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CRYSTALLIZATION KINETICS OF Cu_3Ti_2 FORMING FROM $Cu_{60}Ti_{40}$ GLASS

Continuous heating experiments in XRD and DSC

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Abstract

Amorphous to crystalline transformation in $Cu_{60}Ti_{40}$ alloy has been studied under conditions of constant heating rate experiments, using XRD and DSC. In the high temperature XRD experiment, the transformation has been monitored continuously as the integrated X-ray intensity corresponding to a chosen reflection from one of the two crystalline products forming at close by temperatures. Differentiation of the curve thus obtained gives the transformation rate curve which passes through a maximum. From the peak shift with heating rate, the activation energy for the formation of Cu_3Ti_2 crystalline phase has been obtained. The results have been compared with those obtained by DSC.

Keywords: crystallization, $Cu_{60}Ti_{40}$ glass, DSC, kinetics, XRD

Introduction

Conventionally, X-ray diffraction (XRD) methods have been extensively used for monitoring the progress of a transformation in interrupted experiments. Continuous monitoring of X-ray intensity as a function of transformation process has been attempted by using Guinier-Lenme high temperature camera [1]. Tarling *et al.* [2] demonstrated the advantages of using fixed position geometry in X-ray diffraction experiments to evaluate transformation kinetics. In their experiments X-ray intensity was collected from a chosen reflection of the product phase, using continuous recording on a moving film. Recently experiments using synchrotron radiation source, Anwar *et al.* [3] demonstrated the possibility of obtaining time resolved X-ray powder diffraction pattern. These workers [3]

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have also shown the possibility of continuous observation of different phases simultaneously by energy dispersive mode.

The present paper is an attempt to use an ordinary X-ray diffractometer with a high temperature attachment to evaluate the kinetic parameters such as crystallization temperature, T_x, peak crystallization temperature, T_p, and the activation energy, E for the evolution of stable crystalline phase form from an amorphous structure. Only constant heating rate experiments could be carried out by using the existing equipment. Isothermal experiments could not be attempted because of the considerable rise in temperature prior to stabilization of the system at the isothermal holding temperature. For the amorphous to crystalline transformation such an unavoidable rise of ~5 K is detrimental because of the extremely fast kinetics involved. In order to check the reliability of this experimental technique, results from this method have been compared with that obtained from differential scanning calorimetry (DSC).

Experimental method

Constant heating rate experiments were carried out using RIGAKU high temperature X-ray diffractometer. CuK_α radiation from a rotating anode and a large receiving slit of 2 deg were used in all the experiments. A sample size of $30\times16\times0.04$ mm^3 was inserted into the platinum sample holder placed in the furnace sleeve. The sample was then crystallized at 720 K, which is the known peak transformation temperature [4] and an XRD pattern covering a range of 2 theta from 20 to 80 degrees was recorded. The largest intensity peak was observed at 59.1 deg. corresponding to the (102) reflection from the tetragonal $Cu_3Ti_2$and is well separated from the others. X-ray detector counter was then kept at the fixed position of 59.1. After cooling the furnace a fresh sample was loaded. The measuring thermocouple in the furnace was kept touching the sample. Using the programmable temperature controller, the desired heating rate and final temperature were set and heating started. The X-ray intensity was then recorded as a function of temperature.

DSC experiments were carried out at 10, 20, 40 and 80 deg·min^{-1} heating rates, using Perkin Elmer DSC-II.

Results and discussion

The amorphous to crystalline transformation sequence of $Cu_{60}Ti_{40}$ was identified earlier [4] as follows:

Amorphous alloy $\xrightarrow{A}$ Extremely fine (5 to 7.5 nm) cubic crystals $\xrightarrow{B}$
Equilibrium tetragonal Cu_3Ti_2 crystals.

At constant heating rate DSC experiments the two crystallization events appear as two close exothermic peaks (Fig. 1). The peaks corresponding to the first and second transformations are named as *A* and *B* respectively as shown in the case of 10 deg·min^{-1} heating rate experiment given in Fig. 1. The subject of interest in the present study is the formation of Cu_3Ti_2 tetragonal crystalline phase, represented by peak *B*.

