Effects of Cold Rolling and Heat Treatments on Fe Precipitation in High Purity Aluminum Studied by Mössbauer Spectroscopy

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Abstract. Effects of cold reduction and heat-treatments on the Fe precipitation behavior in high purity aluminum with 50 ppm Fe were investigated by Mössbauer spectroscopy using 90% enriched ^{57}Fe. It has been revealed that the volume fraction of Fe precipitates becomes maximum by a heat treatment at 310 °C in supersaturated solid solutions with strains introduced by 96 % cold reduction. The precipitates in the 310 °C aging sample are probably metastable Al_6Fe compound. Surprisingly, it was found that the precipitation starts even at 120 °C. .

Keywords: aluminum, iron, precipitation, Mössbauer spectroscopy

1. Introduction

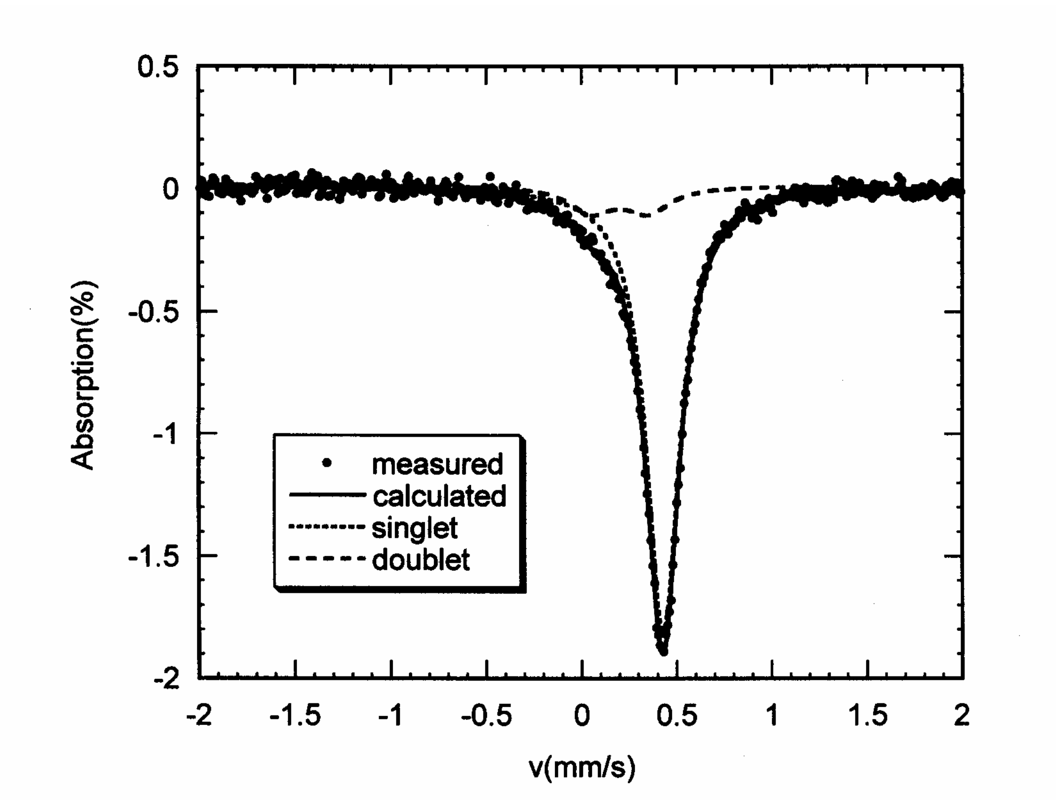
The quality of high purity aluminum foils for electrolytic capacitors sensitively depends on manufacturing factors such as cold rolling and heat treatments. It is believed that the degree of precipitation of impurities, in particular, that of iron impurity is one of the most important factors. Therefore, establishing the methodology for estimating the degree of iron precipitation is highly desired not only for metallurgical interest but also for managing fabrication processes. In this paper, we report on effects of cold reduction and heat-treatments on the Fe precipitation behavior in high purity aluminum with 50 ppm Fe investigated by Mössbauer spectroscopy using 90 % enriched ^{57}Fe.

