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Studies on pre-bainitic transformation in Cu–Zn–Al–Mn alloy*

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Abstract

The behaviour of the pre-bainitic transformation in Cu–Zn–Al–Mn alloy was investigated using internal friction measurements and transmission electron microscope (TEM) observations. The results show that there exists an internal friction peak associated with the appearance of solute atom clusters before the formation of orthorhombic 9R bainite; then the 9R bainite nucleates martensitically in regions depleted of solute atoms in the parent phase (B_2). The changing processes mentioned above were also confirmed by isothermal internal friction and TEM experiments.

1. Introduction

There are two controversial opinions so far on the mechanism of bainite formation. The first view [1, 2] is that bainite crystal with a supersaturated solute concentration nucleates martensitically. The second one [3] is that bainite with an equilibrium solute concentration precipitates initially and then continues to grow while diffusion occurs. However, the first view seems inconsistent with the fact that bainite nucleates at a much higher temperature than the M_s temperature and the second one hardly explains the surface relief accompanying the bainitic transformation. Recently Takezawa and Sato [4], using a high resolution analytical electron microscope with a field emission gun, discovered that the Zn concentration is higher near the outside of a bainite plate than inside the plate and also successfully detected the difference in Zn concentrations in the matrix on opposite sides of bainite plates in Cu–40.5at.%Zn alloy. They thought that the excess and deficient regions of solute atoms are initially produced in the concentrated stress field of the matrix crystal and proposed that the nucleation and growth of bainite occur in the region depleted of solute atoms. However, they did not detect any change in Zn concentration in the incubation period of bainitic transformation in Cu–Zn–Al alloy. Because internal friction is sensitive to the segregation of solute atoms and to shear-type transformation, pre-bainitic and bainitic transformations were investigated by internal friction measurements as well as transmission electron microscope observations during both heating and isothermal transformations in a Cu–Zn–Al–Mn alloy.

2. Experimental details

A Cu–24.38wt.%Zn–4.17wt.%Al–0.89wt.%Mn alloy with $M_s = 86$ °C, $M_f = 48$ °C, $A_s = 82$ °C, $A_f = 126$ °C and $e/a = 1.42$ was used in the experiments. Internal friction, elastic modulus and the zero-point drift of the torsion pendulum were measured simultaneously. The curve of electrical resistance *vs.* temperature was measured *in situ* in the same furnace as the torsion pendulum. The rate of temperature increase was 1 °C min^{-1}. The composition change of the alloy during the bainitic incubation period was measured by a 200 CX transmission electron microscope (TEM) and a Link 860-II energy-dispersive spectrometer. The electron diffraction patterns and the corresponding dark field images at various temperatures were observed *in situ* by means of the TEM.

3. Results and discussion

Figure 1 shows the results of internal friction, elastic modulus, zero-point drift and electrical resistance measurements as functions of temperature for the Cu–Zn–Al–Mn sample. The internal friction peak near 190 °C at 1.4 Hz shows the characteristic of a relaxation

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*Dedicated to Professor T.S. Kê on the occasion of his 80th birthday.

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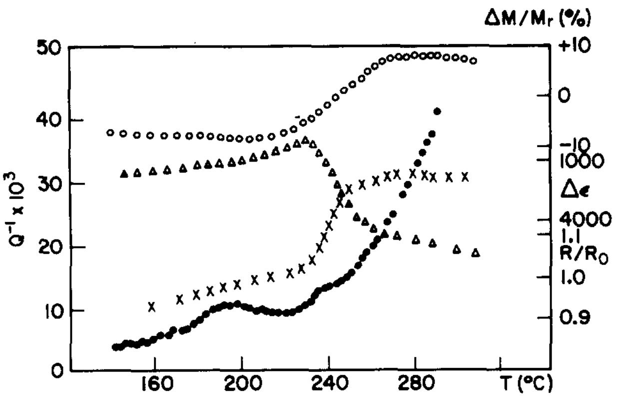

Fig. 1. Q^{-1}, $\Delta M/M$, $\Delta\epsilon$ and R as functions of temperature for Cu–24.38wt.%Zn–4.17wt.%Al–0.89wt.%Mn alloy (f = 1.4 Hz, $\dot{T}$ = 1 °C min^{-1}): ●, Q^{-1}; ×, electrical resistance R; △, zero-point drift $\Delta\epsilon$; ○, elastic modulus $\Delta M/M$.

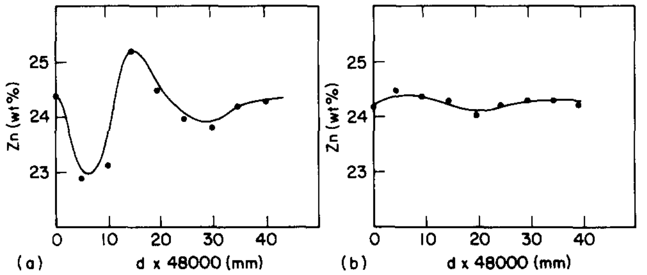

Fig. 2. Curves of solute atom (Zn) concentration *vs.* distance for Cu–Zn–Al–Mn alloy: (a) sample aged at 190 °C for 1 h; (b) as-quenched sample.