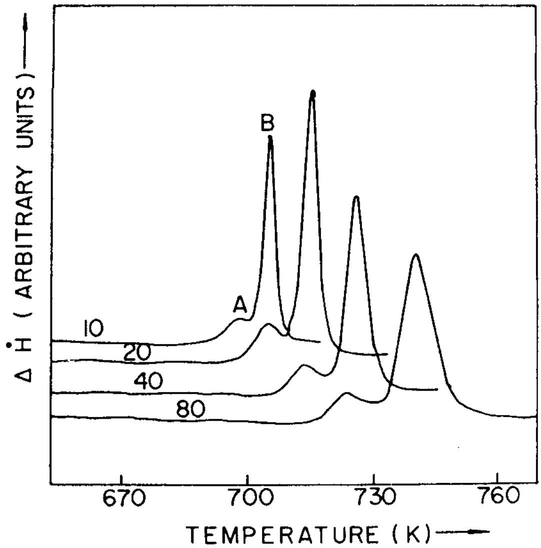

Fig. 1 Constant heating rate DSC exotherms for the amorphous to crystalline transformation of $Cu_{60}Ti_{40}$ obtained at 10, 20, 40 and 80 deg·min^{-1} heating rates

The influence of one peak on the position and content of the other becomes more and more prominent with decreasing separation. However, it is possible to separate any such close or even coinciding thermal events by making use of high temperature XRD. In the example shown in Fig. 2, the continuous evolution of Cu_3Ti_2 phase is represented by the increase in X-ray intensity from (102) reflection of the phase. The observation is not interrupted by the presence or continued formation of the first transformation product.

On the whole, the curve in Fig. 2 represents the integrated form of peak *B* in Fig. 1 as a function of temperature. Crystals of the stable phase start forming at temperatures 10–20 K below the peak transformation temperature of 720 K. With increasing temperature the lattice parameter of the crystals formed can be expected to increase due to thermal expansion, leading to the shift of the maximum intensity position. Such an effect has not been found to influence the present experiment due to the small temperature interval applicable and the use of a large receiving slit. The saturation value of X-ray intensity practically remains constant in spite of heating, in excess of the temperature corresponding to the completion of crystallization (Fig. 2). Such an observation supports the assumption that the peak intensity position does not effectively change within the range of transformation temperatures. Thus the monitoring of the progress of transformation by the continuous increase of X-ray intensity till saturation can be justified to be a reliable method to evaluate kinetic parameters.

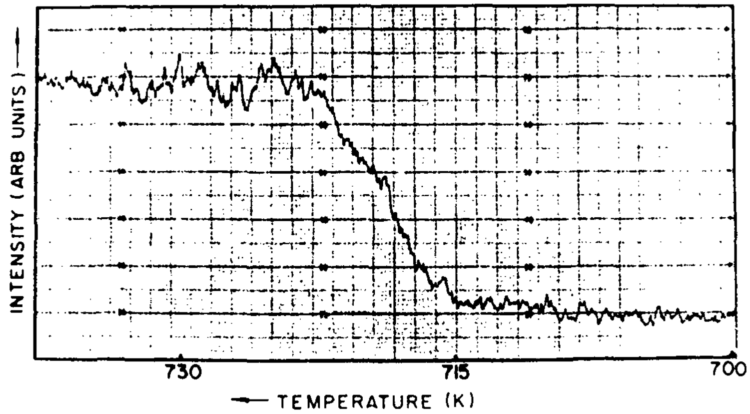

Fig. 2 High temperature XRD of amorphous to crystalline transformation curve for the $Cu_{60}Ti_{40}$ obtained at 20 deg·min^{-1} constant heating rıte in the high temperature XRD experiment

Fluctuations in intensity due to instrumental factors are evident in the plot shown in Fig. 2. These fluctuations have been smoothened and replotted by taking points on the modified curve. The curves thus plotted for 5, 20, 40 and 80 deg·min^{-1} heating rates are shown in Fig. 3(a). These are sigmoidal in shape. The crystallization temperature T_x has been evaluated from each curve, as the point of intersection of the tangent drawn to the straight portion of the curve and the extension of its base line. T_x values for different heating rates are given in Table 1, along with those derived from constant heating rate DSC experiments, presented in Fig. 1. Crystallization temperatures can be seen to increase with heating rate in both the cases. DSC being an extremely sensitive thermal analysis equipment, temperature accuracy from a differential analysis is expected to be high in the case of a single step transformation process. When there are more than one transformation within a small temperature range, the peaks in the thermogram become inseparable. Taking the example of 10 deg·min^{-1} heating rate thermogram given in Fig. 1, it can be seen that there is some enthalpy contribution to peak *B* by *A*. Such a contribution changes the slope of the early part of peak *B*, leading to erroneous assessment of the transformation temperature. The evaluation becomes more and more difficult when the ΔH values for the

