Face-centred cubic to body-centred cubic martensitic transformation of Fe-Co particles in a copper matrix

Fcc → bcc martensitic transformation of Fe-Co particles in a Cu matrix

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Metastable fcc Fe precipitate particles produced by aging of a Cu-Fe alloy with up to ~2wt%Fe are fully coherent with the Cu matrix, when they are less than about 75nm in diameter[1]. The coherent particles do not transform into stable bcc Fe even if the alloy is cooled to the liquid helium temperature[2]. However, the fcc particles martensitically transform into internally twinned bcc structure by plastic deformation of the alloy[3-5], or by partial or complete removal of the surrounding Cu matrix[3,4,6]. Loss of full coherency in larger particles is not sufficient to induce the transformation, at least until the particles coarsen in size to several hundred nanometers[1]. However, ternary addition of Co to a Cu-Fe alloy tends to unstabilize the fcc particles and, thus, the fcc to bcc martensitic transformation in Fe-Co particles can occur by simple cooling without the introduction of plastic deformation[7,8]. The transformed particles are also internally twinned. The present study investigates further details on the transformation characteristics during cooling of Fe-Co particles in Cu-Fe-Co alloys with various Co contents.

98wt%Cu-2wt%($Fe_{1-x}Co_x$) alloy ingots with X=0, 0.2, 0.3, 0.35, 0.4, 0.5 and 0.6 were prepared by melting 99.99%Cu, 99.9%Fe and 99.99%Co in a high frequency induction furnace. To promote homogenization, the ingots were turned upside down, remelted several times and then maintained at 1273K for one week in a vacuum furnace. It was confirmed from chemical analysis that the compositions of the alloys were essentially the same as the initial compositions. Hereafter, the alloys with X=0~6 will be called A-0~6. Sheet specimens, cut from the ingots, were aged at 923K for 6 or 96h after a solution treatment at 1273K for 2h. After the aging, the specimens were slowly cooled to given temperatures above 77K to prevent the introduction of thermal stresses. The 6h aging produced spherical fcc particles with the average diameter of 21nm and the 96h aging those with the average diameter of 52nm. The particle size was essentially independent of the compositions of the alloys. After the cooling, the specimens were annealed at 873K for 1h and quenched into water, except the specimens for structural examination of particles before and after the martenstic transformation. The 873K annealing was done to definitely distinguish the particles which transform martensitically in a bulk state during cooling to a given temperature from those which transform during cooling or thin foil preparation after the annealing: the former change in shape and structure on annealing, while the latter have the same shape as the bcc particles without annealing[9]. Thin foils were examined on a 200kV electron microscope (TEM).

On cooling to room temperature after aging at 923K for 6 or 96h, the martensitic transformation of particles in A-0~3.5 and 6 did not occur. After 6h aging, the fcc particles in these specimens indicated the typical double-lobe contrast arising from coherency strain, but after 96h aging, some dislocations were found near and around large

particles, such as A and B in Fig. 1. A is a semi-coherent fcc particle and B is a bcc particle, which has transformed martensitically presumably by the partial removal of matrix constraint. The dislocations were often found around fcc particles larger than about 50nm in A-6 and 80nm in A-0: the critical size below which the interfacial dislocations cannot nucleate in the fcc state decreased with increasing Co content. This observation can be explained by the dependence of misfit strain on the Co content. The fcc particle/matrix constrained misfit was measured by analysis of the strain contrast observed in TEM following the procedure detailed by Ashby and Brown[10]. The specimens aged for 6h were used for this experiment. It was found that the mean values of the misfit strains for A-0, 3 and 6 were 0.008, 0.009 and 0.010, respectively. That is, the larger the misfit strain, the easier the dislocation generation becomes.

Fig. 1

The particles in A-3~6 transformed during cooling to 77K and the transformed particles consisted of twin bands. As found previously in a Cu-Fe alloy[5], the number of twin bands in the Fe-Co particles tended to be proportional to the particle size despite some scatter. The explanation of this regular pattern is based on the basic idea that twins belonging to different families form in different parts of the particles so as to minimize the total energy consisting of elastic strain energy and twin-interface energy[5]. The average width of parallel twin bands in 6h aged specimens is given against the Co concentration in Fig. 2. The data for Fe particles transformed by plastic deformation of the Cu-2wt%Fe alloy is also shown in this figure at X=0. The average twin width is an increasing function of the Co concentration. This indicates that the ternary addition of Co may cause an increase in the twin-interface energy and/or a decrease in the elastic strain energy which is newly created upon the transformation.

