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SYNTHESIS OF RUBY FILMS BY ANODIC OXIDATION OF ALUMINUM

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An alpha alumina film incorporated with chromium oxide was prepared on aluminum by two-step anodic oxidation. Aluminum was anodized in sulfuric acid and adsorbed chromate ions into the pores of the film. A chromate ions adsorbed alumina film was reanodized in bisulfate melt. The film thus prepared has optical properties similar to a ruby synthesized by the Verneuil method.

In view of the fact that anodic oxidation of aluminum is useful for the improvement of corrosion resistance, abrasion resistance, hardness and decorativeness, etc. of aluminum surface, studies have been carried out on oxide films,[1-4] gamma[5-8] and alpha[9,10] alumina films. Tajima and co-workers examined the mechanism of formation of an alpha alumina film prepared with use of bisulfate melt. No paper seems to have appeared on alpha alumina films incorporated with metal oxide prepared by anodic oxidation. This note deals with the preparation of a reddish violet alpha alumina film incorporated with chromium oxide by anodic oxidation. The film thus prepared has optical properties similar to those of a ruby prepared by the Verneuil method.[11]

The ruby film was prepared on an aluminum plate (purity 99.99%) by two-step anodic oxidation: (a) Aluminum plate was degreased in the usual way and anodized[12] at 25°C in 2.76 mol/dm^3 sulfuric acid with a direct current density of 100 A/m^2. The consumption of quantity of electricity was 204 X 10^3 C/m^2. Chromate ions were adsorbed[13,14] into the pores of the alumina film by dipping in 6.6 X 10^{-2} mol/dm^3 of ammonium chromate at 70°C[15] for 30 min. The temperature for the adsorption of

chromate ion was chosen to be 70°C, since this was found to be suitable for the adsorption of other dyes. (b) A chromate ions adsorbed alumina film was reanodized at 170°C and with a direct current density of 100 A/m^2 for 10 min in molten sodium bisulfate-ammonium bisulfate mixture (mol ratio = 1 : 1.15).[9] A ruby film of thickness 10 micron was peeled off from the aluminum substrate by electrolysis at 25°C in 0.1 mol/dm^3 hydrochloric acid with use of a direct current density of 1000-2000 A/m^2 on the cathode, and its optical properties were examined.

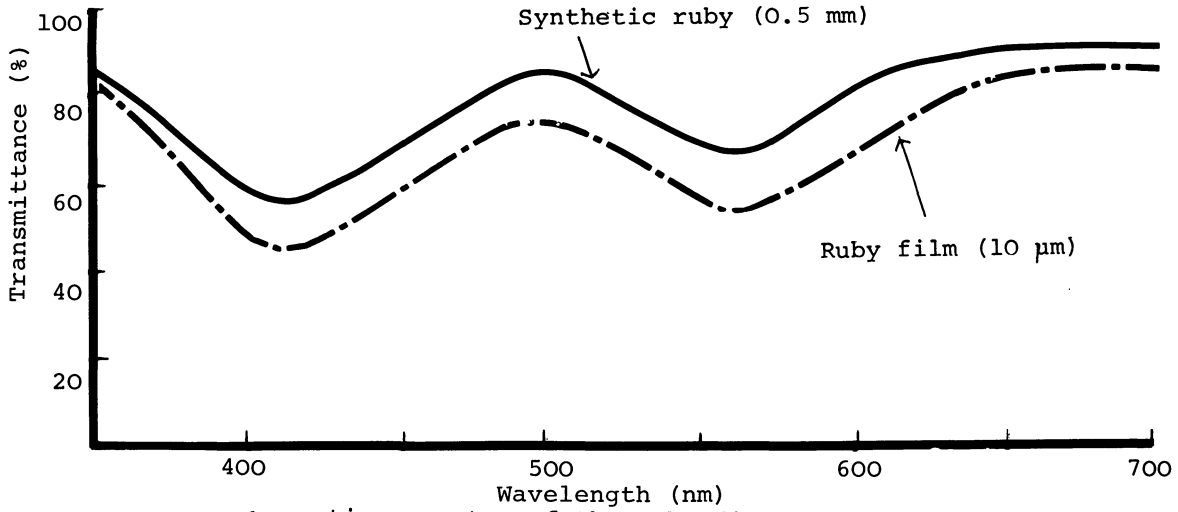

Fig. 1 Absorption spectra of the ruby film and a ruby prepared by the Verneuil method.

