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Electrodeposition and characterization of amorphous Cr–P alloys

B. A. DENEVE, S. B. LALVANI*

Mechanical Engineering and Energy Processes, Southern Illinois University at Carbondale, Carbondale, IL 62901, USA

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The influence of plating variables and bath composition on electrodeposition of chromium–phosphorous alloy composition was investigated. The plating bath, prepared at a pH of approximately 1.25, consisted of a trivalent chromium source, sodium hypophosphite, ammonium sulphate, boric and formic acids, and sodium lauryl sulphate. Energy dispersive spectroscopy and Auger electron spectroscopy were utilized to evaluate alloy composition. These alloys were determined to be amorphous by X-ray diffraction. The influence of temperature, and bath ageing, and deposition time on deposit composition and structure and the deposition rate were also investigated.

1. Introduction

An amorphous material lacks the long range atomic order characteristic of a crystalline material; only short-range order exists over a few atomic distances. An amorphous material possesses properties which are unique to its structure. Amorphous alloys, also referred to as metallic glasses, have hardness properties similar to silicate glass, but the toughness properties similar to metals [1]. Amorphous materials also possess unique electrical and magnetic properties. They typically are one of the easiest materials to magnetize and demagnetize, qualifying them as very good soft ferromagnets.

One of the most widely used engineering coatings is the conventional chromium electrodeposit. It provides a high degree of wear resistance, readily forms a protective oxide film and is esthetically pleasing. Conventional chromium is commonly plated from a bath developed by Sargent [2]. Typical chromium deposits contain a large number of microcracks which are induced by stress relieving during the plating process [3]. Hoare [4] recently proposed a mechanism by which chromium is plated from the Sargent bath, which contains chromic oxide (CrO_3) and sulphuric acid in a weight ratio of 100 : 1. The use of the hexavalent chromium plating bath for chromium deposition has been wide-spread, but this bath has many technical, environmental and health related disadvantages [5].

Modifications to the Sargent bath have been made by various investigators to improve the coating quality as well as the plating process. Yoshida [6] and Ishaguro [7] were probably the first investigators to develop a useful trivalent bath for chromium deposition. A review of the developments in trivalent chromium plating prior to 1975 is provided by Crowther and Renton [8]. Hoshino *et al.* [9] included an organic additive with a –CHO or a –COOH group to a chromic acid bath. They found the incluusion of these additives effective in producing an amorphous carbon-containing chromium coating. X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES) analyses of these coatings were reported by Hoflund, *et al.* [10, 11]. Similar chromium coatings from chromic acid baths containing organic additives have been developed by Dash and Kasaaian [12], Benaben [13] and Furuya *et al.* [14].

Chromium coatings have also been deposited from baths which contain only trivalent chromium ions [15–17]. All of the baths contain an organic additive which prevents the hydrolysis of the chromium ion. Those prepared by Willis and Hammond [17] had an amorphous structure. An electroplated chromium–phosphorus alloy was studied by Bondar and Potapov [18] with no organic additive included in the bath. Watson and coworkers [19–21] have demonstrated sustained deposition of chromium, and its alloys from Cr(III) baths through control of transient Cr(II). They have shown that the transient Cr(II) catalyses interfering olation reactions in the diffusion layer which at the pH values, about 4, found in the diffusion layer would otherwise occur too slowly to be significant.

The addition of phosphorus to a chromium-based coating has a two-fold purpose. First of all, being a metalloid it should aid the formation of an amorphous structure during the electrodeposition process. Secondly, the addition of a metalloid should enhance the corrosion properties of the alloy. Moffat *et al.* [22] have determined the superior corrosion resistant properties of a r.f.-sputtered Cr–P alloy.

This work is an investigation of the electrodeposition of amorphous Cr–P–C alloys from a trivalent chromium plating bath. The effect of bath composition and plating variables on the composition of the alloy was studied. An organic additive was included in

* To whom all correspondence should be addressed.