Fig. 2

The fcc particles formed preferentially along pre-existing dislocations during aging were easily transformed during cooling to 77K. The example is shown in Fig. 3. An A-3.5 specimen was annealed at 873K for 1h after aging for 6h and subsequent cooling to 248K. The elongated bcc particles by the annealing can be seen along a dislocation. This result indicates that the transformation is promoted with the aid of stress fields of a dislocation. Fig. 4 shows the fraction of transformed particles in A-3.5 specimens aged for 6 or 96h against the particle size for several cooling temperatures. The fraction was defined as the ratio of the number of bcc particles to the number of total particles. It can be seen that the smaller the particle size, the lower becomes the transformation temperature, whether or not the fcc particles are fully coherent with the matrix. This tendency was also the case in other alloys examined. The present observation is similar to that of the classical small particle experiments by Cech and Turnball[11], although the Fe-Co particles in the present study are several orders of magnitude smaller than the Fe-Ni particles used in their experiments. Thus, the present result is reasonably understood by assuming that the probability of finding a heterogenity of a given potency within a particle or at a particle/matrix interface decreases as the particle size becomes smaller. An investigation on the martensitic transformation of small fully coherent Fe precipitates in a Cu matrix has shown that localized particle/matrix decohesion resulting from vacancy condensation tends to trigger the transformation[12]. Therefore, the atomic structure of the Fe-Co particle/Cu matrix interface may play some role in the martensitic nucleation of the particle. However, it appears more plausible that dislocations such as those visible at the interface of a large fcc particle in Fig. 1 provide nucleation sites for the transformation of the particle. Such a role of dislocations is substantiated by the result

Fig. 3

Fig. 4

shown in Fig. 3.

Fig. 5 shows the fraction of transformed particles against cooling temperature for several 6h aged alloys. As the Co content increases, the transformation temperature increases, reaching a maximum for A-5 and then decreases again. This situation is similar to the dependence of the fcc to bcc martensitic transformation temperature in Fe-Co alloys on the Co concentration[13]. By assuming that the composition of the precipitated fcc Fe-Co particles is $Fe_{1-x}Co_x$, it can be estimated from the work by Kaufman and Nesor[14] that the chemical free energy differences between fcc and bcc states in A-3, 4 and 6 are 9kJ/mol at 77K, 8kJ/mol at 300 K and 7kJ/mol at 77K, respectively. These values are larger than the free energy difference, 5.4kJ/mol, between fcc and bcc Fe at 4.2K, to which the transformation of fully coherent Fe precipitates in a Cu-Fe alloy does not occur by simple cooling[2]. This means that the driving forces for the transformation of the Fe-Co particles are sufficiently large. Also, it should be recalled that the constrained misfit between a fcc particle and a Cu matrix increases with increase in the Co content. This certainly makes the fcc particles unstable. Therefore, we believe that the combined thermodynamic and mechanical effects promote the spontaneous transformation of the Fe-Co particles by simple cooling.

Fig. 5

References

1. K. E. Easterling and H. M. Miekk-Oja, Acta Metall. 15(1967)1133.
2. S. C. Abrahams, Phys. Rev. 127(1962)2052.
3. K. R. Kinsman, J. W. Sprys and R. J. Asaro, Acta Metall. 23(1975)1431.
4. H. Kubo, Y. Uchimoto and K. Shimizu, Metals Sci. J. 9(1975)61.
5. M. Kato, R. Monzen and T. Mori, Acta Metall. 26(1978)605.
6. K. E. Easterling and P. R. Swann, Acta Metall. 19(1971)117.

7. N. Kuwano, S. Matsumura, H. Nakagawa, M. Watari, T. Tomokiyo and K. Oki, in Proceedings of the International Conference on Martensitic Transformation(Japan Inst. of Metals, 1987) p. 355.
8. R. Monzen, M. Kato and T. Mori, Acta Metall. 37(1989)3177.
9. R. Monzen, A. Sato and T. Mori, Trans. Japan Inst. Metals 22(1981)65.
10. M. F. Ashby and L. M. Brown, Phil. Mag. 8(1963)1083.
11. R. E. Cech and D. Turnball, Trans. Am. Inst. Min. Engrs 206(1956)124.
12. C. H. Li, D. A. Porter and K. E. Easterling, Acta Metall. 33(1985)317.
13. M. Izumiyama, M. Tsuchiya and Y. Imai, J. Japan Inst. Metals 34(1970) 291.
14. L. Kaufman and H. Nesor, Z. Metallk. 64(1973)249.

