorphous alloys containing certain amounts of Cr and P passivate by forming a film consisting entirely of hydrated chromium oxyhydroxide $[CrO_x(OH)_{3-2x} \cdot nH_2O]$. Kawashima *et al.*[15] reported that a Ni-10Cr-20P alloy in 1*N*/HCl showed preferential dissolution of nickel accompanied by increased surface concentrations of chromium and phosphorus yielding chromium oxyhydroxide and chromium phosphate films. Our results are consistent with the above and can be understood in terms of the dissolution of Ni from the surface, and with the film-forming properties of Cr and P in amorphous alloy systems.[7,15,16]

Near-normal reflectance measurements were made *in situ* at wavelengths of 400, 532, and 700 nm during anodic polarization from the corrosion potential up to 1.7 V. Typical results are shown in Fig. 3. As current increases at about 1.0 V the reflectance exhibits an overall decay in intensity with fluctuations which become quite uniformly periodic in the region of constant current. The relative decrease in intensity is strongly dependent upon wavelength. The interferometric measurements of film thickness on a polished surface anodically swept to the point of the first reflectance maximum in 400-nm light indicated the presence of a surface film about 130 nm thick. The above results suggest that overall increase in absorption and the periodic fluctuations of the reflectance can be related to a film-forming process with the film thickness increasing with time and potential.

A simple model was developed which consists of a single dielectric thin film with a single reflection at each of the two

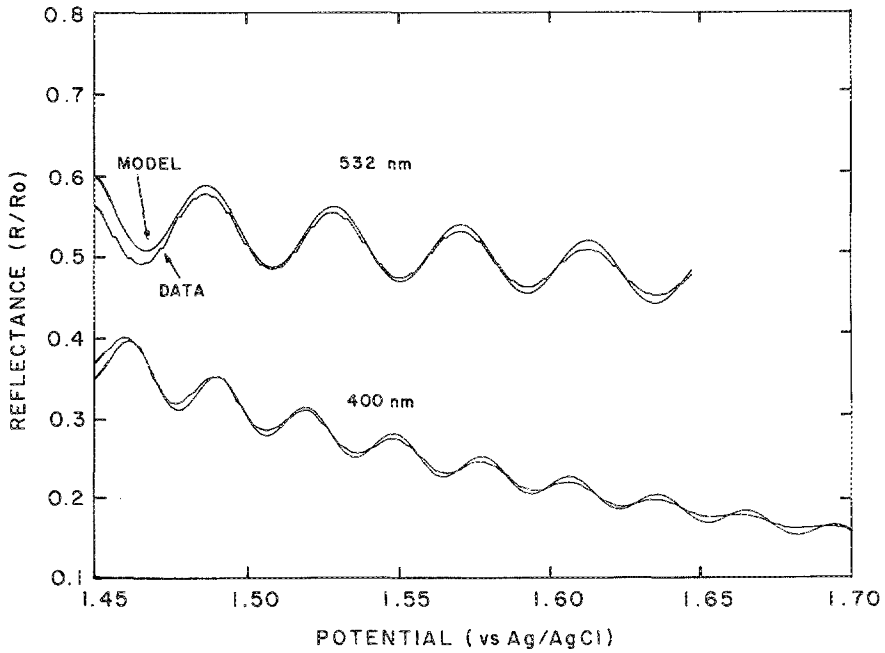

FIG. 4. Plot of normalized reflectance of the surface and the theoretical single-layer model for MBF65 (Ni-14Cr-10P-0.5C) in 1*N* H_2SO_4 at 400 and 500 nm.

interfaces: electrolyte/film and film/metal. Using the data in Table I, the relative intensity, or reflectance, as a function of film thickness t_2 can be expressed as follows:

$$I = [\exp(-2\beta t_1)][\sigma_0^2 + (1-\sigma_0^2)\sigma_1^2 \exp(-2\alpha t_2) + 2\sigma_0\sigma_1(1-\sigma_0^2)\exp(-\alpha t_2)\cos(\delta)], \quad (1)$$

where σ_0 and σ_1 are the reflection coefficients at normal incidence of the top and lower interfaces (a function of their respective indices of refraction n and absorption k), α is the film absorption coefficient equal to $4\pi k_0 \lambda$, and δ is the two-beam phase difference which is a function of the film thickness, its index of refraction, and the phase change of the reflection from each interface. The electrolyte was taken as an optical medium with an index of absorption β and thickness t_1. For the index of refraction of the film we took $n = 1.58$, the value for chromium phosphate reported in the transpassive region in a similar system (Ni-10Cr-10P) by Kawashima[7] in $1N$ HCl. Values of n and k for the untreated polished surface are in general agreement with the published values for nickel.[17]

For a comparison of the results calculated from the model and the experimental data, the potential was related to thickness by assuming the increase in thickness between successive reflectance maxima as 1/2 a wavelength of the monitoring light. This comparison is shown in Fig.4 for wavelengths of 400 and 532 nm. At both wavelengths the overall exponential decay of reflectance shows good agreement with the predicted absorption by both the film and the electrolyte. At both 400 and 532 nm the film growth rate is approximately 7 nm/s at a 1.67 mV/s sweep rate.[18]

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Preparation and characterization of the filled tetrahedral semiconductor LiZnP film on quartz

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A direct wide-gap semiconductor LiZnP has been prepared by rapid evaporation onto a quartz substrate. Various characterization techniques such as x-ray analysis, Rutherford backscattering analysis, and scanning electron microscopy were used to evaluate the quality of the films. Single-phase films were obtained by annealing during 40 min at substrate temperatures ranging from 400 to 440 °C. The grains in the films were oriented preferentially to the ⟨111⟩ direction with increasing substrate temperature. The optical transmission of the LiZnP films was observed to the short wavelength beyond an absorption edge (~600 nm) of bulk materials. This suggests the existence of the imperfection such as accumulated impurities at grain boundaries.

Recently, Wood, Zunger, and de Groot[1] have discussed the susceptibility of zinc-blende semiconductors to band-structure modification by the insertion of small atoms at their tetrahedral interstitial sites. Their electronic structure calculation has predicted that LiZnP [viewed as a zinc-blende-like $(ZnP)^-$ lattice partially filled with He-like Li^+ interstitials] is a novel type of direct-gap semiconductor, not encountered in any cubic III-V material. Among cubic III-