Answers to I.Q. Quiz #406

1. NORM**A**L
2. BI**PO**LAR
3. NANO**TE**C**H**NOLOGY
4. MIL**SP**ECS
5. C**H**ROMIUM

FINAL ANSWER: PHOSPHATE

ABQC's operation in Milwaukee. ABQC has also purchased specific production equipment and tooling used in the Northern Plating operation.

ABQC's 250,000 ft^2 facility makes it one of the largest metal finishing operations in North America. The company, which was established in the 1920s, provides a variety of plating services. Its quality system has been ISO-registered for the past nine years.

Since 1945, Northern Plating has provided zinc, cadmium, copper, nickel and chromium plating. It also provides black oxide, cleaning and decorative finishing services to customers in many industries.

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- Leading edge electroless nickel/immersion gold process is now available lead-free!
- EPL + EZ-Plate = big pwb savings!
- Uyemura introduces first germicidal metallic finish.
- Lead/cad-free electroless nickel meets "October 31 mandate".
- Rhodium TD – the ultimate diamond reflective
- Nickel contact alternative finish is major development for apparel makers.

Uyemura USA has launched a new Web site that features new developments and options for metal finishers.

❑ Imagineering Finishing Technologies (IFT), South Bend, IN, has acquired the assets of Commercial Plating, an established metal finisher based in Indianapolis, IN.

IFT serves customers internationally in the aerospace, automotive, heavy equipment, and military industries.

IFT is accredited for QS-9000 automotive, ISO 9001:2000, AS9100 and the newest international Nadcap accreditations for aerospace and defense. Its processing plant is also accredited for ISO 14001 environmental management program.

❑ Uyemura USA, Southington, CT, has launched a new Web site that covers new developments and options for general metal finishing and seven specific industries. The industries include printed circuit, automotive, apparel, ceramic, jewelry, medical device and connectors.

The site describes new electroless nickel/immersion gold processes, as well as the world's first germicidal metallic finish for use in medical devices, medical and restaurant furnishings and other applications. The site also covers lead-free/cad-free electroless nickel option that meets requirements for automakers.

In Memoriam

AESF was saddened to learn of the recent death of Shirley R. Fotheringham of Tonawanda, NY. She is the wife of past AESF President and long-time National Treasurer Charles Fotheringham, a member of the AESF Buffalo Branch.

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Research Program Objective— *"To arrange for and encourage the development of information in harmony with the objectives of the Society, and to disseminate this knowledge."*

In 1919, Dr. William Blum asked the Society to help fund research efforts of the National Bureau of Standards. This marked the beginning of the AESF Research Program, which expanded its support in 1944 to include such other facilities as universities and colleges, industrial firms, and independent research centers and labs. Please help provide the funding to keep our industry moving forward. Your support is appreciated.

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Chemical Oxidation of Aluminum in Chromic Acid Solutions

by Stojan S. Djokić[*]

Chemical oxidation of aluminum and the formation of thin oxide films on its surface in phosphoric and chromic acid solutions was investigated. The results show that the chemical oxidation of aluminum in chromic acid solutions is a process analogous to the displacement type of reactions. Films formed on the surface of aluminum metal represent a mixture of oxides such as Al_2O_3, Cr_2O_3 and P_2O_5. Chemical oxidation of aluminum in chromic acid solutions and properties of thin surface films depend on the concentration of both H_3PO_4 and CrO_3.

The formation of thin layers of aluminum oxide (alumina) on the surface of aluminum metal significantly improves its surface properties.[1] Alumina is formed as an amorphous film [2 to 3 μm thick (79 to 188 μ-in.)][2] upon exposure of aluminum metal to the atmosphere. Formation of crystalline oxide films is observed when the oxidation is carried out at temperatures above 400°C (752°F), or by anodic oxidation.[3] The oxidation of metals by thermochemical treatment is thoroughly presented in the literature.[4] Similarly, anodizing (anodic oxidation) of aluminum is a well established process and is used for protection of aluminum components from corrosion and mechanical damage.[5] By contrast, relatively little information is available on chemical oxidation of aluminum in aqueous solutions.

Immersion of aluminum in chromic acid solutions has been used for the inhibition of corrosion for a relatively long time.[6] Under these conditions aluminum metal is oxidized, the chromate ions are reduced and oxidation/reduction products in the form of a film are deposited on the surface. Within the pH range of 1.5 to 3.5 the main cathodic reaction is hydrogen evolution.