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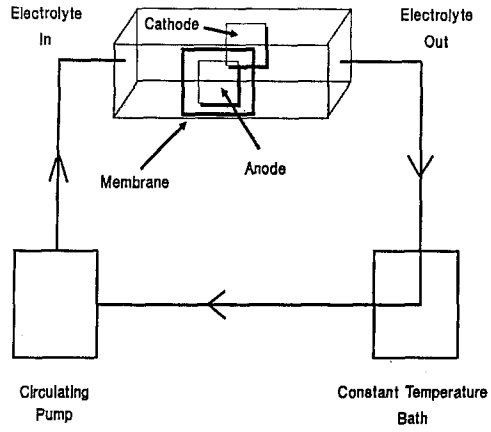

Fig. 1. A schematic sketch of electrodeposition system.

the plating bath as a trivalent chromium complexant. By using this component, carbon is introduced into the alloy. Carbon is also a metalloid and is known to aid in the formation of an amorphous structure.

2. Experimental procedure

2.1. *Electrodeposition*

The electrolyte was prepared with distilled water and reagent grade chemicals. The organic complexant was added to the solution a minimum of one hour prior to plating. The pH adjustments were made by adding either NaOH or H_2SO_4 to the electrolyte. Nitrogen was bubbled through the electrolyte for 10 min prior to deposition. The copper substrate used was a 25 μm thick foil (99.999% purity). Electrodeposition was performed under constant current conditions.

A diagram of the plating system is given in Fig. 1. The electrolyte was pumped through the plating cell to ensure thorough agitation at a rate of 1.5 $dm^3\ min^{-1}$. The anode and cathode were placed parallel to each other, 3.2 cm apart. The area of the cathode was 4 cm^2. A 6.5 cm^2 platinum anode was utilized. The anode and cathode were separated by a DuPont Nafion™ ion selective membrane, thus preventing Cr^{6+}, which is an oxidation product of Cr^{3+} from passing to the cathode. The electrolyte temperature was maintained within $\pm 2°$ C of the desired temperature by a water-jacketed reservoir.

The faradaic efficiencies were calculated with compositional information obtained by energy dispersive X-ray analysis (EDX). The equipment available for this analysis does not detect carbon, so efficiency calculations were based on chromium and phosphorus compositions only.

2.2. *Cyclic voltammetry*

The electrolyte was prepared in the same manner as the electrodeposition solution. Nitrogen was purged through the electrolyte approximately 10 min prior to testing. The programmable potentiostat used for performing cyclic voltammetry was the BioAnalytical System Model 100. A three-electrode cell containing a platinum wire for the counter electrode, a glassy carbon micro-electrode (diameter 3.2 mm) for the working electrode, and a Ag/AgCl reference electrode were utilized.

Table 1. Plating bath for chromium-phosphorous-carbon electrodeposition

Component	*Concentration/g dm^{-3}*
$Cr_2(SO_4)_3 \cdot nH_2O$(20% Cr)	180
$NaH_2PO_2 \cdot H_2O$	0–30
$(NH_4)_2SO_4$	100
H_3BO_3	50
NH_4Br	10
HCOOH	20
$(CH_3(CH_2)_{10}CH_2OSO_3Na)$	0.1
pH $\approx$ 1.25	

2.3. *Composition and structure*

The alloy composition was determined by Energy dispersive X-ray diffraction analysis (EDX) and Auger electron spectroscopy (AES). The surface was cleaned with acetone prior to analysis. The alloy was sputtered to a depth of 20 nm for AES.

The structure of the alloys was determined by X-ray diffraction (XRD). Diffraction was performed in a 2θ range of 5° to 144°.

3. Results and discussion

3.1. *Electrodeposition studies*

Chromium–phosphorus–carbon alloys were plated from the bath listed in Table 1. Chromium sulphate was the trivalent chromium source. Sodium hypophosphite was included as the phosphorus source. Ammonium sulphate is a complexant possibly in the high pH of the diffusion layer. Boric acid (pK 9) served as a source of a borate complex at the pH values involved. The chief acid/base buffer in the electrolyte is the aquo-chromium (III) ion (pK $\approx$ 4). Also included in the bath were ammonium bromide, an anti-oxidant; formic acid, the trivalent chromium complexant; and sodium lauryl sulphate, the wetting agent. The bath was operated at a pH of approximately 1.2–1.3. In the experiments described below, a Nafion™ membrane was used to isolate the working electrode compartment. Thin films of very poor quality were obtained when the membrane separator was not employed.

