Correlation between the Structure and Internal Friction of Metallic Glass $Cu_{45}Ti_{55}$

ZHANG HEN, ZHANG BANGWEI, TAN ZHAOSHENG, and WU LIJUN

The structural change of metallic glass $Cu_{45}Ti_{55}$ from room temperature to 800 K is investigated by combining internal friction using the torsion penulum method with X-ray diffraction (XRD), differential scanning calorimetry (DSC), and transmission electron microscopy (TEM). The internal friction curve exhibits a point of inflection at about 640 K and an internal friction peak between 640 and 780 K, which corresponds to the precipitation of $CuTi_2$ (tetragonal) and a metastable phase I (tetragonal) and the formation of CuTi (tetragonal), respectively. The result shows that internal friction is closely related to the phase transition during crystallization, and there is much correspondence between internal friction and DSC in describing the crystallization behavior of metallic glasses.

I. INTRODUCTION

IT is well known that the internal friction (IF) behavior of solids is highly structure-sensitive. Internal friction therefore is a very sensitive and effective method to study the structural relaxation and crystallization of metallic glasses. Studies indicate that there are two kinds of IF peaks in metallic glasses. One is a inflection IF peak, which is reversible and related to the glass transition without the intervention of crystallization.[1–5] The other is an IF peak related closely to crystallization, which is irreversible.[6,7,8] According to He,[3] the two kinds of peaks can be distinguished clearly as seen in α-$Pd_{77.5}$, $Cu_6Si_{16.5}$, and α-$Pd_{77.5}Ni_6Si_{16.5}$ if $\Delta T = T_x - T_g$ is large enough. Otherwise, they will overlap and only one IF peak in this region will be observed, as in the case of α-$Pd_{80}Si_{20}$.

Although a number of works using the IF technique were related to the structural relaxation of metallic glasses, only a few reports were related to the crystallization. Furthermore, because of the limitation of the method, it is necessary to combine the IF technique with one or more of the other techniques, *e.g.*, X-ray diffraction (XRD), differential scanning calorimetry (DSC), transmission electron microscopy (TEM), *etc.*, to obtain more details for the crystallization of amorphous alloys. The Cu-Ti amorphous alloy is an important and interesting binary amorphous system. The IF behavior of α-$Cu_{70}Ti_{30}$ has been studied,[9] in which only one IF peak was found, as in the case of α-$Pd_{80}Si_{20}$. In order to clarify clearly the crystallization of Cu-Ti amorphous systems, we therefore investigated the correlation of the IF and structure changes of an amorphous alloy $Cu_{45}Ti_{55}$ by combining use of a conventional torsion pendulum with DSC, XRD, and TEM.

II. EXPERIMENTAL

The internal friction of the $Cu_{45}Ti_{55}$ alloy was measured by a low-frequency torsion pendulum under 3.0×10^{-4} torr vacuum from room temperature to 800 K with a heating rate of about 10 K/min. The size of the specimen was $0.035 \times 2.0 \times 300$ mm^3.

An XRD experiment was measured in a RAX-10 diffractometer with CuK_α radiation. Calorimetric data were obtained using a Dupont Model 1090 differential scanning calorimeter at a scanning rate of 10 K/min. The microstructure of the ribbon annealed at 780 K was examined using a H-800 transmission electron microscope at a voltage of 200 KV. The specimens for TEM observation were thinned by twin-jet polishing in an electrolyte containing 75 pct methyl alcohol and 25 pct nitric acid by volume at 10 °C. Specimens for XRD and TEM analyses were heated to differently chosen temperatures at a rate of 10 K/min and then quenched into water.

III. RESULTS

The IF of as-received $Cu_{45}Ti_{55}$ glass in the temperature range from room temperature to 800 K is shown in Figure 1. The IF remains nearly temperature-independent below 420 K and increases substantially with temperature from 420 to 520 K. A shoulder can be observed between 520 and 630 K. Above 630 K, IF increases rapidly and reaches the maximum at 698 K.

