The Electrodeposition and Properties of Amorphous Chromium Films Prepared from Chromic Acid Solutions

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ABSTRACT

The addition of organic compounds containing a —CHO or —COOH group such as formamide, formaldehyde, glyoxal or formic acid to a chromium electroplating bath results in a chromium deposit which has greatly improved properties compared to conventional chromium deposits. These layers have fewer defects, and the as-deposited, amorphous layers have a Vicker's hardness of about 1000, which is comparable to that of conventional chromium plating deposits. With annealing in air, the hardness goes through a maximum of about 1700 at 500°-600°C, while the hardness of a conventional plating decreases monotonically from 1000 to 400, with annealing from 200° to 800°C. X-ray diffraction and differential thermal analysis show that annealing up to about 600°C causes formation and growth of chromium crystallites and that chromium carbides form above this temperature. These layers are also more resistive to corrosion by hydrochloric acid than conventional chromium layers.

Chromium plating has been widely used in the manufacture of machines and instruments in the automobile and other industries. Due to the hardness of chrome plates (Hv > 800), the wear resistance of machine parts is greatly increased by chromium plating. Chromic acid solutions containing a sulfate catalyst for chromium plating have been developed and described by Sargent (1) and Fink (2). However, the chromium plate layers formed in these baths have many defects which may be described as pinhole and crack defects. Moreover, the hardness of the deposits decreases with increasing temperature over the range of 20° to 400°C.

Recently, a trivalent chromium bath (3) has been developed for commercial applications, but it is used only for decorative chromium plating because thick chromium layers cannot be formed in this type of bath. According to x-ray diffraction measurements (4), these chromium deposits show an amorphous structure. Amorphous chromium deposits have been discussed by Furuya, Misaki, and Tanabe (5) and Morikawa and Eguchi (6). They obtained amorphous chromium deposits from chromic acid solutions containing trivalent chromium ions and large quantities of organic compounds, but they also found it difficult to deposit thick chromium layers in these baths. Kasaaian and Dash (7) have reported that the addition of methanol or formic acid increases the current efficiency of chromium deposition from sulfate-catalyzed chromic acid baths, but they did not characterize the structure or properties of these deposits.

In previous investigations of chromium deposition, Hoshino (4) found that the addition of certain organic compounds to the chromic acid solution greatly influences the properties of chromium deposits. A trial-and-error search for effective organic additives for chromium deposition has shown that organic compounds having a —CHO or —COOH group, such as formamide, formaldehyde, glyoxal, or formic acid are most effective in modifying the properties of the deposit. Using these additives, it is possible to prepare electrodeposited amorphous chromium which has a bright surface and no pinhole or crack defects. This paper describes a method for the deposition of thick amorphous chromium layers and the properties of these layers before and after heat-treatment. Although formic acid has been added to similar baths in previous studies, the method described in this paper is new in that it produces chromium films which are amorphous and bright and have desirable mechanical properties. In this paper, it is referred to as the amorphous bright chromium deposition (ABCD) method.

