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EFFECT OF GRAIN BOUNDARY SEGREGATION OF ANTIMONY ON RELAXATION AT GRAIN BOUNDARIES IN SILICON-IRON ALLOYS

Y. Iwasaki and K. Fujimoto

Research Laboratories, Kawasaki Steel Corporation, Kawasaki-cho, Chiba 280, Japan

Abstract. - A sharp grain boundary peak appears in both 2 and 3% silicon-iron alloys due to a substitutional solute of silicon. This peak is highly sensitive to the segregation of the third element of antimony and, contrary to orthodox solute peaks in binary and ternary alloys, largely decreases in magnitude on heating after a segregation treatment. The subsequent measurement on cooling returns the peak to the ordinary magnitude. As a function of annealing time at a temperature of segregation, the height of the solute peak rapidly decreases and then increases slowly to a saturation limit. The effect of antimony on the solute peak is discussed following Guttmann's theory of multisegregation. It is deduced that the interaction between silicon and antimony is repulsive.

1. Introduction. - Commercial silicon steels are classified from their use into two categories of grain-oriented and non-oriented steels. Addition of a small amount of antimony is effective for highly developing the preferred 
\{110\}<001> and \{100\}<0\bar{v}\bar{w}> textures, respectively (1), (2). Since antimony is an embrittling impurity segregating to grain boundaries, the Auger electron spectroscopy may be regarded as a convenient technique to investigate a role of antimony in the steels. The concentration of antimony is, however, too small to perform inter-granular fracture (3).

The grain boundary relaxation is significantly affected by the presence of a small amount of solutes. Addition of substitutional solutes to high-purity metals generates a peak (called a solute peak) at higher temperatures, suppressing an original grain boundary peak (a solvent peak) characteristic of the pure metals. The solute peak is also attributed to grain boundary relaxation, so has a potential ability to reflect sensitively the behaviour of solutes near grain boundaries. The purpose of this report is to establish some fundamental aspects of antimony segregation in silicon-iron alloys through grain boundary internal friction.

2. Experiment. - All the materials were prepared by melting and casting into ingots of 50 kg. The ingots were hot and then cold rolled to either 0.5 mm or 1 mm thick with intermediate annealing at 850°C or...
Table 1 Chemical composition of silicon-iron alloys (wt%).

<table>
<thead>
<tr>
<th>Si</th>
<th>Sb</th>
<th>Mn</th>
<th>Se</th>
<th>C</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.00</td>
<td>-</td>
<td>0.054</td>
<td>0.009</td>
<td>0.005</td>
<td>0.0027</td>
</tr>
<tr>
<td>2.84</td>
<td>0.018</td>
<td>0.056</td>
<td>0.009</td>
<td>0.005</td>
<td>0.0030</td>
</tr>
<tr>
<td>1.79</td>
<td>0.10</td>
<td>0.29</td>
<td>0.41</td>
<td>0.002</td>
<td>0.003</td>
</tr>
</tbody>
</table>

900°C. Specimens 100 mm long and 2 mm wide were cut out of the as-cold-rolled sheets. Encapsulated in silica tube under a vacuum of $10^{-6}$ torr, the specimens were annealed 5 hours at 850°C to complete primary recrystallization and stabilize internal structure, followed by slow cooling at a rate of 40°C/h. The chemical composition of the specimens are given in Table 1.

Internal friction measurements were carried out with much care using a free-decay technique in an inverted torsion pendulum (4)-(6). The whole apparatus was sealed under a vacuum of better than $2 \times 10^{-5}$ torr in order to reduce specimen oxidation and to retain background damping as low as $1 \times 10^{-4}$. Maximum surface strain was $2 \times 10^{-5}$. The influence of magnetic damping was eliminated by an axially applied magnetic field of 300 Oe. The furnace consisting of three zones was wounded non-inductively and controlled by an automatic regulator. This heating equipment ensures good temperature uniformity on the specimen, of less than 1°C. All the measurements were made on heating and cooling at a rate of 2°C/min.

3. Results.

3.1 Fe-3Si.- Internal friction measured at 0.5 Hz over the range of 400°C to 850°C is plotted as a function of temperature in Figure 1 for a specimen which had been primary-recrystallized at 850°C for 5 hours. A pronounced peak appearing at 600°C decreases with increasing grain size (7). Since the grain boundary peak in pure iron occurs at about 500°C (8)-(10), this peak is attributed to a damping process associated with grain boundaries and substitutional solute atoms; thus, the peak is a solute peak.

