Calorimetric studies of non-isothermal crystallization in amorphous Cu$_x$Ti$_{100-x}$ alloys

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Abstract. The present paper reports the composition dependence of pre-exponential factor and activation energy of non-isothermal crystallization in amorphous alloys of Cu$_x$Ti$_{100-x}$ system using differential scanning calorimeter (DSC) technique. The applicability of Meyer–Neldel relation between the pre-exponential factor and activation energy of non-isothermal crystallization for amorphous alloys of Cu–Ti system was verified.

Keywords. Amorphous materials; differential scanning calorimetry (DSC); phase transitions.

1. Introduction

There is a significant attention to two-component amorphous alloys, both as regards to their basic physical properties and industrial applications. Technological applications of amorphous alloys require such materials that should be thermally stable with time and temperature during the application. Scientifically, the kinetics of crystallization is equally important in understanding the atomic processes involved in the formation of crystalline phases. The thermal stability of amorphous alloys can be defined as the resistance to crystallization and is given in terms of the peak crystallization temperature.

Amorphous alloys of Cu–Ti system are of special interest (Koster *et al* 1995) due to the fact that Cu–Ti is a congruently melting compound, which should allow static under-cooling experiments. Several works on the mechanical properties and microstructures of copper–titanium binary alloys have been carried out and some interesting results were obtained (Brunelli *et al* 2001; Suzuki *et al* 2003; Yang *et al* 2006). On the other hand, it is known that copper is the best element to favour the alloy formation when mixed with another metal or rare earth metals (Suzuki *et al* 2003). The addition of titanium is also known to strengthen copper alloys (Suzuki *et al* 2003). Due to this reason, it is supposed to be an ideal system to study crystallization of amorphous alloys and for comparison of under-cooled melts of the same composition. The study of thermally induced crystallization process in such systems is important to determine their thermal stability.

Since the amorphous state is essentially a meta-stable one, it inherently possesses the possibility of transforming into a more stable crystalline state. Understanding of micro-mechanisms of crystallization is, therefore, an essential requirement for most applications. Recently, Mehta *et al* reported the observation of Meyer–Neldel rule (MN rule) in thermally activated crystallization in some semi-conducting glasses (Mehta and Kumar 2006, 2007). They have observed the variation of pre-exponential factor K_0 of the rate constant K with the activation energy of crystallization E_c by changing the variation of composition. In the present paper, we report the applicability of MN rule in the thermally activated crystallization of amorphous alloys of Cu$_x$Ti$_{100-x}$ system.

2. Experimental

Amorphous alloys of Cu$_x$Ti$_{100-x}$ (x = 43, 50, 53, 55) were prepared by the melt-quenching technique under identical conditions. High purity (99·999%) Cu and Ti elements were weighed according to their atomic percentages and were sealed in quartz ampoules (length ~5 cm and internal diameter ~8 mm) with a vacuum ~10^{-5} torr. The ampoules containing the materials were heated to 900°C and held at that temperature for 10–12 h. The temperature of the furnace was raised slowly at a rate ~3–4°C/min. During heating, all the ampoules were constantly rocked, by rotating a ceramic rod to which the ampoules were tucked away in the furnace. This was done to obtain homogenous alloys.

After rocking for about 10 h, the obtained melts were cooled rapidly by removing the ampoules from the furnace

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and dropped into ice-cooled water. The quenched samples were taken out by breaking the quartz ampoules. The amorphous nature of the materials was checked by XRD technique. The XRD pattern of $Cu_{50}Ti_{50}$ alloy is shown in figure 1. Absence of any sharp peak in XRD pattern in figure 1 confirms the amorphous nature of $Cu_{50}Ti_{50}$ alloy. Similar XRD patterns were obtained for the other amorphous alloys.

Differential scanning calorimetry (DSC) was performed on a Rigaku 8230B model attached with a thermal analysis station (TAS 100) at various heating rates. The temperature precision of the equipment was 0·1 K with an average standard error of about ±1 K in the measured values. The samples with masses of 3–4 mg were continuously heated from room temperature to 500°C. The instrument was calibrated prior to measurement by using high purity metal standards with known latent heat. The calibration and measurements of the alloys were carried out using identical conditions for better accuracy.

