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QUANTITATIVE STUDY OF Sb GRAIN BOUNDARY SEGREGATION IN RAPIDLY QUENCHED Cu-Sb ALLOYS

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Abstract

In the present work, we used Cu-Sb alloy system as a model to study grain boundary segregation in specimens prepared by rapid quenching. Ribbons of Cu-Sb alloys of single Cu phase and polycrystalline structure containing 0.01, 0.08, and 2wt% Sb prepared by single roller melt spinning were used as specimens, and the segregation was studied by using energy dispersive X-ray spectrometer attached to a scanning transmission electron microscope. Sb grain boundary segregation was detected in the 0.08 and 2wt% Sb specimens and the degree of segregation in the

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0.01wt% Sb specimen is below detection limit. The effect of rapid quenching in suppressing the segregation was confirmed by comparing the results of as-quenched and annealed 0.01wt% Sb specimens. It is reasoned that the degree of grain boundary segregation increases with Sb concentration from zero up to a value larger than 0.08wt% in the present alloy series. Further, it is concluded that the segregation happens at temperatures above 873K. Upon comparing with previous reports, it is concluded that the degrees of Sb grain boundary segregation observed in the as-quenched 0.08wt% Sb specimen have little effect on the alloys performance in impact test. The present work provides a basis of consideration when both annealing and segregation are concerned in alloy processing.

1. Introduction

It has been reported that trace elements segregation makes metallic materials brittle [7, 12, 15], though occasionally ductile [16]. In the equilibrium state, segregation at high temperatures is lower than at low temperature [13]. At low temperatures, the process to approach equilibrium state takes long time. Practically, no segregation could happen in experimental time scale at room temperature [14, 22]. Therefore, quenching is a practical way to suppress grain boundary segregation. It has been reported that the degree of embrittlement caused by segregation decreases with increasing cooling rate used to cast materials [7, 15], implying a possible change in grain boundary segregation. There are several reports related to trace element segregations to grain boundaries during rapid cooling [5, 11, 23, 25]. These works focused on either the simple detection of segregation [5, 11, 23, 25], or the mutual interaction of multiple trace elements in the segregation process [5].

With respect to the measurement of grain boundary segregation, over the last thirty years, the most widely used one is the Auger electron spectroscopy (AES) [e.g., 18, 20, 21, 24]. With this method, the specimens must be fractured in situ prior to study. Therefore, its application is limited to brittle materials. Since the fracture is likely to follow the most segregated boundaries, the measured distribution of segregation could shift toward the high value side. In recent years, analytical electron microscopy (AEM) has emerged as an effective approach in the study of this field [e.g., 1, 9, 14]. Compared to AES, the application of AEM is not limited to brittle materials and the selection of boundary is not biased. In

AEM, elemental analysis was performed mainly through energy dispersive X-ray spectroscopy (EDS) [e.g., 1, 9, 14] though occasionally electron energy loss spectroscopy (EELS) was used [16].

The present work is set to evaluate quantitatively the degree of grain boundary segregation as a function of trace element concentration in rapidly quenched materials and relate the results to the mechanical behaviours. Cu metal containing Sb is suitable for this purpose. Cu-Bi [e.g., 14, 19] and Cu-Sb [e.g., 4, 7, 11, 12, 26] are two widely documented segregation and embrittlement metal-metal systems. Compared to Sb, the solid solubility of Bi in Cu is extremely low [17]: The maximum solubility of Bi in Cu is ~0.07wt% at 1248K and that of Sb is ~2wt%. Further, the melting temperature of Sb (904K) is close to that of Cu (1358K) as compared to that of Bi (544K). These characters of Sb favourite the preparation of Cu-Sb alloys of varied Sb concentrations with single Cu phase, which is a requirement for the present purpose.