In order to enhance a desirable hardness, corrosion and abrasion resistance, a process to improve the chemical and physical properties of oxide films on the surface of aluminum was developed.[7] This process consisted of two steps. In the first, aluminum was coated with metal oxides or oxyhydroxides either by electrolysis or dipping in solutions containing molybdenum[8] or chromium[7] species. In the second step, aluminum samples were anodically oxidized in 10% H_2SO_4 solution at 15°C (59°F) for 30 min at a constant current density of 3.0 A/dm^2 (27.9 A/ft^2).

In order to form thin composite films on the surface, aluminum samples were treated with the solution containing 0.1 mol/L CrO_3, 0.12 mol/L NaF and 0.49 mol/L H_3PO_4 at pH 1.8, in the temperature range from 30 to 60°C (86 to 140°F) for 2 to 3 min.[5,7] Aluminum samples with a so-called "chromate film" on the surface were then anodized in 10% H_2SO_4 solution as described above. Chromate-fluoride coatings, which were produced by a simple immersion of aluminum samples in chromate-fluoride solutions, exhibited the best properties for corrosion-resistance applications in the radio industry, but their appearance was poor.[9] An addition of phosphoric acid to the above solution led to the precipitation of "chromate coatings" with excellent resistance to finger printing, fair corrosion resistance and other properties important for the use in the electronics industry.[9] However, details about the effect of the solution composition on the formation of "chromate" coatings, as well as the structure and composition of these coatings, have not been found in the literature.

The aim of this work was to investigate the chemical oxidation of aluminum and the formation of oxide films at its surface in chromic acid solutions.

Nuts & Bolts: What This Paper Means to You

Surprisingly little work has been done in understanding what it takes to develop quality chromate films on aluminum by chemical oxidation. This work investigates the subject, shedding light on the factors contributing to corrosion resistance and film properties.

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Experimental

Aluminum samples of 99.99% purity were obtained from a commercial supplier. Specimens with dimensions 20 × 40 × 1 mm (0.79 × 1.57 × 0.04 in.) were used to investigate the oxidation of aluminum in chromate solutions. Aluminum samples of known weight were simply immersed in solution for a certain period of time, and then rinsed carefully with distilled water, dried and weighed. After the oxidation was completed, solutions were analyzed for chromium and aluminum by atomic absorption spectroscopy (AAS). Oxidation of the aluminum samples was carried out using a solution with the following composition: 45 g/L (6.0 oz/gal) H_3PO_4, 4.0 g/L (0.53 oz/gal) NaF, 1.0 g/L (0.13 oz/gal) HF and 6.0 g/L (0.80 oz/gal) CrO_3. The effect of H_3PO_4 on the oxidation of aluminum was determined by increasing the phosphoric acid concentration from 0 to 60 g/L (0 to 8.0 oz/gal). Similarly, the effect of CrO_3 on the oxidation process was investigated by increasing the chromium (VI) oxide concentration from 0 to 10 g/L (0 to 1.33 oz/gal). When the effects of H_3PO_4 and CrO_3 were investigated, concentrations of the other solution components were kept constant. All experiments were performed in solutions stirred with a magnetic stirrer at room temperature (22°C ± 2C°; 71.6°F ± 3.6F°).

Thin oxide films formed at the aluminum surfaces after immersion in chromic acid solutions were analyzed by x-ray diffraction (XRD), x-ray fluorescence (XRF), electron dispersive spectroscopy (EDS) and scanning electron microscopy (SEM). In order to form thick green films on the surface of aluminum, samples were exposed to chromic acid solution for 1 hr. Green films, formed on the surface of the aluminum substrate, were rinsed with water, ethanol and then dried in a laboratory oven at 100°C (212°F) for 1 hr. After drying, the films were easily separated from the aluminum foil. The resultant green powdery material was analyzed by XRF and XRD methods.

