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PREPARATION OF NEW BLACK CHROME SOLAR SELECTIVE COATINGS

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Abstract—The application of the pulse current electrolysis method for black chrome oxide electrocrystallization on nickel substrate, named KIEROME, has been investigated. Pulse plating parameters to optimize the optical properties of KIEROME included the bath composition, current density, plating time, and duty cycle. The bath composition was prepared with the formula of 250-300 *g/l* chromic acid, 10-15 *g/l* propionic acid and 0.5 *g/l* of a proprietary additive. It has been observed that the KIEROME exhibited reasonable optical properties for commercialization when the plating parameters were properly controlled: absorptance (α) of 0.944, and emittance (ε) of 0.084. Thermal aging tests associated with the changes in optical properties, surface microstructures and composition profiles were also performed by aging at 300℃ and 450℃ in air for 24 hours. The surface microstructures of the as-deposited and thermally treated KIEROME coatings were investigated using Scanning Electron Microscopy (SEM), Auger Electron Scopy (AES) and X-ray Photoelectron Spectroscopy (XPS). This study implies that the KIEROME exhibits good optical properties and reasonable thermal stability for the practical application.

Key words: Solar Selective Coating, Black Chrome Oxide, Pulse Current Electrodeposition, KIEROME

INTRODUCTION

It has been well known that the solar collectors require selective coatings for the efficient utilization of thermal energy from the solar spectrum. Efficient selective coatings are indicated by high absorptance (>0.9) over the spectral range of 0.3-2.0 μm and low emittance (<0.1) over the infrared wavelengths to lessen the radiative heat loss for practical use.

Most studies of black chrome selective films have focused on developing suitable bath compositions and optimum optical properties by utilizing the direct current (DC) electroplating method due to its simplicity and low cost [Pettit and Sowell, 1976; Ignatiev et al., 1979; Lampert and Washburn, 1979; Holloway et al., 1980; Lampert, 1980; Pettit et al., 1982; Driver, 1982; Driver and McCormick, 1982]. Especially Ignatiev et al. [1979], Pettit et al. [1976, 1982], Holloway et al. [1980], Lampert and Washburn [1979] and Lampert [1980] observed the microstructural surface of their coatings in detail to investigate the relationship between the optical properties and surface structure of films.

It has been reported that the pulse current (PC) electrolysis has advantages over the DC electrolysis for the general electrodeposition [Avila et al., 1979; Perger et al., 1979]. Its general advantages over the DC electrolysis are as follows : less requirement of additional agents, enhancement of coating uniformity, higher current efficiency, and higher quality coatings, as far as surface microstructure and surface consistency are concerned. Ibl [1980] discussed the effect of pulse current on the electrodeposition of metal surfaces in general. However, the PC electrolysis has not received much attention for the electrodeposition of black chrome oxide. Recently, Lee et al. [1991] have utilized the PC electrolysis for the first time to deposit the black chrome solar selective coatings on the bright nickel substrate with preparing new propionic acid bath solution. We have named this coating KIEROME.

In this study we have concentrated on the production of KIEROME at a low cost and the development of a thin film production process for commercialization by reducing average current density of previous work [Lee et al., 1991]. Black chrome oxide thin films were deposited on nickel substrates of about 30 cm^2, and thin films were thermally treated in air for 24 hr at 300℃ and 450℃ to observe the changes of optical properties and the surface microstructures of PC-applied coatings. Surface microstructures and depth-compositions of the as-prepared and aged KIEROME have been investigated by SEM and AES, respectively. An XPS study was carried out to observe the chemical states of the constituents in the films.

EXPERIMENTAL

1. Plating Apparatus

KIEROME was prepared by utilizing the PC electrolysis method on nickel substrates. Since the optical properties of the coated films are dependent upon the surface condition of the substrates, it is important to create uniform selective coatings. Therefore, the chemical polishing was performed to remove the impurities from the substrate surfaces (Nilaco Co., 99.95% purity) were immersed in a solution of 200 *g/l* of chromic acid in distilled water for 30 minutes and rinsed with acetone and finally with distilled water.

