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FORMATION OF ETA ALUMINA BY ANODIC OXIDATION OF ALUMINUM

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Anodic oxidation of aluminum was carried out in sodium carbonate alone, or in addition with sodium fluoride, sodium chloride, or sodium iodide at 303-353 K with a direct constant voltage of 150 V. Anodic oxidation proceeded with sparking for 120-300 s, and a white coatings of 5-9 μm thickness was formed. This coatings was identified as eta alumina of high crystallinity by X-ray analysis.

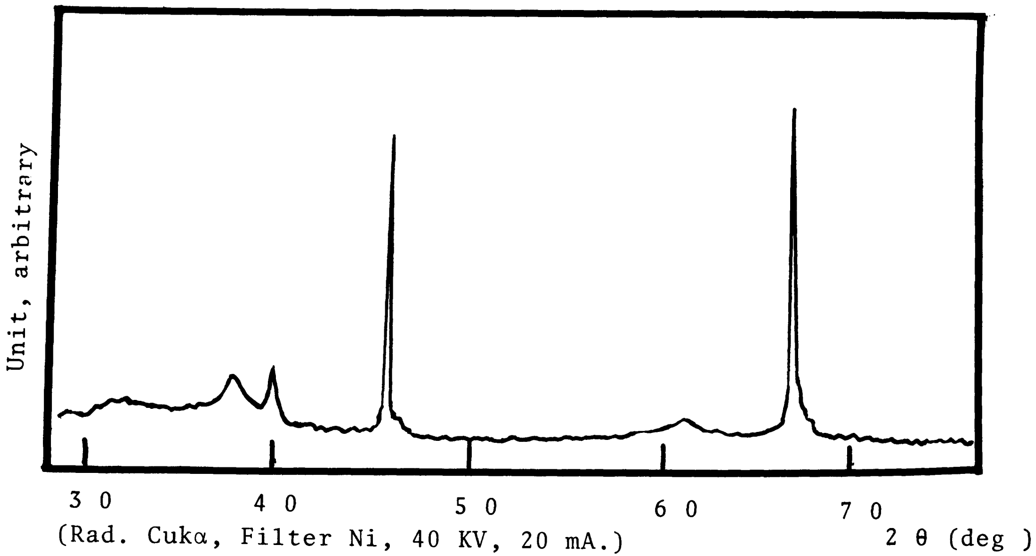
Sparking occurs in anodic oxidation of aluminum under high voltage.1),2) This phenomenon3) has been applied to the formation of integral color coatings in organic acids,4) and of barrier coatings of electrolytic capacitor5) in industry and so on. White coatings was formed6) by anodic oxidation of aluminum in sodium carbonate by use of sparking under high voltage. This paper investigates the crystal structure of these coatings.

The spacimen was aluminum plate of 99.84 % purity with a size of 50 x 100 x 2 mm. The plate was degreased by the usual method and washed with distilled water. The electrolyte used was 2 mol dm^{-3} sodium carbonate aq soln alone, or added with 25-100 x 10^{-4} mol dm^{-3} sodium fluoride, 8-85 x 10^{-4} mol dm^{-3} sodium chloride or 13-17 x 10^{-4} mol dm^{-3} sodium iodide.

Anodic oxidation was carried out under the conditions of electrolytic temperature of 303-353 K, anodic oxidation time of 120-300 s, and constant voltage of 150 V d.c.. The thickness of coatings were meagured using eddy current instrument.

Formation of these coatings differed from that obtained by the conventional anodic oxidation. Electric current did not flow until the electrolytic voltage reached at a range of 80-100 V, and bluish white sparks moved up and down rapidly spinel structure with a=7.9 Å, and the difference between the spacing of gamma and eta alumina is so small, in certain cases, it is almost impossible to distinguish between these two crystal structures.

Yamaguchi[9] defined the gamma and eta alumina as follows: The former shows high diffraction peaks separately corresponding to spinel indexes (440) and (400), while the peaks do not separate in the latter. Sakamoto[10] also supports the above definition. In the present case, above separate peaks were not found for all of the coatings.



(Rad. Cukα, Filter Ni, 40 KV, 20 mA.)

Fig. 4 X-Ray diffraction pattern of the coatings formed in 2 mol dm^{-3} Na_2CO_3 added with 0.25 mol dm^{-3} NaF at 150 V d.c., 313 K.

Table 1 Spacing d(Å) of the coatings formed in various electrolytes.

coatings formed in Na_2CO_3 added with (mol dm^{-3}) NaF(0.25)		NaCl(0.005)		NaI(0.001)		ASTM gamma aluminum oxide		ASTM eta aluminum oxide	
d(Å)	I/I,	d(Å)	I/I,	d(Å)	I/I,	d(Å)	I/I,	d(Å)	I/I,
1.4011	100	1.4011	100	1.4011	100	1.395	100	1.40	100
1.9835	84	1.9835	88	1.9835	75	1.977	100	1.97	80
2.4024	15	2.4086	17	2.3962	12	2.39	80	2.40	60
2.2962	15	2.2962	14	2.2962	13	2.28	50	2.27	30
1.5267	7	1.5222	6	1.5244	7	1.520	30	1.52	20

I/I : relative intensity of X-rays.

over the surface of the aluminum plate. Sparking time continued for a maximum of 120 s, though the time varied according to the electrolytic temperature. Avarage thickness of coatings differed according to the kind and concentration of the additive, but was affected by the electrolytic temperature. Typical examples are shown in Fig. 1. Figure 2 is the scanning electron micrograph of the coatings formed in 2 mol dm^{-3} sodium carbonate added with 0.25 mol dm^{-3} sodium fluoride. Figure 3 is a transmission electron micrograph of a replica of an aluminum surface after being peeled off the coatings.[7] As shown in these photographs, the surface of the coatings (Fig. 2) is not uniform like the coatings formed in acidic electrolyte, and shows the traces of the movement of sparks on the aluminum surface (Fig. 3).