The DSC curves of the as-received specimen and the specimens quenched at different temperatures are shown in Figure 2. For the as-received specimen, two exothermic peaks occur at 669 and 698 K, and the exothermic enthalpy is 6.65 KJ/mol. But the first exothermic peak disappears and the enthalpy is only 5.27 KJ/mol for the sample quenched at 640 K. For the sample quenched at 720 K, two exotherms totally vanish.

The XRD patterns for the as-received and quenched specimens are presented in Figure 3. The XRD pattern of the as-received specimen is a broad ridge typical of the amorphous state. For the specimen heated to 640 K (at the point of inflection on the IF curve), two very weak crystalline lines occur on the main diffuse peak of the amorphous phase. With increase in quench temperature, the diffraction peaks corresponding to crystalline phase increase both in intensity and number.

The TEM observation for the sample quenched at

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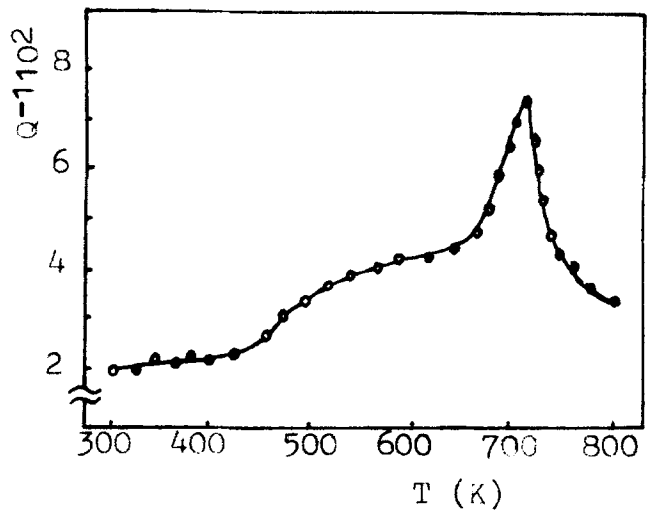


Fig. 1—IF spectrum *vs* temperature of $Cu_{45}Ti_{55}$ metallic glass, heating rate 10 K/min.

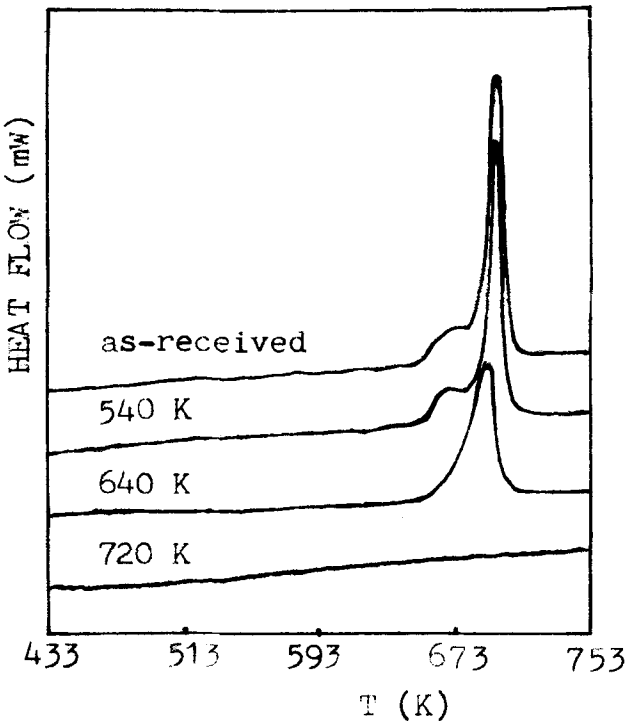


Fig. 2—DSC curves of the specimens quenched at different temperatures, scan rate 10 K/min.

780 K is shown in Figure 4. Two types of stable phases can be identified. "A" is the $CuTi_2$ phase (tetragonal, a_0 = 0.29438 nm, c_0 = 1.07861 nm); "B" is the CuTi phase (tetragonal, a_0 = 0.3108 nm, c_0 = 0.5887 nm). In addition, some traces of a metastable phase can also be detected.