As illustrated in Fig. 1 the PC electrodeposition system consists of pyrex bath container, water cooling glass container, magnetic stirrer, thermometer, anode and cathode. The anode was a Pb-Sn alloy, and the cathode was a nickel substrate. Area ratio of anode to cathode was 2 : 1. The magnetic stirrer was employed to prevent concentration overvoltage effect near the surface of cathode in the bath solution during the operation.

As shown in Fig. 2 the teflon sample holder was used to inhibit

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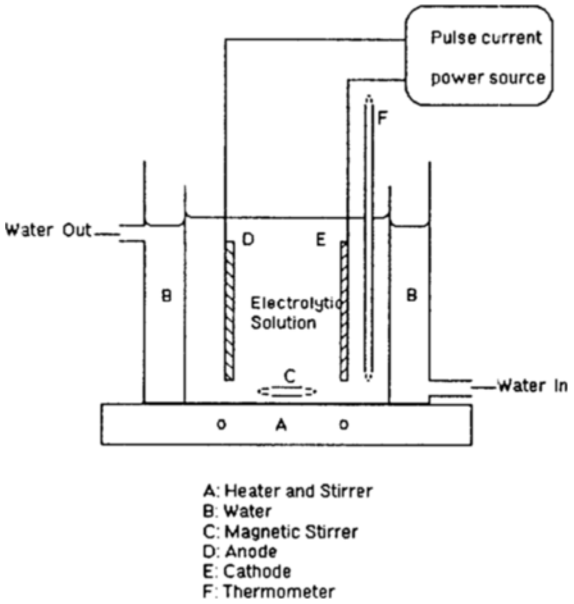


Fig. 1. Schematic diagram of the pulse current electrodeposition system.

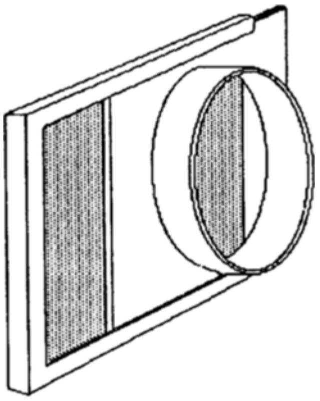


Fig. 2. Teflon sample holder.

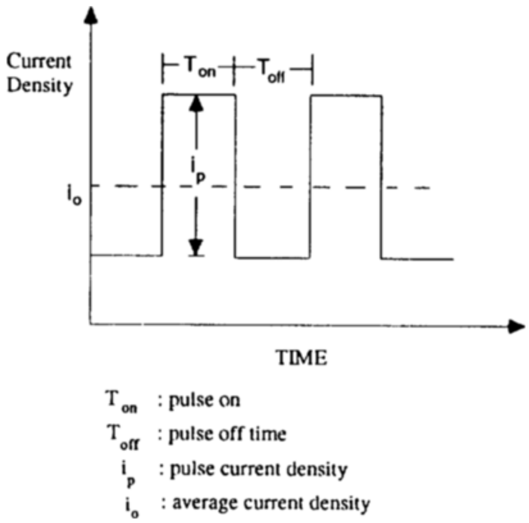


Fig. 3. Schematic diagram of the applied pulse current.