3.2. *Effect of bath composition*

The effect of bath composition on alloy composition was studied by varying the sodium hypophosphite concentration from 0 to 30 g dm^{-3}, while the chromium sulphate concentration was maintained at 180 g dm^{-3}. Figure 2 contains results from depositions performed at 20 A dm^{-2} and 30° C. The phosphorus composition of these alloys, as determined by EDX, was found to increase with the phosphorus content of the plating bath. There is a nearly linear relationship

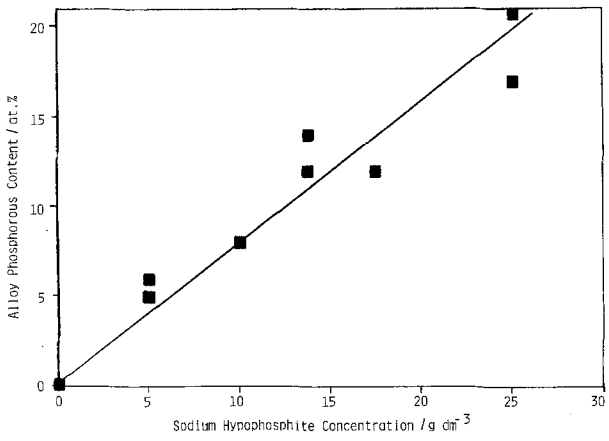

Fig. 2. Alloy phosphorus content against phosphorus in bath. Experiments were conducted at 20 A dm^{-2} and 30° C. The bath composition as in Table 1.

between the amount of phosphorus in the bath and the phosphorus content of the alloy.

The composition of the Cr–21 at % P–C sample was further analysed by AES to determine carbon and oxygen contents. The AES profile is shown in Fig. 3. The sample which was estimated to contain 21 at % P (by EDX) was found to consist of 28 at % P, 8 at % O, and 7 at % C by AES at a sputter depth of 20 nm. The differences in P content can be accounted for by the fact that EDX measures bulk composition, whereas AES is only a surface analysis and also detects the lower atomic weight elements. The discrepancy can also be attributed to the accuracy of the AES system, with a maximum uncertainty in measurement of up to 50 at %, depending on the element analysed. This alloy also contained impurity levels of sulphur, which were not quantified.

Alloys were also prepared with the plating bath stated in Table 1, except that the bath contained no sodium hypophosphite. The Cr–C coatings produced from the bath were bright in appearance. EDX analysis showed 99 at % chromium, while AES analysis indicated 75 at % Cr, 7 at % O, and 18 at % C at a sputter depth of 20 nm for this alloy. These results indicate that under identical reaction conditions, the overall metalloid (i.e. P + C) concentration is much greater for baths that contain a mixture of sodium hypophosphite and formic acid than for those containing formic acid only.

3.3. *Effect of temperature*

Alloys were deposited at 30, 35, 40, and 50° C to determine the effect of temperature on the alloy composition. Experiments were conducted at constant current density of 20 A dm^{-2} using the bath composition shown in Table 1 (15 g dm^{-3} NaH_2PO_2). The results are shown in Fig. 4. A monotonic linear relationship between the alloy phosphorous content and the bath temperature is observed. Since phosphorus deposition from thermodynamic considerations should take place at potentials more positive than chromium deposition, an increase in temperature is expected to favour phosphorus deposition as its deposition is anticipated to be mass transport limited as compared to chromium deposition. The data obtained support this hypothesis.

3.4. *Effect of current density*

The influence of the applied current density on the composition of the Cr–P–C alloys was also investigated. At the lowest applied current density used in this work, 10 A dm^{-2}, no coating could be attained. At the low current density, the cathode potential is probably too noble to induce deposition of chromium.

At a current density of 15 A dm^{-2}, coatings could be obtained, but they were very thin, approximately 1 μm, with incomplete coverage of the substrate. These coatings could be easily scraped off the substrate. Evidently, the rate of chromium reduction is very small at the applied current density of 15 A dm^{-2}. Also very low cathodic efficiencies (less than 2.5%) were observed. The phosphorus content of the two alloys obtained were 15 and 19 at % (by EDX) with a sodium hypophosphite concentration of 5 and 10 g dm^{-3}, respectively (Fig. 5).