2. Experimental

Cu-Sb alloys of 0.01, 0.08, and 2wt% Sb were prepared for the present work. Pure Cu (5N) and Sb (3N) were arc-melted under Ar atmosphere. To ensure the homogeneity, the alloy ingots were reversed and re-melted for several times. From these master alloys, ribbons with a cross section of $0.15 \times 3mm^2$ were prepared by single roller melt spinning. The roller has a diameter of 20cm, operated at a surface speed of 40m/s. This method corresponds to a cooling rate of $\sim 10^6$ K/s [2], which is considered as the highest at present technical level. The 2wt% Sb ribbon was examined by X-ray diffraction (XRD) using RINT2000 of Rigaku to verify the single Cu phase. To prepare specimen for electron microscope, circular disks punched from these ribbons were dimple grinned down to ~10μm, followed by ion milling by using Gatan PIPS with 4keV Ar ion beam incident on the specimen surface at 4˚. The elemental analysis of grain boundary was performed by EDS attached on HB603 scanning transmission electron microscope (STEM), operated at 300kV. Details regarding the STEM-EDS elemental analysis were published elsewhere [11].

3. Results and Discussion

XRD examination verified that the 2wt% Sb ribbon is of single Cu phase. Based on this result, it is safe to conclude that the 0.08 and 0.01wt% Sb ribbons are of single Cu phase too because of their low Sb concentrations. The lack of Sb-rich phase implies that Sb concentration is the same throughout the ribbon and has the nominal value in raw materials.

Figures 1(a) and (b) show bright field STEM and Sb concentration images of the as-quenched 2wt% Sb ribbon centered on a grain boundary. The approach to generate concentration image is reported in previous reports [3, 10]. The lower left part of Figure 1(a) is brighter than the other parts because of reduced thickness. This thickness effect disappears largely in the concentration image (b) because the ratio of Sb X-ray intensity to that of Cu was used in the generation of this image. The bright contrast on the grain boundary in image (b) is a clear evidence of Sb grain boundary segregation. It should be pointed out that, in Figure 1(b), the apparent width of the boundary in the lower part seems narrow compared to the upper part. This is confirmed by line profiles drawn across the grain boundary shown in Figures 1(c) (lower part) and (d) (upper part), respectively. These profiles were obtained by averaging over a width of 11 pixels (12nm) in the direction parallel to the boundary. The apparent width of the boundary in (c) is ~3nm and ~4nm in (d), respectively. The Sb concentration in the peak position of Figure 1(c) is ~12wt% Sb and that in 1(d) ~10wt% Sb. Such change in apparent boundary concentration is considered to be caused by the slight inclination of the boundary plane relative to the incident electron beam. Obviously, this inclination effect is more significant in thicker area.