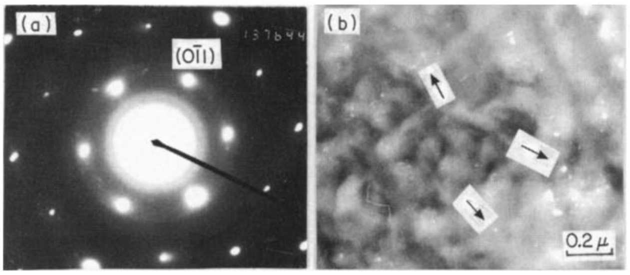

Fig. 3. (a) Some new diffraction rings appear and superpose on the diffraction pattern of the B_2 matrix at 150 °C; (b) corresponding dark field image of the ring.

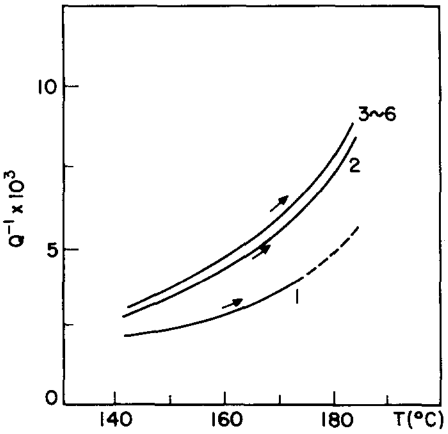

Fig. 4. Change in internal friction under continuous thermal cycling between 142 and 185 °C for Cu–Zn–Al–Mn alloy.

peak with an activation energy of 1.23 eV. The halfwidth of the peak is roughly 1.2 times broader than that of a Debye peak calculated for a single relaxation time; the shape of the peak is asymmetric, which is similar to the internal friction peak caused by the segregation and precipitation of solute atoms in Al–Ag alloy [5]. In order to clarify the origin of this relaxation peak, composition measurement and high temperature TEM *in situ* observation were carried out. Figure 2(a) and 2(b) show the curves of solute atom (Zn) concentration of the B_2 matrix *vs.* distance for a sample aged at 190 °C for 1 h and an as-quenched sample respectively. The distribution of Zn concentration in the aged sample has a larger fluctuation compared with that in the quenched sample, which indicates that the solute atoms (Zn) segregate and may form clusters and that a Zn-depleted region forms in the B_2 matrix before bainite nucleation. High temperature TEM *in situ* observations showed that some new diffraction rings appear and superpose themselves on the diffraction pattern of the B_2 matrix at about 150 °C on heating and become clear with increasing temperature as seen in Fig. 3(a). The corresponding dark field photograph imaged with a segment of the ring showed some small bright spots as seen in Fig. 3(b). This indicates that something starts to precipitate from the B_2 matrix and that the precipitates are randomly distributed in the B_2 matrix. The precipitates may be ZnO, because the condition of extention of the diffraction rings is consistent with that listed in the X-ray powder diffraction file of ZnO (Set 21, No. 1486). It is assumed that the ZnO originates from the oxidation of Zn clusters during high temperature *in situ* observation, because the ZnO precipitates only appear in thin foil specimens which have been heated in the TEM. The appearance of ZnO particles also means that clusters of Zn atoms have formed before bainite nucleates. Ghilarducci and Ahlers [6] and Zhao *et al.* [7] also observed a relaxation internal friction peak near 200 °C in Cu–Zn–Al alloy. They considered this to be a Zener relaxation peak related to point defects, *e.g.* solute atoms. If this is true, the height of the peak should decrease with increasing solute atom precipitation. However, Fig. 4 shows that the height of the internal friction peak increases and then reaches a saturation value under continuous thermal cycling between 142 and 185 °C. On the other hand, in Cu–Zn alloy the activation energy of the Zener peak is larger than that of the present peak and the temperature of the Zener peak is higher (about 300 °C at 0.5 Hz and 400 °C at 640 Hz) [8]. Therefore the

