Effects of Addition of B and P on the Cellular Precipitation in Ni–Sn and Cu–Ni–Sn Alloys*

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The influence of the additions of B and P on the cellular and intragranular precipitation in Ni–8–15 mass %Sn and Cu–80 mass %Ni–8 mass %Sn alloys was investigated by quantitative metallographic methods.

By the additions of B and P, the intragranular precipitation was slightly retarded, while the cellular precipitation was significantly suppressed. The suppressing effects of B and P depended upon the Ni concentration in the Cu–Ni–Sn alloys and were especially large in the 40–60% Ni alloys. These effects increased with increasing amount of addition. It is considered that B and P segregate in the grain boundaries and suppress the nucleation and growth of cells.

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I. Introduction

It is well known that the cellular precipitation in Cu–Be(1)–(6) and Cu–Ti(7)(8) alloys is effectively suppressed by additions of small amounts of elements. But the mechanism by which the additional elements suppress the cellular precipitation is still obscure(9)(10).

One of the present authors(11) examined previously the effects of some additional elements, such as Co, Ni, Fe, Ti, Cd, Zn, Al, In, Mn, Si and Cr, on the cellular precipitation in a Cu–2%Be alloy by quantitative metallographic methods. It was confirmed in that work that no correlation existed between the effects of additional elements on intragranular precipitation of γ' phase and these on cell growth, and that there was a well defined correlation between the effects on grain growth at the solution treatment temperature and those on cell growth at aging temperatures. Based on these observations, it was suggested that the grain boundary segregation of the additional elements was responsible for their suppressing effects on the nucleation and growth of cells.

In order to obtain further informations on the effects of grain boundary segregations of additional elements on cell growth, the effects of additions of B(12)(13) and P(14)(15), which have high segregating potencies to Ni and Cu–Ni alloys, on cellular precipitations of Ni–Sn and Cu–Ni–Sn alloys were examined in the present work. The reason why the Ni–Sn and Cu–Ni–Sn alloys were chosen is that the characteristics of the cellular precipitation in these alloys were fully clarified in the previous work(16)–(18).

II. Experimental Procedure

Table 1 shows chemical compositions of alloys used in the present work. Each alloy was prepared by melting high purity Ni(99.95%), Sn(99.9%), Ni–15%B and Ni–14%P master alloys in a high purity alumina crucible in an Ar atmosphere. Each ingot was annealed and then cut out into plates. After cold rolling, these plates were shaped into specimens suitable for various measurements. Specimens were quenched into water after solution treatment and aged at 723 K or 823 K.

The solution treatment temperatures were 1123 K for 10–20%Ni alloys, 1173 K for 42–60%Ni alloys and 1273 K for alloys containing 80% or more of Ni. The aging temperatures were 723 K for 10–42%Ni alloys and 823 K for alloys containing 60% or more of Ni. Each
specimen was prepared for the grain size to be about 150 μm before aging. After aged, each specimen was examined with optical and scanning electron microscopes, and a micro-Vickers hardness tester. The area fraction of cells and the cell width were measured on optical micrographs taken at a magnification of 150 times. The area fraction of cells was measured by the point counting method. Mean values of the cell width were determined from measurements for about 50 grain boundaries.

Chemical compositions of specimens used in this work are shown by black spots in the phase diagram of the Cu–Ni–Sn system\(^{(18)}\) (Fig. 1).

### III. Results

1. **The additions of B and P to the Ni–Sn alloys**

Figure 2 shows an example of the suppressing effects of B and P on the cellular precipitation in the Ni–8%Sn alloy. Figure 2(a) shows the microstructure in the additive free alloy. As seen in this figure, cells have engulfed all of the matrix. Figures 2(b) and (c) show microstructures in the alloys containing 0.05%B and 0.05%P, respectively. As seen in these figures, the growth of cell is extremely suppressed in these alloys. Therefore, it is clear that B and P have remarkable effects on suppressing the cellular precipitation. The suppressing effect of P appears to be superior than that of B. The similar results are also obtained in Ni–15%Sn alloy.