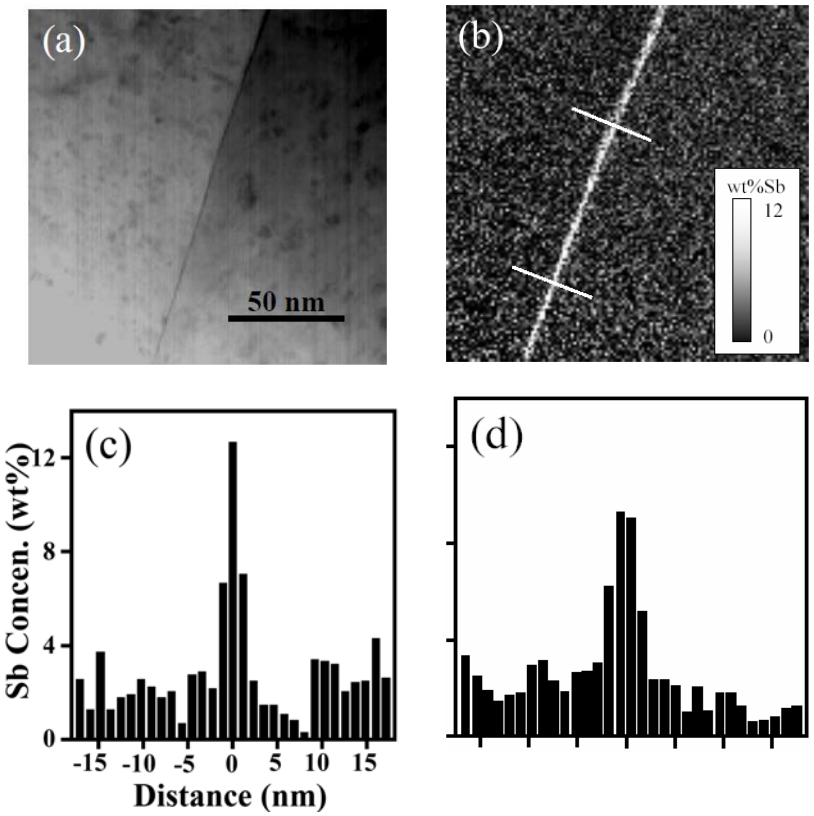

Figure 1. Bright-field: (a) and Sb concentration: (b) images of a boundary in as-quenched 2wt% Sb ribbon. The apparent boundary width in the lower part of (b) seems narrower than the upper part. This is verified by line profiles shown in (c) and (d), which correspond to the lower and upper parts, respectively. Average values over 11 pixels (12nm) in the direction parallel to the boundary were taken in drawing line profiles.

There is other approach to evaluate the degree of segregation on grain boundary. We call it segregant boundary excess with unit of atoms/nm^2. This value represents the excess number of segregant atoms due to the existence of unit grain boundary plane and is less sensitive to the inclination effect mentioned above. Detailed explanation as how to calculate the boundary excess, was given in our previous papers [3, 10], where we used boundary coverage to denote this term. Sb boundary

excesses for the lower and upper parts of Figure 1(b) are both 12 atoms/nm^2 despite the difference in apparent concentration. We adopt boundary excess to evaluate the degree of segregation.

Histograms of Sb boundary excess in the present specimens, as-quenched and annealed, are shown in Figure 2. The boundary excess for the as-quenched 2wt% Sb specimen ranges from 5 to 12 atoms/nm^2. From