Iron containing antimony is often
given 7 days embrittlement treatment at 500°C to accomplish intergranular fracture (11). This heat treatment was applied to specimens of Fe-Si alloys with and without antimony. Although the treatment did not lead to intergranular fracture, the internal friction spectrum exhibits a distinguished reduction in height of the solute peak for the specimen containing 0.018%Sb, while no distinct change is observed in the antimony-free specimen (Figure 2). In the alloy containing antimony, the effect of the segregation treatment disappears during cooling and the curve of internal friction is identical with that for the recrystallized specimen (Figure 1).

3.2 Fe-2Si-0.1Sb. - The segregation treatment yields the same effect on the solute peak in this alloy (Figure 3). Since the peak was due to the equilibrium segregation of solutes (3), it was deemed advisable to measure the change in peak height

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**Fig. 2**: Effect of the grain boundary segregation of antimony on the solute peak. Internal friction measured at 0.5 Hz after annealing at 500°C for 7 days.

**Fig. 3**: Effect of the segregation treatment on the solute peak in 2%Si-Fe ($f_{RT} = 1.3$ Hz).
as a function of time at the embrittling temperature. The data obtained (Figure 4) indicates that the internal friction decreases rapidly during the first 7 days and then increases slowly to a saturation value, which is higher the larger the concentration of antimony absorbed at grain boundaries (3).

4. Discussion.- It can be stated that the solute peak is due to the presence of solutes at grain boundaries. The height of the peak at first rises monotonically with increasing solute content, and then levels off to a saturation value. The deviation from the monotone increase corresponds to grain boundary saturation with the solute atoms. The bulk concentration of solute necessary to obtain boundary saturation, called the saturation concentration, is 2.3wt%Si for Fe-Si alloys (12). The content of silicon in the present case is near or beyond the saturation concentration.

In multicomponent systems of more than two elements, a combination of solutes brings to cumulative effect on the solute peak. Addition of antimony to Fe-Si alloys may, therefore, raise the solute peak in the case where the content of silicon is substantially lower than the saturation limit. The present alloys, however, contain silicon to the content as large as the saturation and hence no contribution of antimony is expected to the magnitude of the solute peak.
The above approach to the problem of explaining the effect of antimony is to consider segregation at grain boundaries in binary combinations taken from elements in the multicomponent system. To account for consistently the behaviour of the solute peak at the presence of antimony, it is necessary to take into account the interaction between silicon and antimony. Attractive interaction simply enhances the segregation of antimony accompanied by silicon, so that the decrease in peak height can not be explained. Therefore, the interaction is necessarily repulsive.

Conversely, it is assumed that Si-Sb interaction is repulsive. Following Guttmann's theory (13), the segregation free energies, $\Delta G$, for Si and Sb in the multicomponent system is represented as

$$
\Delta G_{Si} = \Delta G_{Si}^0 + \alpha'(X_{Si}^\phi - X_{Si}^B),
$$

(1)

$$
\Delta G_{Sb} = \Delta G_{Sb}^0 + \alpha'(X_{Sb}^\phi - X_{Sb}^B),
$$

(2)

where $\Delta G_{Si}^0$ is the segregation energy in binary iron-base alloys, $\alpha'$ the interaction coefficient; $X_{I}^\phi$ is the concentration of I in equilibrium at the grain boundary and $X_{I}^B$ the concentration of I dissolved in the matrix. For a repulsive interaction, the coefficient $\alpha'$ is negative. The grain boundary enrichment ratio $\beta$ defined by $X_{I}^\phi/X_{I}^B$ implies the intensity of segregation in the boundary region. The large enrichment ratio of antimony in $\alpha$-Fe which is 25 times larger than that of silicon (14), (15), is associated with a large segregation energy $\Delta G_{Sb}^0$. Thus, $X_{Sb}^\phi - X_{Sb}^B \gg 0$ and $\Delta G_{Si}^0$ is quite small with respect to $\Delta G_{Sb}^0$. It follows probably that the segregation free energy of silicon $\Delta G_{Si}^0$ takes a negative value which leads to the desegregation of silicon. On the other hand, the second term in equation (2) becomes positive and so increases the segregation energy for antimony. The segregation of antimony is, thus, enhanced at the presence of silicon. During the heat treatment at 500°C, silicon atoms are repelled from grain boundaries. This desegregation involves a large depression of the solute peak in the concentrated silicon iron, despite antimony segregation occurring at the same time. As time elapses, is attained a global equilibrium state that antimony segregates to grain boundaries in place of silicon. The segregation of antimony in turn increases the height of the solute peak due to the solute of antimony passing through a minimal magnitude as seen in Figure 4. Repulsive interaction between silicon and antimony, thus, explains well the results obtained.

5. Conclusions.- Measurement of grain boundary internal friction is a useful technique to investigate non-destructively the segregation
of solutes to grain boundaries in dilute alloys. The technique is particularly applicable to determine species of interaction between solutes. It is shown that antimony exhibits a repulsive interaction with silicon in silicon-iron alloys.

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