IV. DISCUSSION

Combining the DSC, XRD, and TEM analyses with the variation of IF, the structure of $Cu_{45}Ti_{55}$ metallic glass can be described as follows:

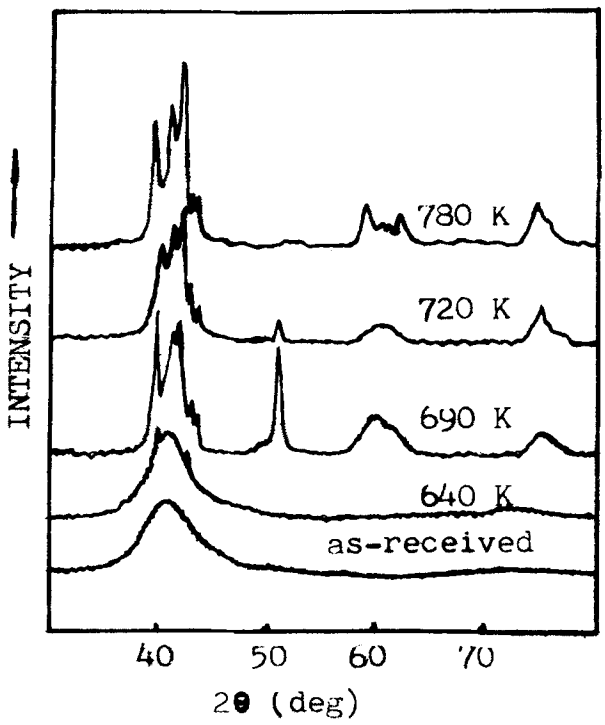
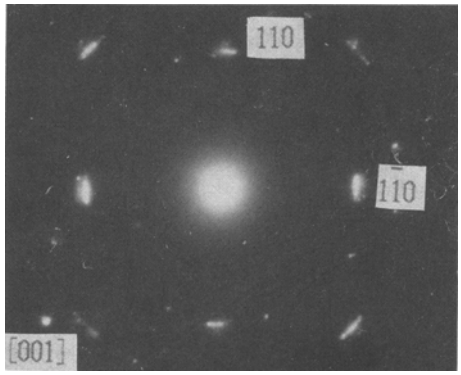
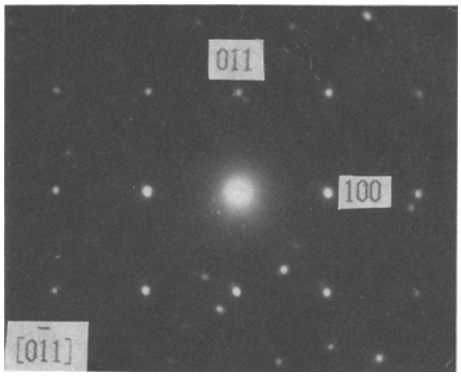


Fig. 3—XRD patterns of $Cu_{45}Ti_{55}$ specimens quenched at different temperatures.



(*a*)



(*b*)

Fig. 4—The electron diffraction patterns of (*a*) $CuTi_2$ and (*b*) CuTi for the specimen quenched at 780 K.

(1) From room temperature to 420 K, the IF varies slightly with the temperature. This stage is attributed to an incubation process of some atomic reorganization phenomenon,[10] but the structure of the amorphous state has not changed much.
(2) In the temperature range of 420 to 520 K, the IF increases rapidly with the temperature, which is regarded as the stress-induced structural rearrangement of atomic clusters in the amorphous matrix by thermal activation.[11,12] There are density fluctuation defects (DF defect) and shear stress fluctuation defects (SSF defects)[13,14] in metallic glasses, and the apparent internal friction of a metallic glass can be described as the sum of two parts:[9]