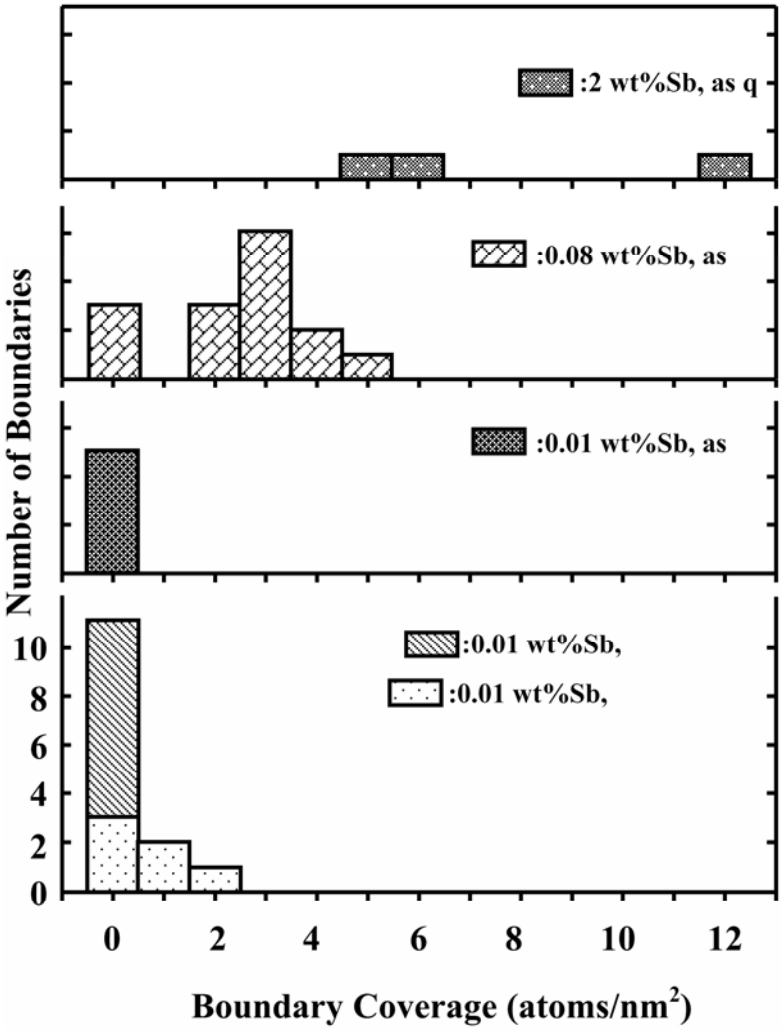

Figure 2. Distribution histograms of Sb boundary excess in the as-quenched and annealed alloys.

the counting statistics, 3σ (one σ is the standard deviation) errors were calculated as 1 and 2 for the boundary excesses of 5 and 12 atoms/nm^2, respectively, implying that the observed range exceeds statistical fluctuation. Different boundary structures are considered as the reason for this inhomogeneous distribution. Using the atomic radius of Sb [8] and the definition of Hondros and Seah [6], one monolayer Sb was estimated as 12 atoms/nm^2. Then, the observed boundary excess values in the as-quenched 2wt% Sb specimen correspond to 0.4 to 1 layers. The Sb boundary excess values for the as-quenched 0.08wt% Sb sample ranges from 0 to 5 atoms/nm^2. No detectable segregation was observed in the as-quenched 0.01wt% Sb specimen. This is true even after the specimen was annealed at 873K for 6hr, where an example of boundary elemental analysis is shown in Figures 3(a) and (b). When prolonged annealing of 72hr at the same temperature is carried out, Sb grain boundary segregation in this specimen was observed, an example of which is shown in Figures 3(c) and (d). The Sb boundary excess for this specimen ranges from 0 to 2 atoms/nm^2, as shown in Figure 2.