Results and discussion

Immersion of aluminum metal into a solution containing phosphoric acid and Cr(VI), led to a reduction of $Cr_2O_7^{-2}$ and oxidation of aluminum. As a consequence, oxide films containing Al_2O_3 and Cr_2O_3 were formed on the metal surface.[9] This process can be represented by the following equation:

$$4Al + 8H^+ + Cr_2O_7^{-2} \rightarrow Al_2O_3 + 2Al^{+3} + Cr_2O_3 + 3H_2 + H_2O \quad (1)$$

The process described by equation (1) is spontaneous at room temperature, since the Gibbs free energy for the reaction is negative (-1751.378 kJ/mol; 1660 Btu/mol). In order to calculate the Gibbs free energy, all thermodynamic data were taken from the literature.[10]

Immersion of aluminum into the solutions under study, according to equation (1), led to the occurrence of the following processes:

1. Aluminum oxidation,
2. Chromium reduction and
3. Hydrogen evolution.

As a result, oxides such as Al_2O_3 and Cr_2O_3 were produced and precipitated on the surface of the aluminum metal.

Increasing the immersion time in the chromic acid solutions, resulted in a weight gain, μm (or change of mass). Figure 1 shows the dependence of μm on time. μm was calculated as:

$$\mu m = m_{in} - m_f \quad (2)$$

where m_{in} is the initial weight of the aluminum samples and m_f is the weight of the aluminum specimens after the immersion process. Figure 1 clearly shows that an increase in the immersion time led to an increase in weight of the aluminum samples. According to equation (1), m_f can be expressed as:

$$m_f = m'_{Al} + m_{Al2O3} + m_{Cr2O3} \quad (3)$$

where m'_{Al} is the weight of aluminum metal that was not involved in the reaction, m_{Al2O3} is the weight of deposited Al_2O_3 and m_{Cr2O3} is the weight of deposited Cr_2O_3. The increase in weight is attributed to an increase in the amount of oxides precipitated on the metal surface.

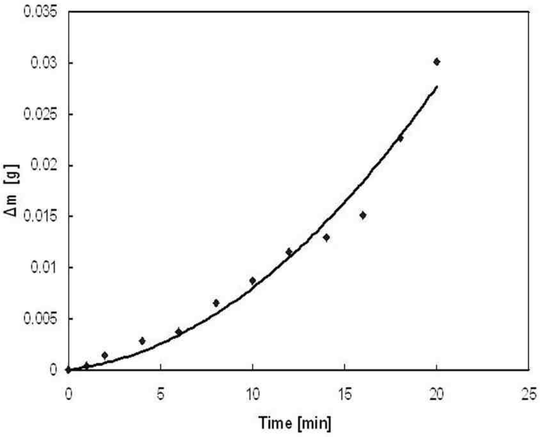

Figure 1—Dependence of Δm on the immersion time.

Effect of H_3PO_4 concentration

An increase in the H_3PO_4 concentration caused a decrease in the weight of the oxide film, Δm, as shown in Fig. 2. On immersion of aluminum into the chromic acid solution for 10 min, Δm decreased from 0.01 to 0.006 g with an increase in the concentration of H_3PO_4 from 10 to 60 g/L (1.3 to 8.0 oz/gal). This weight decrease could be attributed to an increase in the amount of dissolved aluminum. This was confirmed by chemical analysis of the solutions under study.

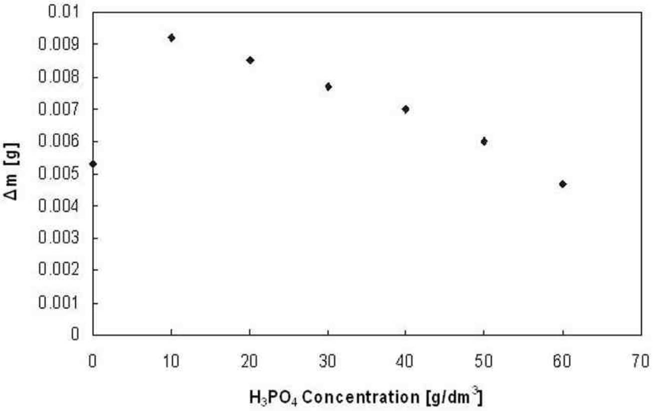

Figure 2—Dependence of Δm on the H_3PO_4 concentration.

Figure 3 shows the dependence of the Al^{+3} concentration in the reacting solution on the H_3PO_4 concentration. An increase in H_3PO_4 concentration from 0 to 60 g/L (0 to 8.0 oz/gal) led to an increase in the Al^{+3} concentration from 0 to 0.06 g/L (0 to 0.008 oz/gal), indicating an increase in the amount of dissolved aluminum. Within the same time frame, the concentration of Cr(VI) in the solution decreased from about 3.07 to 2.93 g/L (0.41 to 0.39 oz/gal)(Fig. 4). A slight decrease in the concentration of Cr(VI) was attributed to a reduction to Cr(III), in the form of green Cr_2O_3 deposited on the aluminum surface .