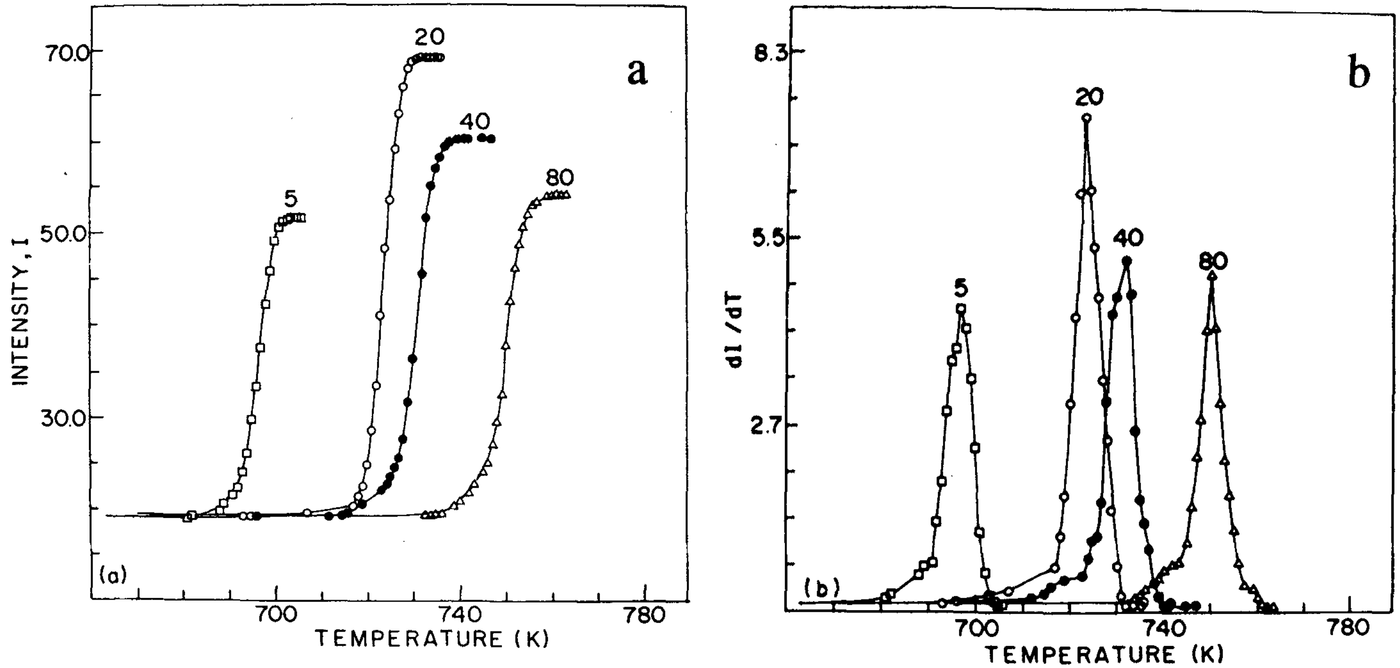

Fig. 3 (a) X-ray intensity plots as a function of temperature at 5, 20, 40 and 80 deg.min^{-1} heating rates.
(b) Differentials of X-ray intensity with respect to temperature; i.e. $d^2c/dtdT$ as a function of temperature

close peaks are comparable. In such a situation it is highly advantageous to use the fixed counter position high temperature XRD for the evaluation of T_x.

X-ray intensity is recorded as count rate d*c*/d*t*, where *c* is the X-ray counts and *t* is the time in seconds. Any point on the curve represents the X-ray count rate (d*c*/d*t*) which continuously increases from a minimum corresponding to the base line value till saturation representing completion of transformation. Taking the minimum intensity as the reference (zero), the height measured from the base line to saturation represents 100% transformation. Hence, the height of any point on the curve, measured from the base line represents the fraction transformed till that time (or temperature). Since each point on the curve represents the integral effect till that temperature, the instantaneous rate of change at each temperature can be evaluated as the differential of X-ray intensity with respect to temperature i.e. $d^2c/dtdT$. A plot of the differentials taken at various intervals as a function of temperature form a peak (Fig. 3(b)). Each point on the peak thus drawn represents the rate of transformation at that temperature, as in the case of a DSC peak. In effect, peak *B* obtained from DSC and the peak derived from XRD experiment should represent the same transformation.