$$Q^{-1} = Q_1^{-1} + Q_2^{-1} \qquad [1]$$

where Q_1^{-1} and Q_2^{-1} are associated with DF defects and SSF defects, respectively. The value of Q_2^{-1} will increase with increase in temperature during isochronal annealing, because SSF defects are not annealed out during structural relaxation.[15] On the other hand, because the number of DF defects activated in the bulk per unit time should be larger than that of the DF defects annihilated, Q_1^{-1} increases as temperature rises when the temperature is not very high. Thus, Q^{-1} increases noticeably during structural relaxation with increasing temperature in the range of 420 to 520 K.
(3) There is a shoulder from 520 to 630 K. The exotherm is not observed for the as-received specimen heated to this range of temperature according to DSC measurement (Figure 2). Differential scanning calorimetry data show that the peak temperature and onset temperature of the exothermic peak for the state quenched at 540 K are nearly the same as those for the as-received state. Moreover, the exothermic enthalpies for the former and latter cases are 6.59 and 6.65 KJ/mol, respectively, and both are nearly the same. Therefore, the amorphous state still remains in this temperature range.
(4) The IF curve has a point of inflection at about 640 K (which is within the first exothermic peak). Some authors reported that it corresponds to the phenomena associated with either the glass transition or a precrystallization stage.[10,16,17] In our experiment, the XRD pattern of the specimen quenched at 640 K produces two very weak crystalline peaks corresponding to a Ti-rich phase of $CuTi_2$ or $CuTi_3$ (the three strongest lines of both phases are totally overlapping). The DSC curve for the specimen quenched at 640 K shows that the first exothermic peak has disappeared and the exothermic enthalpy ΔH decreases to 5.27 KJ/mol. Based on the above experimental facts, it can be concluded that at the point of inflection for Q^{-1}, the amorphous matrix has partly changed and a small amount of a Ti-rich crystalline phase has formed.
(5) The IF increases sharply above 640 K and exhibits an internal peak during 640 to 780 K. The peak has a maximum at about 698 K, which is nearly identical with the temperature of the second exothermic peak on the DSC curve for the as-received specimen. It is evident that the crystallization of the glass takes place generally in the temperature range of the IF peak, and the origin of the IF peak is directly related to the transformation. It first increases and then decreases with temperature during the crystallization of glassy matrix. Hence, the IF peak depends on the rate of transformation from amorphous to crystalline state. In this stage, the IF of the metallic glass is composed of contribution from both glassy and crystalline states and can be expressed in the form of[18]

$$Q^{-1} = (1 - X)Q_{g-1} + XQ_c^{-1} \qquad [2]$$

where Q_g^{-1} and Q_c^{-1} are the IF of the glassy state and crystalline state, respectively, and X is the fraction of transformation. This expression implies that the high-temperature peak results from the softening of the glass matrix (decrease of viscosity) and crystallization (increase of viscosity) near T_g and T_x. The IFs for the crystalline and glassy states both increase monotonically with the increase of temperature on heating, but the IF of the crystalline materials is, as a rule, lower than that of the glassy matrix. The increase of X leads to the appearance of a maximum during crystallization. In brief, the IF peak is due to the steep increase of Q_g^{-1} in the region of T_g and a gradual increase of Q_c^{-1} after the onset of crystallization and attains a maximum at a specified fraction of the transformation.

The crystallization behavior and products corresponding to Q^{-1} peak can be identified based on the DSC, XRD, and TEM analyses. The XRD pattern indicates that besides a Ti-rich phase occurring at 640 K, CuTi also occurs for the glass heated to 690 K. With the rise of temperature, the crystalline peaks corresponding to CuTi and Ti-rich phase increase both in number and intensity. Because of the overlapping of the three strongest lines of $CuTi_2$ and $CuTi_3$, it is very difficult to identify which phase exists. According to the TEM observation for the specimen heated to 780 K, two kinds of stable phases can be identified as (Figure 4): CuTi phase (tetragonal, $a_0 = 0.3108$ nm, $c_0 = 0.5887$ nm) and $CuTi_2$ phase (tetragonal $a_0 = 0.29438$ nm, $c_0 = 1.07861$ nm). In addition, an I phase with tetragonal structure also can be detected. Using results from the XRD patterns, we find that a diffraction peak corresponding to the interplanar space $d = 0.178$ nm decays from strong to weak in the temperature range from 690 to 720 K and nearly vanishes at 780 K. It can be inferred that the I phase is the trace of an intermediate metastable phase which forms during the temperature range of the first exothermic peak of DSC curve and transforms to final stable phase with the increase of heating temperature. It does not vanish completely, because the time is not long enough for this transition. This is similar to the formation of metastable phase of $Cu_{60}Ti_{40}$ glass, but the latter has body-centered cubic structure.[19] Details about the metastable phase will be reported in another article.

