Zone Refining of Aluminum

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99.999% aluminum was zone-refined in vacuum better than 1×10^{-6} Torr, and various zone speeds, zone lengths and numbers of passes were tried to know the optimum refining conditions. The impurity content was estimated from the residual resistivity, and the highest resistance ratio in bulk $R_{300}/R_{4.2}$ obtained in the present work was 50000.

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I. Introduction

Zone refining of aluminum has been tried by several workers. Bratsberg et al.[(1)] carried out the zone refining in high purity nitrogen gas under the zone speed of 25 mm/hr and about 10 cm zone length, and obtained 26500 as the highest resistance ratio $R_{293}/R_{4.2}$.

On the other hand Revel[(2)] obtained 35500 as the resistance ratio $R_{273}/R_{4.24}$ by the zone refining 10 passes at 20 mm/hr in zone speed, followed by 10 passes at 5 mm/hr.

In spite of the works described above, the best method of zone refining for aluminum is still not clear. So the present work has been started with two aims, to get aluminum of higher resistance ratio and to make clear the optimum condition for zone refining of aluminum.

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II. Experimental Procedure

1. Zone refining

Starting material used in the present work was 99.999% aluminum ingot supplied from Sumitomo Chemical Co., Ltd., and the resistance ratio $R_{300}/R_{4.2}$ was about 2000. The material was rolled and cut to a square rod of 22×10 mm^2 in cross section and of 900 mm in length. After the machining, the surface of the rod was cleaned with benzene and was washed in distilled water. The aluminum rod was set in a reactor grade graphite boat and placed inside a quartz tube as seen in Photo. 1 which shows the zone-refining apparatus used in the present work. It was melted by induction heating in vacuum better than 1×10^{-6} Torr. To check the optimum condition for the zone-

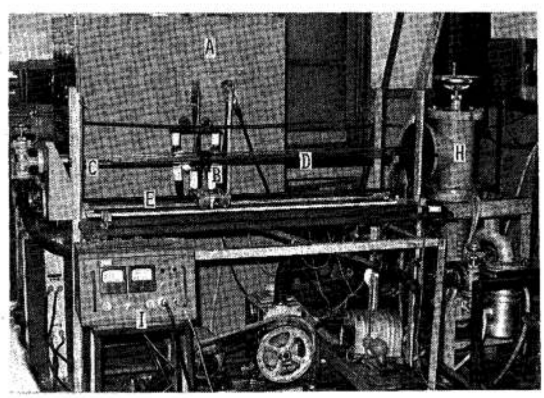

Photo. 1 Zone-refining apparatus.
A: induction heating apparatus, B: heating coil, C: quartz tube, D: graphite boat, E: worm gear, F: motor, G: rotary pump, H: diffusion pump, I: vacuum gauge.

Table 1 Zone-refining conditions and the resistance ratio $R_{300}/R_{4.2}$ without size correction.

Number of specimen	Zone speed (mm/hr)	Number of passes	Zone length (mm)	Maz. *R.R.*	*R.R.* at the tail
ZR– 8	55	10	50	12100	
ZR– 9	24	9	40~50	16200	290
ZR–10	236	8	40~50	12500	1210
ZR–11	24	5	40~50	14700	620
ZR–14	11	5	20~25	15000	310
ZR–15	55	10	30	16800	290
ZR–16	236+11	5+3	30	14000	260
ZR–17	55	20	<30	15700	310
ZR–18	55	6	30	12600	
ZR–19	38	1	30	8800	
ZR–20	38	10	30	13800	
ZR–21	55	10	<30	15100	

refining, various zone speeds, zone lengths and the numbers of passing zone were tried as seen in Table 1.