Table 1. Optical properties for as-deposited and thermally aged black chrome coatings

Mode	Condition	α	ε(100℃)
PC-mode	as-deposited	0.944	0.084
	300℃ , 24 h	0.94	0.08
	450℃ , 24 h	0.854	0.075

Table 2. Experimental conditions for electrodeposition of the black chrome coating on nickel substrates

Run number	Peak current (A)	Pulse on time (msec)	Duty cycle	Plating time (min)
n-1	60	1	1/10	8
n-2	60	1	1/16	6
n-3	60	1	1/16	8
n-4	60	1	1/32	8
n-5	62	1	1/16	8
n-6	70	1	1/12	8
n-7	70	1	1/16	5
n-8	70	1	1/16	8
n-9	70	1	1/16	12
n-10	70	1	1/24	8

the edge current effect, and eventually to form uniform surfaces. The distance between the anode and cathode was kept constant, 15 cm. The bath temperature (20-22℃) was checked by the thermometer and controlled by the water cooling system. The square type of pulse current in Fig. 3 was generated by a Model HCP-301H power supply (Hokuto Denko Co., Japan).

2. Plating Solution and Plating Parameters

Since there exists various plating variables in the PC electrolysis process which affect the quality of deposited coatings, careful control of electroplating conditions as well as chemical composition of black chrome bath has been accomplished by employing the standard Hull Cell test. The new plating bath solution consists of 250-300 *g/l* of chromic acid (CrO_3), 10-15 *g/l* of propionic acid (CH_2CH_3COOH) and 0.5 *g/l* of a proprietary additive. The main reasons why propionic acid has been dissolved are due to the ponderous motion of catalytic propionic acid radicals which could prevent the rapid depletion of Cr^{6+} ions in solution, and due to the outstanding bridging effects of radicals on cathodic film in which Cr^{6+} ions are reduced to Cr^{3+} ions.

The bath composition used in this work along with commercial chromic bath solutions are listed in Table 1. The concentration of chromic acid in the plating bath solution in this work was compared to commercial Chromonyx, Econochrome and Tetrachromate reported by Driver and McCormick [1982]. Other parameters, such as peak current, pulse "on" time, pulse "off" time, duty cycle and plating time are listed in Table 2.

3. Optical Properties and Surface Analysis

The solar absorptance (α) of films was measured by utilizing an AM2 Solar Spectrum over the wavelength range of 0.2 μm-2.5 μm. The emittance (ε) at 100℃ was obtained from the spectral reflectance using 882 IR Spectrophotometer by Perkin-Elmer in the wavelength range of 2.5 μm-25 μm.

Because the coating thermal stability was of utmost importance, annealing experiments were performed in an electric muffle furnace to investigate the effects of thermal degradation on the opti-

Table 3. Optical properties of the black chrome coatings deposited on nickel substrates at different electroplating conditions

Run number	Absorptance (α)	Emittance (ε)	Selectivity (α/ε)
n-1	0.942	0.162	5.8
n-2	0.929	0.078	11.9
n-3	0.944	0.084	11.2
n-4	0.86	0.054	15.9
n-5	0.939	0.09	10.4
n-6	0.96	0.232	4.1
n-7	0.893	0.1	8.93
n-8	0.951	0.172	5.5
n-9	0.939	0.212	4.4
n-10	0.924	0.14	6.6

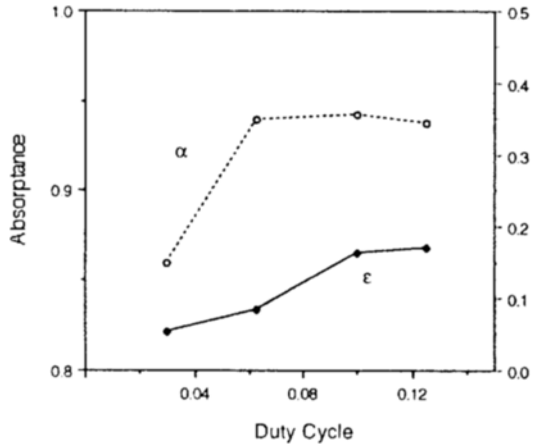


Fig. 4. Absorptance and emittance of black chrome coatings as function of duty cycle.

cal properties and surface structures. A Phillips SEM 505 scanning electron microscope was used to examine the microstructure of the coatings. SEM micrographs of the black chrome oxide thin film were obtained as part of the microstructure characterization study. Besides SEM analysis, AES analysis and XPS study using a V.G. Scientific AES/ESCA were also conducted to observe the depth-composition profiles, and the chemical state of black chrome coatings.

