Effect of Cold Rolling on Anodizing of Aluminum in a Neutrality Solution

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Nobuo Kobayashi* and Hiroyuki Ichinose*

In order to find effect of cold rolling on anodizing in a neutral electrolyte of the cold-rolled aluminum sheets which were cold rolled up to 90% total reduction under the condition of 10% reduction per pass, a study has been carried out anodizing test in a 3mass% ammonium tartrate aqueous solution (pH6.8), with the applied cell voltage of 5,20 and 50V, respectively. The current density rapidly increased just after the immersion at each applied cell voltage, and then rapidly decreased, and finally reached a equilibrium within 10~20 seconds. For the applied cell voltage of 5V, the current density after 600 seconds showed the smallest value at 50%, and the larger values at 30 and 80% total reduction. At the current density of 0.1A/m² which is a slightly larger value than the equilibrium current density, the relation between anodizing time and total reduction showed the maxima at 30% and 80%, and a minimum at 50% total reduction. The anodizing time of recovered sheets became a relatively averaged value at all total reduction and was shorter than that of as rolled sheets. Thickness of oxide film after 600s showed a maximum at 50%, and the minima at 30% and 80% total reduction. If the tendency of the curve is inverted, the relation between thickness of oxide film and total reduction follows the relation between residual stress and total reduction. From these results, it was concluded that the anodizing is greatly influenced by residual stress.

1. Introduction

The corrosion behavior of the cold worked metals have been reported from the following viewpoints of metallic conditions; one is from the stored energy[1,2], and the other from the texture and impurities[3], but the results and the interpretations are in disagreement, respectively. For instance, in the former paper, the exchange current density (i_o) which corresponds to the corrosion rate, increases logarithmic with increasing of microstrain concentration, and in the latter paper, with the increase of rolling the corrosion rate shows nonmonotonic behavior, of which the curve have a maximum (60% total reduction) and a minimum (20% total reduction), stating that the corrosion rate depends on the impurities, especially iron, which was enriched on the surface of cold-rolled specimens.

In the previous paper[4], the authors showed that the relation between corrosion

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rate and total reduction of cold-rolled aluminum sheets follows the behavior of the nonmonotonic increase, which have two maxima at 30 and 80% total reductions and a minimum at 50%, and the relation between residual stress and total reduction shows also the same tendency. Farther, under the condition, in which recrystallization does not occur in heating of the rolled sheet, the corrosin rate of thus recovered aluminun sheets becomes nearly the same value at all total reductions, and is far lower than that of as rolled sheets. On the basis of these results, it was concluded that the main cause, which controls the corrosion rate, is residual stress. Thus, the corrosion behavior in case of aluminum subjected to various rolling degrees has been investigated from the physical situation. However, the effect of electro-chemistry of interface between the solution and aluminum on the corrosion behavior is also the important subject, among which the oxide film is the most important. The corrosion behavior and the effect of oxide film of the specimens in a solution have been reported eleswhere[5], but the report concrening the formation of oxide film on the specimens subjected to various rolling degrees is not yet published.

It is the purpose of this paper to report the effect of cold rolling on anodizing of the cold-rolled aluminum sheets in a neutral electrolyte.

2. Experimental

The sample used for this experiment was the same as previously reported[4], i,e., approximately 3.5mm thick, hot-rolled 99.99% aluminum sheet. Specimens were cut into the size of 20mm×100mm parallel to rolling direction of the sample, and annealed at 573K for 1.8ks in vacuum. The prerolling was carried out to obtain the desired thickness and annealing was performed at 673K for 1.2ks in vacuum. After that, each total reduction was given with one pass reduction of 10%, obtaining the final thickness of 0.3mm. The pass schedule in rolling is the same as previously reported[4].

The cold rolling was carried out in both directions by reversing without a lubricant, and each total reduction from 10% to 90% was performed with 10% per pass. To get recover the cold-rolled sheets without recrystallization heating was carried out at 373K for 10.8ks in vacuum.