Figures 3 and 4 show the effects of B and P
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Fig. 2 Microstructure of the Ni–8%Sn–X alloys aged at 823 K for $2.5 \times 10^5$ s. (a) non, (b) -0.05%B, (c) -0.05%P.

Fig. 3 Change in hardness, area fraction of cell and mean width of cell of the Ni–15%Sn–X alloys on aging at 823 K.

Fig. 4 Change in hardness, area fraction of cell and mean width of cell of the Ni–8%Sn–X alloys on aging at 823 K.

The effects of addition of B and P on the intragranular and cellular precipitations in the Ni–15%Sn and Ni–8%Sn alloys. As seen in Figs. 3(A) and 4(A), B and P hardly affect the hardening of the matrix. It can be seen, from Figs. 3(B) and 4(B), that B and P suppress remarkably the cell growth, and that P suppress more than B. Figures 3(C) and 4(C) show the mean growth rate of cells in the early stage of aging. By the additions of B and P, the growth rates of cells in the Ni–15%Sn and Ni–8%Sn alloys are reduced to 1/2–1/3 and 1/7–1/13 times, respectively.

Figure 5 shows the relation between the suppressing effects and the contents of B and P.
The growth rate of cells gradually (not linearly) decreases with increasing amounts of B and P. The effect of P on the growth rate of cells is larger than that of B.

2. The additions of B and P to the Cu–Ni–Sn alloys

Figures 6 and 7 show examples of the microstructures showing the effects of B and P on the cellular precipitation in the Cu–10%Ni–8%Sn and Cu–42%Ni–8%Sn alloys. As seen from Fig. 6, the suppressing effects of B and P in Cu–10%Ni–8%Sn alloys are not so noticeable, while the effects of B and P in 42%Ni alloys are remarkable as shown in Fig. 7. It is thus apparent that the effects of B and P depend upon the Ni concentration in Cu–Ni–Sn alloys and that P is more effective than B.

Figures 8–10 show changes in hardness, area
fraction of cells and mean width of cells in Cu–Ni–Sn alloys during aging. In the cases of 10% Ni alloys, Fig. 8, B and P delay slightly the intragranular hardening and suppress the cell growth considerably.

In the cases of 20%Ni alloys, Fig. 9, B and P suppress the cell growth remarkably, but do not delay the intragranular hardening so significantly. The effect of P is larger than B.

In 42%Ni alloys, Fig. 10, the suppressing effect of P is more remarkable, i.e. by the addition of P, the growth rate of cells diminishes to about 1/35 of the additive free alloy.

As seen from Figs. 11 and 12, the effects of these elements on 60%Ni and 80%Ni alloys are nearly the same. That is, B and P delay the initiation of the cell growth and diminish remarkably the growth rate of cells, but hardly affect the intragranular hardening in both alloys.

Figure 13 shows the relation between the suppressing effects of B and P and the Ni concentration in the Cu–Ni alloys. In this figure, the suppressing effects of B and P are shown by the values of the area fraction of cells in the alloys containing B and P, at the time of full development of cells in the additive free alloys. Namely, the small values in area fraction of cells in the alloys containing B and P shows the large suppressing effects of B and P. It can be seen from this figure that the suppressing effects of B and P are most remarkable in 40–60%Ni alloys, and that the effect of P is stronger than that of B in every Cu–Ni–Sn alloys. Figures 14 and 15 show electron microstructures in cells in 20%Ni and 60%Ni alloys, respectively, at the late stage of aging. As seen from Fig. 14, the addition of P suppresses considerably the cell growth in the 20%Ni alloy but hardly affects the microstructures in the cells. On the other hand, in the 60%Ni alloys shown in Fig. 15, the microstructures in the cells changes by the additions of B and P. That is, by the addition of
B, the precipitates become shorter and interlamellar spacing becomes wider, and by the addition of P, the cell growth is extremely suppressed and only the grain boundary precipitates are observed.