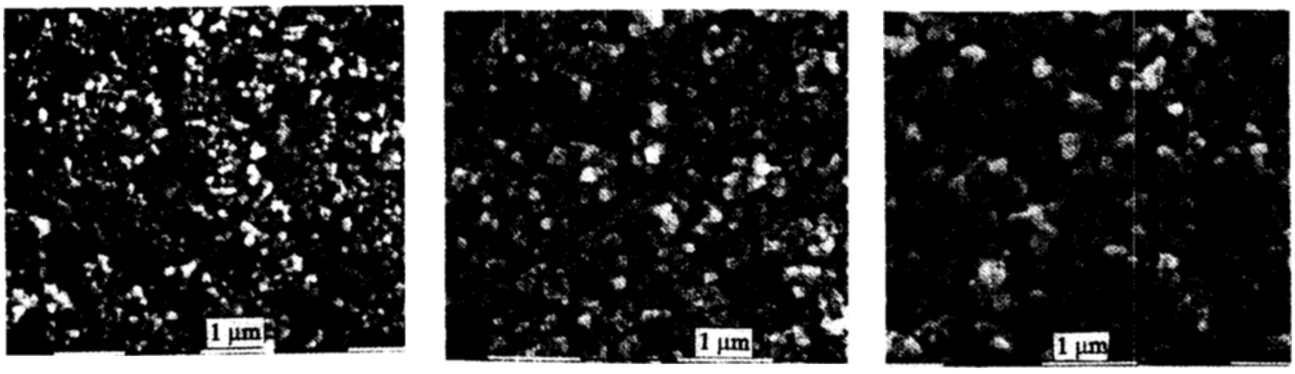
RESULTS AND DISCUSSIONS

1. Optical Properties

The optical properties of the black chrome coatings deposited under the various electroplating conditions are listed in Table 3. It is noted that n-3 and n-8 samples were electroplated under the same conditions, except for bath concentration and the peak current. Their measured absorptance values are 0.944 and 0.951, and the emittances are 0.084 and 0.172, respectively. While the absorptance and emittance of the black chrome coating deposited at the condition of peak current of 70 A are higher, the selectivity (α/ε) is much lower than that of peak current of 60 A. The corresponding average current densities are about 155 mA/cm^2 and 133 mA/cm^2, respectively. Thus, the black chrome coating deposited at the peak current of 60 A seems to be better for commercialization, since the absorptance is high enough and the emittance is much lower than the one obtained at the peak current of 70 A. Furthermore, the bath solution for the peak current 60 A contained 250 *g/l* of chromic acid, 10 *g/l* of propionic acid and 0.5 *g/l* of a proprietary additive while the bath composition used for the 70 A peak current must be composed of more than 300 *g/l* of chromic acid, 15 *g/l* of propionic acid and 0.5 *g/l* of additive. Another achievement in this work is that good quality of KIEROME black chrome coatings were obtained with less average current density than previous work [Lee et al., 1991].

The changes in absorptances and emittances as a function of duty cycle of the samples electrodeposited on nickel sheet under the conditions of the peak current of 60 A and plating time of 8 min are shown in Fig. 4. The absorptances at given conditions are increased in the low duty cycle region and level off in the high duty cycle area; however, the emittances increase as the duty cycle increases. This result shows that the appropriate duty cycle at given conditions is 1/16, since the selectivity is optimum as compared to other conditions.