3. Theoretical basis

The crystallization kinetics of amorphous alloys have been intensively studied using the classical Johnson–Mehl–Avrami (JMA) model (Johnson and Mehl 1939; Avrami 1939, 1940) in which the crystallized fraction (α) is described as a function of time (t) according to the following formula:

$$\alpha(t) = 1 - \exp[-(Kt)^n]. \qquad (1)$$

Here n is the Avrami exponent which depends on the mechanism of growth and dimensionality of the crystal growth. K is defined as the reaction rate constant, which is usually assumed to have an Arrhenian temperature dependency:

$$K = K_0 \exp\left(\frac{-E_c}{RT}\right), \qquad (2)$$

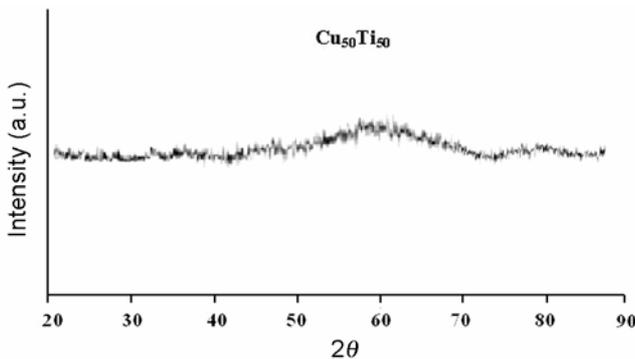where E_c is the activation energy for crystallization and K_0 the frequency factor.

Figure 1. XRD pattern of amorphous $Cu_{50}Ti_{50}$ alloy.

In non-isothermal crystallization, it is assumed that there is a constant heating rate in the experiment. The relation between the sample temperature, T and the heating rate, β can be written in the form:

$$T = T_i + \beta t, \qquad (3)$$

where T_i is the initial temperature. The crystallization rate is obtained by taking the derivative of expression (1) with respect to time, t bearing in mind that the reaction rate constant is a time function through its Arrhenius temperature dependence, resulting in

$$\left(\frac{d\alpha}{dt}\right) = (Kt)^{n-1}\left[K + \left(\frac{dK}{dt}\right)\right](1 - \alpha). \qquad (4)$$

The derivative of K with respect to time can be obtained from (2) and (3) as follows:

$$\frac{dK}{dt} = \left(\frac{dK}{dT}\right)\left(\frac{dT}{dt}\right) = \left(\frac{\beta E_c}{RT^2}\right)K. \qquad (5)$$

Then (4) becomes

$$\left(\frac{d\alpha}{dt}\right) = nK^n t^{n-1}[1 + at](1 - \alpha), \qquad (6)$$

where $a = (\beta E_c/RT^2)$.

Augis and Bennett (1978) developed a method for evaluation of activation energy, E_c of crystallization and the pre-exponential factor of rate constant, K. They took proper account of the temperature dependence of the reaction rate and their approach resulted in a linear relation between $\ln(T_c - T_i)/\beta$ vs $1/T_c$. This can be deduced as follows, substituting u for Kt into (6); the rate of reaction is expressed as

$$\left(\frac{d\alpha}{dt}\right) = n\left(\frac{du}{dt}\right)u^{n-1}(1 - \alpha). \qquad (7)$$

Where

$$\left(\frac{du}{dt}\right) = u\left[\frac{1}{t} + a\right]. \qquad (8)$$

The second derivatives of (7) and (8) are given by

$$\frac{d^2\alpha}{dt^2} = \left[\frac{d^2u}{dt^2}u - \left(\frac{du}{dt}\right)^2(nu^n - n + 1)\right]nu^{n-2}(1 - \alpha), \qquad (9)$$

$$\frac{d^2u}{dt^2} = \frac{du}{dt}\left[\frac{1}{t} + a\right] + u\left[-\frac{1}{t^2} + \frac{da}{dt}\right]. \qquad (10)$$

Recalling that $T = T_i + \beta t$ and substituting for $(da/dt) = -(2\beta/T)a$, (10) can be written as

