Grain Boundary Internal Friction of Ni and Ni–B Alloys

By Hajime Suto* and Shinji Sato*†

In order to investigate the solid solubility of B in Ni as a function of grain size, the high temperature internal friction of pure Ni and Ni-B alloys containing 0.0035, 0.0068 and 0.010 wt% B has been measured with particular attention to the grain boundary damping peaks. The electrical resistivity was also measured to determine the solubility. The results obtained are summarized as follows: (1) The solubility of B in single crystal Ni is given by C(at%)=0.59 exp (−H/*RT*), H=65.6 kJ/mol. (2) The apparent solubility of B in polycrystalline Ni increases remarkably with decreasing grain size. (3) On the $Q^{-1}-1/T$ curves of pure Ni, there are two peaks of grain boundary damping at about 470°C and about 670°C. By addition of 0.0035 wt% B, only one peak can be observed. The peak temperature of every Ni-B alloy used is about 550°C and its activation energy is about 330 kJ/mol.

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I. Introduction

The grain boundary segregation of B is likely to play an important role in improvements of the mechanical properties of B-doped Ni alloys because the atomic size of B in Ni becomes critical; B atoms are too small as substitutional atoms but too large as interstitial atoms, and they must be preferentially segregated to grain boundaries in much the same manner as does B in γ-Fe. The present work is concerned with the severe segregation of B to Ni grain boundaries and the solubility of B in Ni in order to help the considerations of mechanical properties of B-doped Ni alloys[1]~[4].

Internal friction measurements are useful for the investigation of grain boundary segregation, since the observed internal friction peaks are associated with grain boundary damping. If the peaks shift to high temperature by an alloying process, it is suggested that the solute atoms segregate to grain boundaries and contribute to strengthening of grain boundaries[5]. It is widely known that two peaks of internal friction associated with grain boundary damping exist[6]. The lower temperature peak which is usually supressed by alloying, has been called the "solvent peak", and the higher temperature peak the "solute peak". In the stress-relaxation at grain boundaries, the roles of lattice diffusion and grain boundary diffusion may be of importance. It has been considered that the grain boundary segregation supresses the low temperature peak due to a decrease in grain boundary diffusion or a change in grain boundary structure[5]. In this work, the change in damping behavior of Ni grain boundaries with segregation of B atoms was examined.

Electrical resistivity measurements were carried out to obtain a better understanding of the grain size dependency of apparent solubility which might be expected from the small solubility[6] and the expected severe grain boundary segregation of B in Ni.

II. Experimental Procedure

Table 1 gives the chemical composition of a commercially pure Ni, (N-1) and Ni–B alloys, (N-2, N-3 and N-4) which were prepared with electrolytic Ni and elementary B by vacuum melting. Johnson & Matthey Spectroscopically Pure Ni, (JM Ni) (99.99% Ni) was also used.

All specimens were cold swaged to 2 mm in dia., annealed at 900°C, cold drawn to 0.5 mm in dia. and finally annealed at 800°C to 1050°C for 2 to 6 h in order to control the grain size.

The internal friction was measured by means of a tortion-pendulum method[5] in the vacuum of 4×10^{-3} Pa and in a magnetic field of 8 kA/m (100 Oe). The grain size controlled specimen

* Department of Materials Science, Faculty of Engineering, Tohoku University, Sendai, 980, Japan.

† Present address:Technical Research Laboratories, Kawasaki Steel Corp., 1, Kawasakicho, Chiba 260, Japan.

Table 1 Chemical composition of specimens used (wt%).

Alloy	B	C	Mn	P	S	Co	Fe	O
N-1	—	0.002	0.03	0.002	0.013	1.73	<0.01	0.003
N-2	0.0035	0.002	0.02	0.003	0.011	1.74	NA*	0.002
N-3	0.0068	0.002	0.02	0.002	0.012	NA	NA	0.002
N-4	0.0100	0.002	0.03	0.002	0.012	NA	<0.01	0.002

* NA: not analysed

of 15 cm in length was set in the apparatus and heated to 900°C for stress-relief. This heating temperature was restricted to below the final annealing temperature in order to avoid the grain growth. The internal friction was measured during cooling from the stress relief temperature. The cooling rate was controlled to be 2°C/min, the torque strain of specimen surface was limited to 5×10^{-5}, and the frequency was 0.4 Hz. The internal friction, Q^{-1}, was calculated using the ordinery method[6].