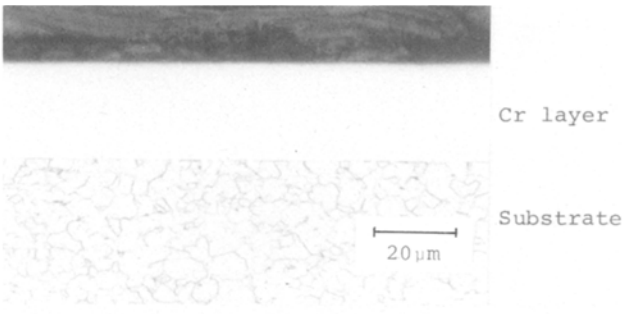
Experimental

The electrolytes used for the electrodeposition of chromium were prepared with reagent grade chromic acid, sulfuric acid, and formic acid as the additive. Conventional chromium layers were electrodeposited from a solution containing 250 g/l of chromic acid and 2.5 g/l of sulfuric acid at a temperature of 50°C and a current density of 40 A/dm^2 for 30 min. In the ABCD method, the chromium was electrodeposited from a solution containing 100 g/l of chromic acid, 5 g/l of sulfuric acid, and 20 ml/l of an 85% solution of formic acid at a temperature of 30°C and a current density of 40 A/dm^2 for 30 min. The chromium layers were electrodeposited on foils of mild steel which were 0.2 mm thick. A PVC jig was used to hold a sample and restrict deposition to a 20 × 10 mm region on the foil. These conditions gave films which were typically 20 μm thick.

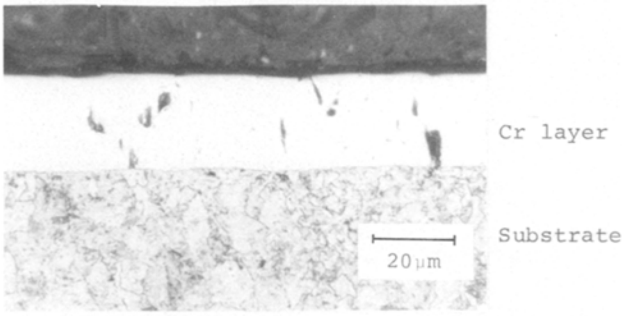
Several techniques were used to characterize the properties of the chromium layers. Electron microscopy, electron diffraction, and x-ray diffraction were used for structural determination. Differential thermal analysis was performed using a heating rate of 10°C/min and a chromium deposit which had been heated to 900°C as a counter material. The hardnesses of the surfaces of the layers were determined using a conventional micro-Vickers hardness tester employing a standard load of 100 gf. Some of the samples were polished with diamond paste after the heat-treatment but before measurement of the hardness. The carbon contents of the chromium deposits were measured using an analytical system constructed by Leco Corporation. This technique is based on measuring the amount of CO_2 produced after heating a sample in oxygen at 1200°C in a high frequency induction furnace. For the differential thermal analysis and electron diffraction experiments, unsupported chromium layers were required. These were prepared by depositing the chromium on copper foils which were 50 μm thick. The copper was then removed by soaking in a 30% ammonium persulfate solution at room temperature.

Results and Discussion

Electrodeposition of amorphous chromium.—Figure 1 shows typical electron micrographs of cross sections of electrodeposited chromium obtained by the conventional



(a) Amorphous chromium deposit



(b) Conventional chromium deposit

Fig. 1. Electron micrographs of the cross sections of amorphous chromium deposits formed using the (a) ABCD method and (b) conventional methods.

method and the ABCD method described in this paper. It is clear from this figure that the film made with the ABCD method does not contain the pinhole and crack defects which are seen in the film made by the conventional method. An electron diffraction pattern of a chromium deposit prepared using the ABCD method is shown in Fig. 2. The broad and diffuse pattern indicates that the structure is amorphous.

Chromium deposits produced by the new method have a mirror-like surface. It is interesting that uniformly bright surfaces are obtained only when the weight ratio of chromic acid to sulfuric acid is between 5:1 and 40:1. This is quite different from the operation of commercial Sargent plating baths, which utilize a ratio of chromic acid to sulfuric acid within the range of 50:1 to 200:1. The ABCD method uses a sulfuric acid concentration which is typically twice as high as that for a conventional bath.

Figure 3 shows the variation of the current efficiency as a function of temperature, sulfuric acid concentration, chromium concentration, and current density. It was determined by measuring the total charge passed in the plating process and the weight of the deposited chromium. Current efficiency decreases with increasing concentrations of both chromic acid and sulfuric acid and temperature, but increases with current density up to about 80 A/dm². This behavior is similar to that of a conventional plating bath.