At a current density of 20 A dm^{-2}, the physical appearance of the coatings ranged from 'matted' to 'bright'. The phosphorus content of these alloys varied from 6 to 21 at % (by EDX), and were discussed previously. The plating efficiencies of these coatings ranged from 6–16%, however they bear no

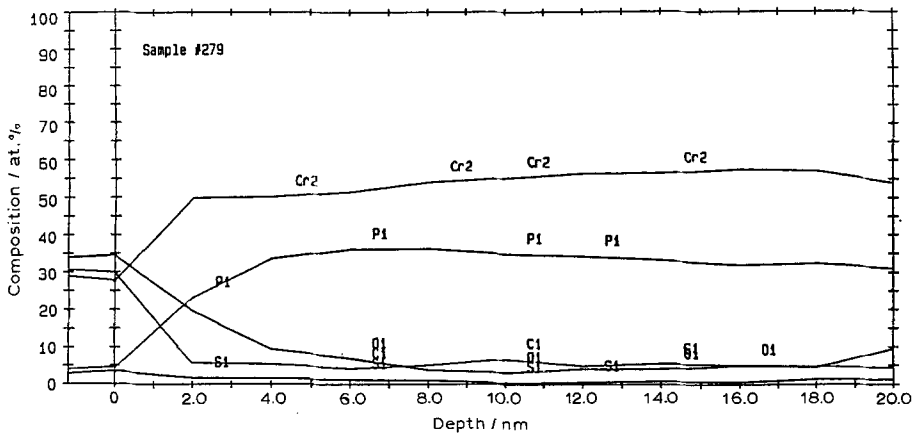

Fig. 3. Auger depth profile of chromium–phosphorus–carbon alloy. The alloy was produced from the bath shown in Table 1 at 20 A dm^{-2} and 30° C containing 20 g dm^{-3} $Na_2H_2PO_2 \cdot H_2O$. The film was found to contain 21 at % P by EDX.

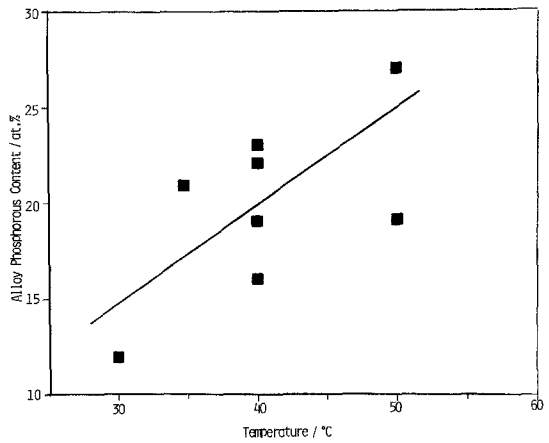

Fig. 4. Alloy phosphorous content against temperature. Experiments were conducted at 20 A dm^{-2}. The plating bath fused shown in Table 1 contained 15 g dm^{-3} of $NaH_2PO_2 \cdot H_2O$.

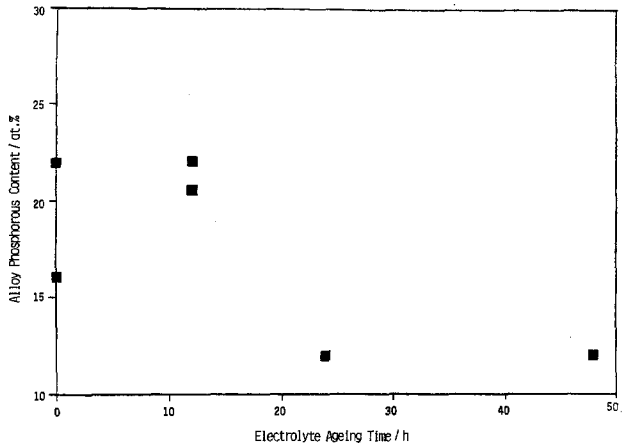

Fig. 6. Alloy phosphorous content against bath ageing time. Plating was carried out at 40° C and 20 A dm^{-2} using the bath shown in Table 1 (15 g dm^{-3} $Na_2H_2PO_2 \cdot H_2O$).

direct relationship to the composition of the deposits. The thicknesses of these coatings varied from 2 to 15 μm.

