

Surface Segregation of Several Elements in High Purity Aluminum Foils

H.Tsubakino¹, Y.Yamamoto², A.Yamamoto¹, L.Liu¹, M.Terasawa¹,
T.Mitamura¹, K.Yoshida³, A.Kinomura⁴, Y.Horino⁴

¹ Graduate School of Engineering, University of Hyogo,
2167 Shosha, Himeji Hyogo 671-2201, Japan

² Graduate Student, University of Hyogo, presently Sumitomo Metal Industry,
Amagasaki, Hyogo 660-0891, Japan

³ Development Department Rolled Products Division, Showa Denko K.K. Sakai, Osaka 590-8576, Japan

⁴ Institute of Advanced Industrial Science and Technology KANSAI, Ikeda, Osaka 563-8577, Japan

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Abstract

Surface segregation phenomena of several elements (Pb, Fe, Mn, Co and Cu) in high-purity aluminum foils were studied by Rutherford back scattering spectroscopy and transmission electron microscopy on heat-treated foils. The degree of surface segregation (content segregated at the surface/bulk content) was also different depending on the elements, i.e., the greatest degree for Pb (140-fold) and the least for Cu (almost nil), and the other elements were in the decreasing orders of Fe (80-fold), Co (13-fold) and Mn (9-fold). This change in the degree of surface segregation of the various elements followed a roughly similar tendency as the order of maximum solubility in aluminum.

1. Introduction

It is well known that surface segregation phenomena are closely similar to those of grain boundary segregation [1], although there is much less information on the former. The surface segregation of lead in high-purity aluminum foils has been studied widely [2-7], because this segregation strongly affects the formation of uniform and fine tunnel etching pits in the foils as an electrolytic capacitor. There remain few studies on the surface segregation phenomena of other elements in aluminum foils, despite the importance of knowing the effect of surface segregation on surface physical, mechanical properties and corrosion behavior except for the lead element.

High-purity aluminum foils containing a small amount of several elements focused on the transition metals of Fe, Mn, Co and Cu, were used in this study. The surface segregation phenomena were studied by Rutherford back scattering spectroscopy (RBS) and transmission electron microscopy (TEM) on the foils, after various heat treatments.

2. Experimental Procedures

The foils were prepared by casting using high-purity aluminum (99.999%) and impurity addition (99.9-99.99%). The chemical compositions of the alloys are shown in Table 1. The ingots were hot- and cold-rolled to foils of ca. 0.1 mm thickness. The foils were cut to a size of 10x10 mm² after electro-polishing both surfaces to avoid surface segregation layer occurring during the hot-rolling stage. The foils were annealed under various conditions in an argon atmosphere, as shown in Table 1. These conditions were selected as the highest segregation at the surface occurring in each element from preliminary experiment.

Table 1: Chemical composition of foils and heat treatment in Ar atmosphere.

Foil Composition (mass-ppm)	Heat Treatment
1. Al-94 ppm Pb	813 K, 4 h
2. Al-1 ppm Pb-25 ppm Cu	813 K, 4 h
3. Al-50 ppm Fe	723 K, 20 h
4. Al-464 ppm Mn	623 K, 20 h
5. Al-199 ppm Co	623 K, 20 h

Rutherford back scattering spectroscopy (RBS) was done on these heat-treated foils using 1.8 MeV He ion. The He ion beam was irradiated on the foils for 20 micro-coulomb with a beam current of about 10 nA, and the scattered ion was detected at 165 degrees in the direction of the incident beam [6,7]. The analyzed area was 2 mm².

Transmission electron microscopy (TEM) was also done using specimens sliced perpendicular to the foil surface. Foils were buried in resin and then sliced with a diamond microtome. These TEM foils were observed by transmission electron microscopy with an energy dispersive x-ray spectroscopic (EDX) apparatus. The observations were performed with a JEM-2010 operated at 200 kV.