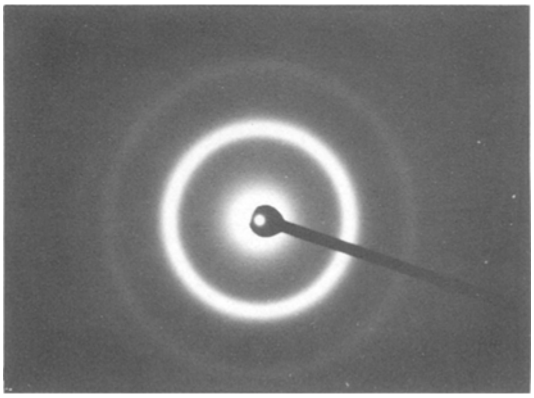


Fig. 2. An electron diffraction pattern of an unsupported chromium deposit produced by the ABCD method. The unannealed sample shows an amorphous structure.

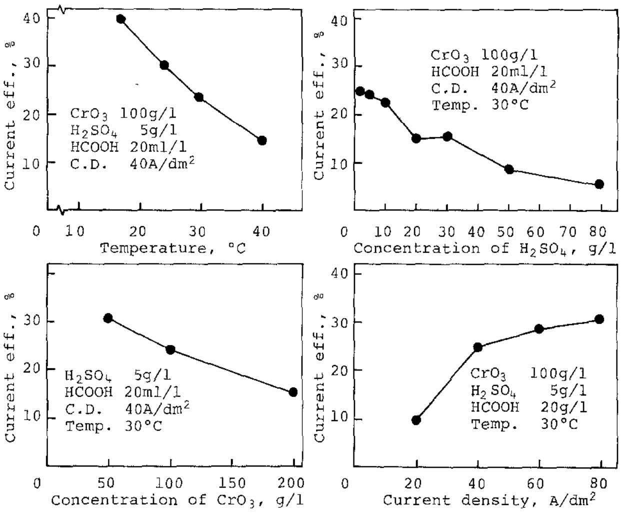


Fig. 3. Current efficiency of chromium deposition as a function of temperature, sulfuric acid concentration, chromic acid concentration, and current density. Each point represents an average of two experimental values.

Bright deposits are obtained using the conventional method over a relatively narrow range of current densities, and this range decreases dramatically with temperatures below 50°C. However, the ABCD method yields bright deposits over a broad range of current densities even at 30°C. Even though the current efficiency decreases with increasing temperature, the deposits were prepared at 30°C, whereas the conventional deposits were prepared at 50°C.

The addition of formic acid to the plating solution causes a decomposition reaction which produces trivalent chromium ions by reduction of the chromic acid. It can be represented by

$$2H_2Cr_3O_{10} + 9HCOOH + 18H^+ \rightarrow 6Cr^{3+} + 9CO_2 + 20\,H_2O \quad [1]$$

Figure 4 shows the concentration of trivalent chromium ions in the bath due to reaction [1] as a function of time for varying chromic acid concentration, sulfuric acid concentration, and temperature. A double-beam UV spectrophotometer manufactured by Hitachi Company, Limited, was used to measure the CrO_3 concentration by its absorption at 350 nm. From this, the Cr^{+3} concentration was calculated. The presence of other ions was found to have no effect on this measurement.

During electroplating, formic acid in the bath is oxidized chemically by chromic acid and anodically on the Pb anode. However, small amounts of formic acid are incorporated into the film, as discussed in a surface study (8) of films prepared by the ABCD method. The oxidation of formic acid increases the concentration of Cr^{+3} and decreases the formic acid concentration. Therefore, the chromium deposits described in this study were prepared within 90 min after adding formic acid to the chromic acid solution which contained 5 g/l of sulfuric acid. In order to prepare smooth and amorphous deposits which are bright, it is necessary that the concentration of Cr^{+3} remain below 7% of the chromic acid concentration. A lower concentration of Cr^{+3} could be maintained by employing a membrane-devised cell for the oxidation of Cr^{+3}. Neither this nor the long-term stability of this type of bath has been considered in detail thus far.

