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KINETIC STUDY OF PRECIPITATION PROCESSES IN Cu-Be ALLOYS BY DSC

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ABSTRACT

The overlapping reaction peaks on DSC curves due to precipitation reactions in Cu-Be alloys were discriminated by peak fittig of the numerical calculation with the aid of Ozawa's and Johnson-Mehl equations to determine the activation energy and the other kinitic parameters. The peak fitting could be made fairly well and the reasonable values were obtained.

INTRODUCTION

Cu-Be alloy is one of the most useful age-hardening alloys and thermal analysis(1), as well as many reports with other techniques, showed that the precipitation processes in supersaturated copper-rich Cu-Be alloys include at least four stages, that is, formation (and dissolution) of G.P.zones and continuous precipitation of the metastable γ''-, γ'-phases and the equilibrium γ-phase. But the problem is that the temperature range of these stages are overlapping each other. The aim of the present study is to discriminate kinetically these stages and to provide data to discuss the interrelation in the precipitation sequence.

EXPERIMENTAL PROCEDURE

Cu-12at%Be binary alloy was made by melting high purity master alloy with high purity copper in a vacuum of 1.3mPa using a high frequency induction furnace. The ingot was worked by hot and cold rolls to a sheet about 0.2mm thickness. The specimens for DSC were cut by a spark-cutting machine to discs of 4.5mmϕ and chemically polished. The 3--5 discs were solution heat-treated at 1093K for 30 min. Within 1h, DSC measurement was started to avoid natural ageing.

DSC measurement was carried out using a Rigaku DSC-YCH type device, from room temperature to 773K in Ar gas flow atmosphere, with heating rates of 3,5,10 and 20K/min. The discs were piled up to make the total mass suitable for DSC 60--100mg. The Pt-discs of

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similar size were used as the references.

The base line was decided by the DSC curve of 2nd heating after the 1st run up to about 773K and natural cooling. Because, it is assured that around 773K, only the equilibrium γ-phase precipitates to its maximum amount, no more reaction occurs during cooling and 2nd heating.

The DSC curves were converted to specific heat change - temperature ($\Delta Cp-T$) curves by heat calibration with In,Sn,Pb,Zn and Al.

Thin foils for TEM observation and diffraction were prepared by chemical and electro-Jet polishing(2), after heat treatments. The foils were examined with a JEOL-200 TEM operated at 200kV.

METHOD OF DISCRIMINATION OF DSC PEAKS

Concerning the relation between the heating rate,B and the peak temperature of a reaction,Tp, there is Ozawa's equation,

$$\log B = -0.4567(E_A /RTp) + C, \quad (20<=E_A/RTp<=50) \qquad (1)$$

where E_A and C are the activation energy and a constant. This is a convenient equation to decide the activation energy if the relevant peak is due to a single reaction mechanism.

On the other hand, the Johnson-Mehl (or Avrami) equation,

$$X = 1 - \exp [-(kt)^n] \qquad (2)$$

is often used in order to characterize various reactions in alloys, where X,k,t and n are the reacted fraction, the rate constant, the reaction time and the dimensionless exponent, respectively. Temperature dependence of k is expressed by a equation of Arrhenius type,

$$k = A \exp (-E_A / RT) \qquad (3)$$

where A,R and T are the frequency factor, the gas constant and the absolute temperature, respectively.

By differentiating the equation (2) with t, we obtain

$$dX/dt = A \exp(-E_A /RT)\, n\, [-\ln(1-X)]^{(n-1)/n} (1-X) \qquad (4)$$

For the numerical calculation of DSC peaks, we used the relations,

$$X_i = \sum_k^i (dX/dt)_{Tk} (\Delta T/B) \qquad (5)$$

where X_i,ΔT and $(dX/dt)_{Tk}$ are the reaction fraction up to temperature T_i, the temperature interval of T_k points in the calculation and the reaction rate at the k-th temperature of ΔT, respectively. And

$$\Delta Cp,_k = Q\, (dX/dt)_{Tk} (\Delta T/B) \qquad (6)$$

where $\Delta Cp,_k$ and Q are the specific heat change at the k-th temperature of ΔT and the heat quantity of the reaction in a peak, respectively.

