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THERMAL PHENOMENA DURING ANODIZING OF ALUMINIUM IN SULFURIC ACID

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The heat developing at the oxide-aluminium interface during anodizing in sulfuric acid has been measured. The temperature of the aluminium anode increases rapidly to attain a steady value after a few minutes, and drops sharply upon current interruption. The rise in temperature increases linearly with the current density. The effects of the concentration and temperature of the electrolyte and the anodizing voltage on the heat developed in aluminium have been examined. The results are discussed with regard to the dispute concerning the conditions necessary at the base of the pores for the relatively high local dissolution.

The characteristics of the porous anodic oxide coatings formed on aluminium in acid solutions and the effects of the different conditions of formation have been the subject of several investigations [1–9]. It is well established that the film is composed of an amorphous oxide with a large number of perpendicular pores extending through the oxide almost to the metal/oxide interphase. At the bottom of the pore, there is a thin layer of non-porous oxide, called the „barrier layer". The mechanism of pore formation and the dissolution of the oxide during anodizing has been extensively discussed [5–8]. Regardless of the exact mechanism, a balance is attained between the rate of oxide formation and factors controlling solvent action, resulting in a constant barrier layer thickness.

The temperature release inside the pores and its effect on the rate of dissolution of the oxide has been subjected to confusing conclusions. Hunter and Fowle [9] demonstrated that the temperature rise inside the pores is the dominant factor for the locally high rate of dissolution at the pore base. Their results showed that the conditions existing at the base of the pores differ vastly from those existing in the body of the electrolyte. The conditions at the pore bases are characterized by high temperatures and high electrolyte concentrations. They assumed, for anodizing at 13 mA/cm^2 in 15% H_2SO_4 solution, that the acid at the pore base has a concentration of approximately 51% at its boiling point of 124^o.

This thermal mechanism has been supported by many workers. Mosan [10] postulated that considerable heat is developed at the base of the pores, especially when high current densities are used. Unless this heat is removed rapidly through the oxide coating by suitable agitation of the electrolyte or by other means, the coating is dissolved at a more rapid rate.

Nagayama and Tamura [11], on the other hand, reject the above thermal mechanism. On the basis of their calculations of the temperature distribution along the pores of the anodic oxide film on Al in sulfuric acid electrolyte, they concluded that the temperature rise at the pore base is always negligibly small, and the locally high rate of dissolution during anodizing should be interpreted as being due to the high electrical field across the barrier layer, as suggested by Hoar and Mott [12].

In this paper, the heat generated inside an aluminium anode during anodizing in H_2SO_4 solutions has been followed with the help of a simple and sensitive technique. The effects of current density, voltage, and concentration and temperature of the electrolyte on the temperature rise in aluminium have been examined.

Experimental

The technique used in the present study resembles that previously used by Zabolotnyi and Frankevich, [13] in the thermometric dissolution of zinc in acids. It simply consisted of a copper-constantan thermocouple with its two branches insulated from each other by a thin-walled porcelain tube. The aluminium anode used was in the form of a rod 8 cm long and 5 mm in diameter. This anode was bored through its centre to a depth of 5 cm. The diameter of the pore was approximately equal to the outer diameter of the porcelain tube containing the thermocouple (about 2 mm). The Al anode was coated with lacquer, except for a definite length (4 cm) in contact with the solution and about 2 cm at the other side for electrical contact. A platinum sheet of relatively large area was used as the other electrode.

In each experiment, 800 ml of chemically pure H_2SO_4 of known concentration was used in a glass vessel immersed in a water bath controlled at the required temperature. Before introduction to the solution, the anode was cleaned and degreased as described before [14]. The variation in temperature of the aluminium during anodizing was measured on a Millivac MV–27E DC Microvoltmeter precalibrated with the working thermocouple to temperatures in degrees centigrade.

Results and discussion

Curves A of Fig. 1 show the variation in temperature of the aluminium during anodizing in 15% H_2SO_4 at different current densities. It is clearly seen that the temperature increases rapidly to attain a steady value after limited anodizing periods. The curves also illustrate that the temperature drops sharply upon interruption of the current. The rate of temperature rise and decay reveals the high sensitivity of the measurement technique. In these experiments, the temperature of the electrolyte was thermostatically controlled at 20°, and there was no agitation. When these experiments were repeated under good agitation (Fig. 1B), some of the generated heat was removed to the solution.