On the whole, the $CuTi_2$ and metastable phase I first precipitate near the point of inflection of the IF spectrum, which corresponds to the first exothermic peak of the DSC curve. In the IF peak, which corresponds to the temperature of the second exothermic DSC peak, CuTi forms universally, and metastable phase I transforms to

Table I. Analysis of Crystalline Phases by X-Ray Diffraction

XRD Data Samples Quenched at Chosen Temperature								X-Ray Data from ASTM Cards Crystalline Phase					
640 K		690 K		720 K		780 K			B (CuTi)		A ($CuTi_2$)		
d	*I*	*d*	*I*	*d*	*I*	*d*	*I*	*d*	*I/Io*	*hkl*	*d*	*I/Io*	*hkl*
2.28	w	2.26	s	2.26	s	2.27	s				2.28	100	103
		2.19	s	2.20	s	2.20	s	2.19	60	110			
		2.15	s	2.14	s	2.15	s	2.13	100	102			
2.09	w	2.08	m	2.08	m	2.08	m				2.08	40	110
		2.06	w	2.06	w	2.06	w	2.05	5	111			
		1.78	m	1.78	m								
		1.54	m	1.54	m	1.56	w	1.56	25	200			
						1.48	w	1.47	10	004			
1.25	m	1.25	m	1.26	m	1.26	m	1.26	40	212	1.24	10	213

Notes: *d* = interplanar spacing, *I* = estimated intensities of XRD lines (w = weak, m = medium, s = strong), *I/Io* = relative intensities.

a stable phase with the rise of temperature. The final stable phases are mainly CuTi and a little $CuTi_2$. This interpretation corresponds to results of other authors.[20,21] The crystallization process of the metallic glass $Cu_{45}Ti_{55}$, therefore, can be expressed as follows:

$$\text{Amorphous} \rightarrow CuTi_2 + I \rightarrow CuTi + CuTi_2$$

(6) The XRD analysis of crystallization phase structure of $Cu_{45}Ti_{55}$ and ASTM data are given in Table I. Two crystallization phases, CuTi and $CuTi_2$, and one metastable phase have been identified.

V. CONCLUSIONS

1. The IF of metallic glass $Cu_{45}Ti_{55}$ is related to structural change of the amorphous alloy. Hence, the IF peak at 710 K is attributed to the transition of an amorphous state to crystalline.
2. The crystallization behavior of metallic glass $Cu_{45}Ti_{55}$ can be effectively expressed by IF and thermal analysis, which are complementary in studying structure change of metallic glass during heating.
3. Combining IF measurement with DSC and TEM analyses, it can be concluded that $CuTi_2$ and metastable phase I first precipitate from the glass matrix near the point of inflection for the IF curve, so that the first crystallization products are $CuTi_2$ and I phase. The CuTi phase forms at the temperature of the IF peak, which is near the end of the first exotherm and the beginning of the second exotherm on the DSC curve. As the heating temperature increases, metastable phase I vanishes, and the final stable phases are CuTi and $CuTi_2$. Therefore, the crystallization process of metallic glass $Cu_{45}Ti_{55}$ can be expressed as follows:

$$\text{Amorphous} \rightarrow CuTi_2 + I \rightarrow CuTi + CuTi_2$$

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