2. Experiments

We prepared 1 kg high purity aluminum ingot using 99.995 % pure aluminum adding small amount of Si, Cu and 90 % enriched ^{57}Fe, so that the final impurity compositions become to 50 ppm Si, 10 ppm Cu and 50 ppm Fe, which are near to the material for electrolytic capacitors. The melt was cast into a book-shaped mold. A part of ingot was subjected to heat treatments: heated at 620 °C for 17 hr, cooled down to 530 °C and then hot rolled into a plate of 7mm thickness. The Mössbauer samples were prepared by cold-rolling this plate into 0.1 to 1 mm thickness. In these treatments, 90 % of Fe exist as solutes as shown later.

Mössbauer measurements were carried out at room temperature using 370 MBq ^{57}Co doped in a metallic Rh foil. Rectangular sheets of 20x20 mm foils were set into the sample holder so as the total thickness to be about 0.8 mm. Data are accumulated for 7 to 10 days, giving a fairy clear spectrum even for such a dilute Fe sample.

The spectra thus obtained were fitted by Lorentzians corresponding to a singlet of Fe solute and a doublet of Al_6Fe precipitate. All of the Mössbauer parameters of the singlet were determined by least square fitting. On the other hand, the fixed parameters were used for the doublet using the values obtained for Al_6Fe compound, which is believed to be the precipitation products in dilute A1(Fe) alloys [1,2] slightly modified to obtain better fitting for the present results, namely, the isomer shift, δ = 0.20 mm/s, the $e^2qQ/4$ = 0.15 mm/s and the half width of each Lorentzian Γ= 0.28 mm/s. Neglecting the difference in recoil-free fractions between solute Fe and Al_6Fe compound, we regarded the ratio of integrated intensities of the both components as the fractions of Fe atoms of solute and in precipitates. This procedure might give rise to somewhat over-estimation of precipitates because the Debye temperature of Al_6Fe should be higher than that of solute Fe.



3. Results and discussion

Figure 1. Mössbauer spectrum of the sample hot rolled from 530 ° C. ● : absorption rate (%), solid line : calculated value, chain line(singlet): solute Fe, dotted line(doublet): precipitated Fe.

Figure 1 shows the Mössbauer spectrum of the as-rolled sample (4 sheets of 0.2 mm thickness foils). As seen in the figure, the spectrum consists mostly of the singlet. Analyzing the spectrum, it becomes evident that approximately 90 % of Fe exist as solutes in the plate prepared by hot-rolling.

Figure 2 shows the Mössbauer spectrum of an aged sample at 310 °C for 6hr after cold rolling the plate sample up to 97% reduction in thickness (7mm to 0.2mm). It is clearly seen that the doublet component growth, indicating the development of precipitation of the Al_6Fe compound. The Fe fraction in precipitates thus estimated for the samples aged for 6h at various temperatures after cold