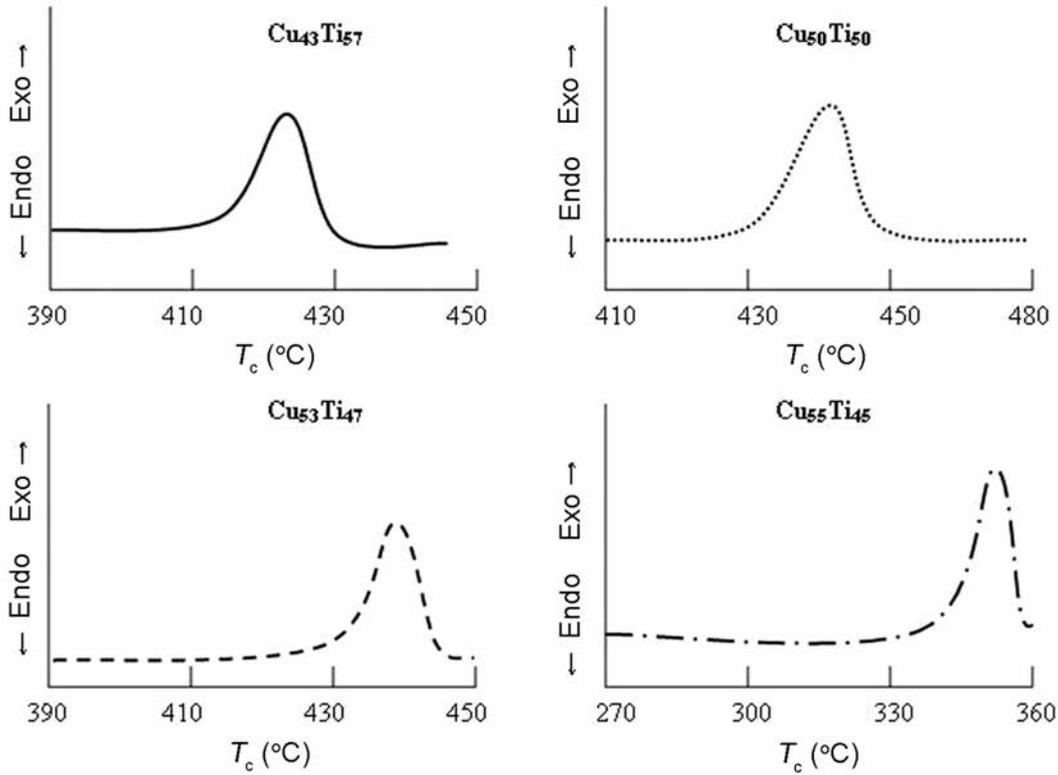$$\frac{d^2u}{dt^2} = u\left[a^2 + \frac{2aT_i}{tT}\right]. \qquad (11)$$

Figure 2. DSC thermograms of Cu$_x$Ti$_{100-x}$ (x = 43, 50, 53, 55) amorphous alloys at the heating rate of 10 K/min.

The last term in the above equation was omitted in the original derivation of Augis and Bennett's ($T_i \ll T$) (Augis and Bennett 1978) and resulted in the simple form

$$\frac{\mathrm{d}^2u}{\mathrm{d}t^2} = a^2u. \tag{12}$$

Substitution of $(\mathrm{d}u/\mathrm{d}t)$ and $(\mathrm{d}u^2/\mathrm{d}t^2)$ from (8) and (12), into (9) gives

$$(nu^n - n + 1) = \left[\frac{at}{1+at}\right]^2. \tag{13}$$

For $E/RT \gg 1$, the right-hand bracket approaches its maximum limit and consequently, u (at the peak) = 1, or

$$u = (Kt)_c = K_0 \exp\left(\frac{-E_c}{RT}\right)\left[\frac{T_c - T_i}{\beta}\right] \approx 1. \tag{14}$$

In logarithm form, for $T_i \ll T_c$, we have

$$\ln\left(\frac{\beta}{T_c}\right) = \left(\frac{-E_c}{RT}\right) + \ln K_0. \tag{15}$$

This equation is used to calculate the activation energy of crystallization by plotting $\ln(\beta/T_c)$ vs $1/T_c$ curve. This method has an extra advantage that the intercept of $\ln(\beta/T_c)$ vs $1/T_c$ gives the value of pre-exponential factor K_0 of Arrhenius equation.

