Improvement in Hot Ductility in a Cu–4.4 mol% Sn Alloy by Adding a Small Amount of Third Elements*

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A small addition of elements such as Y, Ce, La and Ca resulted in two kinds of improvements in ductility in a Cu–4.4 mol% Sn alloy which has poor hot ductility: one appeared at temperatures above 973 K and the other, around 673 K. A series of results obtained in this study suggested that the cause of the former was the same as that obtained in B-bearing alloy which was previously reported. As to the latter, slip band and dislocation structures were regarded to be unaffected by the added elements. On the other hand, EDS analysis showed that yttrium sulfides were present in a Y-bearing alloy showing high ductility, while Auger electron spectroscopy revealed that impurity of sulfur segregated to grain boundaries of the Cu–Sn alloy, showing poor ductility. Thus, the improvement at intermediate temperatures around 673 K was attributed to the increase in grain boundary strength caused by the reduction of sulfur segregation to grain boundaries.

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I. Introduction

According to a previous paper(1), the ductility of a phosphor bronze containing 8 mass% Sn (4.4 mol% Sn) is high enough at room temperature, but it decreases remarkably at elevated temperatures: it has a minimum value at 673–773 K and increases a little at the higher temperatures. This kind of poor ductility is commonly observed in a Cu–4.4 mol% Sn binary alloy prepared by vacuum melting and casting, and is considered to be closely related to the hot shortness of Cu–Sn–(P) alloys.

Recently, the present authors have shown(2) that the hot ductility of a Cu–4.4 mol% Sn alloy can be improved markedly at temperatures above 973 K by adding a small amount of boron or magnesium. In the present study, the effect of additional elements on the hot ductility of the alloy was further investigated.

II. Experimental Procedure

The Cu–4.4 mol% Sn binary alloy and Cu–4.4 mol% Sn alloys with a single addition of such element as calcium, yttrium, lanthanum, cerium or boron in an amount of 1000 mol ppm were prepared by vacuum melting and casting. Ingots of the alloys were homogenized at 973 K for 18 ks in a reducing atmosphere of dissociated ammonia gas. The procedures for fabricating round tensile specimens were the same as reported elsewhere(2), and the specimens were made with a gauge length of 10 mm and a diameter of 4 mm. The mean grain size of specimens controlled by vacuum annealing at 1073 or 973 K, was about 100 μm.

Tensile tests were conducted at temperatures ranging from 573 to 1073 K in a vacuum (1 Pa) by use of an Instron type testing machine. An initial strain rate of 3.3 × 10⁻³ s⁻¹ was adopted and the ductility was assessed by measuring the reduction in area (RA) at the fracture. Metallographic observations were mainly made on etched longitudinal cross sections of gauge lengths of specimens which were quenched after fracturing. Observations of slip bands which developed within grains during deforma-
tion were also made on polished surfaces of specimens. Fractography was performed with SEM, and Auger electron spectroscopic (AES) analysis was carried out on the fracture surface. In addition, energy dispersive X-ray spectroscopic (EDS) analysis was carried out on dispersed particles appearing in specimens.

III. Results

The variation of RA with temperature is shown in Fig. 1. It is clearly seen that the ductility of the binary alloy becomes poor at elevated temperatures: it has a minimum value at about 773 K and a peak at 973 K. On the other hand, hot ductility is markedly improved at temperatures above 973 K in Y- and Ce-bearing alloys in a similar way as in a B-bearing alloy. Although the ductility-trough is commonly observed in each alloy, the ductility around 673 K is also much improved in Y-, Ca- and Ce-bearing alloys compared with that in the binary and B-bearing alloys. In brief, this figure indicates that two kinds of improvements in ductility are brought about by the addition of third elements.

For convenience, the cause of the improvement in hot ductility at temperatures above 973 K was studied first. Observations were made on the cross sections of the specimens after fracture and the results are shown in Fig. 2. In this figure, the Ca-bearing alloy as well as the binary alloy exhibits severe grain boundary

† The results for a La-bearing alloy were omitted in Fig. 1 and in the following figures, since they were similar to those for a Ce-bearing alloy.
cracking, while such grain boundary cracking almost disappears in the Y- and Ce-bearing alloys in the same way as in the B-bearing alloy\(^2\).