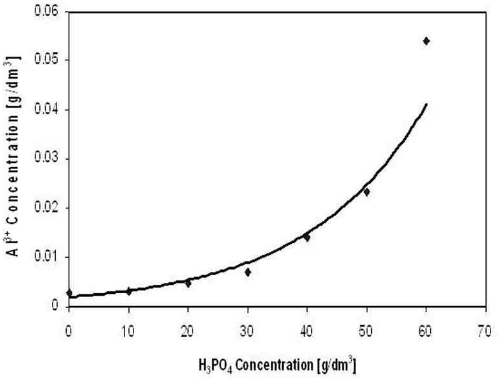

Figure 3—Dependence of Al^{+3} concentration on the H_3PO_4 concentration.

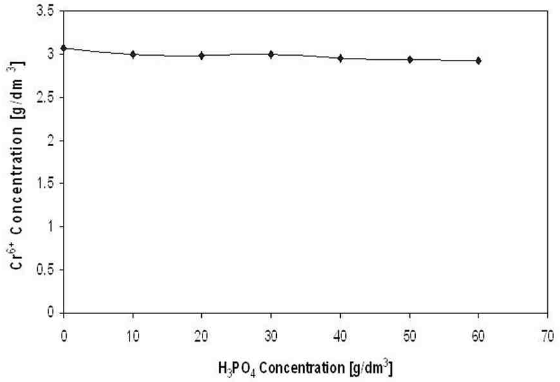

Figure 4—Dependence of Cr^{+6} concentration on H_3PO_4 concentration.

Effect of CrO_3 concentration.

An increase in the CrO_3 concentration led to an increase in the weight of oxide film deposited on the aluminum as confirmed by Fig. 5, showing the dependence of Δm on the Cr_2O_3 concentration. Increasing the CrO_3 concentration from 0 to 10 g/L (0 to 1.33 oz/gal), increased the weight of oxide deposited on the surface from about minus 0.008 to plus 0.008 g. For a CrO_3 concentration above 3.0 g/L (0.4 oz/gal), a weight gain was observed. Below this concentration, since $m_f < m_{in}$ and $\Delta m < 0$, there was a weight loss, indicating that the relative amount of dissolved aluminum was larger then the amount of deposited oxides. It was found that with an increase in CrO_3 concentration above 6.0 g/L (0.8 oz/gal), the amount of precipitated oxides slightly decreased. This result indicates that the surface of aluminum metal was covered with a thin oxide film. Under these conditions, the aluminum surface area available to react with chromic acid was significantly smaller, leading to a decrease in the amount of precipitated oxide film. The chemical analysis results support this conclusion, as follows.

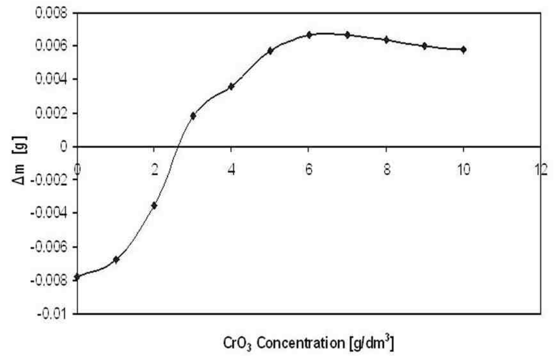

Figure 5—Dependence of Δm on the CrO_3 concentration.

Figure 6 shows the dependence of the Al^{+3} concentration on the CrO_3 concentration after 10 min of immersion. An increase in the CrO_3 concentration from 0 to about 6.0 g/L (0.8 oz/gal) led to an increase in the Al^{+3} concentration in solution. A further increase in the CrO_3 concentration decreased the Al^{+3} concentration. It should be noted that a maximum in the aluminum concentration (Fig. 6) was achieved for the same CrO_3 concentration for which a weight maximum was obtained during the oxidation process (Fig. 5).