The film obtained shows absorption peaks at 410 and 560 nm similar to those of a synthetic ruby[11] (Fig.1).

The fluorescence of the ruby film as well as the synthetic ruby was measured by means of excited light at 410 nm. The intensity of fluorescence at 680 nm changes with the chromate ion in the order $Na_2CrO_4 < K_2CrO_4 < Li_2CrO_4 < (NH_4)_2CrO_4$. Similar fluorescence was observed for the synthetic ruby (Fig.2).

The red fluorescence intensity of the ruby film increases with increase in current density in the range 50-800 A/m^2 in the first step of anodic oxidation. A typical result is shown in Fig.3.

The X-ray diffraction pattern of the ruby film indicates that alpha alumina contains a trace of gamma alumina (Fig.4). The ruby film seems to be formed by highly local heating caused by scintillation on the anode surface. The surface of a ruby film formed in bisulfate melt is porous (Photo.1). The ruby film was heated in an electric furnace attached to a gas-chromatographic apparatus. No

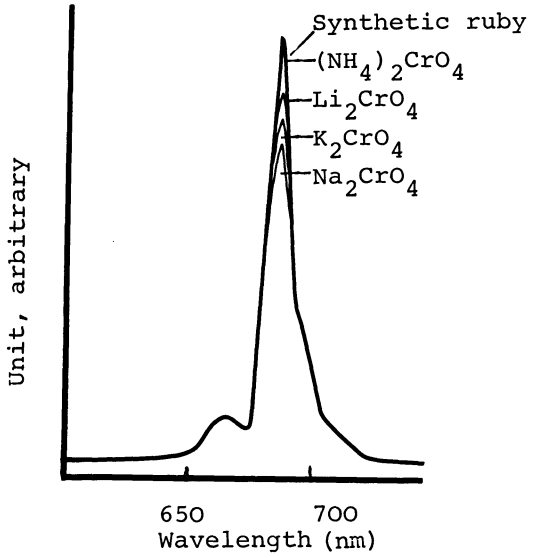

Fig. 2 Effect of chromate on fluorescence intensity.
Chromate concentration: 6.6×10^{-2} mol/dm^3 aq soln.
Thickness: Ruby film 10 μm ; synthetic ruby 0.5 mm.

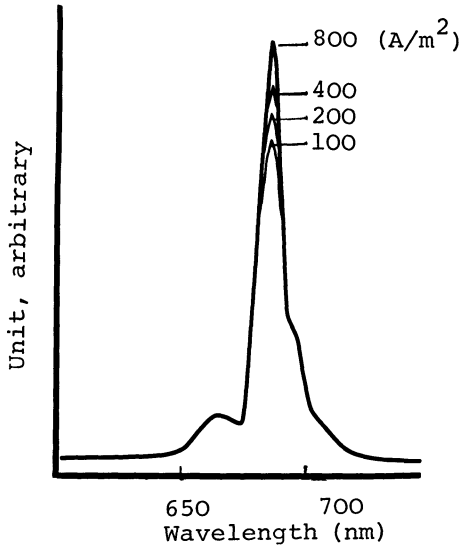

Fig. 3 Effect of current density in the first step of anodic oxidation on fluorescence intensity.
Adsorbing conditions: 6.6×10^{-2} mol/dm^3 of ammonium chromate aq soln at 70°C for 30 min.

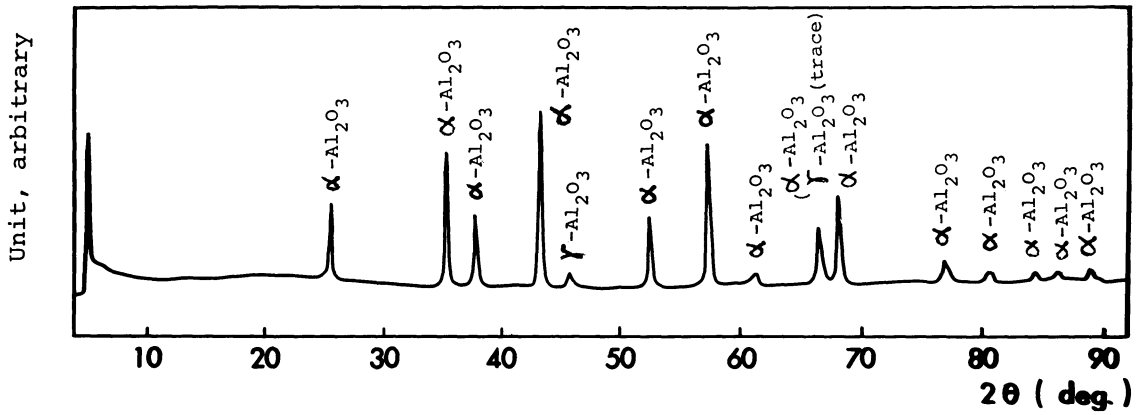

Fig. 4 X-ray diffraction pattern of the ruby film.