In connection with grain boundary cracking, several experiments, including the observation of crack propagation along grain boundaries during hot deformation and the observation of slip band structures were carried out. In the course of these experiments, almost the same results were obtained as those reported previously in B- and Mg-bearing alloys\(^2\). In addition, it was shown that internal oxidation of the alloy or preferential oxidation of grain boundaries was significantly suppressed by Y(Ce) addition in the same way as the addition of B. Hence, it is possible to give the following interpretation of the marked improvement in hot ductility observed above 973 K in the same way as in a B-bearing alloy\(^2\): added yttrium or cerium (lanthanum) suppresses the preferential oxidation of grain boundaries during annealing for grain size control or holding at testing temperatures, and consequently can prevent reduction in the strength of grain boundaries, which results in an improved ductility of the Y(Ce, La)-bearing alloy at temperatures above 973 K.\(^1\)

Next, the cause of the improvement in ductility around 673 K was examined. Micrographs of cross sections of specimens which were fractured at 673 K are shown in Fig. 3. Both the binary and B-bearing alloys exhibit severe grain boundary cracking and almost maintain the initial grain morphology. In contrast, grain boundary cracking is hardly observed in Y-, Ca- and Ce-bearing alloys and grains in these alloys are extended in the tensile direction. Fractographs of specimens tested at 673 K are shown in Fig. 4. The former alloys demonstrate intergranular fracture, and ledges on fracture surface which correspond to the intersections of localized coarse slip bands with a grain boundary are observed. The latter alloys, however, show transgranular fracture accompanying numerous dimples on the fracture surface.

Then, observations of slip band structures were carried out to clarify whether the different fracture morphology was due to the difference in stress concentration caused by localized slip bands at grain boundaries. Localized coarse slip bands are commonly observed in each alloy as shown in Fig. 5, but no essential difference in slip band structures is recognized between these alloys. In addition, no alleviation of stress concentration at grain boundaries can be expected in these alloys, since grain boundary

\[\text{The reason why calcium was ineffective was not made clear, though calcium is known to be a deoxidizer of copper and copper alloys. It might be related to this fact that calcium forms a tin compound which has a much lower melting point than that of the other elements in this study, since calcium and tin were detected by means of Auger electron spectroscopy from intergranular fracture surface obtained at 1073 K.}\]
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Bulging or dynamic recrystallization hardly occurs at intermediate temperatures around 673 K.

Figure 6 shows curves of load versus displacement obtained at 673 K. This figure indicates that the binary and B-bearing alloys are ruptured at a very early stage of work-hardening with such small displacements. On the basis of the results shown in Figs. 3 and 4, it can be said that grain boundary cracks are easily formed when low stress is applied to these alloys. This fact suggests that grain boundary strength is lower in these alloys than that in a Y-bearing alloy. In other words, an alleviation of intermediate temperature embrittlement brought about by the addition of yttrium may be due to the increase in grain boundary strength.

IV. Discussion

In this study, it has been shown that a small amount of additional elements induces two kinds of improvements in ductility in a Cu–Sn alloy. Since the improvement at temperatures above 973 K has already been described in
the former chapter, the improvement at the intermediate temperatures will be discussed below.

It has been reported that an intermediate temperature embrittlement in an $\alpha$-brass is ascribable to the stress concentration on grain boundaries caused by localized coarse slip bands which develop during deformation at elevated temperatures$^{(4)}$. The same mechanism was considered to be operated in Cu–Sn alloys with and without additional boron$^{(2)}$. In this study, however, it was suggested that the alleviation of the embrittlement was due to an increase in the strength of grain boundaries caused by the addition of Y(Ce, La).

