Misorientation dependence of intergranular embrittlement of Cu-2.0 wt.% Sb bicrystals

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Abstract

Bicrystals of a Cu–2.0 wt% Sb alloy with different [001] symmetric tilt boundaries were tensile tested at several temperatures from 77 to 743 K. The dependence of Sb segregation level at [001] tilt boundaries on the misorientation angle also was examined by energy-dispersed X-ray spectroscopy. The fracture behavior was sensitive to the misorientation angle and test temperature. Both the fracture behavior at 77 K and the Sb segregation level showed a good correlation with the grain-boundary energy of pure Cu. The higher the grain-boundary energy, the higher the Sb segregation level and the higher the degree of grain-boundary embrittlemen.

Keywords: Embrittlement, Segregation, [001] symmetric tilt boundary, Cu–Sb bicrystal, intergranular fracture

1. Introduction

It has been widely established that grain-boundary fracture behavior of solids induced by segregates depends strongly on the character of individual grain boundaries. Many investigations have attributed the structural dependence to the tendency of impurity atoms to segregate at various levels to individual boundaries [1]. For example, Miura et al. examined systematically the embrittlement of Bi-doped Cu bicrystals with various [011] [2] and [001] [3] symmetric tilt boundaries. For the two series of grain boundaries, they showed that the bicrystals became more brittle as grain-boundary energy of pure Cu increases, and that the fracture stress and fracture strain of the bicrystals decreased with increasing deformation temperature. For four kinds of [011] tilt boundaries, they also found by energy-dispersed X-ray spectroscopy of thin foils that segregation of Bi atoms became more significant as the boundary energy of pure Cu increases [2]. Monzen et al. [4] carried out a similar investigation for [011] twist boundaries and found that there existed a strong correlation between the degree of boundary embrittlement and the boundary energy. On the other hand, Roy et al. [5] studied the Bi-induced boundary embrittlement in Cu as a function of boundary structure and found that boundaries of least embrittlement were the boundaries of least energy of segregated Cu.

More recently, we have performed tensile tests of Sb-doped Cu bicrystals with various [011] symmetric tilt boundaries at several temperatures between 77 and 773 K. The dependence of Sb segregation level at the boundaries on the misorientation angle has also been examined by energy-dispersed X-ray spectroscopy (EDX). The fracture behavior is sensitive to the misorientation angle, Sb doping time and test temperature. A strong correlation is found among the fracture behavior at 77 and 773 K, grain-boundary segregation level of Sb and grain-boundary energy before Sb doping: a higher-energy boundary has a higher level of Sb segregation and fractures more easily at a lower tensile stress [6].

In the present study, as an extension of this work, we will investigate the correlation between the grain-boundary embrittlement of Cu–2.0 wt% Sb bicrystals with [001] symmetric tilt boundaries and their energy before Sb doping. In addition, the measurements of Sb segregation at the grain boundaries will be performed as a function of the misorientation angle by EDX.

2. Experimental procedure

Cu bicrystals with flat surfaces parallel to (001) and with different [001] symmetric tilt boundaries of misorientation angles θ=12° to 78° were grown by the Bridgman method using two-seed crystals for each. Hereafter, the bicrystal with the misorientation angle θ and its grain boundary will be termed θ bicrystal and θ boundary, respectively. Tensile specimens with the gage dimensions of 1.5×6×30 mm were spark-cut from the grown bicrystals so that straight boundaries ran at 90° with respect to the tensile axis in the center of the specimens. Then they were packed into a mullite tube with a mixture of Cu (10 parts), Al_2O_3 (10 parts) and Sb (1part) powders and heated to 1223 K for 336 h in an Ar atmosphere. The Sb-doped specimens were homogenized in evacuated quartz capsules at 1223 K for 48 h. A chemical analysis showed that the specimens doped for 336 h contained 2.0 wt% Sb. Tensile tests were conducted at various temperatures between 77 and 743 K using an instron-type testing machine at an initial strain rate of 10^{-5} s^{-1}. Tensile tests at high temperatures were carried out in a vacuum of 10^{-3} Pa.