Effect of heat-treatment on the chromium deposits.—Heating samples prepared by the ABCD method in vacuum or air has a dramatic effect on the hardnesses of the films. This is illustrated in Fig. 5 for samples annealed at 10^{-3} torr for 1h. The hardnesses of chromium films pre-

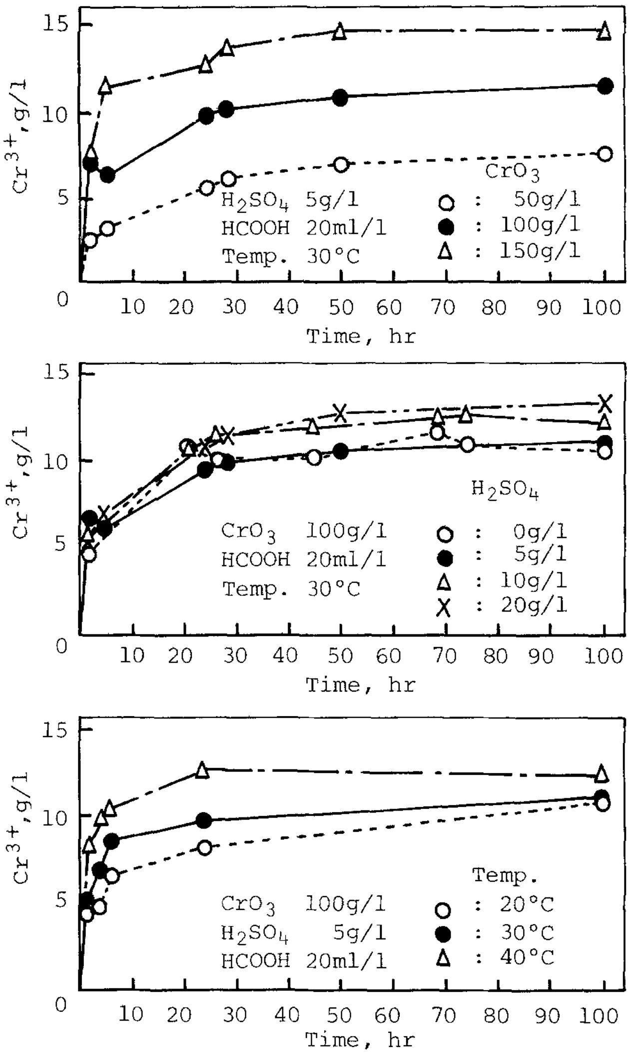


Fig. 4. Concentration of trivalent chromium ions as a function of time for varying chromic acid concentration, sulfuric acid concentration, and temperature.

pared in the conventional manner are also shown as a function of annealing temperature. As stated above, the hardnesses of the conventional samples monotonically decrease with annealing temperature. Also, the hardnesses decrease much more rapidly with heating at temperatures above 400°C. However, the chromium layers prepared by the ABCD method show a very different behavior. Their hardnesses nearly double by heating up to 600°C and then decrease almost to their initial value with heating at 800°C. Varying the trivalent Cr ion concentration up to 15 g/l has essentially no influence on the temperature dependence of the hardness. This same general type of behavior for amorphous chromium was also observed by Morikawa and Eguchi *et al.* (6).

Many processes occur during annealing, such as segregation of carbon and sulfur to the surface region, segregation of oxygen away from the surface region, and the formation of carbides and various chromium oxides (8, 9). Although the chemical compositions and elemental distributions of the films differ between films heated in air and films heated in vacuum, it is interesting that the hardness is only a function of the annealing temperature. Annealing the deposits for periods longer than 1h does not cause further changes in the hardness, but the time dependence of annealing on the hardness remains to be investigated.