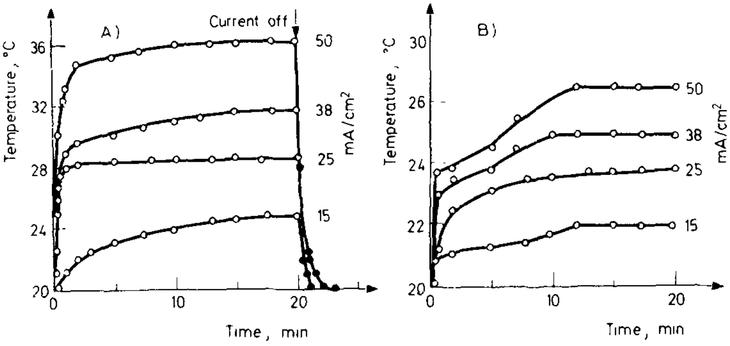

Figure 1 Variation in temperature of aluminium during anodizing in 15% H_2SO_4 at different current densities (20 V, 20°) (A) – stagnant, (B) – stirring

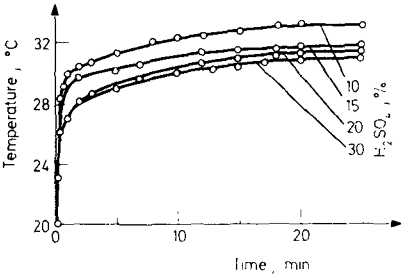

Figure 2 Effect of concentration of H_2SO_4 on temperature rise of aluminium anode. (i = 39 mA/cm^2, 20 V, 20°)

Curves similar to those of Fig. 1 A were obtained in H_2SO_4 solutions of different concentrations. The curves of Fig. 2 represent the variation in temperature of the aluminium during anodizing in 10, 15, 20 and 30% H_2SO_4 solutions at constant current density.

The steady-state rise in temperature (ΔT) increases linearly with the anodizing current density, as given by the lines of Fig. 3. This Figure also shows the effect of the sulfuric acid concentration. It can be seen that the generated heat slightly decreases with the increase of acid concentration in the examined range (10–30%). This may be due to an increase in the dissolution of the oxide in the concentrated acid, which decreases the resistance of the coating. These results are in harmony with the findings of Hunter and Fowle [9]. They reported that increasing H_2SO_4 concentration increases the dissolution rate and decreases the barrier thickness of the coating formed on Al at 15 V.

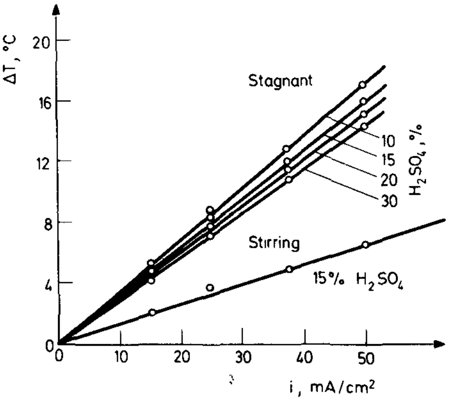

Figure 3 Variation of temperature rise of aluminium anode with current density at different H_2SO_4 concentrations (20 V, 20°)

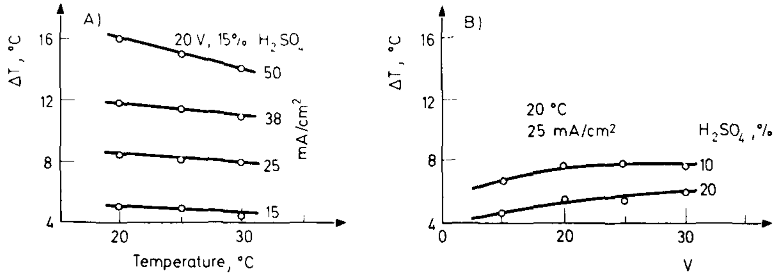

Figure 4 Effects of temperature (A) and applied voltage (B) on temperature rise of aluminium during anodizing in H_2SO_4