3. Results and Discussion

A typical RBS spectrum of an Al-94ppm Pb foil is shown in Figure 1. The edge peaks of lead and aluminum were determined using high-purity standard specimens. Enlargement of the lead peak is shown in Figure 2. As shown in each spectrum, a lead peak can be observed (1) in the foil annealed at 813 K for 4 h, but it disappeared (2) after electro-polishing this annealed foil for 1 min (about 6 micron), and the lead peak can be observed again after re-annealing at the same temperature for 4 h (3). This is again confirmed that the surface segregation of lead at the aluminum foil did occur obviously after electro-polishing. The heights of the lead peak in both (1) and (3) are almost the same, which was estimated as about the segregation degree (which is defined as surface segregation concentration/bulk concentration) [6] of about 140-fold. It was clear, however, that the lead concentration within the foil changed little although the lead element diffused to the surface from inside during the annealing, because the heights of the two peaks are almost the same.

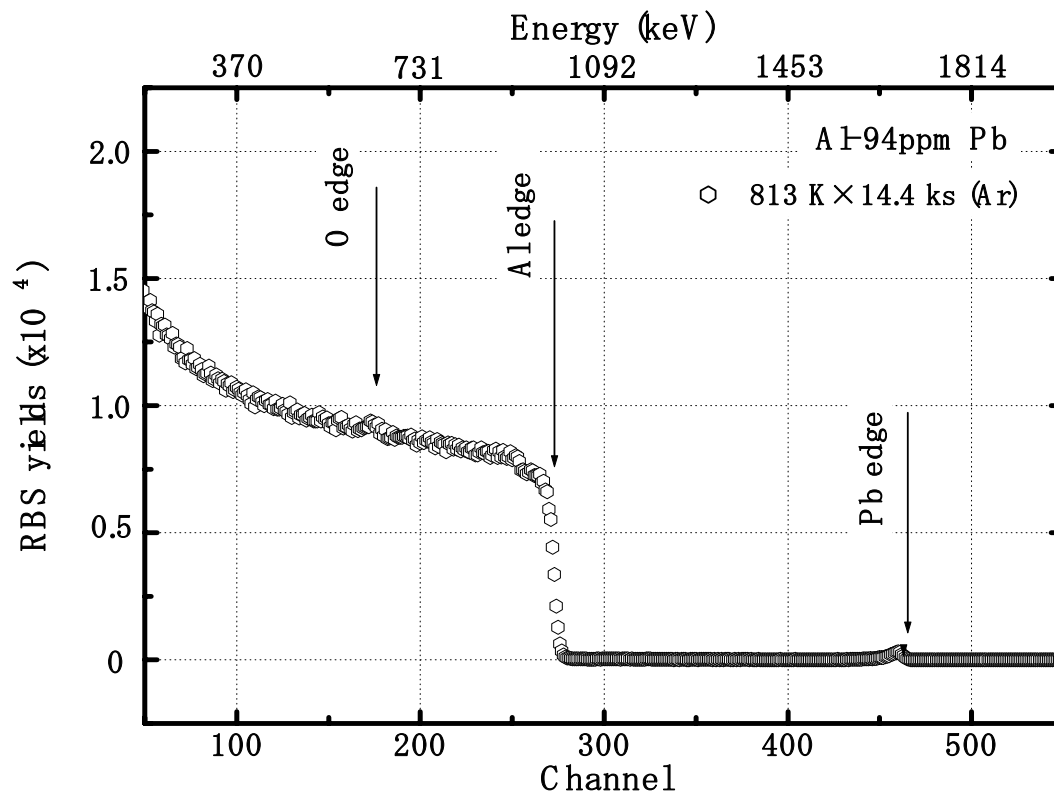


Figure 1 : Typical RBS spectrum in Al-94ppm Pb foil annealed at 813 K for 4 h.
(Several data are superimposed)