**IV. Discussion**

As shown in results, B and P suppressed remarkably the cellular precipitation in the Ni–Sn and Cu–Ni–Sn alloys. The suppressing effects were especially remarkable in 40–60%Ni alloys. So, we discuss here about the suppressing mechanism of B and P for the cellular precipitation.

The following theories have been proposed as the mechanism for the additives to suppress the cellular precipitation: (1) The additives promote the intragranular precipitation and decrease the chemical driving force for the cell growth\(^{(1)(2)(6)}\). (2) Additives suppress the nucleation and growth of cells by segregating in grain boundaries\(^{(19)(20)}\). (3) The distribution of vacancies at the front regions of advancing boundaries of cells is influenced by the difference in varency electron between the solvent and the additives, and the bulk diffusion of the solute atoms to the advancing boundaries of cells is decreased\(^{(21)}\). However, it has not been clarified yet which mechanism is more important.

As seen from the results, B and P hardly affected the intragranular hardening in Ni–Sn and Cu–Ni–Sn alloys except for 10–20%Ni alloys. It is considered from this fact that the influence of B and P on the chemical driving force for the cell growth is very little. Therefore, another mechanisms must be more important. It is reasonable to consider that B and P suppress the nucleation and growth of cells by segregating in the grain boundaries, because B and P are well known to segregate in
Grain-boundary segregants will suppress the cellular precipitation in following manners: (1) Grain boundary-segregants will retard the nucleation of cells by occupying nucleation reaction sites such as steps or ledges on the grain boundaries. In fact, B and P delay the initiation of the cell growth in almost all the Ni–Sn and Cu–Ni–Sn alloys in the present work. (2) Grain boundary-segregants will suppress the cell growth by lowering grain boundary diffusion rate of solute and solvent atoms, and by solute drag effect of these segregants. As seen from Fig. 16, the growth rate of cell is reduced to 1/100 in maximum by the additions of B and P. The suppressing effects of these elements depend upon the growth rate of cells in additive free alloys and are especially strong in the alloys with low growth rate of cells, i.e. in 40–60%Ni alloys. These facts appear to suggest that grain-boundary segregants (B and P) suppress strongly the cell growth.

Thus, it may be concluded that the grain boundary segregation of additional elements (B and P) is mainly responsible for their suppressing effects on the cellular precipitation in Ni–Sn and Cu–Ni–Sn alloys, though these

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**Fig. 12** Change in hardness, area fraction of cell and mean width of cell of the Cu–80%Ni–8%Sn–X alloys on aging at 823 K.

**Fig. 13** Relation between the effect of B or P on the cellular precipitation and the Ni concentration in the Cu–X%Ni–8%Sn alloys.

**Fig. 14** Scanning electron micrographs of the Cu–20%Ni–8%Sn–X alloys aged at 723 K for 3×10^6 s. (a) non, (b) 0.05%B.
predel and gust(24), recently, reported that the difference in valency electron between the additives and the solvent affected the suppressing effects. however, we can not discuss here about the valency electron effect for lack of experimental data.

v. summary

the influence of the additions of b and p on the cellular and intragranular precipitation in ni–8–10%sn and cu–10–80%ni–sn alloys was investigated by the quantitative metallographic methods. results are as follows:

1. the intragranular precipitations in these alloys were slightly retarded by the additions of b and p.

2. the cellular precipitation in these alloys was significantly suppressed by the additions of b and p. the suppressing effects of b and p depended upon the ni concentration in the cu–ni–sn alloys and were especially large in the 40–60%ni alloys.

3. the suppressing effects of b and p depended also upon the growth rate of cells in the b and p free alloys, and were especially remarkable for the alloy with small growth rate of cell.

4. the suppressing effect of p was larger than that of b. the effects of b and p increased with increasing amount of addition.

5. it is considered that b and p segregate in the grain boundaries and suppress the nucleation and growth of cells.

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