Figure captions

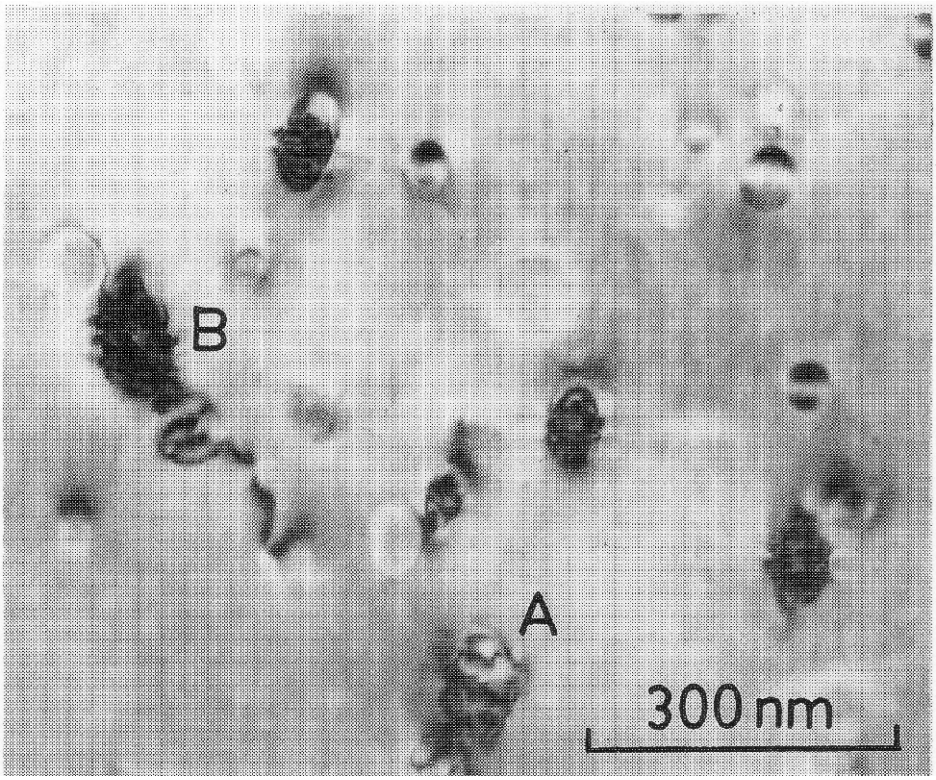
Fig. 1 Fe-Co precipitates in an A-6 specimen after aging at 923K for 96h.

Fig. 2 Average twin width in Fe-Co particles transformed during cooling to 77K plotted against the Co concentration.

