Effects of B Additions on the Intragranular and Cellular Precipitations in a Cu-Be Alloy*

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Effects of B additions on the intragranular and cellular precipitations in a Cu-2 mass% Be alloy on aging at 523 and 623 K after quenching from 1093 K were investigated by means of hardness measurements, optical and electron microscopic observations, and X-ray analysis. The addition of 0.02-0.1 mass% B suppressed the formation of G.P. zones and retarded the precipitation of γ'-phase. The lattice parameter of the α solid solution of the B-added alloy increased with B addition. This result suggests that B atoms exist interstitially in the α solid solution and suppress the formation of G.P. zones and retard the precipitation of γ' phase as a result of the strong interaction with vacancies. The formation and growth of grain boundary cells were suppressed by the addition of 0.02-0.05% B, but promoted by excess additions of B, 0.1%.

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I. Introduction

Recently many studies have been carried out as for the effects of B addition on the mechanical properties, corrosion resistance and heat resistance of Ni base alloys. For example, there are studies on the effects of B additions on the ductility of a Ni₃Al intermetallic compound, the high temperature embrittlement, and hydrogen embrittlement of Ni base alloys.

Moreover, the authors have reported that the B atoms added in Ni-Sn and Cu-Ni-Sn alloys suppressed remarkably the growth of grain boundary cells. Since the B atoms added in Ni or Cu-Ni base alloys tend to segregate at grain boundaries, these segregated atoms must have suppressed the nucleation and growth of cells.

While, a little reports have been published as for the effects of B on the various properties of Cu-base alloys. It is little known how much B atoms segregate at grain boundaries of Cu base alloys. However, it is estimated, from the solid solubility of the equilibrium phase diagram of a Cu–B binary alloy, that B atoms will segregate largely at grain boundaries. Because, it is well known that the tendency of the grain boundary segregation of the solute atom in a binary alloy is inversely proportional to the solid solubility. Therefore, the nucleation and growth of grain boundary cells of Cu-base alloys also will be suppressed by the addition of B.

Moreover, it is expected that B atoms will dissolve interstitially in Cu-base alloys and affect the precipitation process in the matrix grain, because the diameter of a B atom is much smaller than that of a Cu atom. However, little study has been carried out about these points.

Therefore, this study was aimed to elucidate the effects of the B addition on the cellular and intragranular precipitations in the typical Cu-base age-hardenable alloy, Cu–2 mass% Be. Many studies have been done up to now on the precipitation sequence of the Cu-Be alloy and it is α solid solution → G.P. zone → γ' intermediate phase → γ equilibrium phase. In the case of the aging at low temperatures, the
structural change from the $\gamma'$ to $\gamma$ phase occurs by the growth of grain boundary cells containing equilibrium $\alpha$ and $\gamma$ phases into the matrix grain where the $\gamma'$ phase has already precipitated. Many reports\cite{21,22,23} have also been published on the effects of the additional elements on the cellular precipitation, but no report has dealt with the effects of the B addition.

II. Experimental Procedures

Table 1 shows the chemical compositions of alloys used in this work. These alloys were made by melting electrolytic copper (>99.95\%), Cu–4\% Be mother alloy, and Cu–2\% B mother alloy in high purity alumina crucibles in an Ar atmosphere. The ingots were cut out into plates after homogenization at 1093 K for 24 h (8.6 x 10^4 s) and then these plates were cold-rolled to suitable thickness for the following measurements. Specimens prepared from these plates were quenched after solution treatment at 1093 K, followed by isothermal aging at 523 and 623 K.

After aging, various measurements were done. The hardness measurements were performed with a Vickers micro-hardness tester using a load of 2.94 N. Optical photographs enlarged by 150 times were used for measurements of the amount and width of cell. The amount of the cell was measured by the point accounting method and showed in area percent. As for the cell width, the maximum value was taken among the values of the cell width measured at about 50 grain boundaries. Lattice parameters were measured by using an X-ray diffractometer with a Cu target and calculated by the method of mean square root. An experimental error for the measured value of the lattice parameter is ±0.0001 nm. Since the amount of the cell is affected by the grain size in the specimen, the mean grain size of each specimen used in this study was prepared to be about 150 \mu m. The specimens for optical microscopic observations were etched in a solution of HCl and FeCl$_3$ after electropolished in a solution of H$_3$PO$_4$ and Cr$_2$O$_3$. The specimens for electron microscopic observation were electropolished in a solution of H$_3$PO$_4$ and Cr$_2$O$_3$, and the electron microscope was operated at 200 kV.