In order to measure the Sb concentrations at the grain boundaries and in the Cu matrix, thin foils were examined in a HITACHI H-9000NAR microscope operated at 300 kV and equipped with an energy dispersive X-ray spectroscopy (EDX) system. Concentration measurements by EDX were performed with the electron beam, parallel to [001], directed at the grain boundaries. The beam diameter employed was 2 nm and the foil thickness examined was about 20 nm. About 20 points per boundary were measured.

3. Results and discussion

3.1. Effect of test temperature on the fracture behavior

The nominal stress–strain curves of Cu–2.0 wt% Sb bicrystals showed sharp yield points at all temperatures of test between 77 and 743 K and marked serrations at a temperature of 523 K, as exemplified in Fig. 1. This result is in agreement with the result of tensile tests on Cu–1.7 wt% Sb polycrystals by Hopkin [7], who observed sharply defined yield points at all

temperatures examined from 77 to 773 K and marked serrations at some temperatures between 473 and 573 K.

Fig. 2 presents the effect of test temperature on fracture stress (peak stress) for 46° and 53° bicrystals. Open and solid symbols represent transgranular and intergranular fractures, respectively. About three bicrystal specimens were tensile tested for each experimental value. Since dynamic recrystallization often took place at grain boundaries during deformation over about 773 K, values of fracture stress lower than 743 K are shown in Fig. 2. Both bicrystals exhibit intergranular fractures at both low and high temperatures, and the two curves show the peaks at about 400 K. The fracture strain vs. temperature curves for both bicrystals exhibited a similar tendency, as seen in Fig. 1. This result is analogous to the results of impact and tensile tests on polycrystals of Cu alloys with 1.7 wt% Sb and 2.0 wt% Sb, reported by Hopkin [7]. The embrittlement at low temperatures in Fig. 2 may be influenced by stress concentrations set up at the end of slip planes [7].

Miura et al. observed that fracture stress and strain generally decreased with increase in test temperature between 77 and 503 K [2,3,8], and there was a sharp reduction in the fracture strains when the test temperature is raised from 503 to 553 K [8]. It was considered that the sharp reduction in the fracture strains was caused by premelting of the Bi layers at grain boundaries. Similarly, the embrittlement around 743 K in Fig. 2 seems reasonable to be promoted by premelting of segregated Sb layers at the grain boundaries, since the eutectic temperature at 76.5 wt% Sb in the Cu–Sb phase diagram [9] is 799 K, although the melting point of Sb is 904 K.

3.2. Dependence of fracture behavior on the misorientation

Fig. 3 shows the misorientation dependences of fracture stress σ_f at (a) 743 K and (b) 77 K. The fracture stress is dependent sensitively on the misorientation θ at the test temperatures. The fracture strains at 743 K were about two times larger than those at 77 K, as seen in Fig. 1. Thus, although the fracture stresses at 77 K are larger than those at 743 K, the fracture stresses at 77 K are considered to better reflect the inherent character of grain boundaries. The $\sigma_f - \theta$ curve at 77 K shows local peaks near θ =28.1° (Σ=17), 36.9° (Σ=5), 53.2° (Σ=5) and θ =61.9°

(Σ=17). At the same misorientation angles, the fracture strain showed local maxima. However, no peaks are observed at misorientation angles corresponding to relatively low-Σ boundaries, e.g. θ =22.6° (Σ=13) and θ =67.4° (Σ=13). Such boundaries can be expected to show peaks according to the Σ-value criterion [10]. That is, the criterion does not explain sufficiently the existence of the observed peaks. On the other hand, the positions of the four peaks in Fig. 3 agree with those of cusps in the relative boundary energy γ_B/γ_I–the misorientation θ curve for pure Cu reported by Mori et al. [11] in Fig. 4. Therefore, we conclude that higher-energy boundaries of pure unsegregated Cu are more brittle and fracture more easily with lower tensile stresses by the Sb addition.

