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Phase transformation in martensite of Cu–12.4% Al

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Phase transformations in a Cu–Al alloy which was in the martensitic state were examined by the use of differential thermal analysis. The influence of the speed of temperature changes on the character of the phase transformation was determined. The new sequence of phase transformations in martensite is discussed and related to the physical properties (the "shape memory effect"). Characteristic temperatures and heats of transformation in the alloy are also estimated.

1. Introduction

Alloys in which a high-temperature bcc β phase is transformed into martensite during quenching have recently been the subject of considerable research. This is due to the fact that systems with martensite transformation possess unique mechanical phenomena asssociated with shape recovery, such as "pseudo-elascity" and the "shape memory effect" [1–3]. Copper–aluminium alloys containing 9 to 14 wt % Al are among those showing a martensitic transformation on rapid cooling from high temperatures; the β phase undergoes the transformation (Fig. 1). When quenching from the β state, alloys containing more than ~ 11% Al first become ordered to the β_1 phase (DO_3) and then transform martensitically to either β_1', $\beta_1' + \gamma'$ or γ'.

It may be noted that β alloys containing less than 11% Al transform to an fcc type of disordered martensite β' [4]. During the heating of martensitic Cu–12.4% Al alloy, a reverse martensitic transformation, $\beta_1' \rightarrow \beta_1$, takes place in the temperature range 340 to 400° C. Afterwards during slow heating the β_1 phase transforms into a eutectoid α and γ_2 phase mixture in the temperature range 400 to 550° C. At a temperature of 565° C, from an α and γ_2 mixture the reaction of β phase formation occcurs [4–10].

The main object of the present paper is to determine which phase transformations take place during heating at different rates, for Cu–12.4 wt % Al alloy which exists in the martensitic state.

2. Experimental procedure

The Cu–12.4 wt % Al alloy was prepared from 99.97% copper and 99.95% aluminium by induction melting. After the casting and rolling of the material, rods about 6 mm diameter were obtained. Polycrystalline samples were homogenized at 800° C and quenched in water. Experiments were performed with a Mettler Thermoanalyzer TA1 and Du Pont Instruments DSC/DTA Calorimeter. Heating runs from 25 to 600° C were carried out in a protective argon atmosphere. Pure copper was used as a standard.

To determine the temperature of phase transformation, cylindrical samples with a bored aperture were placed directly at the end of the thermoelement. To determine the heat of transformation, samples were placed in a crucible, thus simulating the conditions in which the calibration curve and measurements were obtained. The heats of transformation were calculated from the areas under DTA peaks by multiplying them by the equivalent calories per unit area. The areas under DTA peaks were deliminated by the straight line from the beginning of the effect to the return of the DTA curve to the baseline, as in Figs. 3 and 9 below.

The calibration coefficient K, from the equation $\Delta H = KA$, where ΔH is the heat of the process and $A = \int \Delta T dt$ is the area under the peak, was calculated for the Mettler Thermoanalyzer over the range 100 to 600° C (Fig. 2a). For the macro Pt–PtRh thermocouple (ME-93523, Mettler crucible holder) using Al_2O_3 crucibles and an argon atmosphere, the temperture dependence of K is $K = a + bT^3$ where $a = 4.94$ and $b = 15.02$.

For the Du Pont Calorimeter the following equation was used to determine the heat of transformation: $\Delta H = (A/m)(60\, BEq)$ where m = mass of the sample, A = peak area, B = time base, q = sensitivity of calorimeter ($\text{mcal sec}^{-1}\,\text{in}^{-1}$). E is the coefficient obtained experimentally and the temperature dependence of E is shown in Fig. 2b.

Phase analysis of the specimens was performed using a Dron X-ray diffractometer with a high-temperature Philips programmer. Filtered Cu$K\alpha$ radiation was used. The X-ray diffractometer tracing was obtained during heating of the quenched specimens. The lines used for identification of the phases are shown in Table I [10]. The lines of the β and β_1 phases overlap, but they exist at different temperatures.

