Thermoanalytical Studies Of Anodic Oxide Coatings on Aluminum

By A.K. Sharma and H. Bhojaraj

Data derived by thermogravity, derivative thermogravity and differential scanning calorimetry revealed that (1) anodic oxide coatings on aluminum are dehydrated during heating at temperatures up to 550° C and (2) aluminum sulfate in the oxide films is decomposed at higher temperatures. The residue after heating at 1100° C is α Al₂O₃. Kinetic data during the decomposition reaction are examined.

he inherent lightness and good strength-toweight ratio of aluminum has focused attention on increasing applications in aerospace and allied fields. Conventional anodizing is required primarily for protection against atmospheric corrosion, but also provides a base for thermal-control paints. Hard anodizing is a prime requirement for reducing friction on sliding surfaces such as spacecraft deployment mechanism components, aircraft undercarriage legs, naval magazine ammunition guides and hydraulic gears. Hard coats act as a base for dry lubricants.

A study of the thermoanalytical behavior of anodic oxide coatings was undertaken to explore the composition of the coatings before and after heating at different temperatures. The mechanism of decomposition, kinetic parameters such as activation energy and order of reaction and heat of decomposition at different temperatures were examined.

Experimental Procedure

Anodic oxide coatings were produced on AA 6061 by using the following practices:

1. Ultrasonic decreasing for three to five min in trichloroethylene.

2. Alkaline cleaning at 55 to 60° C for three to five min in a solution of sodium hydroxide (1 O percent), sodium fluoride (2.0 percent) sodium polyphosphate (0.2 percent) and a wetting agent (0.2 percent).

3. Water rinsing and desmutting in 30 percent nitric acid for 30 sec.

4. Water rinsing and anodizing.

Conventional anodic coatings were produced in a 150 to 165 g/L solution of sulfuric acid at 20 to 25° Cat a current

Composition of Anodic Oxide Coatings					
Compound	Conventional anodic film, 1/10	Hard anodic film, %			
A I.O .	66.0	65.8			
Al ₂ (SO ₄)	16.5*	15.4**			
H,O	17.4	18.5			
co.		0.3			

Table 1

*Based on a SO, content of 11.6 percent **Based on a SO, content of 18.5 percent.

density of 1.5 A/din'; anodizing time was 30 min. After water rinsing, the coatings were sealed in boiling water for 30 min.

Hard oxide coatings were obtained in a solution containing 100 g/L of sulfuric acid and 15 g/L of oxalic acid, maintained at $5 \pm 2^{\circ}$ C. Current density was 3.6 A/dm² and anodizing time was 75 min.

Anodic oxide films were removed from the aluminum substrate' by (1) scraping the films away from two or three 4 x 4 mm areas using a sharp scalpel; (2) immersing the specimen in 100 mL of pure dry methanol and adding 2 mL of bromine; (3) gently heating, if necessary, to start the dissolution of aluminum; and (4) washing the film several times with pure methanol after all aluminum had been dissolved. After drying in air, the films were gently ground into a fine powder.

Coating composition was determined by using infrared spectrometry. Infrared spectra were recorded in KBr pellets in the wave number region of 200 to 4000 cm⁻¹. The thermal stability of the oxide films was investigated by using thermogravimetry (TG), derivative thermogravimetry (DTG) and differential scanning calorimetry (DSC). With a heating rate of 10° C/min, TG and DTG curves were recorded simultaneously up to 1000° C. DSC data were limited to a temperature of 500°C, due to a limited temperature capability.

Weight Loss Data for Anotic Oxide Coatings						
	Conventional oxide weight loss, %		Hard oxide weight loss, %			
	Observed	Calculated	Observed	Calculated		
Dehydration *	17.42	17.43	18.63	18.84		
Sulfate decomposition	11.58	11.61	10.58	10.80		
Fotal weight loss at 1100° C	29.08	29.04	29.62	29.64		

Table 2							
Weight Loss	Data for	Anodic	Oxide	Coatings			

"Weight loss over the range of 27 to 515°C for the conventional oxide coating and 27 to 550 °C for the hard coating. "Weight loss over the range of 625 to 1000°C for the conventional oxide coating and 680 to 1000° C for the hard coating. "Weight loss including loss of CO, from decomposition of oxalate.



Fig. 1—TG and DTG curves of(a) normal anodic and (b) hard anodic oxide coatings. Sample sizes (a) 21.95 mg (b) 35.46 mg.