The Cu−Sb phase diagram shows a solid-solubility limit of about 2 wt% at 473 K, going up to about 10 wt% at 743 K. Bicrystal specimens were cooled from about 500 K to room temperature within half an hour after homogenization at 1223 K or tensile tests at higher temperatures. Therefore, although the Sb concentrations at all grain boundaries examined by EDX were greater than 2 wt% (Fig. 5), no precipitates were detected on the grain boundaries by transmission electron microscopy (TEM).

When comparing the fracture stresses of the Sb-doped bicrystals with those of the Bi-doped bicrystals [3], the fracture stress of the Sb-doped bicrystals appears higher than that of the Bi-doped bicrystals. It can thus be regarded that embrittlement caused by boundary segregation of Sb is less significant than that of Bi. Furthermore, Bi precipitates are formed during cooling to room temperature after Bi doping treatment from the oversaturated Bi atoms on grain boundaries in the Bi-doped bicrystals. The existence of the precipitates could be enumerated as one of the possible causes of acute embrittlement [4]. On the other hand, no precipitates were detected by TEM in the present study, as stated above. We believe that the absence of precipitates on boundaries may be one of the possible origins of lower embrittlement of the present Sb-doped bicrystals in comparison with the Bi-doped bicrystals.

3.3. Dependence of segregation level on the misorientation

Fig. 5 shows the Sb concentration at grain boundaries measured by EDX against the misorientation angle θ. The value at θ =0° is for the Cu matrix and the grain boundary

segregation is apparent. The existence of local cusps is noticed near θ=28.1°, 36.9°, 53.2° and 61.9°. The positions of these cusps are in disagreement with those in the misorientation dependence of Bi segregation in Cu at [001] symmetric tilt boundaries, previously reported by Fraczkiewics and Biscondi [12]. In the Bi segregation–misorientation curve, two cusps are observed at about 30° and 60° misorientations. Furthermore, comparison between Figs. 3 and 5 reveals that the higher the Sb segregation level, the more easily the brittle fracture occurs. Therefore, it is concluded that higher-energy boundaries of pure Cu are more susceptible to Sb segregation to cause boundary embrittlement.

4. Summary

Both tensile tests at several temperatures between 77 and 743 K and energy-dispersed X-ray spectroscopy analyses have been carried out to examine the misorientation dependence of fracture behavior and Sb segregation level for different [001] symmetric tilt boundaries in Cu–2.0 wt% Sb alloy bicrystals. The fracture behavior depends strongly on the misorientation angle and test temperature. As the test temperature increases, the degree of embrittlement of grain boundaries decreases up to about 400 K and then increases. The fracture stress at 77 K and Sb segregation level vs. misorientation angle diagrams display several peaks and cusps at the same angles, and the positions of these peaks and cusps are in accordance with those of cusps in the grain-boundary energy of pure Cu vs. misorientation diagram. That is, higher-energy boundaries are more susceptible to Sb segregation to cause grain-boundary embrittlement.

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Figure captions

Fig. 1 Stress–strain curves of 46° bicrystals of a Cu–2.0 wt% Sb alloy, tested at different temperatures.

Fig. 2 Variation in fracture stress of Cu–2.0 wt% Sb bicrystals with test temperature. Open and solid symbols represent the transgranular and intergranular fractures, respectively.

Fig. 3 Dependence of fracture stress of Cu–2.0 wt% Sb bicrystals on the misorientation angle, tested at (a) 743 K and (b) 77 K. Open and solid symbols represent the transgranular and intergranular fractures, respectively.

Fig. 4 Relative boundary energy γ_B/γ_I plotted against the misorientation angle [11].

Fig. 5 Dependence of Sb Concentration estimated at each boundary in Cu–2.0 wt% Sb bicrystals by EDX on the misorientation angle. A representative error bar is shown.