Additionally, electron microscopic investigations of the alloy structure were carried out. Specimens for these studies were thin foils cut from rods in a spark cutter and then electrolytically polished in a solution of 50g CrO_3 in 400 ml H_3PO_4. Polishing conditions employed were 10 V at room temperature. Foils were

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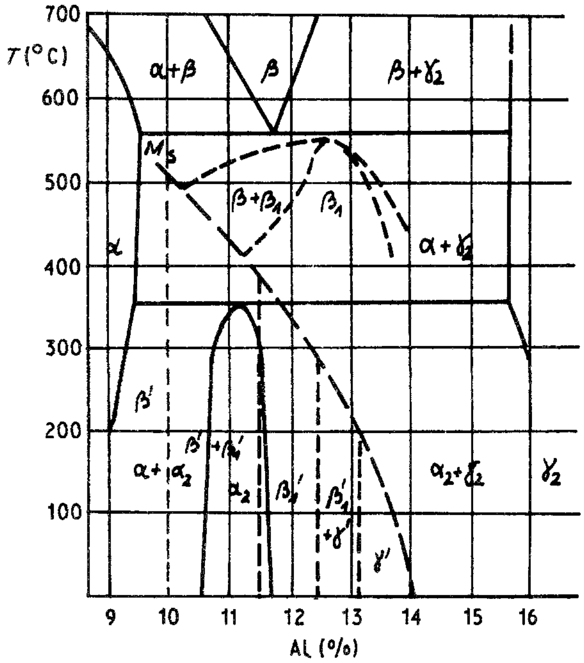

Figure 1 Partial phase diagram for the Cu–Al system.

observed with a JEM 200B transmission electron microscope operated at 200 kV.

3. Results and discussion

From the thermal effects on DTA curves it was found that the speed of heating was the main factor determining the type and quantity of the phase changes which take place during linear heating of martensite. DTA registered during the heating of martensite can be divided into three groups (Figs. 3 and 4):

(a) curves obtained for speed 1° C min^{-1} and lower,
(b) for speeds between 2 and 100° C min^{-1}, and
(c) for speed 100° C min^{-1}.

During the heating of martensite at a speed of 1° C min^{-1}, one exothermic transformation was found in the temperature range 210 to 310° C (the P_1 peak) as well as two endothermic effects which occur at higher temperatures (Fig. 3a). The first of them (P_2) at 380 to 490° C was caused by the transformation of martensite into the β_1 phase and then the β_1 phase into a eutectoidal mixture of α and γ_2 phases. The second one (P_3), starting at 565° C, is due to the transformation of the eutectoid to the β phase. The X-ray measurements confirm this interpretation (Fig. 5).

The exothermic effect in the temperature range 220 to 310° C occurs also during heating at higher speeds.

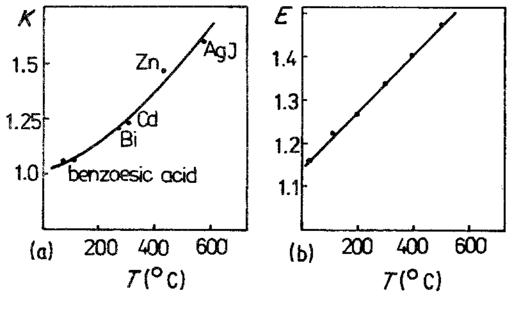

Figure 2 The calibration coefficient against temperature for (a) the Mettler Thermoanalyzer and (b) the Du Pont Calorimeter.

TABLE I Diffraction lines used for identification of the phases

Phase	2θ (deg.)	d_{hkl} (nm)	hkl
β	50.8	20.9	110
β_1	50.8	20.9	220
β_1'	52.4	20.3	208
α	58.5	18.3	200
γ_2	51.8	20.5	411, 330

From electron microscopic results one can suppose that this DTA effect is due to an ordering process in the martensite. This can be seen from electron diffraction patterns on which extra spots appear for samples which after quenching were isothermally heated at 300° C (Fig. 6). Since after quenching the Cu–12.4 wt % Al alloy the ordered β_1' martensite was obtained, we should talk rather about the process of reordering of martensite which takes place during heating. One can therefore propose the notation $\beta_1' \rightarrow \beta_1''$ for the transformation associated with the P_1 exothermic peak.

