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INVESTIGATION OF THE DISTRIBUTION OF RARE EARTH ELEMENTS IN PURE Al BY THE METHOD OF INTERNAL FRICTION (PART 1)

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Abstract - In this paper, the distribution of rare-earth elements in pure Al was investigated by the method of internal friction with a high vacuum Ke's pendulum. The samples are pure Al (99.99%) with various contents of RE (0-3%, nine in number). The effect of rare-earth addition on grain-boundary relaxation of Al, and the unpinning of dislocations at room temperature was measured. It has been found that the peak height and background decrease with increasing RE content up to 0.5%, and that when RE > 0.5%, the peak height changes little but the background rapidly increases with RE content increase. In view of these facts, the distribution of RE in Al was inferred. The binding energy between RE impurity and dislocations was estimated to be about 0.19 eV.

I - INTRODUCTION

In recent years, the use of rare earths (RE) and their alloys have been growing fast, especially in the cable industry. But little is known about the distribution of RE in Al. It is known that the difference between the rare earth atom and the Al atom in diameter and electronegativity are considerable. Therefore, the solubility of RE in Al is very small /1/. However, reliable values of solubility have not been obtained. It can be shown that the RE atoms in the state of solid solution, if any, should have a preference for segregating in grain boundaries and dislocations when the RE content is high; the eutectic compound or intermetallic compound of Al-RE may be formed in grain boundaries./2/ Since internal friction is especially sensitive to impurities, we use this method to study, in particular, the effect of RE on grain boundary internal friction of Al and discuss the behavior of RE in Al.

II - EXPERIMENTAL PROCEDURE AND RESULTS

Nine samples with different RE contents (see Table 1, RE = mischmetal, Al = 99.99%) were kindly supplied by Guangzhou Institute of Non-ferrous Metal Research. These samples are all in cold-drawn states with diameters of 1.2 mm. They were redrawn to a diameter of 0.9 mm for internal friction measurement by Ke's torsional pendulum in a vacuum of about 5x10^-8 Torr. These samples are about 300 mm long, and annealed at 720 K for two hours in the internal friction apparatus. Measurements were carried out with the temperature decreasing about 1°C/min. The experimental grain-boundary internal friction curves were obtained as shown in Fig. 1 and Fig. 2. The background of experimental curves is subtracted according to the method provided in another paper, and the true grain boundary internal friction was obtained as shown in Fig. 3. These curves are fit by following equation.
where $\Delta$ is the relaxation strength, $W = z/\beta, Z = \ln (\tau/\tau_m) \tau$ is the relaxation time, $\tau_m$ the most probable value of $\tau$, $\beta = [\beta_0 + \beta_H]$, where $\beta_0$ and $\beta_H$ are the distribution widths of $\ln \tau$, $\ln \tau_m$, and the activation energy $H$ respectively, and $H_m$ is the most probable value of $H$. $T_m$ is the temperature when $\omega = 1$. Thus the series parameters are obtained and listed in Table 1.

III - DISCUSSION

It is thought that there exists a dislocation network in the grain boundaries. Under the application of stress, the dislocation moves by glide and climb /3/. In the case of Al–RE alloys, since RE’s atom size is large compared with Al, there is a strong tendency of RE atoms to segregate to the grain boundaries, and the movements of grain boundary dislocations is restricted by the RE atoms, so that the peak height or the relaxation strength, $\Delta$, rapidly decreases with RE content, as indicated in Table 1, No. 1 to No. 5 to (from 0.01% to 0.50% RE). When $\Delta = 0.50\%$, the solid solution state RE in grain boundaries is saturated, and $\Delta$ changes little or increases slightly, which may have a contribution by phase boundaries, since an amount of Al–RE eutectic compound has been observed in specimens by metallographic microscope. So for the relaxation strength, $\Delta$, of specimen 1 to be greater than specimen 2, it may be caused by the clearing action. When the RE content is small, i.e. RE $< 0.01\%$, some non-RE impurity atoms form a compound out of RE, so that the grain boundaries of 1 become more clean than pure Al (99.99%). Consequently, the grain boundary relaxation height of specimen No. 1 is greater than that for ultra-pure Al, like our specimen No. 0. There is evidence that if No. 1 and No. 0 specimens are annealed at the same condition (720K), the grain size of the former is about 0.32 mm, and the latter 0.20 mm. Thereafter the grain size decreases with RE content increase (see Table 2), except for specimen No. 3.

From Table 1, it can be seen that both $H_m$ and $\beta_H$ change with RE content. Reference /4/ describes that the distribution of impurities grain boundary behaves as a Gaussian distribution. From this we deduced that $\beta_H = G \sigma c^2$ when $c$ is very small, where $G$ is constant, $c$ is RE content. Taking small RE content specimens No. 1, 2 and 3 in Table 1, the plot of $\beta_H$ versus $\sigma c^2$ is made as shown in Fig. 4 which appears to show a good linearity. Therefore, it is verified that the distribution of $H$ arises from concentration fluctuations of solute atoms of RE in the grain boundary.