An applied current density of 25 A dm^{-2} resulted in 'matted' coatings. The phosphorous content varied from 5 to 17 at % (see Fig. 5), with efficiencies comparable to those obtained at 20 A dm^{-2}. There is little compositional effect due to an increase in current density from 20 to 25 A dm^{-2}. The compositional difference was much more pronounced when the current density was increased from 15 to 20 A dm^{-2}.

A metallic coating could not be obtained at a current density of 30 A dm^{-2}. A deep greenish film, probably a chromium hydroxide precipitate, resulted which could be easily scraped off the substrate.

The data show that for a given bath composition, an increase in the current density generally results in a corresponding decrease in the P content (Fig. 5). This is explained as follows. As compared to Cr, P deposition takes place (on thermodynamic basis) at more positive potentials hence an increase in the current density would result in higher rates of Cr(III) reduction. The influence of varying the current density from 20 to 25 A dm^{-2} on alloy composition is not as distinguishable as it is by changing the current from 15

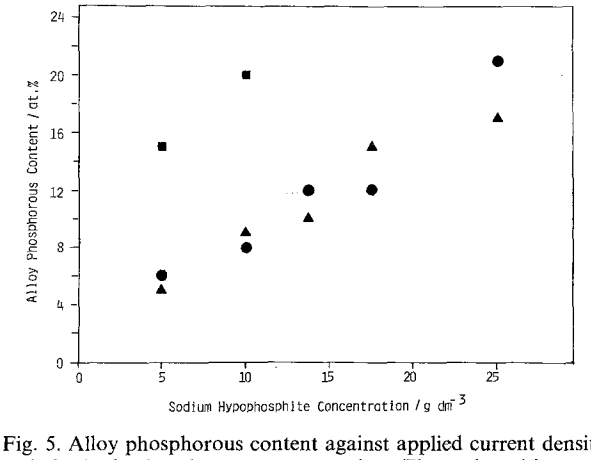

Fig. 5. Alloy phosphorous content against applied current density and the bath phosphorous concentration. Electrodeposition was carried out from the plating bath shown in Table 1 at 30° C. C.d.: (■) 15, (●) 20 and (▲) 25 A dm^{-2}.

to 20–25 A dm^{-2}. We speculate that at high current densities, in addition to phosphorous deposition being mass transport limited, the chromium deposition is also partially mass transport controlled. Thus, the influence of increasing the current density on the alloy composition at high rates (20–25 A dm^{-2}) is small. We would also like to draw the attention of the reader to the method of analysis used for the determination of elemental composition (i.e. EDX) which is not very sensitive to small difference in composition.

3.5. *Effect of electrolyte ageing and additives*

The influence of electrolyte ageing on the deposit composition was also investigated. Plating was carried out at 40° C and 20 A dm^{-2} using the bath composition shown in Table 1 (15 g dm^{-3} NaH_2PO_2). The data show that freshly prepared baths have higher metalloid content than the ones that have been aged for 10 h and more (Fig. 6). For example, about 22 at % phosphorous was observed in a deposit prepared from an unaged bath as compared to about 11 at % phosphorous content in a deposit prepared from the bath that was allowed to age for 24 h. The influence of various additives on deposition characteristics was also studied and the results obtained are shown in Table 2. When ammonium sulphate was not added to the plating bath, the phosphorous content of the deposit was observed to increase while the coulometric efficiency decreased sharply. The cell voltage needed to maintain the desired current density (20 A dm^{-2}) was found to increase sharply to $\simeq$ 14–15 V as compared to about 9 V needed for deposition when bath shown in Table 1 was used. Thus, in addition to acting as a complexant possibly in the high pH of the diffusion layer, we also believe that $(NH_4)_2SO_4$ enhances the bath conductivity significantly. Again, when NH_4Br was not present in the bath, the coulometric efficiency declined sharply. In the absence of $(NH_4)_2SO_4$ and NH_4Br, the deposits obtained were nonuniform and of poor quality.