Therefore KIEROME obtained from n-3 was selected for a detailed investigation of thermal aging behavior. After thermal aging at 300, 450°C for 24 h in air, solar absorptance and emittance were remeasured. After thermal treatment at 300°C it was observed that there was a marginal decrease in absorptance to 0.94 compared with the value of as-deposited film, 0.944. However, a remarkable decrease in absorptance to 0.854 has been observed after annealing at 450°C. Meanwhile, little change in solar emittance has been observed and their measured values are 0.08 and



(a) (b) (c)

Fig. 5. SEM micrographs of the KIEROME
(a) as-deposited, (b) thermally aged at 300°C in air for 24 hours, (c) thermally aged at 450°C in air for 24 hours.

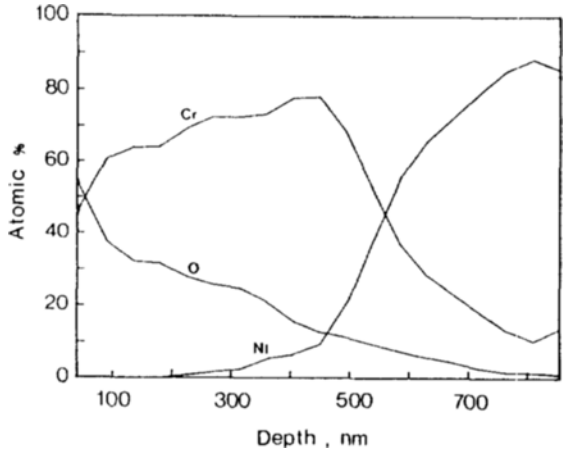


Fig. 6. Auger sputter profiles for as-deposited KIEROME.

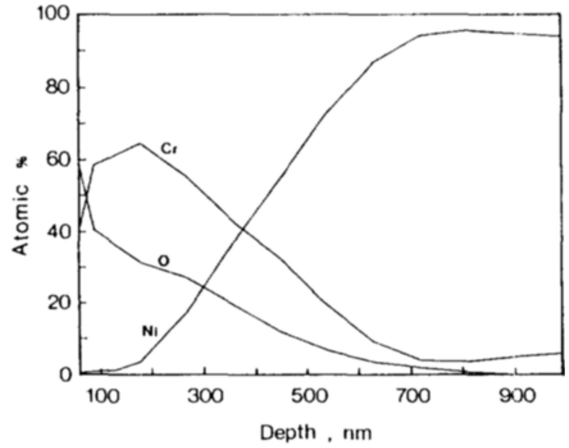


Fig. 7. Auger sputter profiles for KIEROME thermally aged at 300°C.

0.075 for the aged films at 300 and 450℃, respectively. From these results it is seen that as the heating temperature was increased, both the absorptance and emittance values decreased after aging as indicated elsewhere with DC-applied coatings [Pettit and Sowell, 1976; Lampert and Washburn, 1979; Ignatiev et al., 1979; Holloway et al., 1980; Lampert, 1980; Pettit et al., 1982].

2. Surface Analysis

2-1. SEM Photomicrograph

A SEM micrograph of KIEROME is shown in Fig. 5(a). KIEROME coating consists of sphere-like particles with a diameter in the range 0.08-0.1 μm. It was also observed that these small sphere-like particles have agglomerated to form clusters which are typically 0.3 μm across. Figs. 5(b) and (c) show SEM micrographs of the aged KIEROME at 300 and 450℃ in air for 24 h, respectively. As shown in Fig. 5(b), there is no remarkable difference in grain shape between as-deposited and aged film at 300℃, but small spherical grains form clusters which are approximately 0.5 μm across. There is a detectable change in coating surface microstructure and grain size after 24 h exposure to 450℃ in air as seen in Fig. 5(c). Although the changes in particle size and shape were observed from Fig. 5, it can be said that heating upto 300℃ does not significantly change particle size or shape. These SEM photomicrographs support the hypothesis that smaller grain size in these films is responsible for the higher solar absorptance.