Coating Compositions

The appearance of infrared absorption bands at wave numbers of 3200 to 3525 cm⁴ and 1600 to 1630 cm⁴ indicate water attached to a lattice structure.²Strong bands observed at 1059 and 1143 cm⁴, the medium band at 1227 cm⁴ and the shoulder at 989 cm⁻² support the presence of A I₂(SO₄)₃³. The moiety of AI₂O₃ in the coatings was confirmed ⁴⁵ by the very strong bands occurring at 1180, 745 to 752 and 825 cm⁴, the strong band at 432 cm⁴ and the shoulders at 375, 432 and 575 cm⁴. The strong band observed at 2350 cm⁻² in the infrared spectrum of the hard anodic oxide coating must have been due to the asymmetric stretching mode of free carbon dioxide⁶, which implies the entrapment of CO₂ in the coating. On the basis Of the chemical analyses and observed infrared absorption bands, the compositions in Table 1 were derived.

The infrared spectra of anodic oxide particles heated at 600° C did not show absorption bands characteristic of hydrated water or carbon dioxide. The residues consisted Of AI_2O_3 and $AI_2(SO_4)_3$ only.

Particles heated at 1100° C showed strong absorption bands at 432 and 575 cm⁻¹ and a shoulder at 375 cm⁻¹, which confirmed the α form of Al₂O₃⁵.







Fig. 2—DSC curves of (a) normal anodic and (b) hard anodic oxide coatings. Sample sizes: (a) 20.55 mg; (b) 17.57 mg.

Thermal Analysis

Figure 1 shows TG and DTG curves and Fig. 2 shows DSC data for conventional and hard anodic oxide coatings. These thermograms reveal two major changes that occur when particles of the oxide films are heated: (1) dehydration and (2) decomposition of aluminum sulfate.

Dehydration of both the conventional and hard anodic oxides starts at 27° C, slows down at about 375° C, but continues until 515° C in the case of the conventional oxide or 550° C for the hard oxide coating. The release of entrapped carbon dioxide could not be distinguished from dehydration in the thermograms for the hard oxide particles.

After heating at 600° C, a completely dehydrated, carbon-dioxide-free residue with the composition of AI_2O_3 + $AI_2(SO)_4$ was isolated. The total weight loss due to heating at 600° C corresponded to the amounts expected from Table 1 data. As expected, endothermic behavior during the dehydration process was observed from the DSC curves.

When the temperature was raised to the range of 635 to 680° C aluminum sulfate began to decompose. The maximum weight loss occurred at 900 to 935° C in the case of the conventional anodic oxide and at 890 to 920° C for the hard oxide. The residue after heating at 1000" C contained a trace of sulfate. When heating was continued in an oven at 1100° C, an additional slight weight loss was detected, but no further change occurred as a result of heating at higher temperatures. According to chemical analysis and infrared spectra, the residue that remained after heating at 1100° C is α Al₂O₃. Table 1 summarizes the chemical compositions and Table 2 shows weight loss data of the anodic oxide coatings due to heating.

Calculations of the apparent activation energy (E) and order of reaction (n) were performed for the decomposition reaction that occurred during the temperature range of 880 to 940° C, employing the graphical method of Coats and Redfern.⁷ The plot of -log $[-log(1-\alpha)/T^2 vs. 1/T^3 for n = 1 is a$ straight line (Fig. 3) with a slope of -E/2.303 R, where R is the gas constant. The activation energy, as calculated from Fig. 3 curves, was 3188.2 J/g for the decomposition of sulfate in the conventional anodic coating and 3847.6 J/g for the hard coating.

The heat of reaction for the dehydration step was

calculated from the DSC curves using the expression H = KA/m, where H is the heat of reaction, K is the calibration constant, A is the area under the peak and m is the sample mass. At the peak temperature of 117.5° C, the heat of reaction for the dehydration of conventional oxide was 349 J/g. At the peak temperature of 114.3° C for the hard oxide, the heat reaction was 321 J/g.

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References

- 1. V.F. Henley, Anodic Oxidation of Aluminum and Its Alloys, Pergamon Press, Oxford, England, 1982; p. 88.
- 2. A.K. Sharma, S. Kumar and N. K. Kaushik, *Thermochim.* Acts, 47, 149 (1981).
- 3. H. Tai and A.L. Underwood, Anal. Chem., 29, 1430 (1957).
- 4. H. Hafner, Z. Kristallogr., 115, 331 (1963).
- 5. N.T. McDevitt and W. L. Baun, Spectrochim. Acts, 20, 799 (1 964).
- 6. S. Mittal, A.K. Sharma and N.K. Kaushik, *Thermochim.* Acts, 89, 195 (1985).
- 7. A.W. Coats and J.P. Redfern, *Nature* (London), 68,201 (1964).



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