For an estimate of the binding energy between RE atoms and dislocation, the unpinning strain of dislocations was measured at various temperatures near room temperature for two samples (RE=0.01%wt, RE=0.06%wt). According to reference /5/, the following expression can be deduced:

$$\ln A^* = B_0 + G/KT$$

where $A^*$ is the amplitude which corresponds to the unpinning strain; $\sigma^*, G$ are constant. The experimental data is listed in Table 3, and the plot $\ln A^*$ against $1/T$ is shown in Fig. 5. These two curves are well fit by two straight lines with the same slope:

$$\ln A^* = -4.5 + 2143/T \quad \text{for } 0.01\% \text{wt RE}$$
$$\ln A^* = -5.0 + 2143/T \quad \text{for } 0.06\% \text{wt RE}$$

From the above empirical expression the binding energy between RE atom and dislocation is obtained. The value is about 0.19 eV.
From the discussion above, it may be concluded that:

1. When \( \text{RE} < 0.01\% \), the clearance action is mainly due to the activity of RE.
2. When \( \text{RE} > 0.01\% \), the RE elements act as solute atoms segregating to the grain boundaries up until about 0.5% and meanwhile part of RE elements act as solute atoms existing in the interior of the grains. These RE atoms are located mainly in the defects of dislocations. In the case of Al, the 0.5% RE content is a saturating content for grain boundaries.
3. When \( \text{RE} > 0.5\% \), the AT-RE eutectic compound is formed.

### Table-1 Grainboundary relaxation parameters

<table>
<thead>
<tr>
<th>No.</th>
<th>( \beta_{m} \times 10^{6} )</th>
<th>( \Delta t )</th>
<th>( \gamma(\text{op}) \times 10^{6} )</th>
<th>( \Delta )</th>
<th>( T_{m} )</th>
<th>( \eta )</th>
<th>( \text{RE}% )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.944x10³, 0.944x10³</td>
<td>3.03</td>
<td>0.56</td>
<td>0.57</td>
<td>0.57</td>
<td>0.57</td>
<td>D</td>
</tr>
<tr>
<td>1</td>
<td>1.72±0.1</td>
<td>5.18</td>
<td>0.57</td>
<td>0.57</td>
<td>0.57</td>
<td>0.57</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>2</td>
<td>4.0±0.2</td>
<td>2.88</td>
<td>0.57</td>
<td>0.57</td>
<td>0.57</td>
<td>0.57</td>
<td>0.04</td>
</tr>
<tr>
<td>3</td>
<td>50.2±0.1</td>
<td>0.56x10³</td>
<td>0.57</td>
<td>0.57</td>
<td>0.57</td>
<td>0.57</td>
<td>0.06</td>
</tr>
<tr>
<td>4</td>
<td>38.4±0.1</td>
<td>5.39</td>
<td>0.57</td>
<td>0.57</td>
<td>0.57</td>
<td>0.57</td>
<td>0.097</td>
</tr>
<tr>
<td>5-1</td>
<td>35.4±0.1</td>
<td>8.87</td>
<td>0.57</td>
<td>0.57</td>
<td>0.57</td>
<td>0.57</td>
<td>0.31</td>
</tr>
<tr>
<td>5-2</td>
<td>32.7±0.1</td>
<td>2.47</td>
<td>0.57</td>
<td>0.57</td>
<td>0.57</td>
<td>0.57</td>
<td>0.12</td>
</tr>
<tr>
<td>6</td>
<td>39.6±0.1</td>
<td>5.39x10³</td>
<td>0.57</td>
<td>0.57</td>
<td>0.57</td>
<td>0.57</td>
<td>0.12</td>
</tr>
<tr>
<td>7-1</td>
<td>38.4±0.1</td>
<td>4.79x10³</td>
<td>0.57</td>
<td>0.57</td>
<td>0.57</td>
<td>0.57</td>
<td>0.33</td>
</tr>
<tr>
<td>7-2</td>
<td>38.4±0.1</td>
<td>0.79x10³</td>
<td>0.57</td>
<td>0.57</td>
<td>0.57</td>
<td>0.57</td>
<td>0.33</td>
</tr>
</tbody>
</table>

Note: \( \Delta = \text{Hm/R}(1/T_{m}-1/T) \), No. 5-2 630°C 3hr, No. 7-2 620°C 7hr annealed.

### Table-2 Grain size with different RE content (450°C 2hr annealed)

| No. 5-2 630°C 3hr, No. 7-2 620°C 7hr annealed |
|-----|-------|------|-------|------|-------|------|
| dx10² (mm) | 20 | 32 | 16 | 6 | 3 | 11 | 2.0 | 18 | 1.2 | 0.78 | 2.4 |

Note: No. 5-2 and 7-2 is annealed at 640°C 3hr and 620°C 7hr respectively.

### Table-3 lnA* value at different T for specimen. No. 2 and 3.

<table>
<thead>
<tr>
<th>Temp. (K)</th>
<th>282</th>
<th>283</th>
<th>293</th>
<th>296</th>
<th>303</th>
<th>313</th>
<th>320</th>
</tr>
</thead>
<tbody>
<tr>
<td>RE=0.01%</td>
<td>2.60</td>
<td>2.23</td>
<td>1.70</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>RE=0.06%</td>
<td>3.10</td>
<td>2.80</td>
<td>2.58</td>
<td>2.35</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Fig. 1 $Q^{-1}$ versus $T$ experimental curves (various RE content in pure Al).

Fig. 2 $Q^{-1}$ versus $T$ experimental curves for specimens No. 6-8.

Fig. 3 $Q^{-1}$ versus $1/T$ curves obtained from Fig. 1 and Fig. 2 after subtraction of background.

Fig. 4 $B_H$ as a function of RE content.

Fig. 5 Curves of $\ln A^*$ as a function of reciprocal temperature for specimens Al-0.01%RE and Al-0.06%RE.

Reference
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