The specimen of 10 cm length having 4 terminals for electrical resistivity measurements was heated in the same manner as in the case of internal friction measurements, and the electrical resistivity was measured during cooling. The cooling rate was controlled to be 2°C/min. It was considered that the kink point on each resistance-temperature curve indicates the starting of precipitation in the specimen. Since the precipitation took place preferentially on the grain boundaries, the metallographical observation of specimens quenched from various temperatures was also useful in the study of the solubility.

III. Experimental Results and Discussion

Figure 1 shows the $Q^{-1}-1/T$ (T: the measuring temperature in K) curves for the commercially pure Ni (N-1) and JM Ni. Since the grain growth easily took place in JM Ni, the measuring temperatures for specimens having fine grains were restricted to within the low annealing temperature range. In Fig. 1, two peaks appear in each of the $Q^{-1}-1/T$ curves except for the curve for fine grained JM Ni (87 μm) cooled from 600°C. All the observed peaks must be due to grain boundary damping[6]. The observed high temperature internal friction Q_{ob}^{-1} of annealed polycrystalline metals and

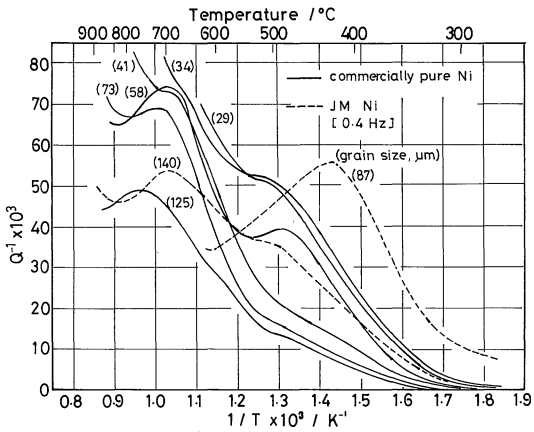

Fig. 1 $Q^{-1}-1/T$ curves for commercially pure Ni, (N-1) and JM Ni having various grain sizes.

dilute alloys is the sum of the back ground internal friction Q_b^{-1} and the grain boundary internal friction Q_g^{-1}. Let us assume that $Q_b^{-1}=A\exp(-U/RT)$, where A and U are materials constants and R is the gas constant. The A and U values were given experimentally on condition that Q_b^{-1} was nearly equal to Q_{ob}^{-1} at the temperature far from the peak temperature of grain boundary internal friction, e.g., at room temperature and 900°C in the present case.

Figure 2 is a typical example of Q_b^{-1} and Q_g^{-1} separated from an observed $Q_{ob}^{-1}-1/T$ curve. In this case, Q_g^{-1} can be further separated to two peaks, assuming that the $Q^{-1}-1/T$ figure of each peak is symmetric with respect to each peak temperature. The two peaks are called the "high temperature peak" and the "low temperature peak", respectively. The temperatures and heights of the high and low temperature peaks are expressed as T_H, T_L, Q_H^{-1} and Q_L^{-1}, respectively.

Similar experiments with high purity Ni have been performed by Roberts *et al.*[8] They found three kinds of peaks at 400 to 450°C, 570 to

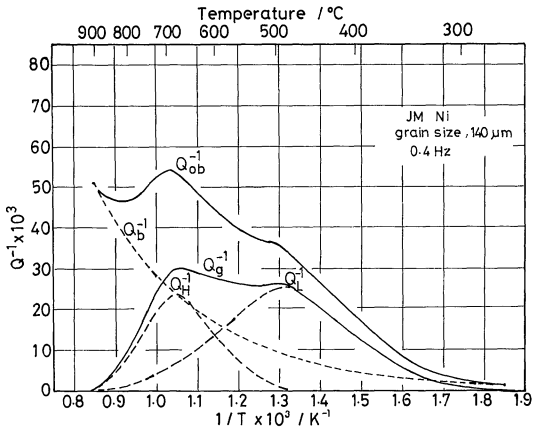

Fig. 2 A typical example of separation of Q_g^{-1} by subtracting Q_b^{-1} from Q_{ob}^{-1} of JM Ni. It is shown that this Q_g^{-1} is composed of two peaks.

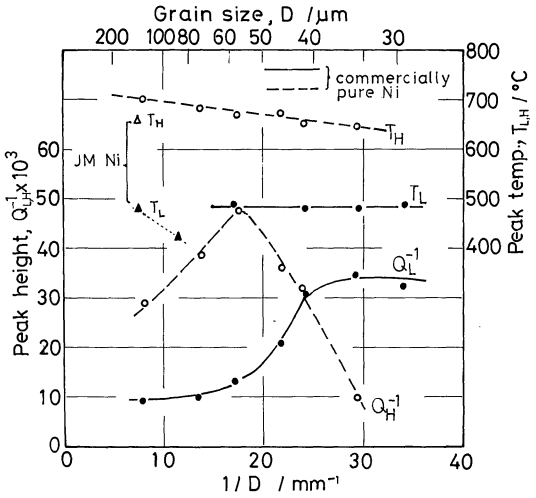

Fig. 3 Grain size dependence of peak height and peak temperature of grain boundary internal friction in pure Ni (N-1 and JM Ni).