The specimens for the anodizing test were cut from the cold-rolled sheets into the size of 20mm×20mm. Each specimen was pickled in trichloroethylene, benzene and methanol for 300s respectively, pickled in 5mass% NaOH solution at 288K for 600s, and then rinsed with distilled water and dried. A teflon tape and vinyl paints were applied to cover the specimen, except the central portion of 10mm×10mm on one surface. The coverings of the small parts on two surfaces at one corner of the specimen were peeled off, and a forked lead-wire was attached to these parts and then the coverings were repaired. Anodizing test was carried out in a 3mass% ammonium tartrate aqueous solution (pH6.8) held at 298K. Apparatus used was a simple anodizing cell by conventional means; pure aluminum cathode and specimen was connected to DC power, a resistace 100Ω was inserted in the circuit, and the

recorder was connected at both sides of this resistance. The measurements were carried out on anodizing voltage at the applied cell voltage of 5V, 20V and 50V, respectively.

3. Result and Discussion

3. 1 Anodizing

The continuously recorded current density at the applied cell voltage of 5V, 20V and 50V, as a typical example on 30% cold-rolled sheets is shown in Fig.1. It is found that the current density rises very rapidly immediately after immersion at each applied cell voltage, then falls rapidly, and finally reaches the equilibrium within approximately 10~20 seconds. Moreover, the values of the current density immediately after immersion and the final, steady current density are depend on the applied cell voltage.
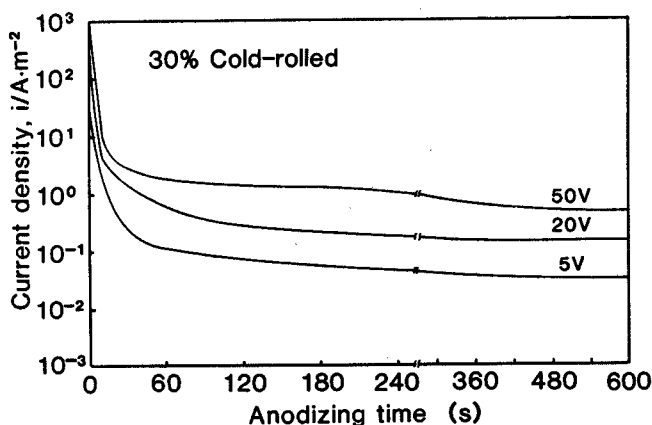

Fig. 1 Relation between the current density and anodizing time at each applied cell voltage on 30% cold-rolled sheets.

Figure 2 shows the relation between the current density and anodizing time for various total reductions at the applied cell voltage of 5V. In case of each applied cell voltage (including 20V and 50V), the diference in anodizing current density by total reduction becomes clear after the immersion of 15~25 seconds, and the current density after 600 seconds shows the smallest value at 50% total reduction, and the larger values at 30% and 80% total reductions.

On the cold-rolled and recovered sheets at the applied cell voltage of 5V, Fig.3 shows the relation between the anodizing time and total reduction, in which the current density reaches to a value (0.1A/m²), a slightly larger value than the equilibrium current density. It is found that the anodizing time of the cold-rolled sheets shows the maxima at 30% and 80%, and a minimum at 50% total reduction, and in addition the anodizing time of recovered sheets becomes a relatively averaged