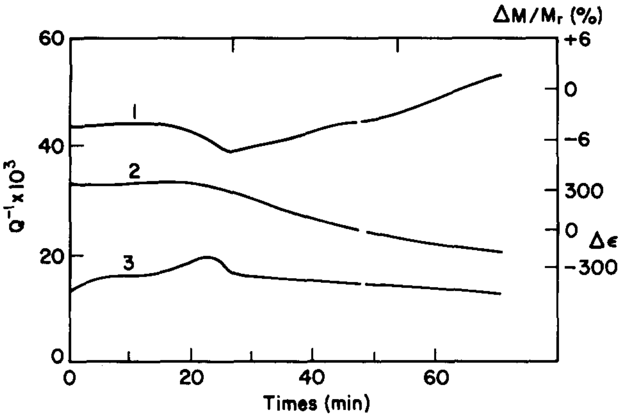

Fig. 5. Q^{-1}, $\Delta M/M$ and $\Delta\epsilon$ as functions of time in the isothermal process at 190 °C for Cu–Zn–Al–Mn alloy: 1, elastic modulus $\Delta M/M$; 2, zero-point drift $\Delta\epsilon$; 3, Q^{-1}.

internal friction peak near 190 °C at $f = 1.4$ Hz is not a Zener relaxation peak. The origin of the internal friction peak is attributed to the correlative movement of disordered solute atoms at the boundaries between clusters and matrix [9].

The transformation from B_2 to 9R bainite is also observed by the internal friction experiment as shown in Fig. 1. A number of anomalies appear at about 240 °C, *e.g.* the electrical resistance increases rapidly, the elastic modulus exhibits a minimum at first and then increases, the internal friction exhibits a shoulder peak with a zero-point drift and the peak temperature is independent of the measuring frequency. These anomalies are almost the same as those occurring during martensitic transformation at lower temperature and could indicate the occurrence of a shear-type phase transformation near 240 °C. Han *et al.* [10] also observed bainite plates with the orthorhombic 9R structure by TEM in a Cu–24.3Zn–4.7Al–0.8Mn sample aged at 350 °C for 4 min and thought that the bainite plates are initially formed by shear. The shear mechanism of bainite formation has also been supported by many other results [1, 2, 4, 11–13]. It is known that the M_s temperature of the tested alloy increases with decreasing solute concentration. This implies that the driving force of martensitic transformation in the solute-depleted regions increases. When it is equal to or larger than the resistance of bainitic transformation, bainite can form martensitically in the solute-depleted regions. Yang and coworkers [12, 13] have observed that bainite plates nucleate in the Zn-depleted regions in both Cu–Zn and Cu–Zn–Al alloys.

The changes in structure observed above during heating were also observed during the isothermal internal friction experiment at 190 °C as shown in Fig. 5. The increasing internal friction (Q^{-1}) at first is due to increasing clusters of solute atoms; then orthorhombic 9R bainite forms martensitically. This transformation is characterized by the occurrence of a Q^{-1} peak, a zero-point drift and a minimum of the shear modulus, which are very similar to the results obtained near 240 °C in Fig. 1.

The above results indicate that diffusion indeed occurs during the incubation period of bainitic transformation, *i.e.* clusters of solute atoms form and regions depleted of solute atoms in the matrix appear before the formation of orthorhombic 9R bainite; then bainite plates with the 9R structure nucleate and grow martensitically in the regions depleted of solute atoms (Zn) in the B_2 matrix with increasing temperature and/or increasing aging time.

References

1 P.E. Flewitt and J.M. Towner, *J. Inst. Met., 95* (1967) 273.
2 I. Cornelis and C.M. Wayman, *Acta Metall., 22* (1974) 301.
3 G.W. Lorimer, G. Cloff, H.I. Aaronson and K.R. Kinsman, *Scr. Metall., 9* (1975) 271.
4 K. Takezawa and S. Sato, *Metall. Trans. A, 21* (1990) 1541.
5 A.C. Damask and A.S. Nowick, *J. Appl. Phys., 26* (1955) 1165.
6 A. Ghilarducci and M. Ahlers, *J. Phys. F: Met. Phys., 13* (1983) 1757.
7 Z.Q. Zhao, F.X. Chen, X.M. Li and D.Z. Yang, *Adv. Mater. Sci., 2* (1988) 29 (in Chinese).
8 A.S. Nowick and B.S. Berry, *Anelastic Relaxation in Crystalline Solids,* Academic, New York, 1972, p. 248.
9 Y.N. Wang, M. Gu and L.H. Sun, in T.S. Kê (ed.), *Proc. ICIFUAS-9,* Pergamon, Oxford, 1990, p. 465.
10 M. Han, F.M. Chen, J.M. Chen, Y.Y. Chen and W.X. Liu, *Acta Metall. Sinica, 26* (1990) A81 (in Chinese).
11 M.H. Wu, J. Perkins and C.M. Wayman, *Acta Metall., 37* (1989) 1821.
12 Y.Q. Yang, Z.F. Zhang, H.M. Shen, Y.N. Wang, X.N. Zhao, J.M. Hong and M.K. Kang, *Mater. Lett., 17* (1993) 369.
13 M.K. Kang, J.L. Sun and Q.M. Yang, *Metall. Trans. A, 21* (1993) 853.