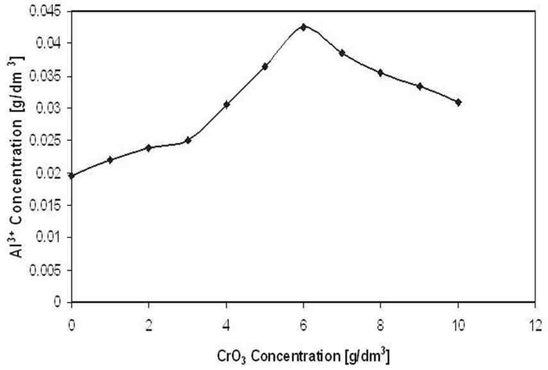

Figure 6—Dependence of Al^{+3} concentration on the CrO_3 concentration.

Properties of the oxide films.

SEM photomicrographs of the oxide films at two different magnifications are presented in Fig. 7. As can be seen, cracks appeared on the surface of the oxide films. An increase in the immersion time produced thick oxide films. It was possible to obtain films up to 5 μm (~200 μ-in.) thick from the chromate solutions. The films could be separated from the substrates with relative ease. The SEM photomicrographs of "thick" films for fractured samples are presented in Fig. 8. Their thickness is estimated to be about 5 μm (~200 μ-in.). The XRF analysis of the green material separated from the metal surface showed that it contained about 2% Al, 18% P, 37% Cr and 42% O with the rest consisting of trace elements. The EDS surface analysis showed that the film formed by immersion of aluminum in the chromic acid solution consisted of 8% Al_2O_3, 42% Cr_2O_3 and 50% P_2O_5. Both the XRF and XRD results showed that the oxide films contained a significant amount of phosphorus which was probably in a form of phosphates incorporated into films during the oxidation process by adsorption. A typical XRD pattern of the green material, after separation from the aluminum substrate, is shown in Fig. 9. This pattern exhibited a broad peak, indicating that the material produced had an amorphous structure.

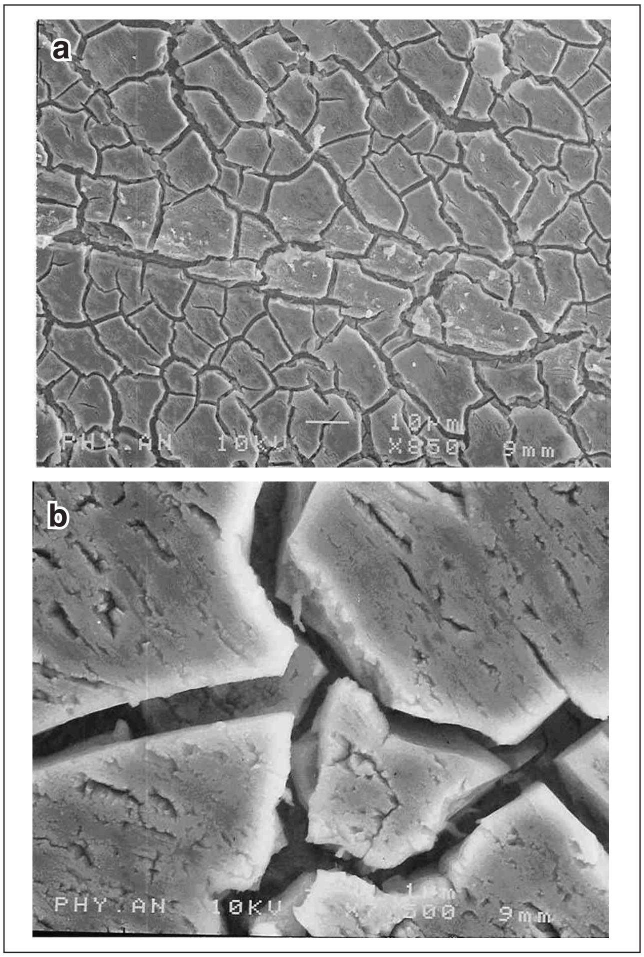

Figure 7—SEM micrographs of oxide films: (a) 900X; (b) 9000X.