The alloy deposition rate as a function of the time of deposition was also determined. Experiments were conducted at 35° C and 20 A dm^{-2} using the plating

Table 2. The influence of various additives on deposition characteristics. Experiments carried out at 40° C and 20 A dm^{-2}. 15 g dm^{-3} of $Na_2H_2PO_2$ used in the plating bath.

Bath	*Cell voltage*/V	*Phosphorous content*/at %	*Coulometric efficiency*/%	*Deposit quality*†
1. As in Table 1	≃9	16.02; 23.15; 22.37	7.12; 6.79; 3.72	homogeneous, bright
2. No $(HN_4)_2SO_4$	≃14–15	26.20	1.45	not uniform
3. No NH_4Br*	≃9–10	24.00	1.25	not uniform; "streaky" surface

* Otherwise the bath composition as in Table 1
† Visual observation

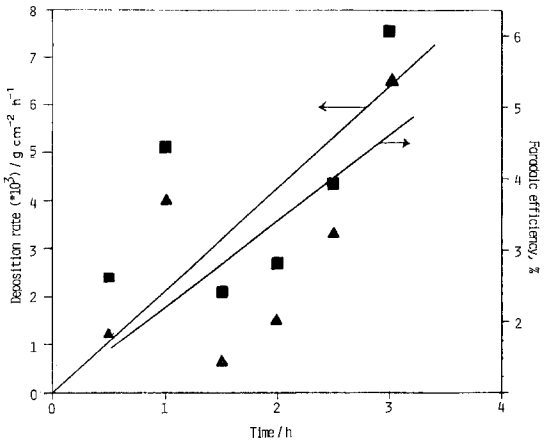

Fig. 7. Alloy deposition rate against plating time. (■) Deposition rate; (▲) efficiency. Plating was carried out at 35° C and 20 A dm^{-2} using the bath shown in Table 1 (15 g dm^{-3} $Na_2H_2PO_2 \cdot H_2O$).

bath shown in Table 1 (15 g dm^{-3} NaH_2PO_2). The deposition rate expressed in g cm^{-2} h^{-1} is observed to increase with the time of reaction (Fig. 7). It is also interesting to note that although the coulometric efficiencies are low, they also increase with the time of reaction. The data suggest that the Cr–P alloy acts as a better substrate than the Cu discs used for alloy deposition in our experiments.

3.6. *Structure of electrodeposits*

All of the alloys that were analysed by XRD were found to be amorphous. In a related study, DeNeve [23], using transmission electron microscopy, has shown the deposits to consist entirely of an amorphous phase. A more detailed analysis of the physical properties of the electrodeposits will be reported at a later date. The diffraction pattern of an alloy prepared at 25 A dm^{-2} and 30° C (5 at % P) is given in Fig. 8. The broad Gaussian peak at an angle of approximately 43° indicates the alloy is amorphous. The chromium–carbon alloy was also found amorphous by XRD. The diffraction pattern of a conventional chromium electrode is also shown in Fig. 8. Bright chromium plate is strongly grain-oriented, with the (1 1 1) plane parallel to the basic metal (2 2 4). This preferred orientation was observed to persist after recrystallization (2 2 2).

3.7. *Cyclic voltammetry studies*

Figure 9 is a cyclic voltammogram for the deposition of the chromium alloy from the chromium–phosphorus–carbon plating bath utilized for alloy deposition, on a glassy carbon microelectrode. The potential scan in the negative direction resulted in a