Equation (15) has been used by various workers (El-Oyoun 2000; Abu-Sehly 2003; Mehta *et al* 2004). Their results show that E_c values obtained by (4) are in good agreement with the E_c values obtained by well known Kissinger's relation (Kissinger 1957) and relation of Matusita and Sakka (1979, 1981). We have therefore used the method of Augis and Bennett (5) (Augis and Bennett 1978) to evaluate activation energy of crystallization, E_c. This method has an extra advantage that the intercept of $\ln \beta/T_c$ vs $1/T_c$ gives the value of pre-exponential factor K_0 of Arrhenius equation, which is in good agreement with the value that obtained directly from Arrhenius (1) using isothermal method.

4. Results and discussion

Amorphous alloys of Cu$_x$Ti$_{100-x}$ (x = 43, 50, 53, 55) were scanned at six different heating rates; 5, 10, 12, 15, 17 and 20 K/min. Figure 2 shows the DSC thermograms for all the four samples at a heating rate of 10 K/min. A sharp peak is observed for all the amorphous alloys during the crystallization process. The values of the peak crystallization temperature at different heating rates are given in table 1.
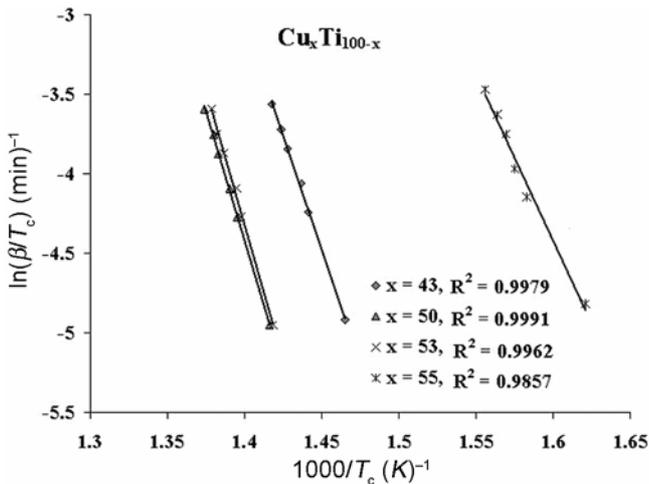
In amorphous alloys, the thermal stability represents the resistance to divitrification of the alloy through the nucleation and growth process. This means that higher

Table 1. Peak crystallization temperatures (T_c) of Cu_xTi_{100-x} ($x = 43, 50, 53, 55$) amorphous alloys.

Heating rate (°C/min)	$Cu_{43}Ti_{57}$	$Cu_{50}Ti_{50}$	$Cu_{53}Ti_{47}$	$Cu_{55}Ti_{45}$
		T_c (°C)		
5	409·6	433·1	432·0	344·0
10	420·9	443·7	442·4	358·8
12	422·9	446·2	444·0	361·9
15	427·4	450·0	448·2	364·2
17	429·4	451·6	450·5	366·5
20	432·4	454·8	452·3	369·7

Table 2. Activation energy of crystallization (E_c) and pre-exponential factor (K_0) of rate constant for Cu_xTi_{100-x} ($x = 43, 50, 53, 55$) amorphous alloys.