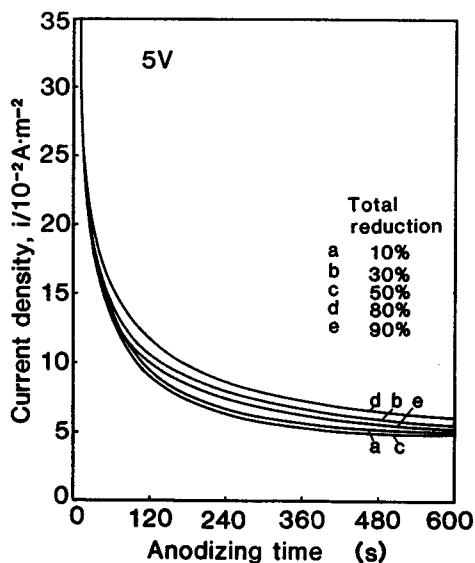Nobuo KOBAYASHI* and Hiroyuki ICHINOSE*

Fig. 2 Relation between current density and anodizing time for
various total reductions at the applied cell voltage of 5V.
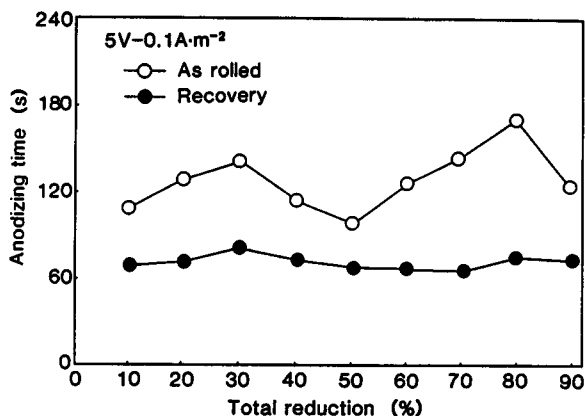

Fig.3 Relation between the anodizing time and total reduction, in whch
the current density is 0.1A/m² at the applied cell voltage of 5V.

value at all total reductions and is shorter than that of as cold-rolled sheets. In case
of 20V and 50V, the curves showed also the same tendency, if the comparison is made
at about 0.5A/m², 1A/m², respectively.

In the anodizing based on the constant potential method of the pure aluminum, the
initial rise of the current density at the measurements (Fig.1) is controlled by the
applied cell voltage[5]. The decreasing current density approches gradually a constant
value, of which value is dependent on the total reduction (Fig.2) and proportional to
the applied voltage. At each applied cell voltage, if the current density which means
the growth of film is compared in the condition which is just before reaching the

constant value, the current density of 50% total reduction is smaller than these of 30% and 80% (Fig.3), and reaches earlier to the final steady state (Fig.2). From these results, the film formation on the specimen of 50% reduction is easier than that of 30% and 80%, and is also easier in the formation of the stable oxide film. Therefore, the thichness of film formed by anodizing has been examined as follows.
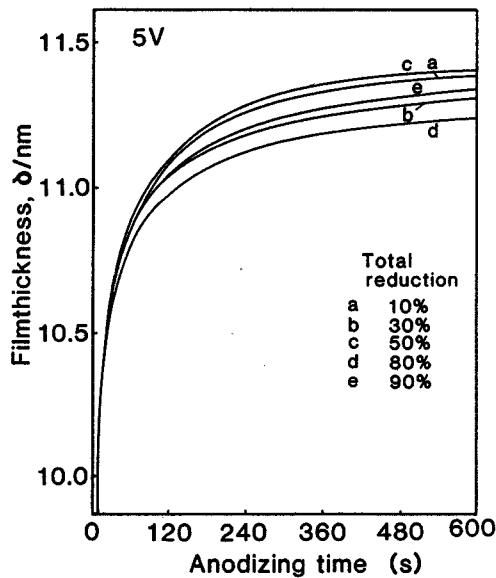

Fig. 4 Relation between the anodizing time and the thickness of anodized oxide film calculated by using the anodized current density for various total reductions at the applied cell voltage of 5V.