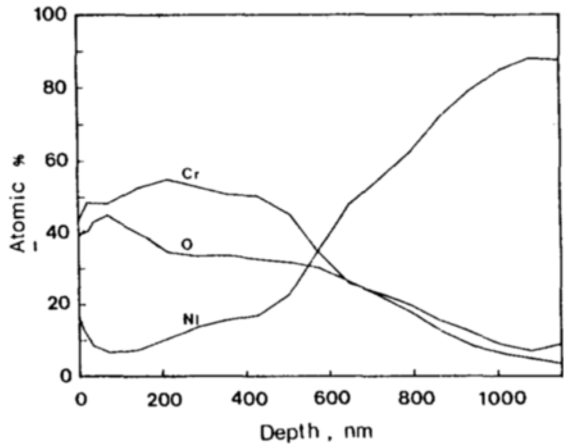


Fig. 8. Auger sputter profiles for KIEROME thermally aged at 450°C.

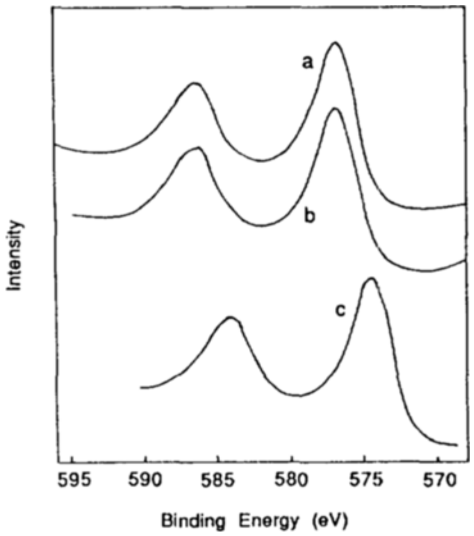


Fig. 9. XPS spectra of the Cr 2p levels for initial KIEROME; the surface (curve a), after etching 5 min (curve b), after etching 15 min (curve c).

2-2. Auger Depth Profiling

The Auger sputter profiles of as-deposited KIEROME is shown in Fig. 6. Figs. 7 and 8 illustrate the composition depth profiles of the aged KIEROME films at 300 and 450℃. Upon heating, the coating oxidizes and the oxygen signal increases slightly at the surface. However, the rate of oxidation at 300℃ is much slower than at 450℃. The major difference between the two aged sample profiles is the presence of a large oxygen signal at a much greater depth for the sample aged for 24 h at 450℃ than for the relatively lightly aged for 24 h at 300℃. Another feature observed in the AES depth profiles is diffusion of nickel into the film from the substrate. This diffused nickel probably exists in the form of nickel oxide and may contribute to the degradation of the coating.

2-3. XPS Measurements

Fig. 9 shows XPS spectra of the chromium 2p level at the surface of KIEROME. In order to survey the chromium 2p level in detail at the surface, the binding energy (BE, eV) values of chromium 2p3/2 level are observed in Fig. 10. Comparing the BE values of the Cr 2p and O 1s levels between the as-deposited

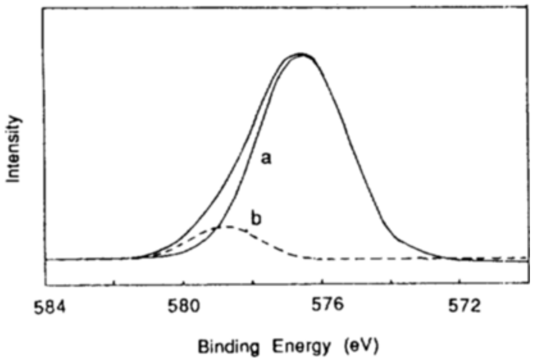


Fig. 10. Detailed XPS spectrum of the Cr 2p levels for Cr_2O_3 (curve a) and CrO_3 (curve b) at the surface of KIEROME.