During the heating of martensite at a speed of 1° C min^{-1} one can observe that the P_2 peak starts to be asymmetrical. For a rate of heating of 2° C min^{-1} two overlapping thermal effects, marked as P_2 and P_3 in Fig. 3c, appear in the temperature range 350 to 450° C. They are associated with a reverse martensitic transformation at 400° C, and the subsequent decomposition of the β_1 phase into a eutectoidal mixture at 420° C. At 505° C a small but sharply outlined endothermic effect is visible. With an increase in the speed of heating the height of this effect increases too.

For speeds of heating from 4 to 25° C min^{-1}, six thermal effects (P_1 to P_6 in Fig. 3d) were noticed. In the temperature range 480 to 550° C two simultaneous transformations were registered. The above-mentioned

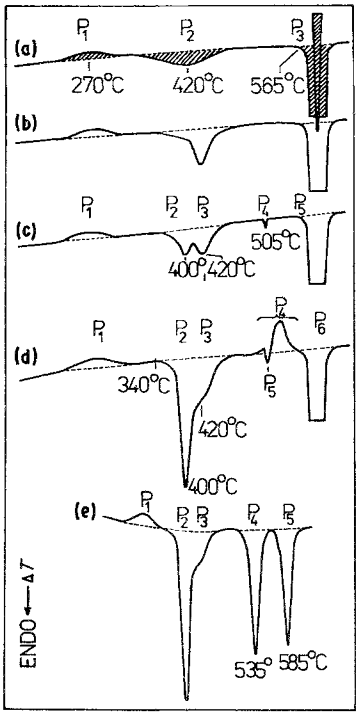

Figure 3 DTA curves for Cu–12.4% Al alloy obtained at a heating rate of (a) 0.5° C min^{-1}, (b) 1° C min^{-1}, (c) 2° C min^{-1}, (d) 6° C min^{-1}, and (e) 25° C min^{-1}, using the Mettler Thermoanalyzer.

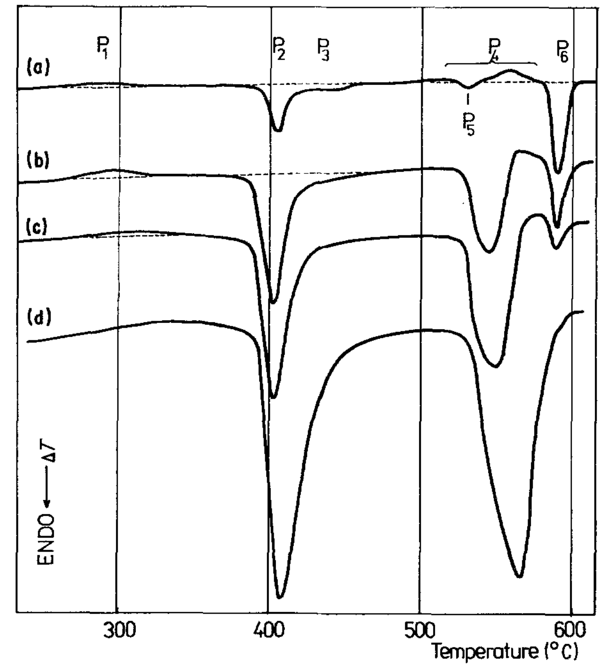

Figure 4 DTA curves for Cu–12.4% Al alloy obtained at a heating rate of (a) $5^\circ\,C\,min^{-1}$, (b) $30^\circ\,C\,min^{-1}$, (c) $50^\circ\,C\,min^{-1}$, and (d) $100^\circ\,C\,min^{-1}$, using the DSC/DTA Du Pont Calorimeter.