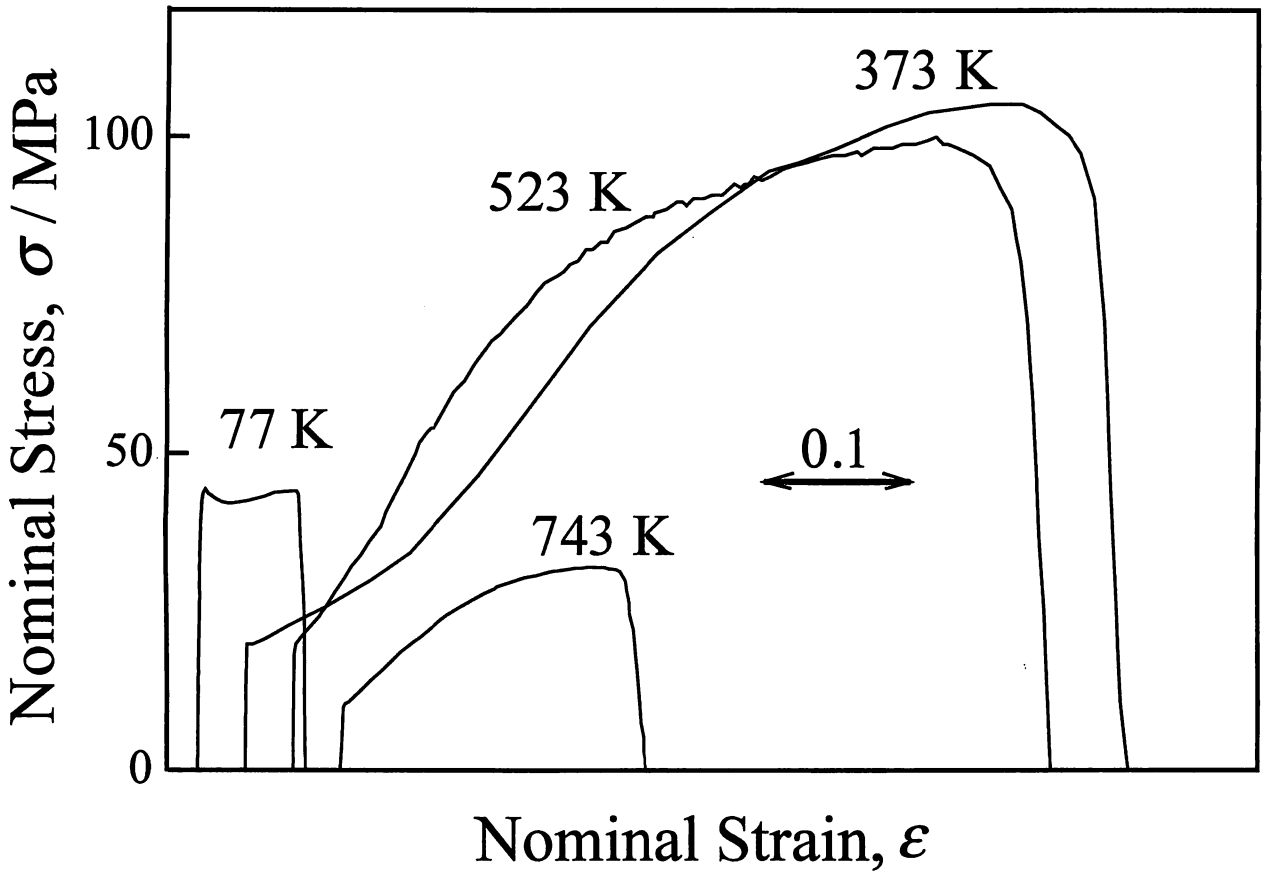


Fig.1 Monzen et al.