The discrimination and kinetic analysis have been made in the following steps:

1) E_A is decided preliminarily by the data of $(B,Tp)_n$ of each peak in the real ΔCp-T curves, where n means different heating rates.
2) After estimating Q's of all peaks by calculation of area between 2 minima of both sides of a peak, $\Delta Cp,_k$ of the peak in lowest temperature were calculated by using a fixed E_A value, with the aid of equations,(4),(5) and (6), where A and n were decided as to fit the calculated $\Delta Cp,_k$ to the actual ΔCp by trial and error.
3) The calculated $\Delta Cp,_k$'s were subtracted from the real curve to make residual curves of the different heating rates, respectively.
4) After this, on the next peak in a higher temperature, the similar calculation was applied, when E_A and Q values were checked or corrected with the peak in the residual curves.
5) By the similar way, all the parameters were decided on each peak.
6) And then calculated ΔCp's were synthesized to make each whole DSC curve and compared with a relevant real curve and then the parameters were corrected to be consistent if needed.

The decision of A and n by trial and error as in 2), was not so difficult because A has a effect mainly to shift the temperature range of a peak, while n affects only the shape of a peak and so they could be decided almost independently.

RESULTS AND DISCUSSION

Fig.1 shows an ΔCp-T curve with the heating rate of 10K/min, as an example(the bold curve). There are five continuous peaks, that is, P,Q,R,S and T. After one set of calculation the five peaks were discriminated as the peaks, P*,Q*,R*,S* and T*. The peaks are due to formation of G.P.zones, dissolution of it, precipitations of γ''-, γ'- and γ-phases, respectively. Only peak Q is endothermic and the discrimination between peaks P and Q could not be made with the method explained in the previous section and were made with two assumptions that (1)n=1 in the reaction of Q, and that (2)the net heat quantity of Q equals to the peak P*'s one, that is, G.P.zones once formed in the reaction P, dissolved fully in the reaction Q. The assumption(1) is reasonable(3,4).

In order to verify the assumption(2), TEM observation and electron diffraction were carried out. The specimens were heat-treated with the heating rate of 10K/min and quenched into water at several temperatures, as shown in Fig.1. The <100> streaks in the diffraction patterns, which is due to G.P.zones, were very weak in the specimen quenched at 623K and disappears at 653K, while the peak Q* made by the calculation, tails off between these temperatures, as shown with "⟶" in Fig.1. So it can be said that the assumption(2) is appropriate.

Table 1 shows the calculated values of the kinetic parameters. It is remarkable that E_A of the reaction R was widely changed from an apparent values, 277 to a normal value, 192 kJ/mol after the calculation. The value almost equals to the activation energy for diffusion of Be in Cu(5). The values of n have a tendency to increase along with the increase of temperature range of peaks, which suggests some change in the mechanism of nucleation and growth.

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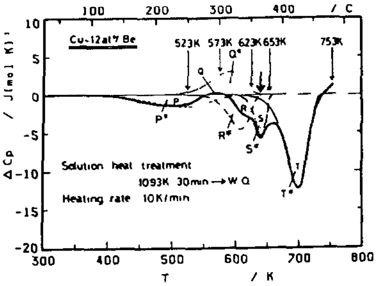

Fig.1 DSC(ΔCp-T) curves of Cu-12at%Be after solution heat treatment(the bold curve). The arows show the temperature at which the speciments for TEM observation were quenched into water, respectively.

The peaks P*,Q*,R*,S* and T*(the fine curves) were discriminated by peak fitting of the numerical calculation.

Table 1 Kinetic parameters of precipitation from supersaturated Cu-12 ar%Be. The values in parentheses were calculated using data read directly from DSC curves.

Peak	P* (P)	Q* (Q)	R* (R)	S* (S)	T* (T)
Exo or Endo	Exo	Endo	Exo	Exo	Exo
E_A/kJ(mol)$^{-1}$	89 (89)	101 (101)	192 (277)	150 (152)	100 (101)
n	0.5	1.0	0.9	2.2	2.0
A/s^{-1}	8×10^6	3×10^6	2×10^{14}	2.7×10^{10}	2.0×10^5
Q/J †	190 (145)	190 (2.7)	200 (78)	130 (161)	570 (505)

† The values of Q are in case of 10K/min.