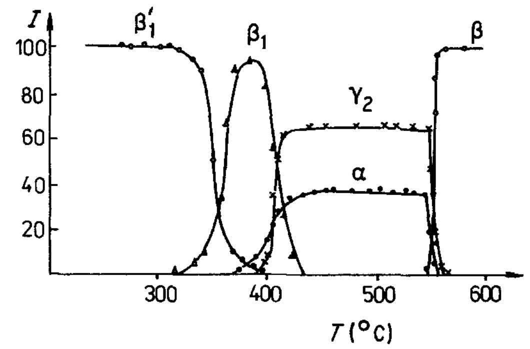

Figure 5 Relative intensities of X-ray peaks for different phases as a function of temperature.

endothermic effect (at 505° C), occurring during heating at a rate of $2^\circ\,C\,min^{-1}$, overlaps the exothermic one. In order to analyse fully these DTA effects the martensite specimens were heated at different speeds (4 to 25° C min^{-1}) to different temperatures in the range 480 to 550° C, and then quenched in ice-water. Samples obtained in such a way were examined by X-ray diffraction (Fig. 7) and electron microscopy (Fig. 8). The results of these investigations indicate that a $\beta_1 \rightarrow \alpha + \gamma_2$ reaction takes place in two stages. Over the temperature range of the P_3 effect the γ_2 phase (Cu_9Al_4) forms from the β_1 phase. Formation of the γ_2 phase causes a decrease in the concentration of solute aluminium atoms in the matrix. Changes of chemical composition arising in this way cause the precipitation of the copper-rich solid-solution α phase, which is evident from an exothermic effect P_4.

It was found that less than the whole amount of the β_1 phase changed into the eutectoid $\alpha + \gamma_2$. When the rate of heating was more than $4^\circ\,C\,min^{-1}$ in the range 400 to 550° C, two competitive transformations of the β_1 phase took place. Part of the β_1 phase transforms into eutectoid (P_3 and P_4 in Fig. 3d) and part into the high-temperature β phase (P_5). When the speed of heating increases the $\beta_1 \rightarrow \beta$ transformation starts to dominate the $\beta_1 \rightarrow \alpha + \gamma_2$ reaction. This was confirmed by the increase in the height of the P_5 peak and the reduction of the P_3 and P_4 peaks.

When the speed of heating was equal to about 25° C min^{-1}, the β phase was created with approximately half from the β_1 phase ($\beta_1 \rightarrow \beta$ at 535° C, P_4 in Fig. 3e) and half from the eutectoid mixture ($\alpha + \gamma_2 \rightarrow \beta$ at 585° C, P_5 in Fig. 3e). The maximum rate of heating on the Mettler Thermoanalyzer is $25^\circ\,C\,min^{-1}$. Therefore the Du Pont Calorimeter was used for higher rates of heating. In order to compare these two thermal techniques, the results obtained at similar rates of heating are shown in Figs. 3 and 4 (5 and $30^\circ\,C\,min^{-1}$ for the Du Pont Calorimeter, 6 and $25^\circ\,C\,min^{-1}$ for the Mettler Thermoanalyzer). Using different thermal methods, the same sequences of phase transformation for similar heating rates were obtained (Figs. 3d and e and Figs. 4a and b). However, the temperatures of phase transformations which were registed on the Du Pont Calorimeter were higher than those from the Mettler Thermoanalyzer. This is a result of the higher thermal inerta of the DSC/DTA Du Pont Calorimeter [11].