The effect of the temperature of the sulphuric acid bath on the temperature rise of the aluminium anode is shown by the lines of Fig. 4 for different current density values. These results show that the bath temperature affects the rise in temperature of the aluminium in a nearly similar manner to that described above for the effect of the acid concentration (Figs 2,3). The effect of this factor on the formation of oxide coatings on aluminium in sulfuric acid has been discussed previously [9,11]. Decreasing the temperature results in a greater barrier thickness. From the trend observed [9], it appears that at very low temperatures the barrier thickness will approach the value characteristic for electrolytes that do not dissolve the oxide. These authors [9,11] also demonstrated the great effect of the temperature of the electrolyte on the rate of dissolution of the oxide. The dissolution rate was doubled for every 8.6° increase in temperature of 15% H_2SO_4. It was therefore concluded that the conditions existing at the base of the pores differ greatly from those existing in the body of the electrolyte.

The conditions at the pore bases are characterized by high temperature and high electrolyte concentrations, both of which are necessary for a relatively high rate of dissolution.

Figure 4 B shows the effect of voltage on the temperature rise of the aluminium anode in 10% and 20% H_2SO_4 solutions. The results illustrate the slight effect of this factor.

From the above results on the effects of the different formation conditions on the temperature rise inside aluminium during anodizing in H_2SO_4, it appears that the current density has the major influence. According to the calculations of Nagayama and Tamura [11], on the basis of Kellers's pore model [5], the Joule heat and the formation heat of oxide are expected to evolve at the barrier layer. Part of this heat is absorbed by the dissolution reaction, and the evolved heat will be transferred to both the bulk solution and the substrate metal. For a real surface area of 1 cm^2 at the bottom of the pores, the rate of evolution of Joule heat was expressed as:

$$q_J = i_a \Delta E/4.184\, N\pi r^2,$$

where ΔE is the immediate fall of potential observed when the anodizing c.d., i_a is stopped, r is the radius and N is the density of the pores. The rate of heat evolution due to the formation and the dissolution of oxide was also given by:

$$q_f = H_f\, i_a/6N\pi r^2$$

and

$$q_d = V_b d\, H_d/M_o$$

where

H_f = molar heat of formation of Al_2O_3,
H_d = heat of dissolution of Al_2O_3 to form Al^{3+},
d = density of the oxide,
M_o = molecular weight of the oxide.

Thus, the rate of heat evolution at the pore base as a whole is

$$Q_b = q_j + q_f + q_d$$

The rate of heat evolution at the side wall of the pores due to the dissolution of oxide was assumed to be negligible. Nagayana and Tanura [11] reported the following data:

q_j = 0.162 cal/S.cm^2
q_f = 3.85×10^{-2} cal/S.cm^2
q_d = -6.23×10^{-3} cal/S.cm^2, and
Q_b = 0.194 cal/S.cm^2

It can be seen from these data that the rate of evolution of the Joule heat, q_j, amounts to almost 80% of the total rate of heat evolution, Q_b. The Joule heat ($i_a \cdot \Delta E$) can be affected through the variation of the anodizing current density and the applied voltage. The variation in i_a in addition affects the evolution of heat through the formation heat (q_f). This might clarify why the current density of anodizing is the factor most influencing the elevation in temperature of the metal.

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Zusammenfassung — Es wurde die an der Oxid-Aluminium-Grenzfläche während der Anodisierung in Schwefelsäure entwickelte Wärme gemessen. Die Temperatur steigt in der Aluminiumanode schnell an, erreicht einen konstanten Wert nach wenigen Minuten und sinkt bei Unterbrechung des Stromes abrupt ab. Der Temperaturanstieg ist proportional der Stromdichte. Auswirkungen von Konzentration und Temperatur des Elektrolyten und der Anodisierungsspannung auf die Wärmeentwicklung in Aluminium wurden untersucht. Die Ergebnisse wurden im Zusammenhang mit jener Diskussion diskutiert, die sich auf die nötigen Bedingungen der relativ grossen lokalen Dissolution auf Grund der Poren bezieht.

Резюме — Измерена теплота выделения на межфазной границе окись — алюминий во время анодизации в серной кислоте. Температура алюминиевого анода быстро увеличивается, достигнув действитель ного значения после нескольких минут и затем капли резко прерывают ток. Рост температуры увеличивается линейно с плотностью тока. Исследовано влияние концентрации, температуры электролита и анодного напряжения на теплолоту выделения в алюминии.