2. Resistance ratio measurement

In order to investigate the efficiency of purification, the electrical resistance was measured. The zone-refined aluminum rod was cut to 40 mm length from the top and the remainder was cut into 100 mm pieces as shown in Fig. 1. Furthermore the top of each piece was cut into a 10 mm length piece for the resistance measurement. The surface of the small pieces was scraped off to remove the contamination, rolled to 0.5 mm thickness, and then cut in the form of $0.5 \times 3 \times 120\ mm^3$ as the sample for the resistance measurement. These samples were cleaned with benzene and set on a quartz frame for the resistance measurement. After the annealing at 600°C for 3 hr in air followed by the furnace cooling, resistance measurements were made in a temperature controlled oil bath at 300 K and in a liquid helium cryostat. The ratio of the resistance at 300 K to that at 4.2 K, $R_{300}/R_{4.2}$, was used as a scale of purity through the present work.

The sample thickness was changed from $20\ \mu$ to 1.5 mm, and the resistance were measured in the temperature range from 4.2 K to 300 K using a double chamber cryostat, in order to determine corrections necessary for the size effect. The details of apparatus have been published elsewhere[3].

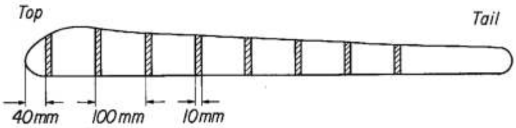

Fig. 1 Zone-refined aluminum rod showing the parts for electrical resistance measurement.

III. Results and Discussion

Several zone-refining conditions, i.e. zone speed, zone length and the number of passing zone, in the present work are given in Table 1, and the maximum resistance ratio obtained under such conditions are also tabulated in the table. It is necessary to know the distribution of impurity, that is, the resistance ratio $R_{300}/R_{4.2}$ along the aluminum rod, in order to investigate the efficiency of zone refining. The resistance ratios along the rod are shown in Figs. 2~6 for several samples.

Impurity distributions for several zone speeds, 24, 38, 55 and 236 mm/hr, are plotted in Fig. 2. It is shown that 70~80% from the top of sample has a resistance ratio more than 13000 for the speeds of 24, 38 and 55 mm/hr, whereas for the speed of 236 mm/hr the ratio is high at only at the top side and becomes gradually lower in the tail side. An example of the 11 mm/hr zone speed, which is the slowest speed in the present work, is compared with the speed of 55 mm/hr in Fig. 3. It is evident from the figure that the resistance ratio is high only at the top side as is the case with the speed of 236 mm/hr. Therefore the best zone speed

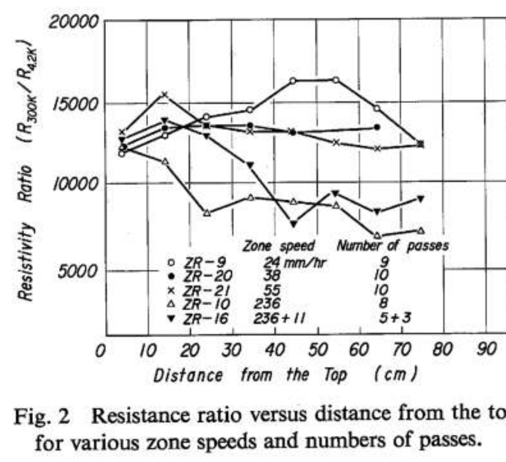

Fig. 2 Resistance ratio versus distance from the top for various zone speeds and numbers of passes.

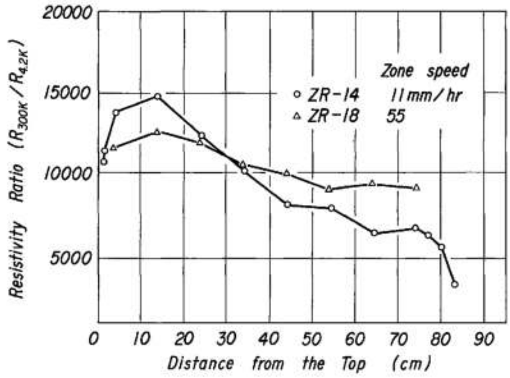

Fig. 3 Resistance ratio versus distance from the top for the zone speeds of 11 and 55 mm/hr.