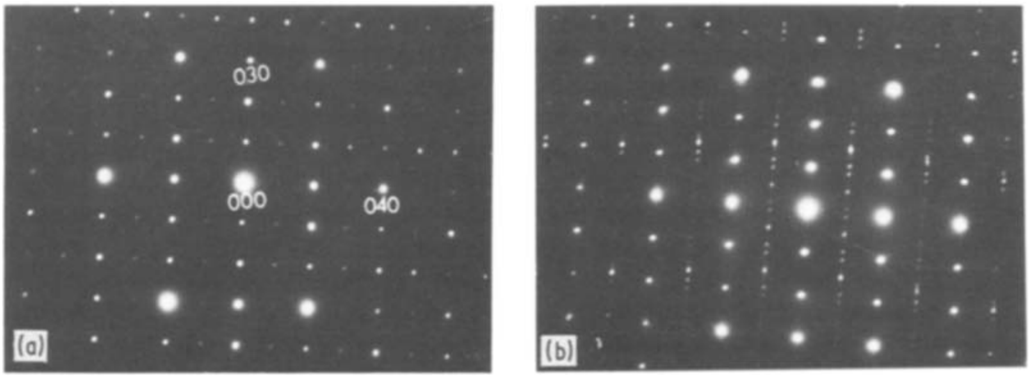

Figure 6 Electron diffraction patterns obtained (a) for a quenched sample (700° C/ice-water) of Cu–12.4% Al alloy, and (b) for a quenched and homogenized sample after 300 h at 300° C. Zone axis [0 0 1].

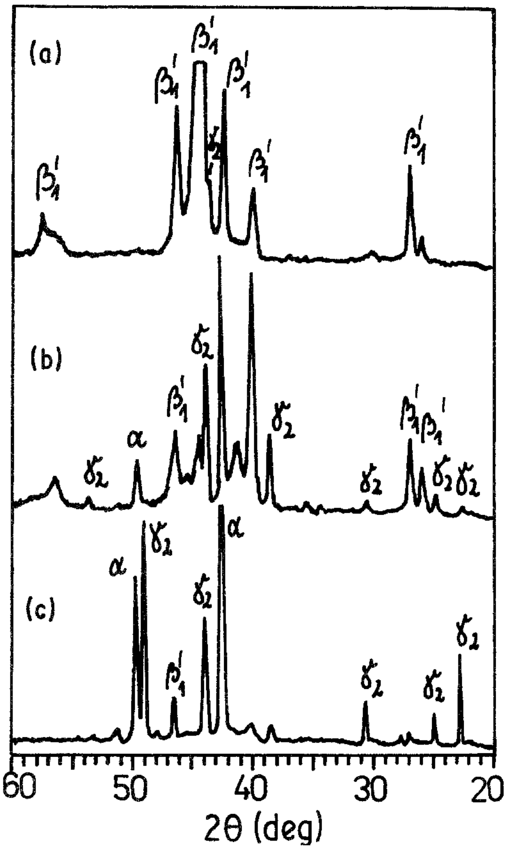

Figure 7 X-ray diffraction pattern (Cu$K\alpha$ radiation) of samples of Cu–12.4% Al alloy which after quenching were heated at 6° C min^{-1} to (a) 490° C, (b) 510° C and (c) 550° C.

As can be seen from Fig. 4 the $\alpha + \gamma_2 \rightarrow \beta$ transformation (P_6 in Fig. 4a) diminishes when the heating rate rises. At the same time the P_5 peak of the $\beta_1 \rightarrow \beta$ transformation increases. For heating at a rate of 100° C min^{-1} β phase arose wholly from the ordered β_1

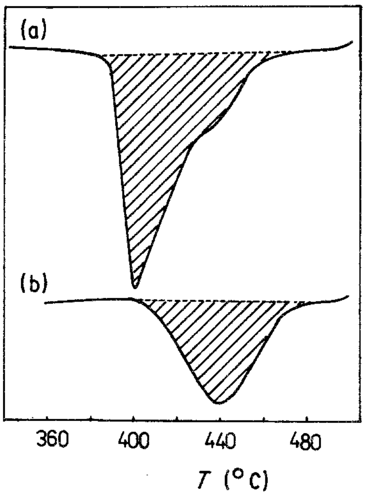

Figure 9 DTA curves of Cu–Al alloy obtained for (a) a martensitic sample and (b) a sample homogenized for 100 min at 380° C.

phase. The $\beta_1 \rightarrow \alpha + \gamma_2$ reaction did not take place at this rate of heating. Heating martensite at this rate was sufficient to cause the reverse martensitic transformation $\beta_1' \rightarrow \beta_1 \rightarrow \beta$. A thermoelastic reversible martensitic transformation is a necessary condition to obtain the shape memory effect in Cu–Al alloys.