In order to investigate the hardness behavior shown in Fig. 5, x-ray diffraction was used to examine chromium deposits which were annealed at different temperatures. The results are shown in Fig. 6. A deposit with no annealing shows a broad feature which corresponds to an amorphous structure. This is consistent with the interpretation of the electron diffraction pattern shown in Fig. 2. Annealing at 300°C causes the formation of a peak characteristic of metallic chromium. Three metallic chromium peaks dominate the spectra in the 400°-600°C range, and the broad feature, due to the amorphous structure, is gone. Formation of the metallic chromium structure from

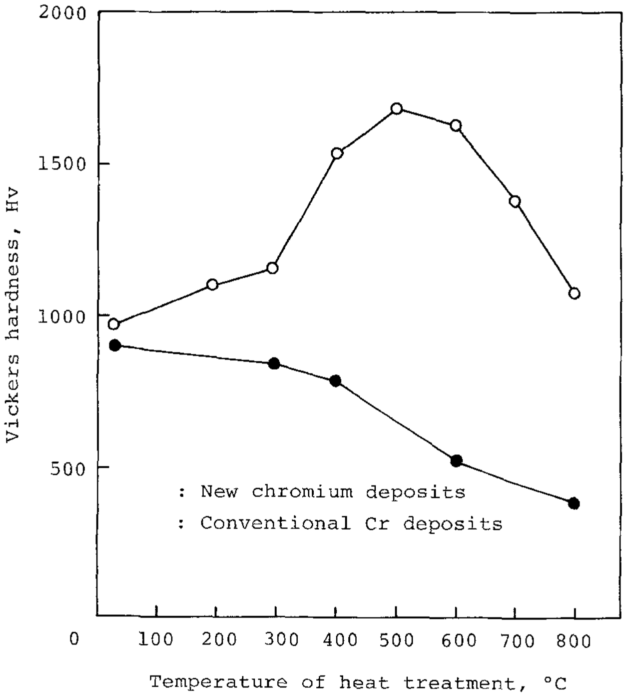


Fig. 5. Vickers hardness of chromium deposits formed by the conventional method and ABCD method as a function of annealing temperature.

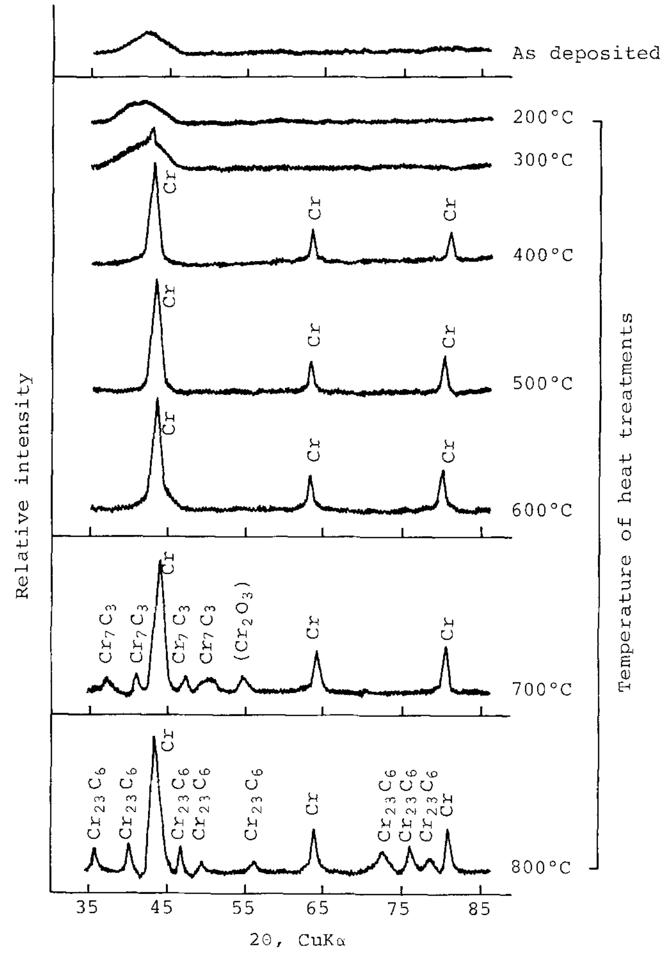


Fig. 6. Variation of x-ray diffraction patterns of chromium deposits formed by the ABCD method with annealing temperature.