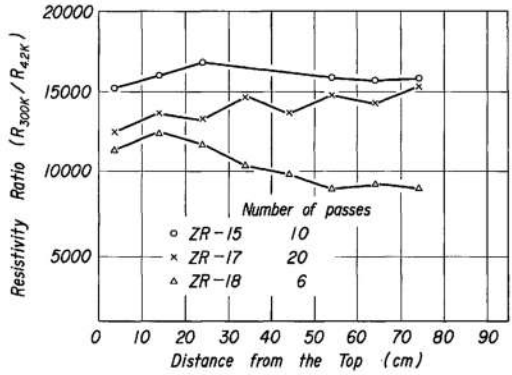

Fig. 5 Resistance ratio versus distance from the top for various numbers of passes at the zone speed of 55 mm/hr.

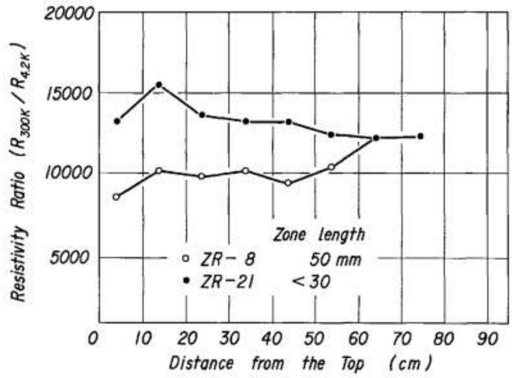

Fig. 4 Resistance ratio versus distance from the top for the zone length 30 and 50 mm.

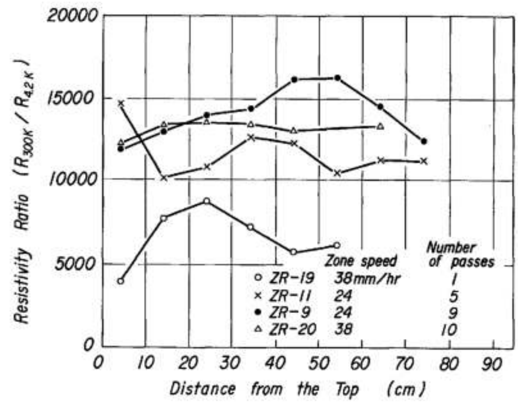

Fig. 6 Resistance ratio versus distance from the top for various numbers of passes at the zone speeds of 24 and 38 mm/hr.

seems to be 24~55 mm/hr.

Figure 4 is a similar figure to compare the zone length, and the two samples are zone-passed ten times at the 55 mm/hr speed, so the difference in resistance ratio is attributed to the difference of zone length.

The effect of the number of passing zone is seen in Fig. 5. The zone speed and the sample length are 55 mm/hr and 30 mm, respectively, and the resistance ratio increases with the number of passing zone until 10 times passing. However, 20-time passing decreases the ratio when compared with 10-time passing. It seems that the purification saturates at a level and the further zone passing rather contaminate the sample. The data for the zone speeds of 24 and 38 mm/hr are given in Fig. 6.

The impurity concentration is estimated from the resistance ratio in the following way. The measured resistivity should be corrected taking into account the size effect to know the bulk resistivity ρ_b on such a high purity metal. By the Fuchs-Sondheimer formula[(4)], the ratio of the measured resistivity to the bulk resistivity ρ/ρ_b varies with the ratio of specimen thickness t to the electron mean free path l as follows:

$$\frac{\rho}{\rho_b}=\left[1-\frac{3l(1-p)}{2t}\int_1^\infty\left(\frac{1}{x^3}-\frac{1}{x^5}\right)\times\frac{1-\exp(-tx/l)}{1-p\exp(-tx/l)}\,dx\right]^{-1} \tag{1}$$