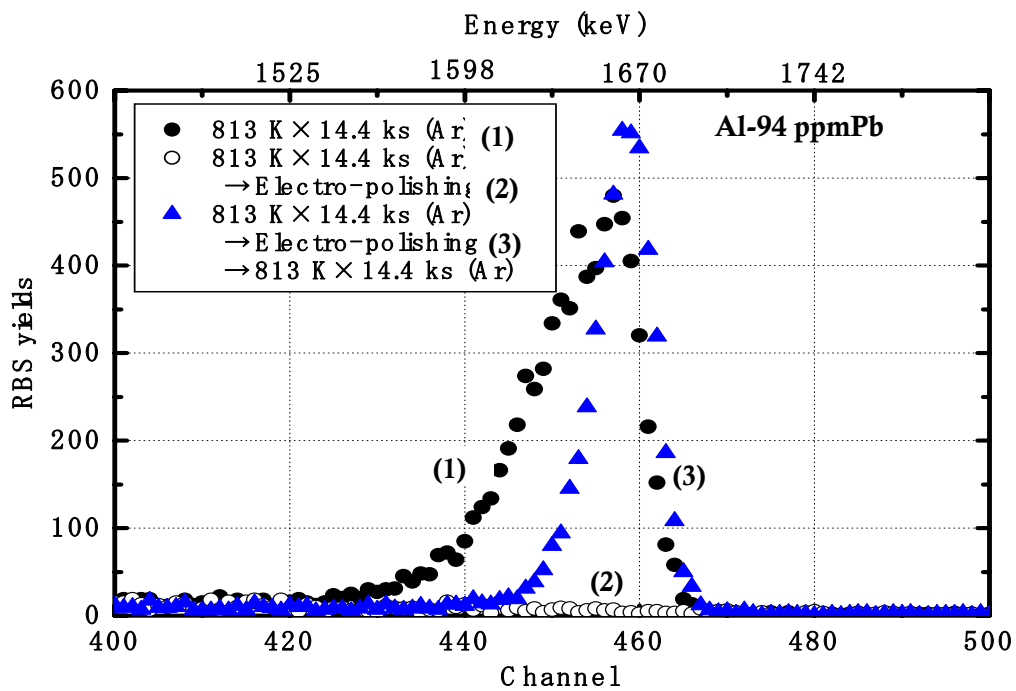


Figure 2 : Enlargement of lead peaks of RBS spectra in Al-94 ppm Pb foil.

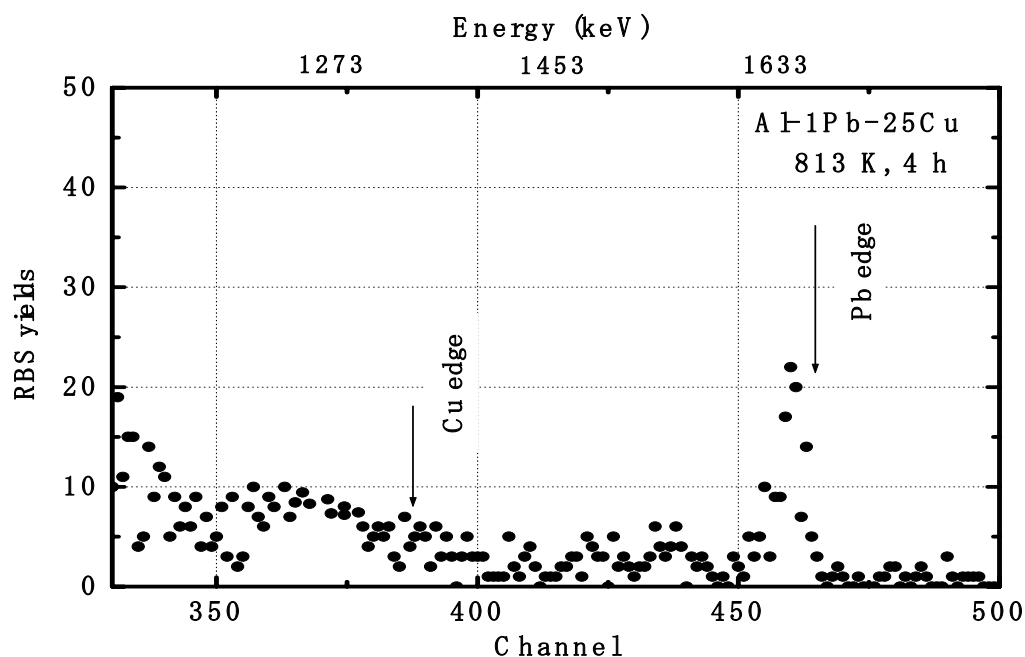


Figure 3 : RBS spectrum in Al-1ppm Pb-25ppm Cu foil annealed at 813 K for 4h, showing no obvious Cu edge peak.