an amorphous structure in the 300°-600°C temperature range corresponds to an increase in the Vickers hardness value from about 1100 to 1700. The hardness value increases greatly in the 300°-400°C range, while relatively small changes occur in the 400°-600°C range. This is also consistent with the x-ray diffraction studies in which a dramatic change is observed between 300° and 400°C but little change is observed between 400° and 600°C. Further structural changes occur in the 600°-700°C and the 700°-800°C ranges, which correspond to decreases in hardness from about 1700 to about 1100. Annealing at 700°C causes the appearance of diffraction peaks due to Cr_7C_3 and Cr_2O_3. This step results in a decrease of 300 in the hardness. X-ray diffraction shows that annealing at 800°C converts the Cr_7C_3 into $Cr_{23}C_6$. Also, the peak due to Cr_2O_3 is no longer present. These changes correspond to a further reduction in hardness of about 300.

The carbon content of the deposit as a function of formic acid concentration, temperature, and current density is shown in Fig. 7. It generally lies between 2 and 4 weight percent (w/o). The codeposition of organic compounds and metals has been used in other applications. For example, saccharin is often codeposited with nickel as a brightener. Generally, the role of the organic additive is to limit the growth of metal crystallites during the electrodeposition. The additive adsorbs on the surfaces of the small crystallites, thus inhibiting growth and resulting in a nearly amorphous layer. It is believed that some of the formic acid behaves in this manner in this application.

Differential thermal analysis provides another means of studying the transformations caused by annealing. The sample temperature was increased at a rate of 10°C/min to a maximum of 900°C, and its weight remained constant between 300° and 750°C. The resulting DTA spectrum is shown in Fig. 8. Two distinct peaks are seen in this spectrum with maxima at 400° and 590°C. One possible interpretation of this spectrum is that the low temperature peak is due to the growth of crystallites with the structure of bulk chromium metal. This gives the peak its broad structure over the 400° to 600°C temperature range. This is also the same range over which a tremendous increase in hardness is observed. The second peak is quite sharp and could be due to a chemical reaction such as the formation of chromium carbide. This temperature marks the onset of the decrease in hardness and the appearance of chromium carbides in the 700° and 800°C x-ray diffraction patterns. The carbide most likely does not appear in the 600°C x-ray diffraction pattern because it has not agglomerated sufficiently for detection by x-ray diffraction. At about 800°C, another rather structureless feature is seen which may correspond to the formation of $Cr_{23}C_6$ by the reactions

$$23Cr_7C_3 \rightarrow 7Cr_{23}C_6 + 27C \tag{2}$$

$$6C + 23Cr \rightarrow Cr_{23}C_6 \tag{3}$$

The behavior and chemical nature of the carbon in these layers have been examined using Auger electron spectroscopy (AES), electron spectroscopy for chemical analysis (ESCA), and other surface techniques (8, 9).

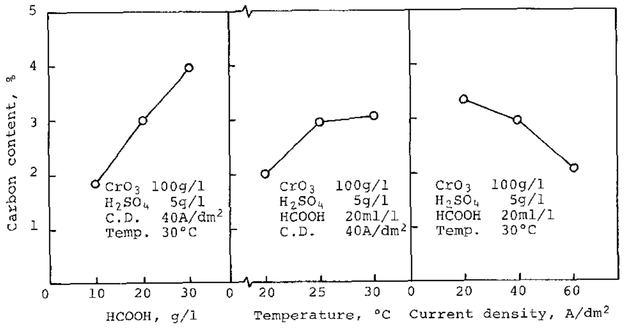


Fig. 7. Variations of carbon content of chromium deposits with electrodeposition variables: formic acid concentration, temperature, and current density.