620°C and 680 to 800°C, and the highest temperature peak was observed when the grains were of the so-called bamboo structure. In the present work, such large grain specimens were not used. The intermediate and the lowest temperature peaks observed by Roberts *et al.* may correspond to the high and the low temperature peaks in the present work, respectively.

In the previous papers[9][10], it was reported that the grain boundary damping was proportional to the grain boundary area, or to the reciprocal mean diameter of grains, $1/D$. In the present work, Q_L^{-1} and Q_H^{-1} were not proportional to $1/D$. The most probable reason for this is that the low temperature damping is replaced by the high temperature damping as a result of stabilization of grain boundaries during annealing for grain coarsening.

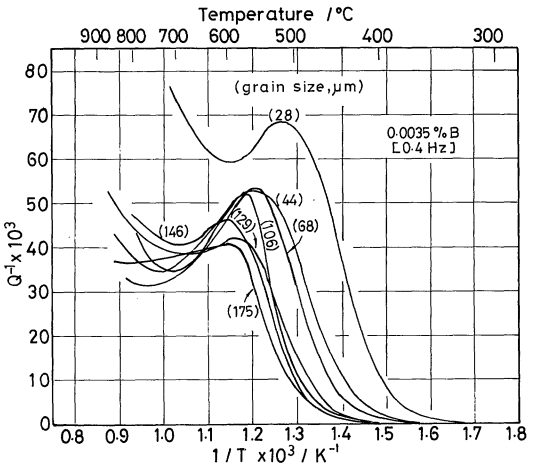

Fig. 4 $Q^{-1}-1/T$ curves for the N-2 alloy.

From the shift of T_L produced by changing the torque frequency from 0.4 to 1.2 Hz, the activation energies for the low temperature peaks of N-1 and JM Ni were obtained to be 290 and 190 kJ/mol, respectively. Roberts *et al.* reported the value to be 290 kJ/mol[8]. Previous papers[6] have reported that the activation energy for the low temperature peak of pure metals has an intermediate value between the activation energies of the grain boundary and of lattice difusion, U_b and U_1. The U_b and U_1 values of Ni were reported to be 120 and 260 kJ/mol, respectively[11]. The values of activation energy for the low temperature peak of N-1 in the present work and of high purity Ni by Roberts *et al.* are as large as the U_1-value. This is considered due to the effect of grain boundary segregation of impurities.

Figures 4, 5 and 6 show the $Q^{-1}-1/T$ curves for three kinds of dilute Ni–B alloys having various grain sizes. Only one peak can be seen on each curve at the temperatures ranging from 500 to 600°C. The peak temperature, T_P, is lower than that of the high temperature peak of pure Ni. From the facts described above, we may conclude that the grain boundary segregation of B does not contribute to the improvement of strength of grain boundaries in Ni

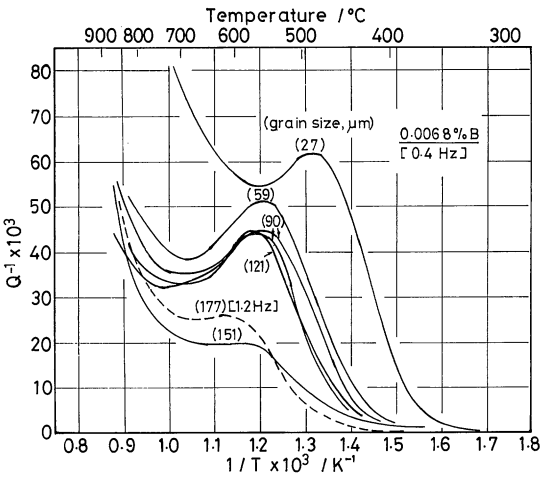

Fig. 5 $Q^{-1}-1/T$ curves for the N-3 alloy.