It is generally accepted that the grain boundary strength of alloys is lowered by the segregation of trace impurities to grain boundaries$^{(5)}$. According to the results reported elsewhere by the present authors$^{(1)}$, a tin bronze which was prepared from high purity metals with less sulfur showed a higher ductility than an alloy prepared from commercially available copper and tin. Additionally, it was reported that sulfur tended to segregate to grain boundaries of a copper$^{(6)}$. Hence, it can be considered that the intermediate temperature embrittlement of tin bronzes is closely related to the segregation of sulfur impurity to the grain boundaries.

Auger spectra obtained from intergranular fracture surface of the binary alloy tested at 673 K are shown in Fig. 7. Although the concentration of the sulfur impurity in the binary alloy is only about 8 mol ppm, sulfur is surely detected from the fracture surface (Fig. 7(a)). No sulfur, however, can be detected after sputtering by argon ions for 600 s (Fig. 7(b)). This figure reveals that impurity of sulfur is significantly segregated to grain boundaries in the tin bronze. If sulfur segregation to grain boundaries causes a substantial decrease in the strength of the grain boundary, then the alleviation of the intermediate temperature embrittlement, due to the addition of elements, is attributed to a reduction in the amount of sulfur segregated to grain boundaries on account of desulfurization.

The composition of dispersed particles appearing in Y-bearing alloy was examined by EDS. Figure 8 demonstrates that the particles contain copper, tin and yttrium, but that not sulfur. Then, a Cu–4.4 mol%Sn alloy, with only 50 mol ppm of yttrium added, was prepared and dispersed particles appearing in this alloy were examined. Naturally, the number density of the dispersed particle in this alloy was markedly reduced compared with that in the alloy containing 0.1 mol% Y. The results of EDS analysis on the particles in the alloy with 50 mol ppm yttrium is shown in Fig. 9. It is evident that sulfur is detected in every particle in this alloy together with copper, tin and yttrium. The reason why sulfur is detected in this case may be that sulfur concentration in these particles is much higher than that in Fig. 9.

To make sure that the alleviation of the embrittlement can be brought about by a trace addition of yttrium, the variation of hot ductility with temperature of the alloy is shown in Fig.
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It is obvious that the addition of yttrium in quantities of only 50 mol ppm is effective. It is known that elements such as yttrium, cerium, lanthanum and calcium are strong sulfide formers. In addition, it was reported that the addition of these elements could induce desulfurization in pure copper\(^{(9)}\). Since the affinity of boron for sulfur is not so strong as that of the other elements in this study\(^{(10)}\), sufficient desulfurization may not occur in the Cu–4.4 mol%Sn–0.1 mol%B alloy. To confirm this, the dispersed particles appearing in Cu–4.4 mol%Sn alloys, with 0.1% and 0.01% B, were examined by EDS analysis. No sulfur was detected in any of the particle appearing in these alloys, as was expected.

After all, it can be concluded that the alleviation of the intermediate temperature embrittlement, a result of the addition of a small amount of yttrium, cerium, lanthanum and calcium, is attributed to an increase in grain boundary strength on account of sulfide formation. The mechanism of the decrease in grain boundary strength, caused by sulfur segregation, is a significant problem in the future.
V. Summary

The hot ductility of a Cu–4.4 mol%Sn alloy affected by a small amount of additional elements such as yttrium, cerium, lanthanum and calcium was studied and compared with that of the alloy having additional boron.

(1) Two kinds of improvements in ductility were brought about by these additional elements: one appears in Y-, Ce- and La-bearing alloys at temperatures above 973 K, and the other appears in Y-, Ce-, La- and Ca-bearing alloys at intermediate temperatures around 673 K. The cause for the former improvement is considered to be the same as that in a B-bearing alloy.

(2) In connection with the latter improvement, the following results were obtained: a trace impurity of sulfur was detected at the intergranular fracture surface of the alloy without added elements, while dispersed particles of sulfides containing yttrium were detected in an Y-bearing alloy. Each element connected to the latter improvement was known to be a strong sulfide former.

(3) The latter improvement was attributed to an increase in the grain boundary strength caused by a reduction in the amount of sulfur segregation to grain boundaries on account of sulfide formation.

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