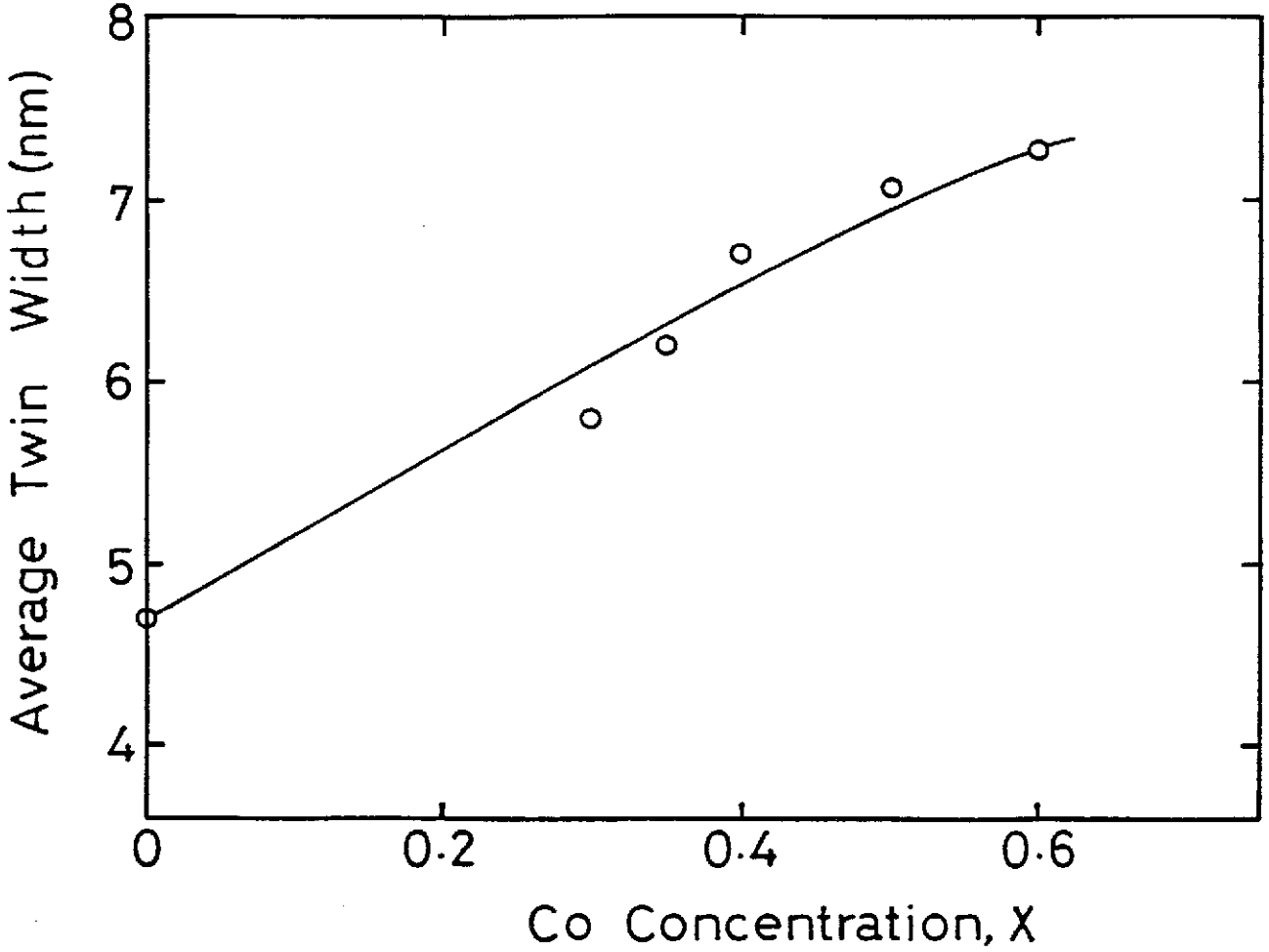
Fig. 3 Chain of bcc Fe-Co particles along a dislocation in an A-3.5 specimen. The specimen was aged for 6h, followed by cooling to 248K and then annealed at 873K for 1h.

Fig. 4 Particle size dependence of the fraction of transformed particles in A-3.5 specimens cooled to various temperatures.

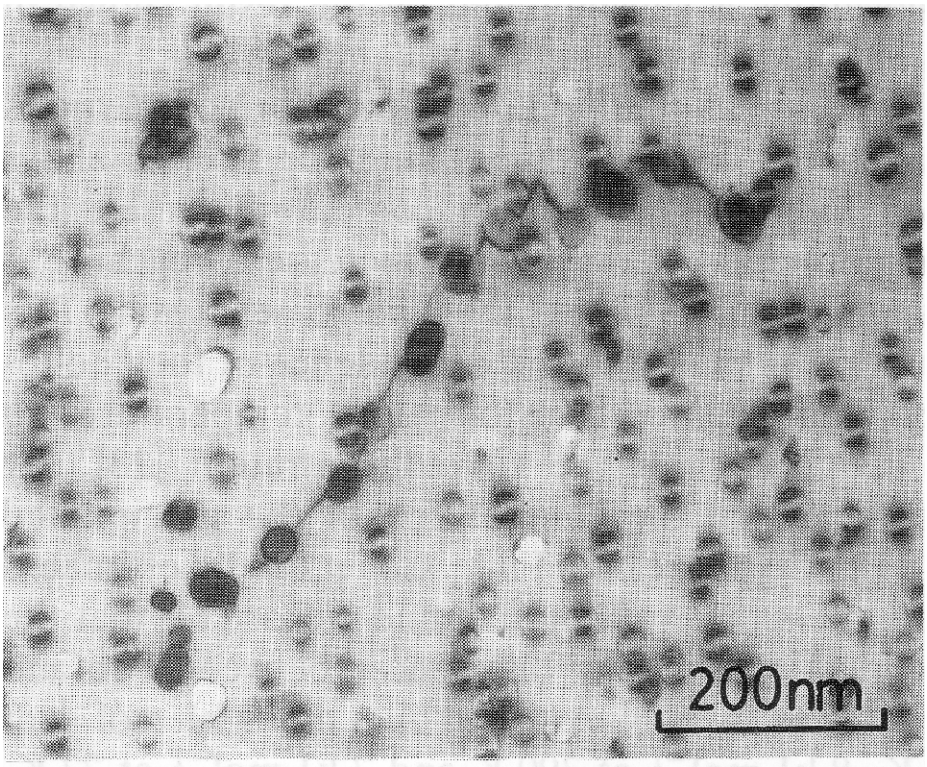
Fig. 5 Fraction of transformed particles against cooling temperature in Cu-Fe-Co alloys with different Co contents after aging at 923K for 6h.