The formula for calculating the thickness of oxide film quantitatively has been proposed by Güntherschulze and Betz[6], and has been examined by Hore and Yahalom[5], and Charlesby[7]. The current density induced by the electric field F is given as follows.

$$i = A \exp(BF/\delta) \tag{1}$$

where i is the current density (A/m²), F the voltage between the metal and the solution (V), and δ the film thickness (nm). A and B are the constants in the case of Charlesby[7], and are 10^{-14}A/m², 3.0×10^{-6}m/V, respectively. Since the film thickness (δ) can be obtained from Eq.(1), the values which are calculated by using the anodizing current density shown in Fig. 2, are plotted aganist the time as in Fig. 4. At the applied cell voltage of 5V, the thickness of oxide film after 600s is plotted as a functioin of total reduction in Fig.5. The thickness of film shows the maximum at 50%, and the minima at 30% and 80% total reduction. At the other applied cell voltage (20V and 50V), the same tendency was observed.
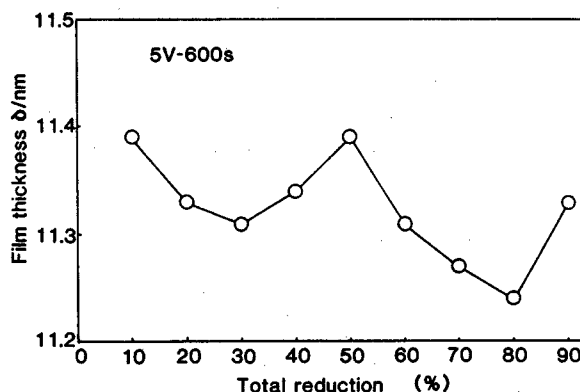
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Fig. 5 Relation between the thickness of anodized oxide film after 600s and the total reduction at the applied cell voltage of 5V.

In the previous report[4], the corrosion rate of aluminum calculated from hydrogen volume generated in 0.5kmol/m³ NaOH solution showed the maxima at 30 and 80%, and the minimum at 50% total reduction. If the tendency of the curve is inverted, it follows the same tendency with the relation between the film thickness and total reduction.

3. 2 Anodizing and residual stress

The relation between the residual stress and total reduction has already been reported in the previous paper[4]. That shows the maxima at 30% and 80%, and a minimum at 50% total reduction. In the relation between the thickness of film and total reduction, if the tendency of the curve is inverted, it follows the same tendency with the relation between residual stress and total reduction. From these facts it can be deduced that the residual stress has a strong relation to the anodizing of alumi-num; i.e., 50% cold-rolled sheet with small residual stress is easily anodized, on the contrary, 30% and 80% cold-rolled sheets with large residual stress are difficult to anodizing. In order to ascertain this, the anodizing test has been carried out on the heated sheet at 373K, 10.8ks. As shown in Fig.3, in which removal of the residual stress was done only with recovery and without recrystallization, the anodizing time becomes relatively averaged value at all total reduction and is shorter than that of cold-rolled sheets. Thus, it is deduced that the residual stress has great influence on the anodizing. As reported in previous paper[4], the residual stress depends on strain and texture due to cold rolling. In evaluating the influence of residual stress on the thickness of film, which was obtained from continuous record of anodizing, the thickness of film at the maximum of 50% reduction is 11.39nm, and at the minimum of 80% reduction is 11.24nm in Fig. 5. The difference is 0.15nm, and corresponds to 1.3% at the average value of film thickness. At the other applied voltage of 20V and 50V the rate is 1.5% and 1.2%, respectively. As obtained in this experiment, the difference of the thickness of oxide film ranges from 1.2 to 1.5% at the average value.

5. Conclusions

The anodizing test on the aluminum sheet (99.99%) which was cold-rolled up to 90% total reduciton under the condition of 10% per pass has been carried out in a 3mass% ammonium tartrate solution by means of the constant voltage method. From the comparison of the results obtained in this experiment with these on residual stress, the following conclusions are drawn.

(1) In the effect of cold rolling on the anodizing of aluminum, the formation of oxide film is easier at 50%, but difficult at 30% and 80% total reduction, which is inversely related to the behavior of the corrosion rate in the sodium hydroxide aqueous solution and the residual stress.

(2) The anodizing time of the recovered aluminum sheets becomes a relatively averaged value at all total reduction and is shorter than that of the cold-rolled sheets; thus the residual stress has great influence on the anodizing.

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