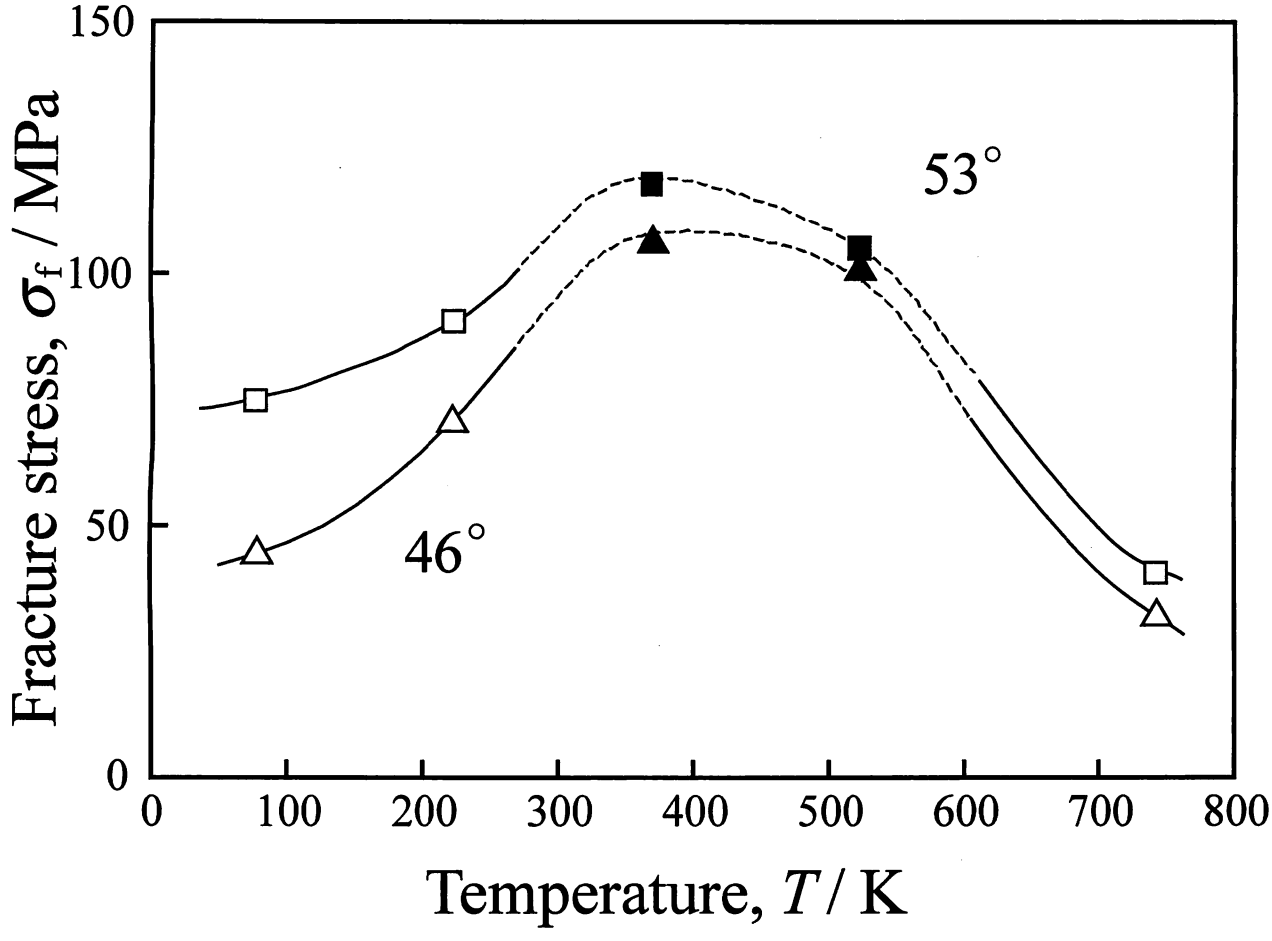


Fig.2 Monzen et al.