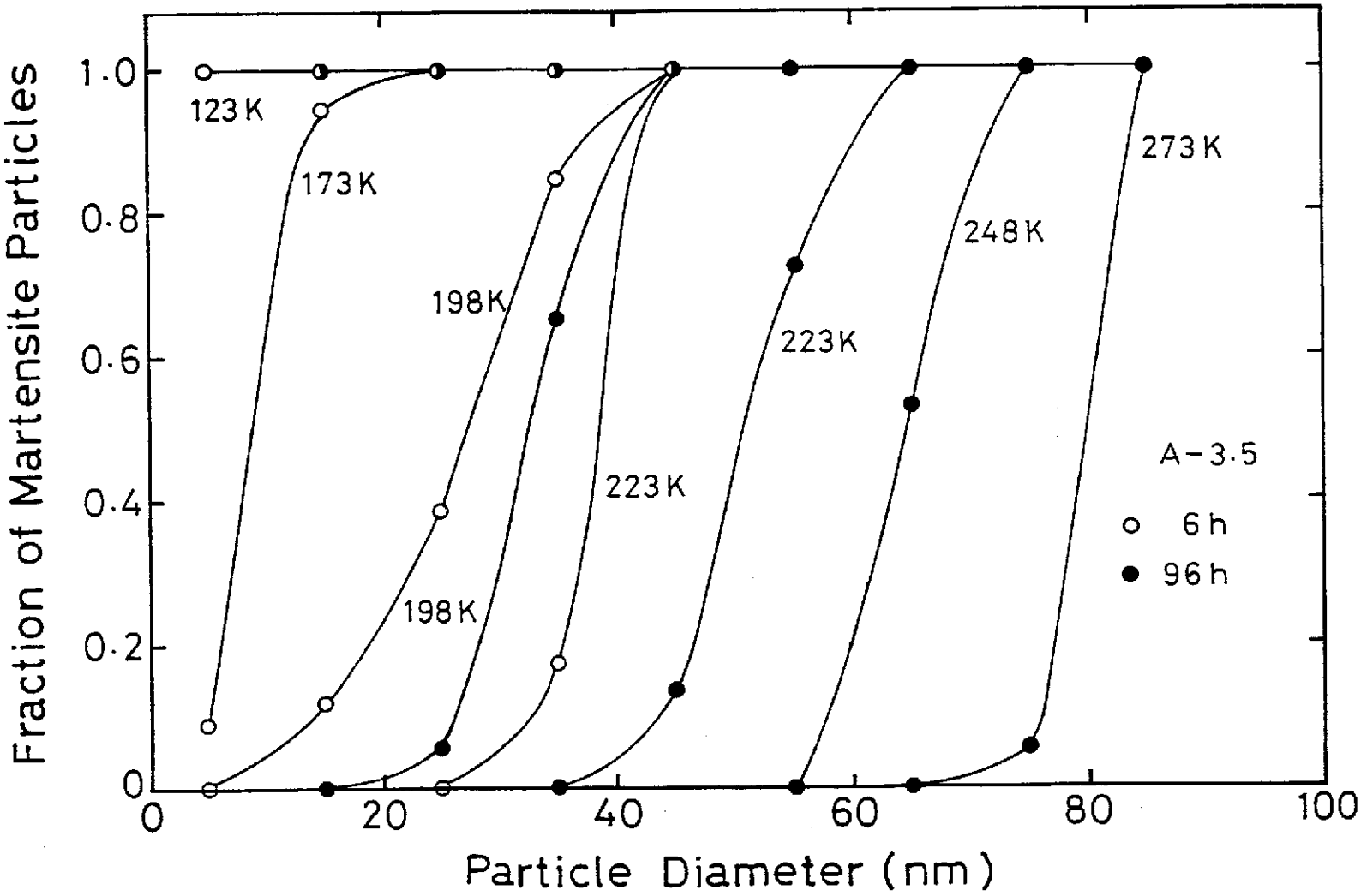
Monzen and Kato Fig. 1



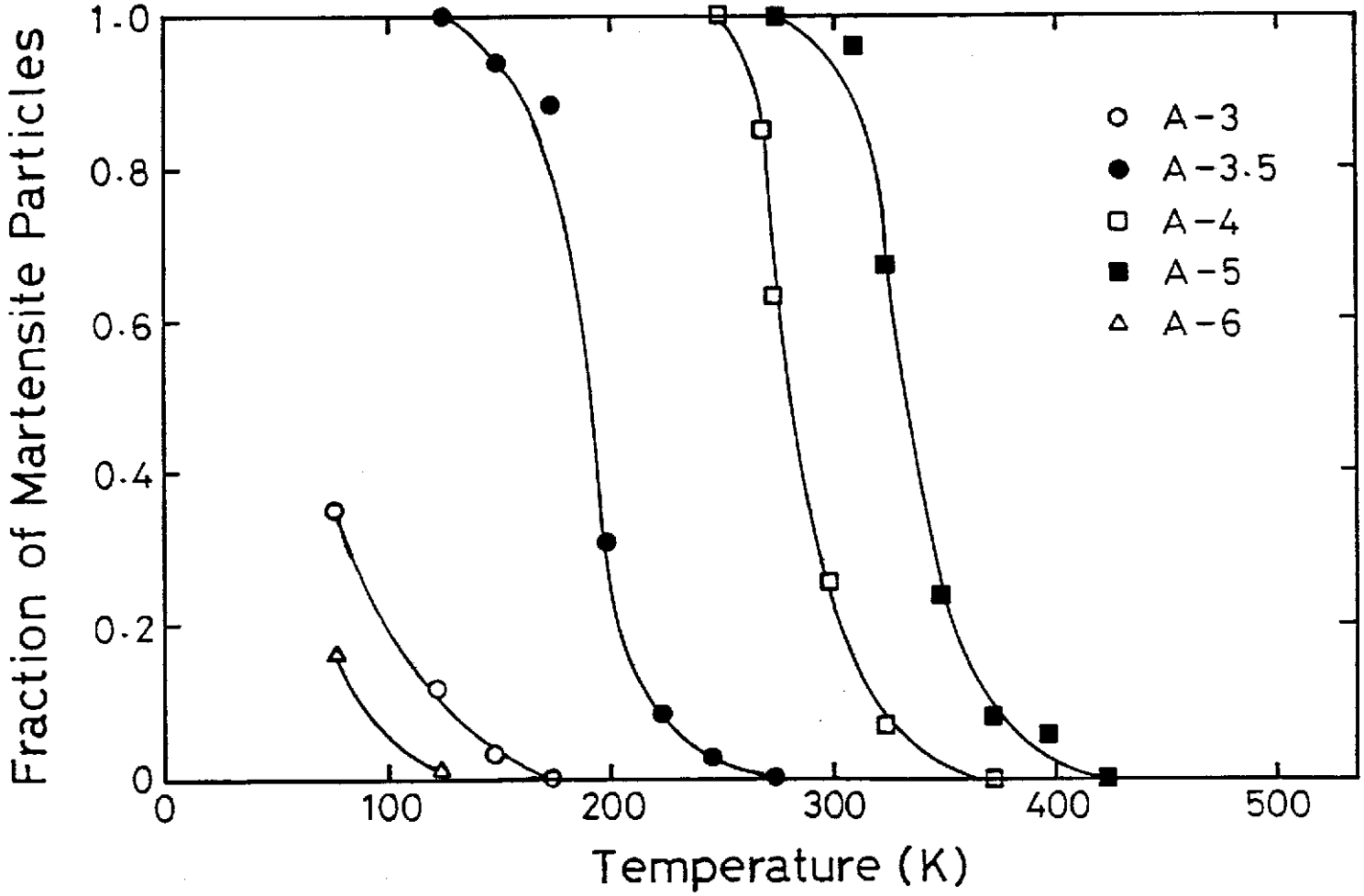
Monzen and Kato Fig. 2



Monzen and Kato Fig. 3



Monzen and Kato Fig. 4



Monzen and Kato Fig. 5