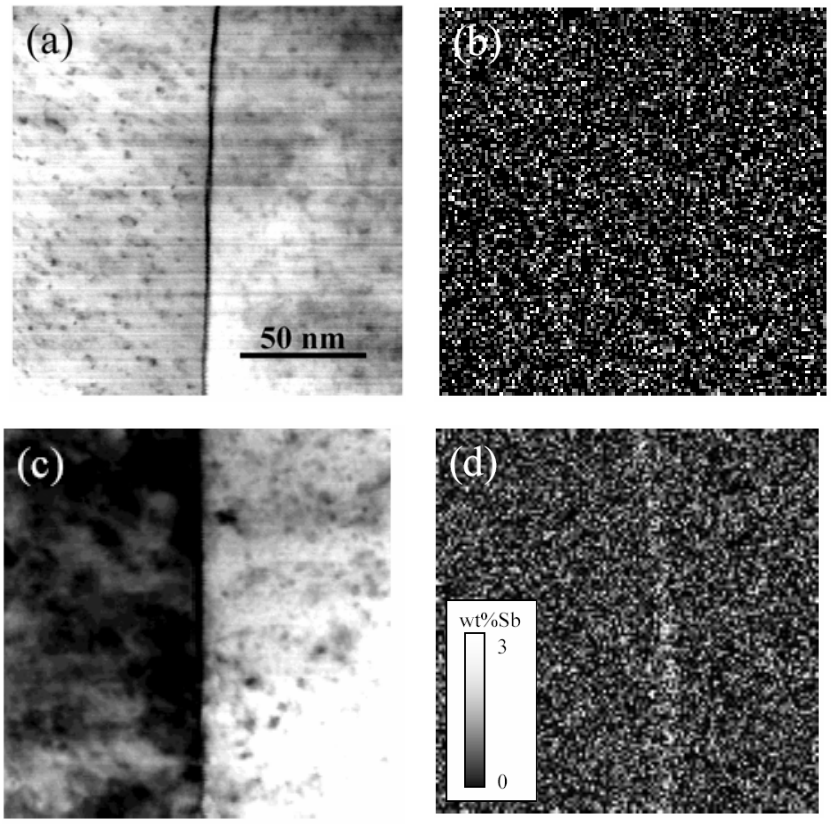

Figure 3. Bright-field ((a) and (c)) and Sb concentration ((b) and (d)) images of boundaries of 0.01wt% Sb specimen. The boundary corresponding to (a) and (b) is from the alloy annealed at 873K for 6hr, where Sb segregation was not detectable. Sb segregation in the boundary corresponding to (c) and (d) was observed, where the alloy was annealed at 873K for 72hr.

The present results indicate that rapid quenching does affect grain boundary segregation. The suppressing effect is evidenced by the change in the degree of segregation in the 0.01wt% Sb specimen before and after the 873K, 72hr annealing. This result is in accordance with the experimental report by Hopkin [7] that slowly cooled Cu-Sb alloys are more brittle than the rapidly quenched one. The cooling rate of 10^6 K/s used in the present work represents the upper limit achievable in the

present technical level. Even this cooling rate is not high enough to prevent Sb grain boundary segregation completely in the 0.08 and 2wt% Sb specimens. It is further speculated that segregation in the present as-quenched alloys happens mainly at temperatures above 873K for the following reasons. In the process of melt-spinning, the temperature of the ribbons drops to room temperature in less than 10 min from the melting temperature. In other words, the ribbons pass through the temperature range from 873K to room temperature in less than 10 min. In the present experiment, it has been shown clearly that annealing of 0.01wt% Sb sample at 873K for even 6hr does not cause significant segregation. Therefore, grain boundary segregation at temperatures below 873K proceeds so slowly that it causes virtually no change.

It is predicted that Sb boundary excess increases with its concentration in the alloy up to certain value. When this Sb concentration is over certain level, the boundary segregation may be saturated for the following reasons. First, the atomic sites suitable for segregation are limited to several atomic layers around the boundary. When all these sites are occupied by Sb atoms, further increase in the Sb concentration may have no effect. Second, high degree of segregation implies that some segregants need to diffuse long distance from the inner part of the grain to the boundary. The rapid quenching used in the present experiment shortens the time span that the segregant atoms have enough mobility to diffuse. The experimental fact that, the degree of Sb boundary excess in 2wt% Sb specimen is higher than the 0.08wt% Sb one is explained as that this higher Sb concentration limit for the saturation of grain boundary segregation is above 0.08wt% Sb.

McLean [12] conducted impact test on 0.08, 0.14, 0.24, 0.56, and 1.29wt% Sb Cu-Sb alloys. In his experiment, the water-quenched ingots were annealed for 36hr at 948K, followed by cold rolling. The cold rolled products were annealed at 923K for 1hr, and then cooled to 373K at a rate of 10K/hr. Impact test experiments revealed that the toughness of 0.08wt% Sb alloy was the same as that of pure Cu, while others showed obvious embrittlement. The thermal process used in his experiment favourites Sb grain boundary segregation as compared to the present as-quenched 0.08wt% Sb specimen, implying that a higher degree of Sb grain boundary segregation is expected in McLean's case. Therefore, it is

concluded that the degree of Sb segregation observed in the present as-quenched 0.08wt% Sb specimen does not affect the performance of impact test significantly.