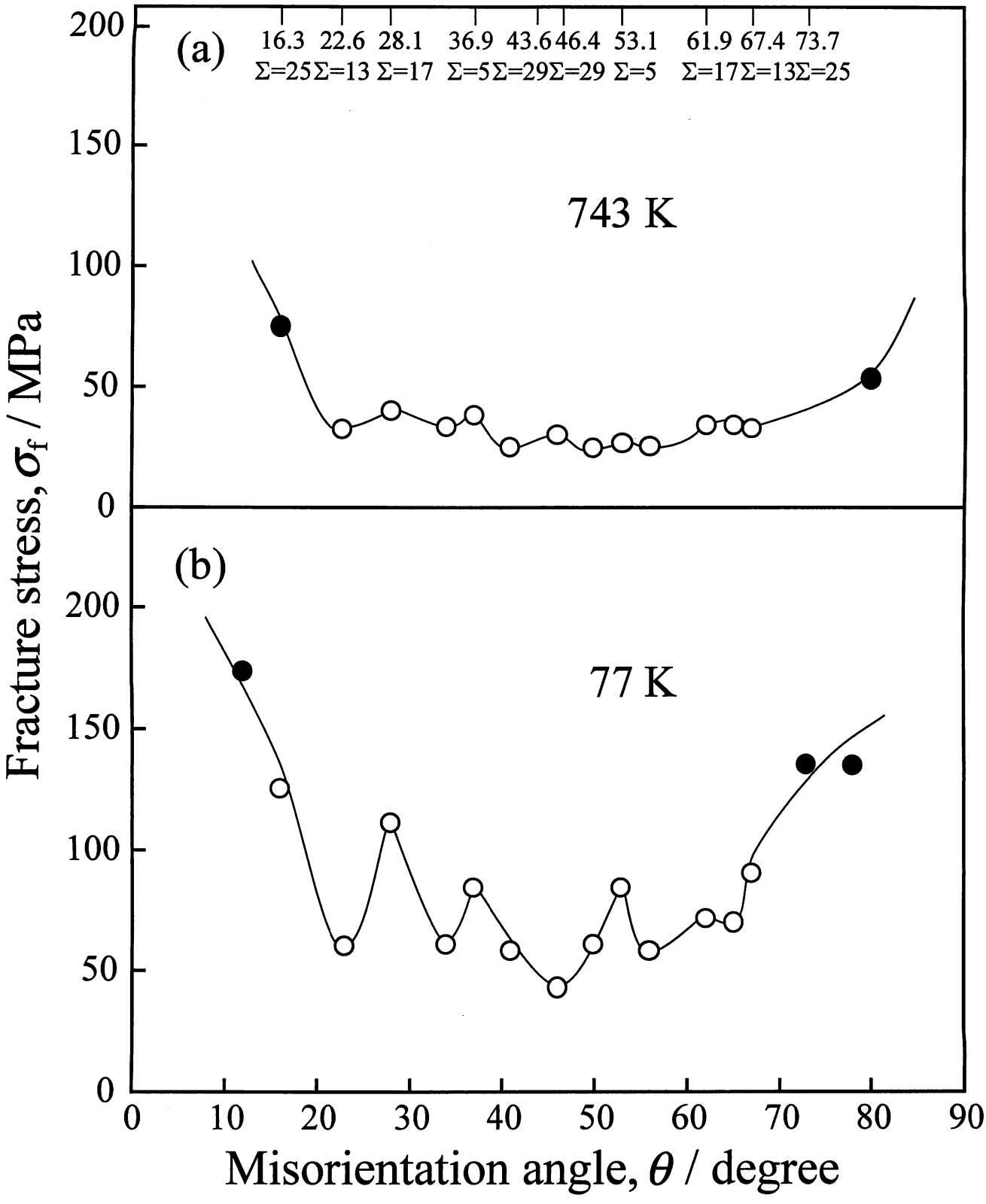