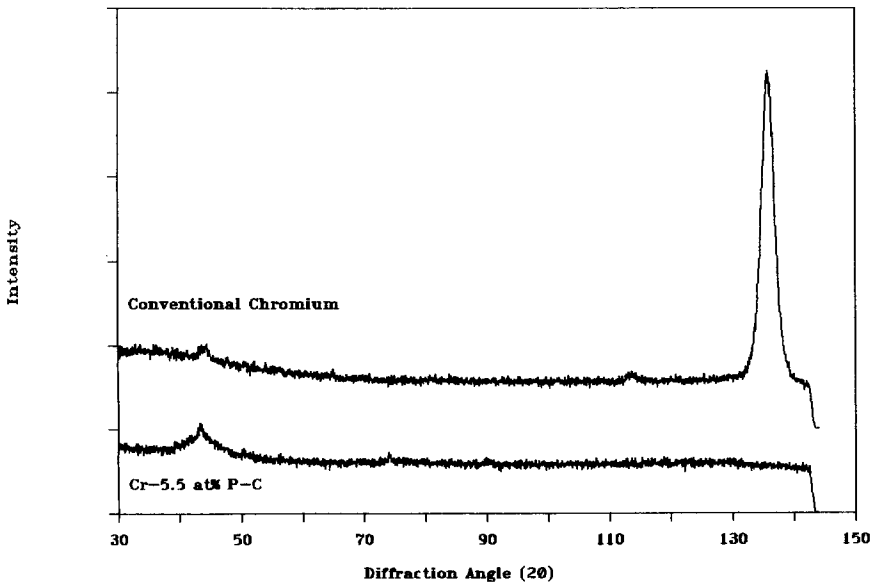

Fig. 8. X-ray diffraction pattern for Cr–5 at % P–C alloy prepared at 25 A dm^{-2} and 30° C.

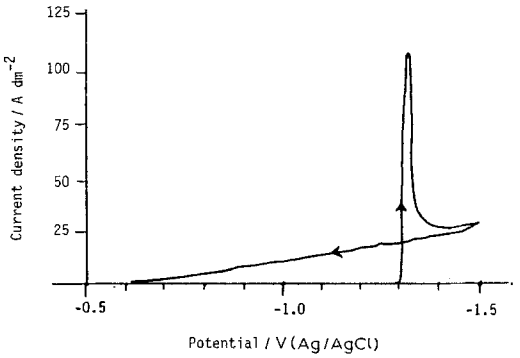

Fig. 9. Cyclic voltammetry on glassy carbon electrode at 100 mV s^{-1}. Bath composition as in Table 1 (15 g dm^{-3} $Na_2H_2PO_2 \cdot H_2O$).

pronounced sharp peak at -1.31 V against Ag/AgCl. This peak corresponds to the potential necessary for nucleation of the chromium alloy on the glassy carbon surface. The peak current corresponding to this potential is 9.2×10^{-2} A with a scan rate of 100 mV s^{-1}. The standard redox potential for the Cr(III)/Cr reaction is -1.03 V against Ag/AgCl. When the electrode was scanned to -1.5 V against Ag/AgCl, the resulting current density was found to be approximately 25 A dm^{-2}. This is in the current density range used for alloy deposition on the copper substrate in this work.

On the reverse scan in the positive direction, the current remains cathodic, but decreases as the applied potential becomes more positive. Very small anodic currents, on the order of 10^{-5} A, were measured at potentials more positive than -0.15 V against Ag/AgCl, but no pronounced peaks corresponding to the oxidation of the alloy were apparent, even up to a potential of 0 V against Ag/AgCl. This indicates that the electrodeposited alloy is resistant to stripping. This behaviour is similar to that observed by Howarth and Pletcher [24] for Cr(III) deposition.

Cyclic voltammetry was performed with the plating bath used in this study, without the phosphorus and carbon-containing components. With a scan rate of 100 mV s^{-1}, the nucleation potential occurred at -1.32 V against Ag/AgCl, with a peak current of 4.5×10^{-2} A, which is half of that obtained when the chromium complexant was present. Although in our experiments, there was not significant shift in the deposition potential due to the presence of formic acid and sodium hypophosphite, the high deposition currents observed in solutions containing formic acid lead us to speculate that it may act as a ligand for Cr(III). However, it is also known that ideally the ligand should also catalyse the metal ion reduction and several sulphur ligands which adsorb on the surface of metals, which are known to reduce the overpotential of Cr(III) reduction [24–27].

4. Conclusions

A new bath for electrodeposition of amorphous Cr–P thin films has been developed and tested. The alloys were electroplated from a trivalent chromium salt, with sodium hypophosphite as the phosphorous source and formic acid as the chromium complexant and the source of metalloid. The alloys were found to be amorphous by XRD spectroscopy. The phosphorous content of the alloys could be controlled by varying the sodium hypophosphite concentration in the bath, current density, and temperature.

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