4. Summary

Sb grain boundary segregation in Cu-Sb alloys containing 0.01, 0.08, and 2wt% Sb quenched from melt at a rate of 10^6 K/s was studied by STEM-EDS. While no grain boundary segregation was found in the 0.01wt% specimen, the ranges of Sb boundary excesses in the 0.08 and 2wt% specimens are 9 to 5, and 5 to 12 atoms/nm^2, respectively. Analysis of annealed 0.01wt% Sb specimens confirmed that quenching suppresses grain boundary segregation. It is believed that the degree of Sb grain boundary segregation increases with Sb concentration in the alloy from zero up to certain higher value, after which it may saturate. This upper limit is determined to be higher than 0.08wt% Sb. Analysis of the annealed sample also leads us to believe that segregation observed in the as-quenched specimens happens mainly at temperatures above 873K. Combining the present results with previous report, it is concluded that the degree of segregation observed in the as-quenched 0.08wt% Sb alloy has no significant effect on the material performance in impact test. The present work provides a basis of consideration when both annealing and segregation are concerned in alloy processing.

References

[1] S. M. Bruemmer and L. E. Thomas, Surf. Interface Anal. 31 (2001), 571-581.

[2] R. W. Cahn and A. L. Greer, In: R. W. Cahn, P. Hassen (ed.), Physical Metallurgy, Volume 2, Amsterdam, North-Holland, 1996.

[3] D. T. Carpenter, M. Watanabe, K. Barmak and D. B. Williams, Microsc. Microanal. 5 (1999), 254-266.

[4] T. H. Chuang, W. Gust, L. A. Heldt, M. B. Hintz, S. Hofmann, R. Lucic and B. Predel, Scripta Metall. 16 (1982), 1437-1441.

[5] J. R. Cowan, H. E. Evans, R. B. Jones and P. Bowen, Acta Mater. 46 (1998), 6565-6574.

[6] E. D. Hondros and M. P. Seah, Metall. Trans. 8A (1977), 1363-1371.

[7] L. M. T. Hopkin, J. Inst. Met. 84 (1955-1956), 102-108.

[8] Japan Institute of Metals, Data Book for Metals, Maruzen, Tokyo, 1996, (in Japanese).

[9] E. A. Kenik, J. Electron. Micro. Tech. 18 (1991), 167-171.

[10] C. Li and D. B. Williams, Micron. 34 (2003), 199-209.

[11] C. Li, M. Watanabe, D. W. Ackland and D. B. Williams, Mater. Lett. 57 (2003), 1345-1350.

[12] D. McLean, J. Inst. Met. 81 (1952-1953), 121-123.

[13] D. McLean, Grain Boundaries in Metals, Oxford University Press, New York, 1957.

[14] J. R. Michael and D. B. Williams, Metall. Trans. A15 (1984), 99-105.

[15] R. D. K. Misra, Surf. Interface Anal. 31 (2001), 509-521.

[16] D. A. Muller, S. Subramanian, P. E. Batson, J. Silcox and S. L. Sass, Acta Mater. 44 (1996), 1637-1645.

[17] H. Okamoto, R. R. Subramanian, L. Kacprzak, In: B. Thaddeus, T. B. Massalski (editor-in-chief), Binary Alloy Phase Diagrams, 2nd edition, William W. Scott Jr, USA, 1992.

[18] P. W. Palmberg and H. L. Marcus, Trans. ASM 62 (1969), 1016-1018.

[19] B. D. Powell and D. P. Woodruff, Phi. Ma. 34 (1976), 169-176.

[20] M. P. Seah, Surf. Sci. 53 (1975), 168-212.

[21] M. P. Seah, J. Vacuum Sci. Tech. 17 (1980), 16-24.

[22] P. Sevc, J. Janovec, M. Lucas and H. J. Grabke, Steel Research 66 (1995), 537-542.

[23] S. H. Song, R. G. Faulkner and P. E. J. Flewitt, Mater. Sci. & Eng. A281 (2000), 23-27.

[24] D. F. Stein, A. Joshi and R. P. Laforce, Trans. ASM 62 (1969), 776-783.

[25] V. Vorlicek and P. E. J. Flewitt, Acta Metall. Mater. 42 (1994), 3309-3320.

[26] K. S. Yu, A. Joshi and W. D. Nix, Metall. Trans. 14 (1983), 2447-2454.

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