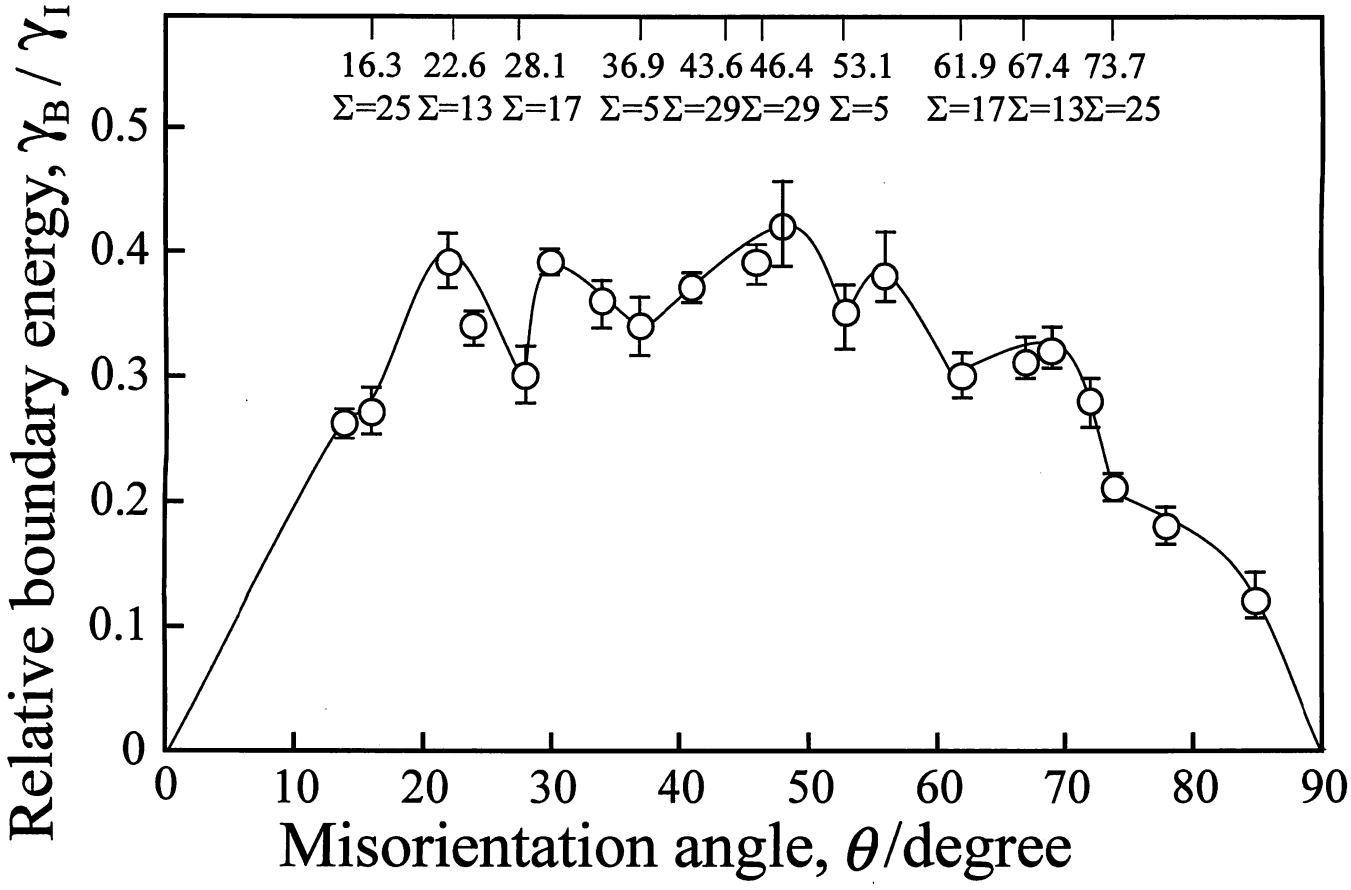