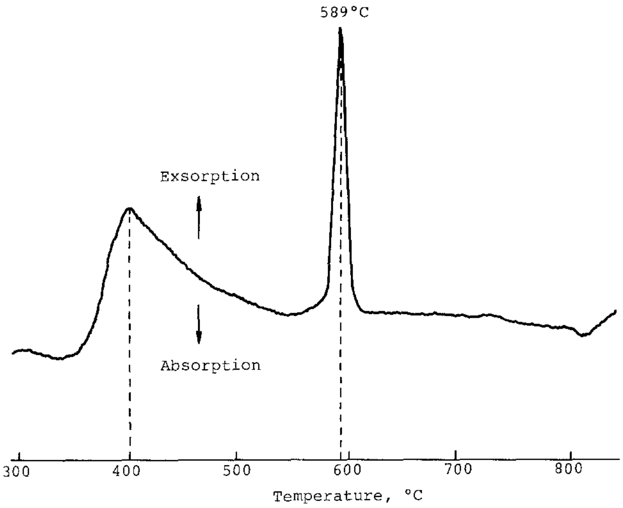


Fig. 8. Differential thermal analysis spectrum of a chromium deposit

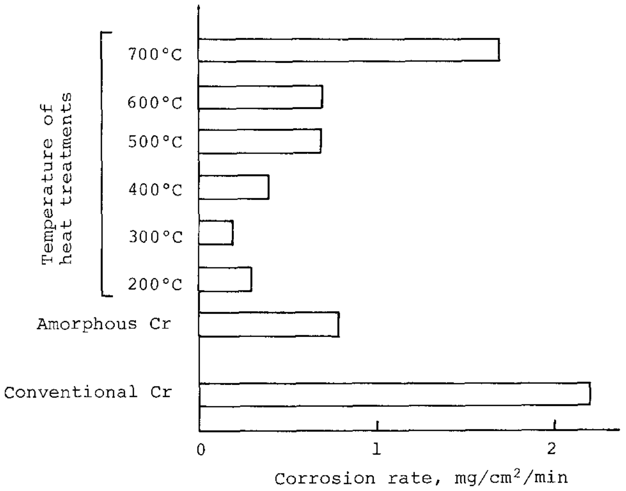


Fig. 9. A comparison of the corrosion rates in an HCl (1:1) solution of chromium deposits prepared by the conventional method and by the ABCD method (annealed at various temperatures).

Corrosion resistance of chromium deposits.—It is generally believed that amorphous metals have better corrosion resistance than polycrystalline metals. However, due to the formation of a passivation film, conventional chromium deposits show excellent corrosion resistance, except toward hydrochloric acid. Figure 9 shows the dissolution rates of chromium deposits with exposure to an HCl (1:1) solution at 30°C. The deposits made by the ABCD method were annealed at the various temperatures shown. Amorphous chromium, which has not been annealed, exhibits a corrosion rate which is 1/3 that of conventional chromium deposits. With annealing, the corrosion rate decreases in temperatures up to 300°C and increase in temperatures from 300° to 700°C. Even with annealing at 700°C, the corrosion rate is lower than that of conventional chromium deposits.

The good corrosion resistance of the unannealed deposit is most likely due to its amorphous structure. It is possible that annealing up to 300°C oxidizes the surface, causes carbon segregation in the grain boundaries, or causes the formation of chromium carbide which inhibits corrosion further. However, the growth of chromium metal crystals or possibly chromium carbide crystals at higher temperatures is responsible for an increase in the corrosion rate. After the corrosion test, a black paste-like substance was observed on the chromium deposits. This suggests that corrosion of annealed deposits proceeds at metallic regions leaving a carbon or carbide deposit at the surface, but the composition of this paste has not been determined yet. No such deposit is observed on conventional deposits. Another point of interest is that chromium deposits prepared by the ABCD method dissolve with a potential of about −0.45V *vs.* SCE in a HCl (1:1) solution whereas conventional Cr deposits dissolve with a potential of about −0.75V *vs.* SCE (4). This suggests that chromium deposits prepared by the ABCD method form stronger passivation films on the surface than conventional chromium deposits.