Table 4. XPS binding energy (eV) for Cr 2p and O 1s levels

Species	Cr 2p1/2	Cr 2p3/2	O 1s
Cr_2O_3	586.2	576.4	530.2
	586.0	576.5	530.0
$Cr(OH)_3$	586.4	577.1	530.9
	-	-	531.2
CrO_3	587.0	578.3	529.7
	588.3	579.1	530.1
Cr(metal)	583.5	574.1	-

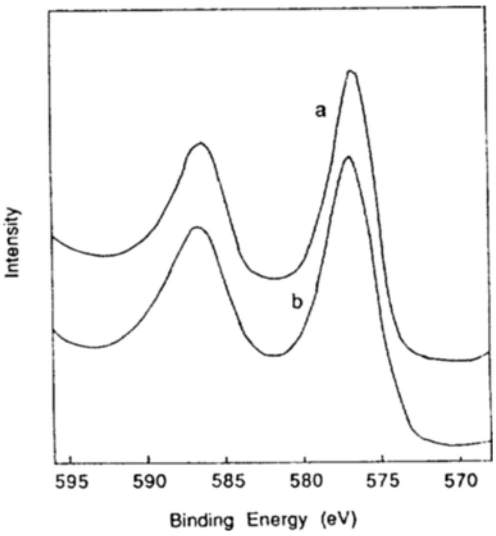


Fig. 11. XPS spectra of the Cr 2p levels for KIEROME thermally aged at 300°C; the surface (curve a), after etching 15 min (curve b).

film and published data in Table 4, the measured Cr 2p level value of 576.7 eV at the surface of film is equivalent to that of 2p3/2 level for Cr^{3+} in Cr_2O_3. The measured O 1s level value of 530.3 eV at the surface is also equivalent to that of O 1s level in Cr_2O_3. However, Fig. 10 indicates that 11% of CrO_3 with the Cr 2p3/2 value of 578.8 eV for Cr^{6+} is detected at the surface of film. This XPS result indicates that both Cr_2O_3 and CrO_3 are present at the surface of as-prepared film. XPS depth profilings of KIEROME were also performed after etching for 5 min and 15 min by an argon ion bombardment with 5 mA/cm^2 at 10 keV, and their profiles are also presented in Fig. 9. The Cr 2p level of the as-deposited film does not change after etching for 5 min, but it undergoes a 2 eV shift to lower BE, 574.3 eV after etching for 15 min. This implies that the film becomes more metallic at this point.

Fig. 11 shows XPS spectra of the chromium 2p level at the surface and 15 min-etched sample of a heated KIEROME. There is no detectable shift in the Cr 2p levels for heated samples with a BE value for Cr_2O_3, indicating that the chrome oxide component increases with depth. Thus, it is predictable that solar absorptance decreases due to thermal oxidation.

CONCLUSIONS

The main purpose of this study was to produce KIEROME for commercialization by the pulse current electrolysis method with lower average current density than that of our previous work [Lee et al., 1991]. The main component of the bath solution used in this work is chromic acid, of which the amount is less than that of commercial products summarized in Table 1. Efforts have been directed toward minimizing the average current density and electroplating time with the suitable optical properties of black chrome coatings.

The absorptance and emittance for commercializable KIEROME was 0.944 and 0.084, respectively under the conditions of a peak current of 60 A in the bath composition of 250 g/*l* of chromic acid and 10 g/*l* of propionic acid. The thermal stability of KIEROME is also acceptable for commercial use. The thermal aging characteristics of KIEROME suggest that the degradation of coating optical properties could be a direct result of the oxidation of metallic chromium crystallites in the coating to Cr_2O_3. This hypothesis is consistent with the increased oxide content of aged films as seen in Auger sputtering profiles and XPS depth profilings for Cr 2p peaks, and also indicates a possible explanation for the observed relationship between microstructure and aging properties.

From results of this investigation, it was concluded that we were able to produce the commercializable KIEROME which exhibits high solar absorptance and selectivity with good thermal stability with 130-155 mA/cm^2 of average current density. This average current density is almost 50% less than the value reported [Lee et al., 1991].

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