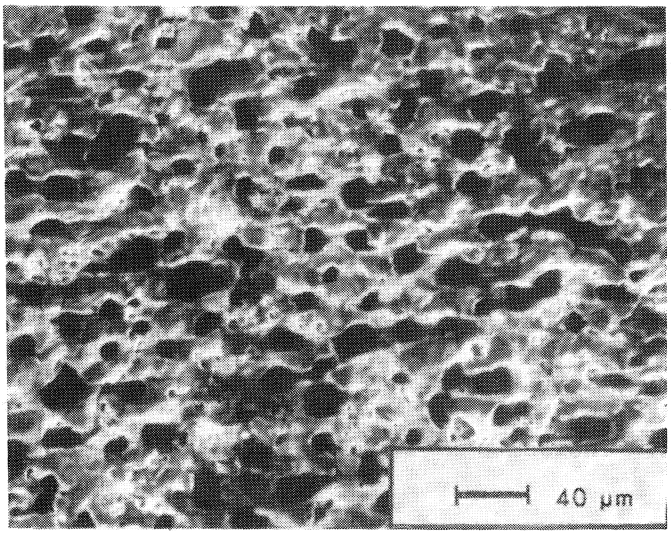

Photo. 1
Scanning electron micrograph of the ruby film.

water was detected in the temperature range 200-950°C. The chromium oxide incorporated with the gamma alumina film showed no fluorescence. Thus the ruby film seems to be transformed into alpha alumina from amorphous alumina via gamma alumina. Chromium oxide is incorporated into alpha alumina when the gamma alumina film is transformed into alpha alumina. Coloration of the ruby film seems to be caused by trivalent chromium ions replacing trivalent aluminum ions in the alpha alumina structure. The ruby film which absorbed the light of 410 and 560 nm from daylight emits deep red fluorescence.

References

1) S.Tajima, Electrochim. Acta, 22, 955 (1977).
2) S.Ikonopisov, N.Elenkov, E.Klein, L.Andreeva, Electrochim. Acta, 23, 1209 (1978).
3) M.Nagayama, H.Takahashi, M.Koda, J. Metal Finish. Soc., Japan, 30, 438 (1979).
4) G.E.Tompson, R.C.Furneaux, G.C.Wood, Trans. Inst. Metal Finish., 57, 123 (1979).
5) C.S.Taylor, C.M.Tucker, J.D.Edwards, Trans. Electrochem. Soc., 88, 325 (1945).
6) A.J.Brock, M.A.Hein, J. Electrochem. Soc., 119, 1124 (1972).
7) I.Mita, M.Yamada, The 56th Metal Finish. Conference, The Metal Finish. Soc., Japan, Sapporo, 24 Sept. 1977, Abstr. No. A 6.
8) I.Mita, M.Yamada, The 60th Metal Finish. Conference, The Metal Finish. Soc., Japan, Nagoya, 20 Nov. 1979, Abstr. No. B 11.
9) S.Tajima, M.Soda, T.Mori, N.Baba, Electrochim. Acta, 1, 205 (1959).
10) S.Tajima, Y.Tanabe, M.Shimura, T.Mori, Electrochim. Acta, 6, 127 (1962).
11) The synthetic ruby containing 0.05 wt% chromium oxide was prepared according to the Verneuil method by Shinko-sha Co. Ltd., Tokyo.
12) JIS H 9500-(1979), Anodic Oxidation Practice by Sulphuric Acid Process on Aluminium and Aluminium Alloys.
13) I.Mita, S.Kikuta, Reports of the Tokyo Metropolitan Industrial Research Inst. No. 14, 59 (1962).
14) G.C.Wood, V.J.J.Marron, B.W.Labert, Nature, 199, 4890 (1963).
15) Metal Finishing Handbook, edited by the Metal Finishing Society of Japan. p.635 (1976).

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