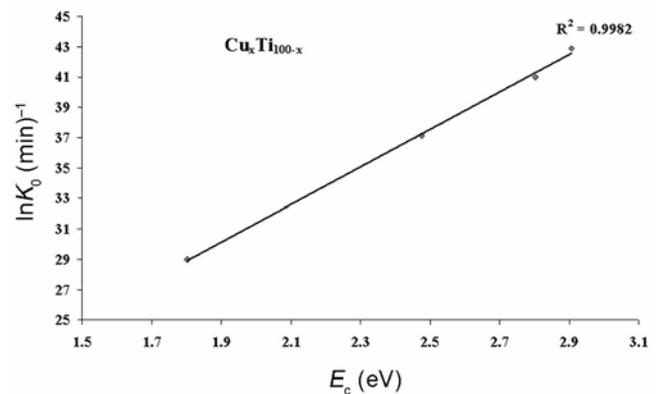| Sample	E_c (eV)	K_0 (min)$^{-1}$ from (15)	K_0 (min)$^{-1}$ from (16)
$Cu_{43}Ti_{57}$	2·50	$1·4 \times 10^{16}$	$2·3 \times 10^{16}$
$Cu_{50}Ti_{50}$	2·80	$6·4 \times 10^{17}$	$8·2 \times 10^{17}$
$Cu_{53}Ti_{47}$	2·90	$4·3 \times 10^{18}$	$2·5 \times 10^{18}$
$Cu_{55}Ti_{45}$	1·80	$3·9 \times 10^{12}$	$1·5 \times 10^{13}$

Figure 3. $\ln(\beta/T_c)$ vs $10^3/T_c$ plots for Cu_xTi_{100-x} ($x = 43, 50, 53, 55$) amorphous alloys.

Figure 4. Plot of $\ln K_0$ vs E_c for Cu_xTi_{100-x} ($x = 43, 50, 53, 55$) amorphous alloys.

the thermal stability of the alloy, maximum is its crystallization temperature. From table 1, it is clear that crystallization temperature is maximum for $x = 50$ in Cu_xTi_{100-x} system. This shows that $Cu_{50}Ti_{50}$ alloys are most thermally stable.

According to (15), the plot of $\ln(\beta/T_c)$ vs $10^3/T_c$ leads to a straight line. This has been verified for the amorphous Cu_xTi_{100-x} system in figure 3.

The activation energy of crystallization, E_c and pre-exponential factor, K_0 of the amorphous alloys have been calculated from the slopes and intercepts of the plots of $\ln(\beta/T_c)$ vs $10^3/T_c$. The values of E_c and $\ln K_0$ for the present amorphous system obtained from (15) are given in table 2.

It is clear from this table that E_c and K_0 are composition dependent and K_0 is not a constant but depends on E_c. Figure 4 shows the plots of $\ln K_0$ vs E_c for the present amorphous system. Curve fitting is done by least square method and the square of coefficient of correlation (R^2) of each $\ln K_0$ vs E_c plot is indicated in the figure. It is clear from each figure that $\ln K_0$ vs E_c plot is a straight line of good correlation coefficient indicating that K_0 varies exponentially with E_c following the relation

$$\ln K_0 = \ln_{00} + \frac{E_C}{RT}. \tag{16}$$

From the slope and intercept of each line, we have calculated the values of $(kT_0)^{-1}$ and K_{00}. Using these values, the expected values of K_0 have been calculated for the present amorphous alloys and compared with the reported

values (see table 2). An overall good agreement between these two values confirms the validity of MN rule in the present amorphous system.

Koga and Sestak (1991) have shown that the kinetic compensation effect mathematically results from the exponential form of the rate constant. A change of activation energy is thus compensated by the same change in temperature or in the logarithm of the pre-exponential factor. In the present study also, the increase in E_c is compensated by the increase in the pre-exponential factor K_0. This may be probably the reason for the observation of compensation effect in the present amorphous system as suggested by Koga and Sestak (1991).

5. Conclusion

Amorphous alloys of Cu$_x$Ti$_{100-x}$ (x = 43, 50, 53, 55) system have been prepared by quenching technique. The observation of compensation effect between the pre-exponential factor and activation energy in the crystallization process has been investigated in the present study for this amorphous system. The crystallization temperature is found maximum for Cu$_{50}$Ti$_{50}$ alloy. This indicates maximum thermal stability in Cu$_x$Ti$_{100-x}$ (x = 43, 50, 53, 55) system for x = 50.

It has been found that the activation energy of crystallization and pre-exponential factor of crystallization rate constant satisfies the MN rule for the present amorphous system. This shows that the MN rule, which is observed for the thermally activated crystallization in semiconductors-conducting glasses, is also applicable for amorphous alloys. Thus, the present results support the generality of MN rule for glassy and amorphous materials.

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