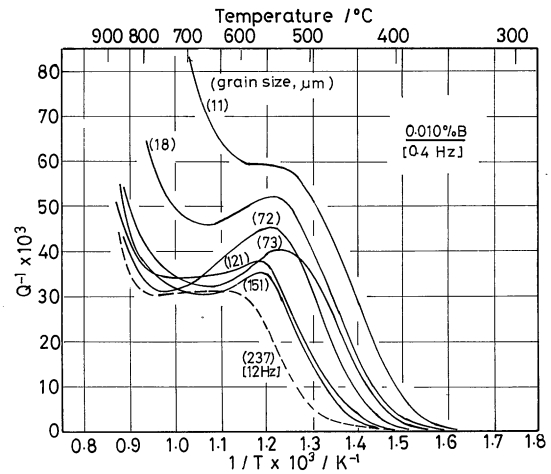

Fig. 6 $Q^{-1}-1/T$ curves for the N-4 alloy.

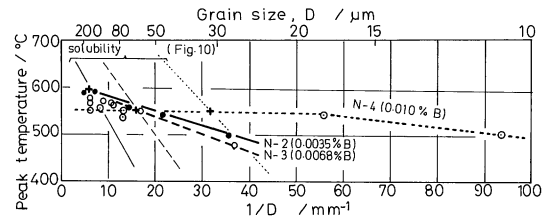

Fig. 7 Grain size dependence of peak temperature of grain boundary internal friction in Ni-B alloys.

alloys, probably due to the high diffusivity of B in Ni.

Figure 7 shows the T_P of Ni–B alloys as a function of $1/D$. (The meaning of three thin lines will be described later.) The T_P increased

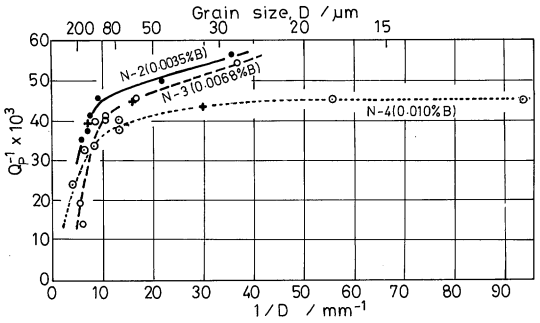

Fig. 8 Grain size dependence of peak height of grain boundary internal friction in Ni–B alloys.

with the increase in grain size and was saturated beyond a critical grain size. The critical grain sizes of the N-3 and the N-4 specimens are about 80 and 20 μm, respectively.

Figure 8 shows the peak height, Q_p^{-1} of the dilute Ni–B alloys as a function of $1/D$. (The meaning of cross marks on the curves will be described later.) The value of Q_p^{-1} decreases slowly with increasing grain size, but it decreases sharply beyond a critical grain size. The critical sizes are not clear but they are about 130 μm for the N-2, 80 μm for the N-3 and 50 μm for the N-4 specimens. By means of optical microscopy, grain boundary precipitates, probably Ni_3B[7] can be observed in specimens having grains coarsened beyond these critical sizes.

The activation energy for the grain boundary damping of every Ni–B alloy used was 330 kJ/mol. This value is larger than the activation energy of self-diffusion of Ni, U_1, 260 kJ/mol.

Figure 9 shows some of electric resistance-temperature curves on cooling. Assuming that the kink point on each curve corresponds with the temperature of precipitation beginning during the slow cooling, the temperature of solubility for each Ni–B alloy is shown as a function of $1/D$ in Fig. 10. The three curves shown in this figure were also drawn with thin lines in Fig. 7. As we would expected, the interaction point of each couple line for the same specimen, indicated by a cross mark, is in approximate agreement with the kink point of the T_P-1/D curve. The cross marks are transcribed on the curves in Fig. 8, and the grain sizes showed by these marks almost agree

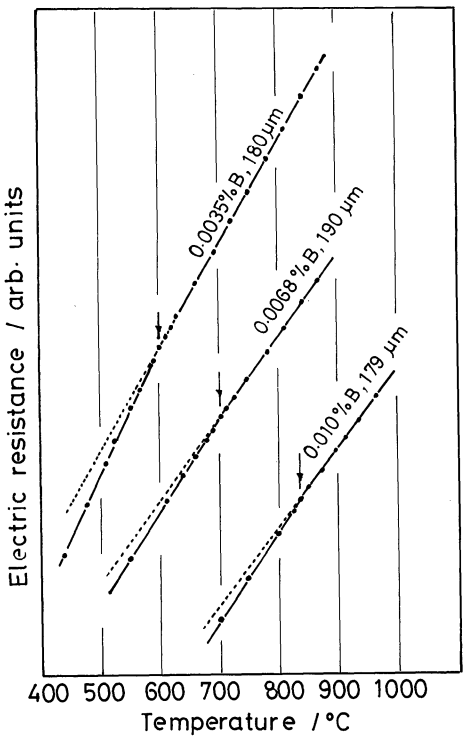

Fig. 9 Temperature dependence of electric resistance of Ni-B alloys having grains of about 180 μm in size.