where p is the surface reflection parameter, and it is assumed to be zero in the present estimation, corresponding to the extreme case of perfectly diffuse reflection. Equation (1) has been numerically integrated by Sondheimer, and the calculated curve was compared with the present experimental results. The best fit for the sample which has about 13000 as the resistance ratio without the size correction is seen in Fig. 7. The values of the bulk resistivity ρ_b and the electron mean free path l estimated from the fit are seen in Table 2, and the values of $\rho_b l$ are also shown in the table. As seen from the table, the resistance ratio is raised from 13000 to 26000 by the size correction, using 2.85×10^{-6} ohm cm as the resistivity at 300 K. Therefore the corrected resistance ratio is not less than 30000 for samples which has the resistance ratio more than 15000 as sample ZR–15. Sometimes we got the value more than 20000 as the resistance ratio without size correction. Such a value must be converted into 50000 by the same size correction. The details of size correction to obtain the bulk resistivity will be published elsewhere[5]. The impurity concentration is estimated from the bulk resistivity, assuming the resistivity contribution due to one atomic per cent impurity to be

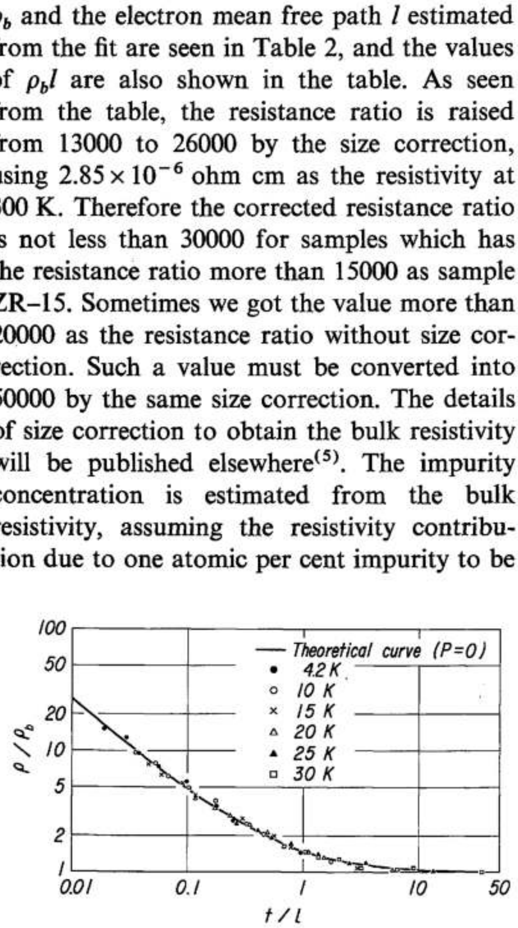

Fig. 7 Comparison of the present experimental results and Fuchs-Sondheimer theory.

Table 2 Bulk resistivity ρ_b and mean free path l.

Temperature (K)	ρ_b (10^{-9} Ωcm)	l (mm)	$\rho_b \cdot l$ (10^{-11} Ωcm^2)
4.2	0.111	1.03	1.1
10	0.204	0.560	1.1
15	0.386	0.326	1.3
20	0.795	0.167	1.3
25	1.86	0.0729	1.4
30	4.53	0.0281	1.3

1.0×10^{-6} ohm cm. Because the resistivity contribution due to dissolved copper, silicon and iron, which are considered to be the principal impurities usually contained in high purity aluminum, are 0.80, 0.65[6] and 6.4×10^{-6} ohm cm[7]/atomic per cent, respectively. By a rough estimation, the impurity concentrations at the top and tail of the zone-refined aluminum ZR–14 are about 1 ppm and 100 ppm, respectively.

It is necessary to know what kinds of impurities are remained and how they distribute along the zone refined aluminum rod, so the activation analysis is in progress with collaboration of the Research Reactor Institute of Kyoto University.

IV. Summary

99.999% aluminum was zone refined in vacuum better than 1×10^{-6} Torr. The optimum conditions for purification are zone speed of 24~55 mm/hr, zone length less than 30 mm and about 10 times of zone passing. Under such conditions, 80% of the rod was purified more than 30000 in the resistance ratio corrected the size effect, and the highest resistance ratio obtained in the present work was 50000.

Acknowledgments

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