In the RBS spectrum of the Al-1ppm Pb-25ppm Cu foil (Figure 3), the peak of the lead edge can also be observed, however there is no obvious copper peak (Cu edge peak=386 channel). The copper element thus has a tendency of being hard to segregate at the foil surface. The segregation degree for lead was estimated as 1200-fold in the multi-component foil, so the degree of segregation of lead differs greatly between binary and multi-component systems. In the Al-Pb binary system, the degree of segregation tends to increase in the foil with a lower concentration of lead [8]. Furthermore, surface segregation of lead will be different depending on which other elements coexist, i.e., the presence of copper may affect the surface segregation of lead. The actual reason for the different degree between elements is not clear right now, but the following factors may be involved: chemical attractive interaction between solutes, enhanced diffusivity of solutes in a multi-component aluminum matrix and/or simultaneous segregation.

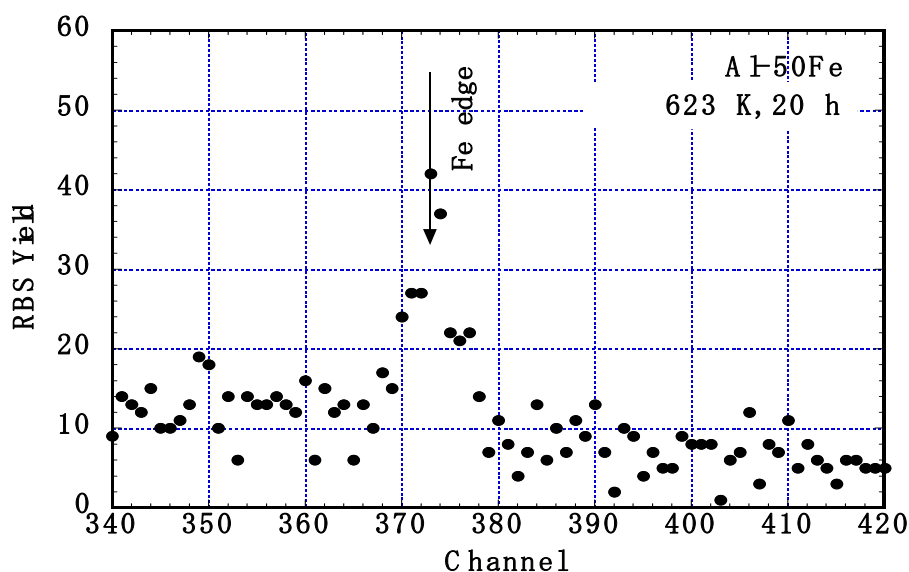


Figure 4 :
RBS spectrum in Al-50ppm Fe foil annealed at 623 K for 20 h

A RBS spectrum of high-purity Al-50ppm Fe foil is shown in Figure 4. From these data, the degree of segregation is estimated as about 80-fold. TEM-EDX analysis data show the segregated iron can be found at the interface between the aluminum matrix and an oxide film, which is different from the previous results concerning the segregation of lead in aluminum oxide film[6-8]. This will be due to the binding energy difference between the elemental oxide and alumina.