Fig.3 Monzen et al.



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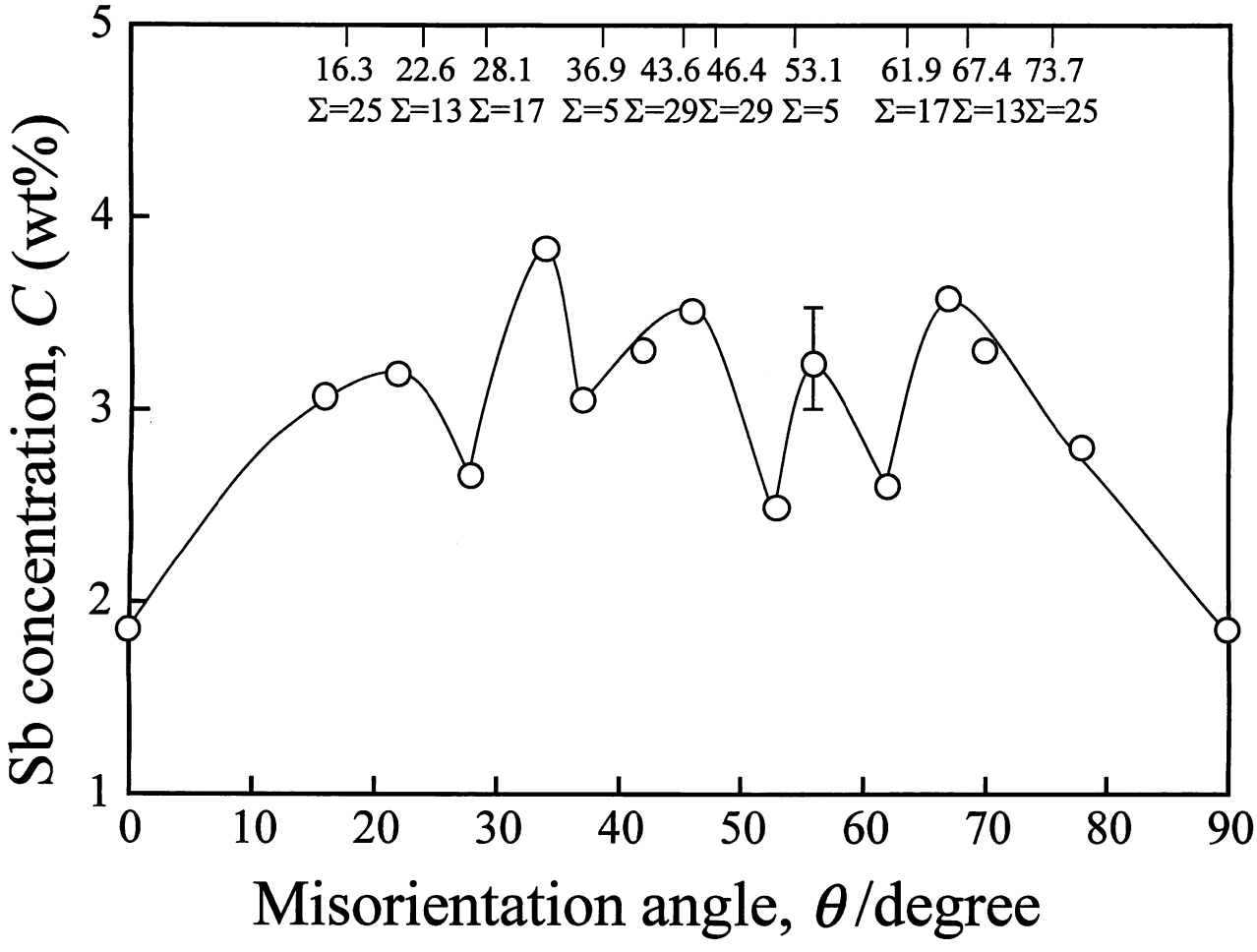

Fig.5 Monzen et al