According to the results obtained in the present work, the green film formed on the aluminum on immersion into chromic acid solutions can be attributed to the formation of oxides such as Al_2O_3 and Cr_2O_3. The process is somewhat analogous to the cementation or galvanic displacement types of reactions. In reference to a displacement reaction (*e.g.*, cementation of copper onto iron scrap or aluminum[11]), the anodic reactions in the system studied here arise from the oxidation of aluminum:

$$Al \Leftrightarrow Al^{+3} + 3e^- \quad (4)$$

and

$$2Al + 3H_2O \rightarrow Al_2O_3 + 6H^+ + 6e^- \quad (5)$$

The cathodic process in this system is the reduction of dichromate to Cr_2O_3, according to the following reaction:

$$Cr_2O_7^{-2} + 8H^+ + 6e^- \rightarrow Cr_2O_3 + 4H_2O \quad (6)$$

and hydrogen evolution

$$2H^+ + 2e^- \rightarrow H_2 \quad (7)$$

The sum of reactions (4) to (7) gives reaction (1), which again is:

$$4Al + 8H^+ + Cr_2O_7^{-2} \rightarrow Al_2O_3 + 2Al^{+3} + Cr_2O_3 + 3H_2 + H_2O \quad (1)$$

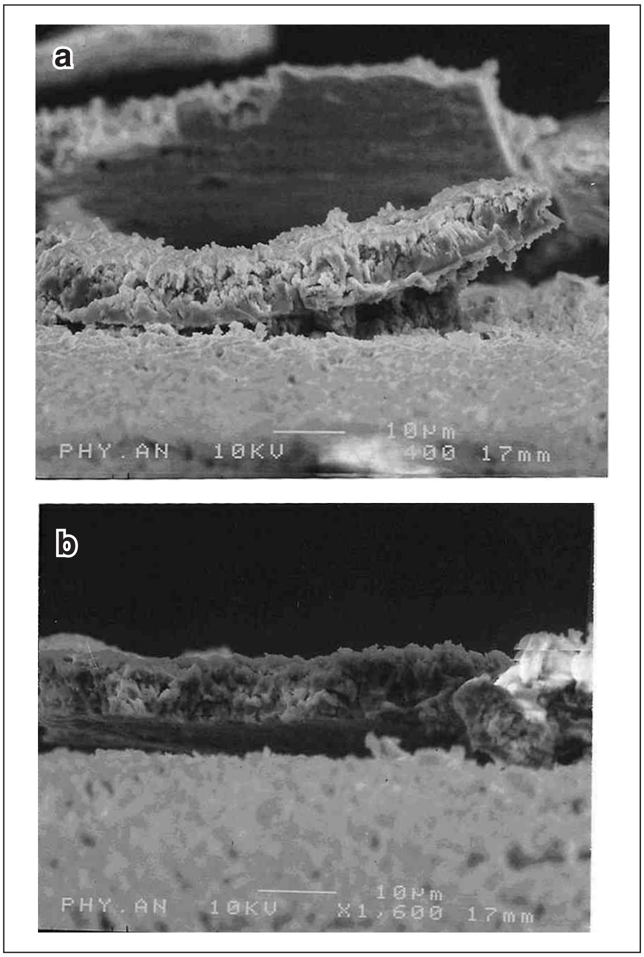

Figure 8—SEM of "thick" films fractured samples: (a) 1700X; (b) 1700X.

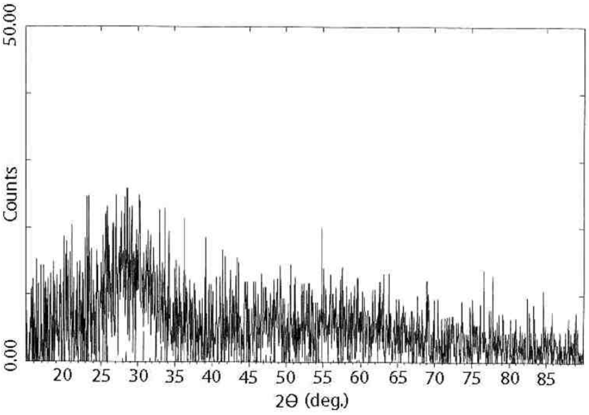

Figure 9—XRD pattern of the green material at the surface of aluminum metal.

Conclusions

Chemical oxidation of aluminum metal in chromic acid solution is a process analogous to the galvanic (displacement) type of reaction. It was found that this process depended on the concentrations of phosphoric and chromic acids. The films formed during the chemical oxidation represent a mixture of oxides (Al_2O_3 and Cr_2O_3).

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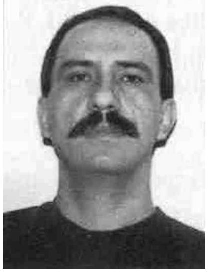
About the Author



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