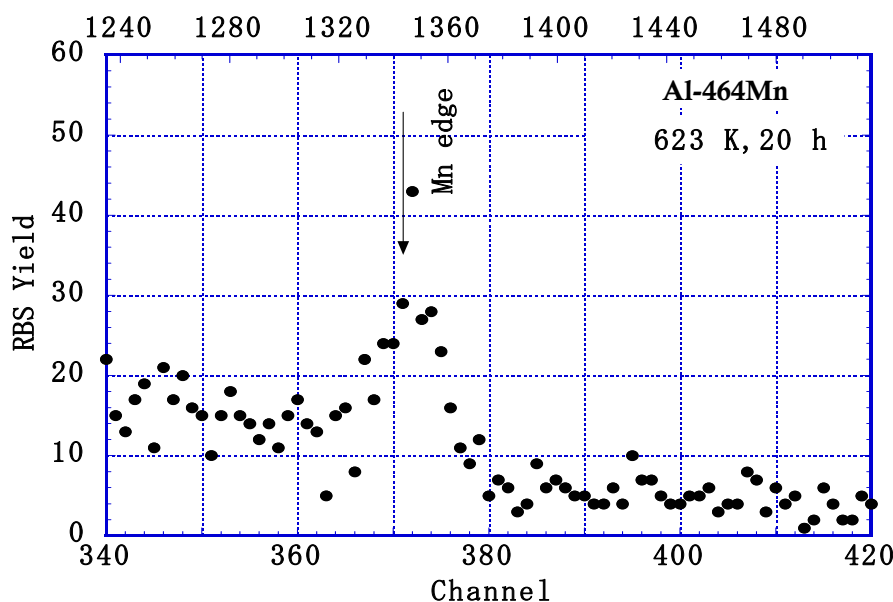


Figure 5 :
RBS spectrum in
Al-464 ppm Mn
foil annealed at
623 K for 20 h

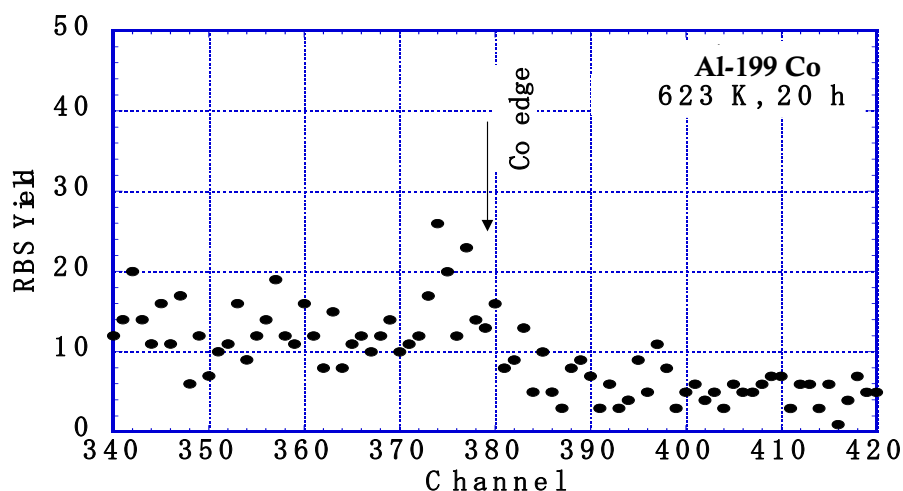


Figure 6 :
RBS spectrum in
Al-199 ppm Co
foil annealed at 623 K
for 20 h

The RBS spectra of manganese and cobalt are shown in Figures. 5 and 6, respectively. It is seen that these elements segregated at the surface of high-purity aluminum, though the height of each edge peak is lower than that of lead in aluminum. The degrees of surface segregation of these elements estimated from these data, were 9 and 13-folds.

Table 2 summarizes the segregation data obtained from RBS. The degree of segregation was the maximum for lead, 140-fold, and the least for copper at nearly nil of the elements used in this study. The maximum solubility data in aluminum [9] are also listed in Table 2. The tendency of the degree of surface segregation is similar to that of the maximum solubility of each element in aluminum. Therefore, the degree of surface segregation is a very similar phenomenon to that of grain boundary segregation [1, 10].

Table 2: Summary of surface segregation obtained from RBS.

Foil	Degree of surface segregation (=segregation c. / bulk c.)	Max.solubility (mass ppm)
Al-94ppmPb	140	nearly nil
Al- 1 ppmPb-25 ppmCu	1200(Pb), nearly nil(Cu)	5.7%(Cu)
Al- 50ppmFe	80	517
Al- 464ppmMn	9	1.4%
Al- 199ppm Co	13	200

4. Conclusions

Surface segregation phenomena of Pb, Fe, Mn, Co and Cu were studied by RBS and TEM methods with the following results:

- (1) The surface segregation phenomena of elements other than copper were observed. The degree of segregation was the maximum for lead and least for copper.
- (2) The degree of surface segregation of lead is much higher in multi-component system than in the binary system.
- (3) Surface segregation has a fundamentally similar tendency to the maximum solubility of each element in aluminum.

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