III. Results

1. The effects of B additions on the intragranular precipitation

Figure 1 shows hardness changes of Cu–2\% Be and B-added alloys during aging at 573 K. The hardening of the Cu–2\% Be alloy occurred in two stages, while that of the B added alloys occurred in one stage and the initiation of the hardening was retarded strongly. It is well known that the hardening of the first and second stages arises from the formation of

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|c|c|}
\hline
Nominal & Cu & Be & B* & Co & Fe \\
\hline
Cu-2Be & Bal. & 2.02 & — & 0.011 & 0.032 \\
Cu-2Be-0.02B & Bal. & 2.08 & 0.02 & 0.011 & 0.036 \\
Cu-2Be-0.05B & Bal. & 2.05 & 0.05 & 0.011 & 0.035 \\
Cu-2Be-0.1B & Bal. & 2.04 & 0.10 & 0.006 & 0.037 \\
\hline
\end{tabular}
\caption{Chemical compositions of alloys (mass\%).}
\end{table}

* not analyzed, showing the amount of addition.
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G.P. zones and the precipitation of the γ' phase, respectively\(^{(17)}\). Therefore, it is concluded that the addition of B suppresses the formation of G.P. zones and retards the precipitation of the γ' phases.

In Fig. 2, hardness changes during aging at 673 K are shown. The Cu-2% Be alloy strongly hardened from the early stage of aging, while B-added alloys began to harden after a long time of aging. This will mean that the precipitation of the γ' phase was retarded by the addition of B.

The change in lattice parameter of the α phase during aging at 573 K is shown in Fig. 3. The lattice parameter of the Cu-2% Be alloy increased corresponding to the second stage of hardening and reached a maximum value after \(1 \times 10^5\) s aging. On the other hand, the lattice parameters of the B-added alloys began to increase corresponding to hardening of the matrix grain and reached a maximum value after \(3 \times 10^5\) s aging. Since the increase in lattice parameter implies the decrease of the Be concentration in the α matrix owing to the precipitation of the γ' phase\(^{(13)}\), it is considered from Fig. 3 that the B atoms retard the precipitation of the γ' phase. The lattice parameter of a as-quenched specimen containing B are slightly larger than that of the Cu-2% Be alloy, suggesting that the B atoms exist interstitially in the matrix lattice.

Figure 4 shows the change in lattice parameter of the matrix α phase on aging at 623 K. The lattice parameter of the Cu-2% Be alloy increased corresponding to the hardness change in Fig. 2 and kept a constant value after \(3 \times 10^3\) s aging. The lattice parameter of the 0.02% B alloy began to increase after a longer incubation period than the Cu-2% Be alloy and kept a constant value after \(2 \times 10^4\) s aging. This retardation of the beginning of the increase of the lattice parameter by the addition of B results from the retardation of the precipitation of the γ' phase by the addition of B.

In Fig. 5, change in X-ray diffraction pattern of these specimens on aging at 523 K. Two lines observed at \(2\theta=33.2^\circ\) (0.5794 rad) and \(2\theta=34.2^\circ\) (0.5969 rad) arise from the γ and γ' phases, respectively\(^{(27)}\). Therefore, it is evident from Fig. 5 that the precipitations of γ' and γ phases were retarded by the addition of B. As will be mentioned later, the precipitation of γ phase occurred by the growth of cells containing the γ phase from the grain boundaries to the matrix grain. Therefore, B atoms must have suppressed the formation and growth of cells.
Figure 6 shows the electron diffraction patterns of Cu–2% Be alloys with or without B aged at 523 K for 300 s. Strong streaks to <200> direction are observed in the diffraction pattern of a Cu–2% Be alloy (a), while streaks are scarcely observed in that of a B-added alloy (b). The above results imply that the G.P. zones exist in the matrix of the Cu–2% Be alloy but scarcely exist in the matrix of the B-added alloy, and that the added B suppresses the formation of G.P. zones. These are consistent with the results of the hardness change in Fig. 1.

2. Effects of B additions on the cellular precipitation

In Fig. 7, changes in optical microstructures of Cu–2% Be and B-added alloys during aging at 523 K are shown. Small additions of B (≤0.05%) suppressed the growth of cells, while an excess addition of B (0.1%) promoted it.

Figures 8 and 9 show the change in the amount of cells by aging at 523 and 623 K, respectively. The addition of B (≤0.05%) retarded the initiation of cell growth and its completion. However, in the case of 0.1% B addition, the initiation and completion of cell growth occurred earlier than those of 0.02–0.05B alloys. This is because insoluble borides which existed in the as-quenched specimen acted as the nucleation sites of cells both in the grain boundaries and in the matrix grain on the aging that followed.

In Figs. 10 and 11, the effects of B additions on the growth of cells in a Cu–2% Be alloy are shown. In the cases of 0.02 and 0.05%B addition, the initiation of the cell growth was delayed, and the cell growth rate became smaller. In the case of 0.1% B addition, the cells were formed around the precipitates of borides in the matrix as well as at the grain boundaries. Therefore, it was impossible to carry out an accurate measurement of the cell width.

IV. Discussion

1. Effects of B additions on the intragranular precipitation

As mentioned above, it has been clarified in this study that the addition of B suppresses the formation of G.P. zones and retards the precipitation of the γ′ phase. The reasons are considered as follows:

Figure 12 shows the relation between the B
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Fig. 7 Optical microstructures in the Cu-2% Be-X% B alloys aged at 523 K for $6.0 \times 10^4$ s((a)-(d)), $1.8 \times 10^5$ s((e)-(h)), and $6.0 \times 10^5$ s((i)-(l)).