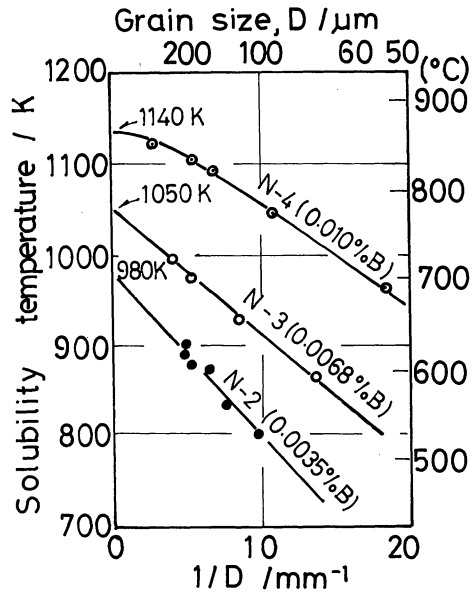

Fig. 10 Grain size dependence of solubility temperature for Ni-B alloys.

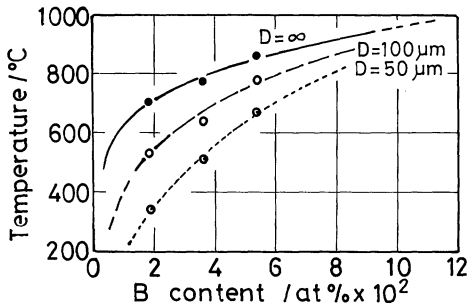

Fig. 11 Grain size dependence of the apparent solvus line for B atoms in Ni.

with the critical grain size mentioned above. These results mean that the apparent solubility of B in Ni as the function of temperature and grain size obtained by electrical resistivity measurements agree with those suggested from the grain boundary internal friction measurements.

It has become clear that the apparent solubility of B in Ni at a given temperature depends upon the grain size. It may be reasonable to assume that the apparent solubility of B is the sum of the amount of B atoms solved in grains and that trapped at grain boundaries. The former, that is, the solubility in a single crystal $(1/D=0)$,C, is given as an exponential function of the heat of solution, H, as follows:

$$C = B \exp(-H/RT) \quad (1)$$

where B is a constant. From Fig. 10, eq. (1) is given numerically by

$$C(\text{at}\%) = 0.59 \exp(-H/RT),$$
$$H = 65.6 \text{ kJ/mol}. \quad (2)$$

The maximum solubility of B in Ni was reported to be 0.15 at% B at the eutectic temperature, 1080°C[7]. The value calculated from eq. (2) is 0.22 at% B at the same temperature.

The apparent solvus curves for the specimens with given grain sizes as calculated from the results in Fig. 10 and eq. (2) are shown in Fig. 11. Assuming that the grain boundary is perfectly smooth, the number of B atoms trapped in grain boundaries per one Ni atom plane at boundaries was calculated to be 5 to 10. These values are unexpectedly large. However, in order to quantitatively discuss the number of B atoms adsorbed to grain boundaries, there

are some problems which should be improved; e.g., (1) accuracy of chemical analysis of B in Ni, (2) estimation of grain boundary area, (3) dislocation density and the B atmosphere arround dislocations, and (4) possibility of formation of a two-dimensional grain boundary compound which was suggested by Guttmann[12]. Rellic *et al.*[13] showed experimentally that grain boundaries were facetted by adsorption of impurities. The change in grain boundary structure by impurity segregation, e.g. facetting, should not be ignored in the considerations of the number of atoms segregated to grain boundaries.

IV. Conclusions

The results are summarized as follows:

(1) The solubility of B in a single crystal Ni is given by

$$C\ (\text{at}\%) = 0.59 \exp\ (-H/RT)$$
$$H = 65.6\ \text{kJ/mol}.$$

(2) The apparent solubility of B in polycrystalline Ni increases with decreasing grain size.

(3) Two grain boundary internal friction peaks are observed on the $Q^{-1} - 1/T$ curves of pure Ni. By addition of B more than 0.0035 wt%, only one peak can be observed. The activation energy was 330 kJ/mol. The peak temperature is lower than that of the high temperature peak of pure Ni.

It was concluded from the experiment described above that B atoms doped in Ni alloys severely segregate to grain boundaries but the high temperature strength of the grain boundaries is not improved greatly by segregation of B atoms.

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