Conclusion

A method is described for the electrodeposition of amorphous chromium layers from a plating bath containing chromic acid, sulfuric acid, and formic acid as an additive. These layers have a very low defect concentration compared to conventional chromium deposits. They are quite hard, exhibiting hardness values of about 950 as-deposited and about 1700 after annealing at 600°C. Annealing above 600°C causes a decrease in hardness to about 1000. These deposits incorporate approximately 2-4 w/o carbon. It is clear from the x-ray diffraction studies that chromium carbides appear above 600°C, but the behavior and nature of the carbon in these layers are still under investigation. These deposits also exhibit much better corrosion resistance toward hydrochloric acid solutions than conventional chromium deposits.

Acknowledgment

The authors acknowledge NSF grants CHE-8309445 and CPE-8210776 for financial support of this research.

Manuscript submitted Aug. 27, 1985; revised manuscript received Dec. 30, 1985.

The University of Florida assisted in meeting the publication costs of this article.

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The Structure of Electroless Cobalt Alloy Films for Perpendicular Magnetic Recording Media

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ABSTRACT

Two types of electroless Co alloy films, $Co_{40.1}$-$Ni_{44.2}$-$Re_{6.0}$-$P_{9.7}$ and $Co_{23.6}$-$Ni_{58.5}$-$Re_{5.3}$-$Mn_{0.2}$-$P_{12.4}$, were prepared for perpendicular magnetic recording media. The correlation between their structure and magnetic properties was investigated and discussed as a function of film thickness. The magnetic properties of these two types of films showed different patterns of dependence with respect to the film thickness. The Co-Ni-Re-P alloy film gave a higher $H_c(\perp)$ (perpendicular coercivity) in regions where it was very thin; on the other hand, the Co-Ni-Re-Mn-P alloy film displayed a lower $H_c(\perp)$ at the initial film thickness. The composition was observed with AES measurements to be nearly independent of film thickness. The clear columnar structure of both types of films was confirmed by scanning electron microscopy (SEM) and especially by transmission electron microscopy (TEM) observations. Only the reflection high energy electron diffraction (RHEED) patterns for both types of film clearly showed different dependence patterns with respect to the film thickness. The Co-Ni-Re-P film displayed a very highly c-axis oriented structure even at the initial thin film stage. On the other hand, the Co-Ni-Re-Mn-P film showed a dependence of the degree of c-axis orientation on the film thickness, which increased with film thickness. The differences in magnetic properties as a function of thickness were assumed to be due to the degrees of c-axis orientation and change in magnetic domain structure.

In longitudinal recording, the recording medium thickness is a very important factor in the determination of recording density (1). It is impossible to avoid decreases in the medium thickness if the recording density is to be increased. In perpendicular recording, a reduction in medium thickness may theoretically not be needed to improve recording density (2). Practically, however, in the case of single pole head with a composite anisotropy medium (3), it is necessary to reduce medium thickness because a strong interaction must occur between the single pole head and the back layer of the composite anisotropy film to allow ideal perpendicular magnetic recording conditions (4).

The authors earlier reported electroless cobalt alloy films for perpendicular magnetic recording media and also discussed their read/write characteristics (5-10). In these research works, it was found that there were two kinds of electroless magnetic films whose magnetic properties displayed quite different degrees of thickness dependence (8, 10). Typical data of perpendicular coercivity, $H_c(\perp)$, already discussed in the previous paper (10), are shown in Fig. 1 as a function of the film thickness. In the above paper (10), the thickness dependence of magnetic properties was discussed from the viewpoint of perpendicular magnetic recording medium applications. The present paper describes further investigations of the correlation between magnetic properties and crystal structure as a function of film thickness and discusses

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