On the basis of the X-ray results it was found that after 100 min of isothermal heating at a temperature of 380° C, martensitic phase transformation into the parent β_1 phase takes place. An attempt was therefore made to separate the P_2 and P_3 peaks in Fig. 3d. For this purpose the quenched sample was aged for 100 min at 380° C in the Thermoanalyzer and next heated from 380 to 600° C (Fig. 9). Fig. 9a represents the DTA curve obtained in the coarse of heating the martensitic sample. Fig. 9b was obtained during heating of a

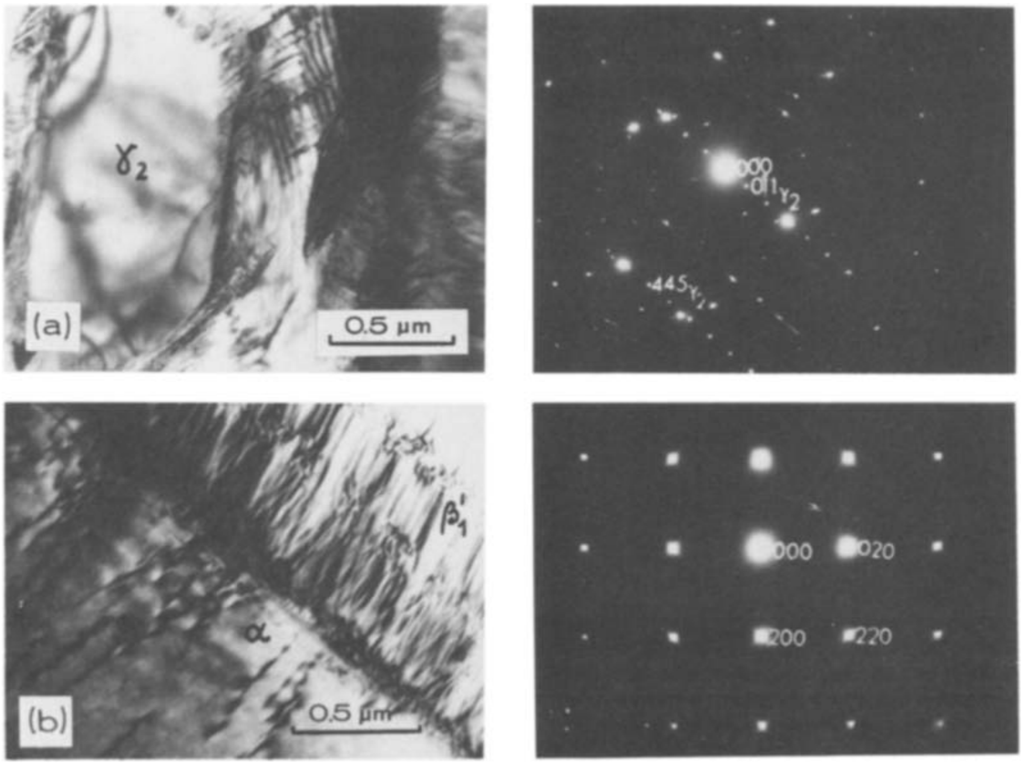

Figure 8 Structure and electron diffraction patterns of samples of Cu–12.4% Al alloy which after quenching were heated at 6° C min^{-1} to (a) 490° C and (b) 510° C. Observed at room temperature.

sample which after being quenched was heated at a temperature of 380° C for 100 min. The effect achieved at its minimum at 440° C is associated with the $\beta_1 \rightarrow \alpha + \gamma_2$ transformation. The thermal effect calculated from the area under the curve of Fig. 9a was $217 \pm 10\,\mathrm{cal\,mol^{-1}}$ ($909 \pm 42\,\mathrm{J\,mol^{-1}}$). The thermal effect of transformation for $\beta_1 \rightarrow \alpha + \gamma_2$ (Fig. 9b) was $163 \pm 7\,\mathrm{cal\,mol^{-1}}$ ($682 \pm 29\,\mathrm{J\,mol^{-1}}$). The difference between these two effects, which is the thermal effect of the reverse martensitic transformation, was $53.7 \pm 3\,\mathrm{cal\,mol^{-1}}$ ($225 \pm 13\,\mathrm{J\,mol^{-1}}$). This value is within the range 40 to $60\,\mathrm{cal\,mol^{-1}}$ (167 to $251\,\mathrm{J\,mol^{-1}}$) quoted in the literature [2] as the heat of martensitic transformation for Cu–Al alloys.