Fig. 8 Change in amount of cell in Cu-2% Be-X% B alloys on aging at 523 K.

Fig. 9 Change in amount of cell in Cu-2% Be-X% B alloys on aging at 623 K.
content and the lattice parameter of the \( \alpha \) solid solution of Cu–2% Be–X% B alloys quenched from 1093 K. The lattice parameter of the \( \alpha \) solid solution increased with B content. The atom radius of B is much smaller than that of a Cu or Be atom\(^{(10)}\). Therefore, if the B atom dissolves substitutionally in the Cu base alloy, the lattice parameter is expected to decrease with B content. However, in this study the lattice parameter increased with B content, implying that B atoms dissolve interstitially in the Cu–Be alloy. Laughlin et al.\(^{(28)}\) have studied the influence of B addition on the lattice parameter of a pure copper and observed an increase of the lattice parameter with B content. This experimental result was consistent with their calculation based on a model for the case in which B atoms exist interstitially in the copper lattice. So, they concluded that the B atoms existed interstitially in the Cu–B solid solution. It is considered from the above facts that the B atoms also exist interstitially in the Cu–Be–B solid solution.

When the B atoms exist interstitially in the Cu–Be–B alloy, they are deemed to give compression to neighboring atoms or vacancies around them. As a result, the B atoms will be expected to have elastic interactions with vacancies\(^{(29)}\). If so, the binding energy between a B atom and a vacancy will be larger than that between a Be atom and a vacancy. So, the number of vacancies needed for the formation of G.P. zones and for the precipitation of the \( \gamma' \) phase will decrease, resulting in the suppression of the formation of G.P. zones and the retardation of the precipitation of the \( \gamma' \) phase. For example, it is well known that Sn atoms added in an Al–Cu alloy suppress the formation of G.P. zones\(^{(30)}\). It is considered, therefore, that the largeness of the binding energies between the additional elements and the vacancies is an important factor in the role of the additional elements.

2. The effects of B additions on the cellular precipitation

As shown in Figs. 10 and 11, the start of the cell growth is retarded and the growth rate of the cell is suppressed by the addition of B. This reason is explained as follows:

The B atoms segregated at grain boundaries must have retarded the formation of cells by occupying the formation sites of the cells, and decreased the cell growth by decreasing the mobility of the advancing boundaries of the

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**Fig. 10** Change in maximum cell width of Cu–2% Be–X% B alloys on aging at 523 K.

**Fig. 11** Change in maximum cell width of Cu–2% Be–X% B alloys on aging at 623 K.

**Fig. 12** Relation between the B content and the lattice parameter of the \( \alpha \) solid solution of Cu–2% Be–X% B alloys quenched from 1093 K.
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The drag effect by the B atoms segregated at the advancing boundaries of the cells may be also important. In the present work, no direct evidence was obtained for the grain boundary segregation of B. However, as seen in Fig. 13, the mean grain diameter in the Cu-2% Be-B alloys quenched from 1093 K after a 50% cold-rolling decreased with B content. This means indirectly that the B atoms segregated at grain boundaries decreased the grain boundary energy and the mobility of the grain boundary migration.

In the case of the excess addition of B, 0.1% B, a incubation period for the cell growth was inversely shorten and cell growth was accelerated. This phenomena will be explained as follows: As seen from the Cu-B binary phase diagram, the amount of insoluble compounds of B will increase with the B addition. Such compounds (unidentified in this work) will offer the sites for the nucleation of cells not only in the grain boundaries but also in the matrix grain. Therefore, the amount of cells in the 0.1% B alloy reached 100% sooner than the 0.05% B alloy. As for the formation of the cell within the matrix grain, the following explanation may be reasonable. That is, the interphase boundaries between B compounds and the matrix will act as the formation sites of cells in the same way as in the grain boundaries. However, a more detailed study is needed to clarify this. Similar phenomena have been already observed in the Cu–Be alloys containing such elements as Zr, Nb and V which are difficult to dissolve in copper.

V. Conclusion

Effects of B additions on the intragranular and cellular precipitations in a Cu–2 mass% Be alloy on aging at 523 and 623 K after quenching from 1093 K were investigated. The results obtained are as follows:

1. The addition of 0.02–0.1 mass% B suppressed the formation of G.P. zones and retarded the precipitation of the γ' phase.

2. The lattice parameter of the α solid solution of the B-added alloy increased with B addition. This result suggests that B atoms exist interstitially in the α solid solution and suppress the formation of G.P. zones and retard the precipitation of the γ' phase as a result of the strong interaction with vacancies.

3. The formation and growth of grain boundary cells were suppressed by the addition of 0.02–0.05% B, but promoted by an excess addition of B, 0.1%.

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