Table 1 Variation of T_x and T_p with heating rates

Heating rate / deg·min^{-1}	T_x* / K		T_p** / K	
	DSC	XRD	DSC	XRD
5	–	691	–	697
10	701	–	705	–
20	710	715	715	723
40	721	725	726.5	732
80	732	746	740.5	750

*T_x – Crystallization temperature
**T_p – Peak crystallization temperature

In both the XRD and DSC experiments the peak positions represent maximum transformation rates. Table 1 gives the peak transformation temperatures (T_p) evaluated from Fig. 1 and Fig. 3(b). It can be observed that T_p values increase in both the cases, with increasing heating rate. Activation energy for the transformation, *E* is related to the heating rate (*C*) and peak transformation temperature T_p by the relation

$$\ln\left(\frac{C}{T_p^2}\right) = -\frac{E}{RT_p} + \text{const.}$$

where R is the gas constant, E is evaluated from the slope of a plot of $\ln(C/T_p^2)$ against $1/T_p$ [5]. Such plots based on DSC (o) and XRD (x) experiments are given in Fig. 4.

It is interesting to note that both the Kissinger plots give nearly the same activation energy of 240 kJ/mole, in spite of the fact that the points on the plot derived from XRD experiments show larger scatter in comparison with those from DSC. Such a scatter appear to be due to the large thermal inertia of the ceramic furnace used in the high temperature XRD and the use of single thermocouple to measure temperature.

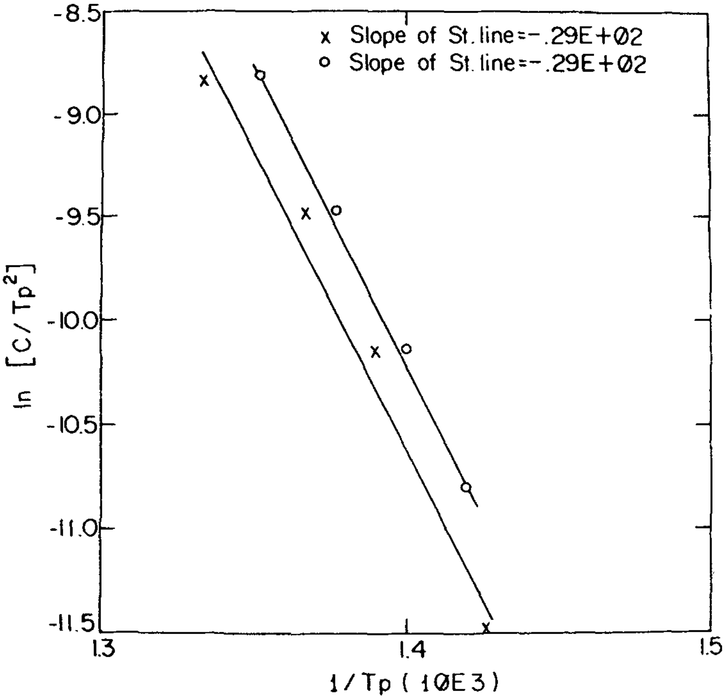

Fig. 4 Kissinger plots using DSC (o) and XRD (x) experiments

It can be mentioned here that there are similarities and differences between the two experiments. In DSC, there is a temperature lag between the occurrence of a transformation and its observation, while in the XRD method the transformation is recorded instantaneously. However, the temperature control in the present-day high temperature XRD equipment is poorer compared to that in DSC. With improved methods of temperature control, it should be possible to carry out isothermal experiments as well, using the high temperature XRD equipment.

Conclusions

The onset of crystallization temperature T_x, the peak crystallization temperature T_p and the activation energy for crystallization E evaluated by constant heating rate XRD experiments match with the results obtained by similar DSC experiments. Hence it is possible to use the high temperature XRD for the evaluation of the kinetic parameters of a chosen phase.

The XRD method does not depend on the energy changes and hence it can be applied to transformations involving enthalpy changes undetectable by calorimetry. The technique can be employed especially for studying the kinetics of formation or dissolution of a selected phase which is evolving along with other phases in a transformation process. Since there is no time lag between the transformation and its observation, the technique can also be employed to prepare a sample of known amount of fraction transformed.

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Zusammenfassung — Mittels Röntgendiffraktion und DSC wurde in Versuchen mit konstanter Aufheizgeschwindigkeit die Umwandlung vom amorphem zum kristallinen Zustand in $Cu_{60}Ti_{40}$-Legierungen untersucht. Bei Hochtemperatur-Röntgenversuchen wurde die Umwandlung kontinuierlich als integrierte Röntgenstrahldichte einer ausgewählten Reflexion eines der beiden bei nahen Temperaturen gebildeten kristallinen Produkte verfolgt. Differenzieren der so erhaltenen Kurve ergibt die Umwandlungsgeschwindigkeitskurve, die ein Maximum durchläuft. Aus der Peakverschiebung in Abhängigkeit von der Aufheizgeschwindigkeit wurde die Aktivierungsenergie für die Bildung der kristallinen Phase Cu_3Ti_2 ermittelt. Die erhaltenen Ergebnisse wurden mit denen der DSC verglichen.