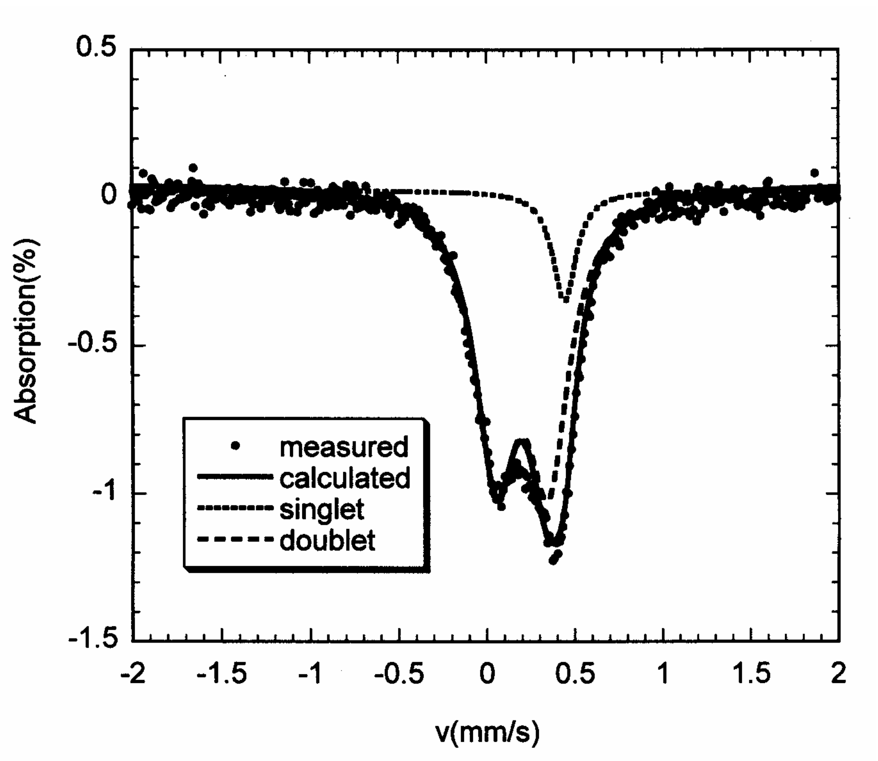


Figure 2. Mössbauer spectrum of the sample aged 6 hrs at 310 oC after cold rolling by 97 % reduction. ● : absorption rate(%), solid line : calculated value, chain line(singlet): solute Fe, dotted line (doublet): precipitated Fe.

rolling is shown in figure 3. It was found that the precipitation develops at surprisingly low temperatures even at 120 °C . The maximum precipitation occurs at 310 °C. Above 310 °C, the Fe fraction in precipitates decreases with increasing temperature and becomes almost 0 at 500 °C. In this temperature range, the alloy should be in the thermally equilibrium state and the solubility limit of Fe in Al is 50 ppm at 500 °C.

Open circles in figure 3 indicate Fe fraction in precipitates for the samples aged for 6 hrs at various temperatures after solidification treatment, namely, rapidly cooled the Mössbauer sample from 550°C . In this case, no precipitation takes place even at 300°C, indicating that high density dislocations are necessary for developing precipitation.

So far, we have considered that the precipitates developed in the present conditions are Al_6Fe. In fact, the fitting of the Mössbauer spectra by the singlet of solute Fe and the doublet for Al_6Fe is fairly good. However, looking carefully, a tiny misfit is observed around the central dip of spectrum as observed in the spectrum of figure 2. We noted that this misfit becomes more distinct for the samples aged at lower temperatures than 300 ºC. Furthermore, we found that the precipitates grown at the lower temperatures are rather unstable and easily destroyed by additional cold rolling, although such a phenomenon is not observed for the samples aged above 250 °C. Probably, the precipitates developed at the low temperatures are not complete Al_6Fe but something like precarious clusters leading to the formation of Al_6Fe compound with a very small size. Since we can not know the size of precipitates from the Mössbauer spectrum, some other experiment like TEM is desirable.

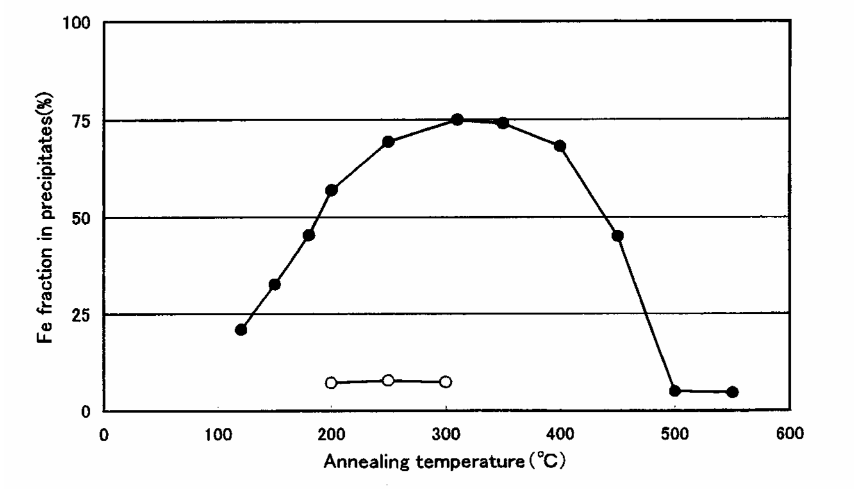


Figure 3. Fe fraction in precipitates for the samples aged 6 hrs at various temperatures from 120 ºC to 550 ºC. ●: aged after 90 % cold rolling, ○ : aged without rolling

References

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