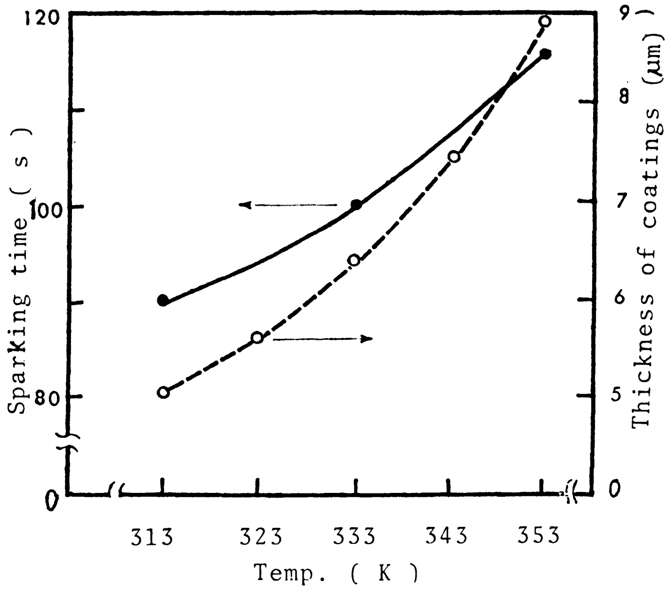


Fig. 1 Sparking time and thickness of coatings.

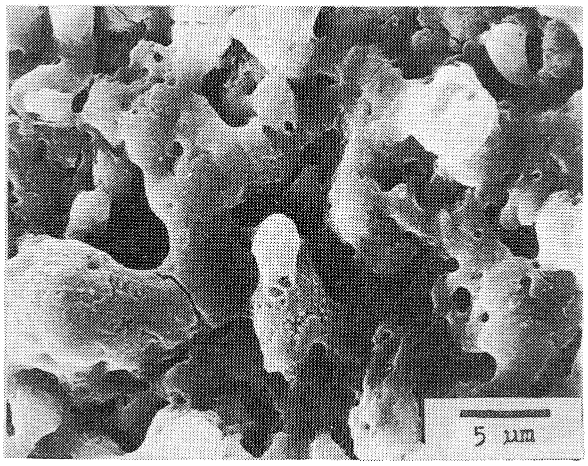


Fig. 2 Scanning electron micrograph of the coatings formed in Na_2CO_3 added with Naf.

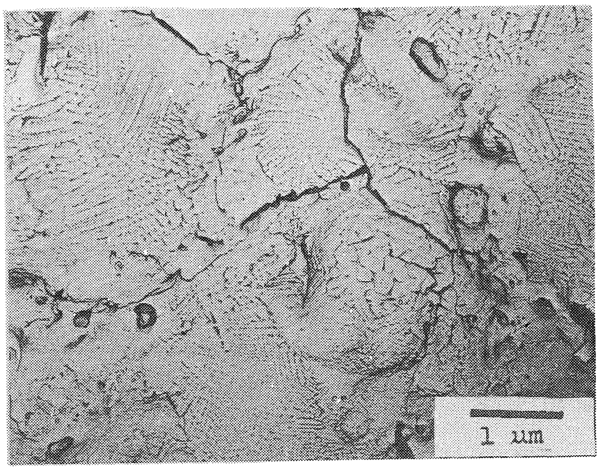


Fig. 3 Transmission electron micrograph of an aluminum surface after being peeled off the coatings.

Figure 4 shows X-ray diffraction pattern of the coatings formed in an electrolyte of 2 mol dm^{-3} sodium carbonate and added with 0.25 mol dm^{-3} sodium fluoride at 150 V d.c., 313 K. X-Ray diffraction apparatus is Regakudenki Co. D-10 C type.

Table 1 shows the spacing d(Å) of the coatings and gamma and eta alumina listed in the ASTM card. As shown in Table 1, the crystal structure of the coatings corresponds to gamma or eta alumina. Funaki et al.[8] reported that eta alumina has a

Table 2 shows the spacing and its integrated intensity ratio of the diffraction peaks. Table 3 shows the corrected spacings using standard silicon and the unit cell dimension of the coatings. The values of the three coatings agree with each other and are very close to 7.92 Å the value of the eta alumina in litarature.[9] These results suggest the formation of eta alumina belong to gamma alumina group.

Table 2 Comparision of the integrated intensity ratio.

electrolyte (mol dm^{-3})	Na_2CO_3 (2) added with		
(Å)	NaF(0.25)	NaCl(0.005)	NaI(0.001)
1.3992	100	100	100
1.9795	85	75	75
2.3962	40	35	40

Table 3 Spacing and lattice constant of various coatings.

electrolyte	hkl	2 θ obs.	2 θ cor.	d(Å)	a₀(Å)
Na_2CO_3-NaF	440	66.769	67.002	1.3967	7.901
	400	45.750	45.974	1.9740	7.596
Na_2CO_3-NaCl	440	66.750	66.983	1.3970	7.903
	400	45.725	45.949	1.9750	7.900
Na_2CO_3-NaI	440	66.750	66.983	1.3970	7.903
	400	45.713	45.937	1.9755	7.902

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