Calculated on the basis of the peak area in Fig. 3, the heat of $\alpha + \gamma_2 \rightarrow \beta$ transformation was $351 \pm 10\,\mathrm{cal\,mol^{-1}}$ ($1470 \pm 42\,\mathrm{J\,mol^{-1}}$).

4. Conclusions

1. The major factor determining which transformations take place during heating of a martensitic sample of Cu–12.4 wt % Al alloy was the speed of heating.

2. For different rates of heating the schema of phase transformation was as follows (Fig. 10):

(i) When martensite was heated at a rate of not more than $1°\,\mathrm{C\,min^{-1}}$ the β_1 phase was obtained and it was then transformed into a eutectoid mixture $\alpha + \gamma_2$.

(ii) When martensite was heated at a rate of $100°\,\mathrm{C\,min^{-1}}$, the β_1 phase was wholly transformed into a high-temperature β phase.

(iii) For intermediate speeds of heating (between 2 and $100°\,\mathrm{C\,min^{-1}}$) the ordered β_1 phase was transformed into eutectoid and then into β phase. If the rate of heating increases, from the two competitive transformations of the β_1 phase, $\beta_1 \rightarrow \alpha + \gamma_2$ and $\beta_1 \rightarrow \beta$ (Fig. 10b), the last one starts to dominate.

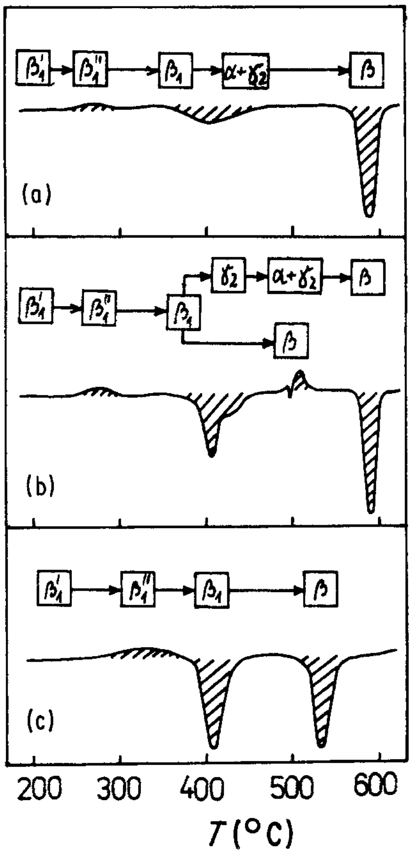

Figure 10 Sequence of phase transformations for the martensite of Cu–12.4% Al alloy during heating at rates (a) lower than $1°\,\mathrm{C\,min^{-1}}$, (b) between 2 and $100°\,\mathrm{C\,min^{-1}}$, and (c) $100°\,\mathrm{C\,min^{-1}}$.

3. The temperatures of martensitic and reverse transformations determined from DTA curves were as follows: $A_s = 340°\,\mathrm{C}$, $A_f = 400°\,\mathrm{C}$, $M_s = 300°\,\mathrm{C}$ and $M_f = 270°\,\mathrm{C}$.

4. From the areas of the DTA peaks, thermal effects of transformations were determined as follows: heat of reverse transformation $53.7 \pm 3\,\mathrm{cal\,mol^{-1}}$ ($22.5 \pm 13\,\mathrm{J\,mol^{-1}}$), heat of $\beta_1 \rightarrow \alpha + \gamma_2$ transformation $163 \pm 7\,\mathrm{cal\,mol^{-1}}$ ($682 \pm 17\,\mathrm{J\,mol^{-1}}$), and heat of $\alpha + \gamma_2 \rightarrow \beta$ transformation $351 \pm 10\,\mathrm{cal\,mol^{-1}}$ ($1470 \pm 42\,\mathrm{J\,mol^{-1}}$).

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