Thermochimica Acta, 217 (1993) 115–121
Elsevier Science Publishers B.V., Amsterdam

A kinetic study of continuous heating crystallization in $Cu_{0.08}Ge_{0.18}Te_{0.74}$ chalcogenide glass

M. Casas-Ruiz [a,*] R.A. Ligero [a], J. Vázquez [b] and R. Jiménez-Garay [b]
[a] *Escuela Superior de la Marina Civil, Universidad de Cádiz, Cádiz (Spain)*
[b] *Facultad de Ciencias, Universidad de Cádiz, Cádiz (Spain)*

(Received 5 August 1992)

Abstract

The $Cu_{0.08}Ge_{0.18}Te_{0.74}$ bulk glass was prepared by the melt quenching technique. Differential thermal analyses were performed at different heating rates. Crystallization occurs in two stages at peak temperatures of 484.8 and 492.8 K (at 8 K min^{-1}), with enthalpies $\Delta H_1 = 0.19$ and $\Delta H_2 = 0.10$ kJ mol^{-1}. The crystallization mechanism was examined through analysis of the data under non-isothermal conditions and the activation energies for crystal growth were also evaluated. The results indicate that surface nucleation occurs in the first stage, and bulk nucleation with three-dimensional growth dominates in the second. The values of the activation energies obtained by this method and by the Kissinger method have been compared and it has been observed that the values obtained are in agreement only when the quotient $m/n = 1$.

INTRODUCTION

Chalcogenide glasses are a class of materials that are easily produced in the amorphous state by the technique of melt quenching; they exhibit many useful properties.

The crystallization kinetics of amorphous alloys have been intensively studied using the Johnson–Mehl–Avrami–Erofeev theoretical model [1–5] which, although developed for isothermal processes, can be applied, under certain conditions, to continuous heating experiments [6].

Studies of kinetics are always connected with the concept of activation energy for crystallization, which is defined as the energy that must be reached by the atoms to transfer them from the amorphous state to the crystalline state. Crystallization phenomena are associated with nucleation and growth processes, and consequently, separate activation energies must be identified with the individual nucleation and growth steps in a transformation. However, they have usually been combined with an

---

[*] Corresponding author.

activation energy representative of the overall crystallization process [7–12].

The present work is concerned with the study of the crystallization kinetics and the evaluation of the activation energy for crystal growth for $Cu_{0.08}Ge_{0.18}Te_{0.74}$ chalcogenide glass by using the non-isothermal method proposed by Matusita and Sakka [13].

EXPERIMENTAL

Quenched samples were prepared by melting weighed amounts of the elements (5N purity) in evacuated, sealed quartz ampoules. The molten alloys were held at 1373 K for 72 hours in a rotary furnace to ensure homogeneity, and were subsequently quenched in liquid nitrogen. The amorphous state of the quenched sample was checked by X-ray diffraction, using a Siemens D500 automatic powder diffractometer.

The calorimetric measurements were carried out in a Rigaku Thermoflex DSC, using sample weights of about 20 mg, in aluminium pans which were crimped. An empty aluminium capsule was used as a reference.

The crystallizing experiments were carried out by continuous heating at rates of 2, 4, 8, 16 and 32 K min^{-1} and a filtered flow of inert gas was maintained at 60 ml min^{-1}. The instrument was calibrated using the melting peaks for the pure elements tin, indium and lead, supplied with the device.

THEORETICAL BACKGROUND

For non-isothermal crystallization, the volume fraction x of crystals precipitated in a glass heated at constant rate β is shown [13] to be related to the activation energy for crystal growth E through the expression.

$$\ln[-\ln(1-x)] = -n \ln \beta - 1.052\frac{mE}{RT} + \text{constant} \tag{1}$$

where n and m are constants having values between 1 and 4, depending on the morphology of the growth. The values of n and m for the various crystallization mechanisms are listed in Table 1. When nuclei formed during

TABLE 1

Values of n and m for various crystallization mechanisms

Mechanism	n	m
Bulk nucleation		
Three-dimensional growth	4	3
Two-dimensional growth	3	2
One-dimensional growth	2	1
Surface nucleation	1	1

the heating at constant rate are dominant, n is equal to $m+1$, and when nuclei formed during any previous heat treatment prior to thermal analysis are dominant, n is equal to m.

It is possible to evaluate $\ln[-\ln(1-x)]$ as a function of $\ln \beta$ at any fixed temperature. As indicated by the expression (1), n is obtained as the slope of the resulting straight line.

In order to obtain the activation energy, eq. (1) is rewritten as

$$\ln \beta = 1.052 \frac{m}{n} \frac{E}{RT} - \frac{1}{n} \ln[-\ln(1-x)] + \text{constant} \tag{2}$$

Thus the plot $\ln \beta$ against $1/T$, where T is the temperature at which the crystal volume fraction reaches a specific value, gives a straight line and the slope supplies the value of $1.052\, mE/nR$.

The activation energy can be obtained when the ratio m/n is known. One way for determining m/n is to observe the change of n with the annealing. If n does not change with the previous heat treatment, a large number of nuclei exist already in the as-quenched glass and $n = m$. If n decreases with the reheating, the nuclei are produced in the prior heat treatment and $n = m + 1$ before reheating, and $n = m$ after reheating.

RESULTS AND DISCUSSION

Figure 1 shows the DSC dynamic scan obtained by continuous heating at a rate of 8 K min^{-1} under a dry He atmosphere, for a sample of 20.3 mg of

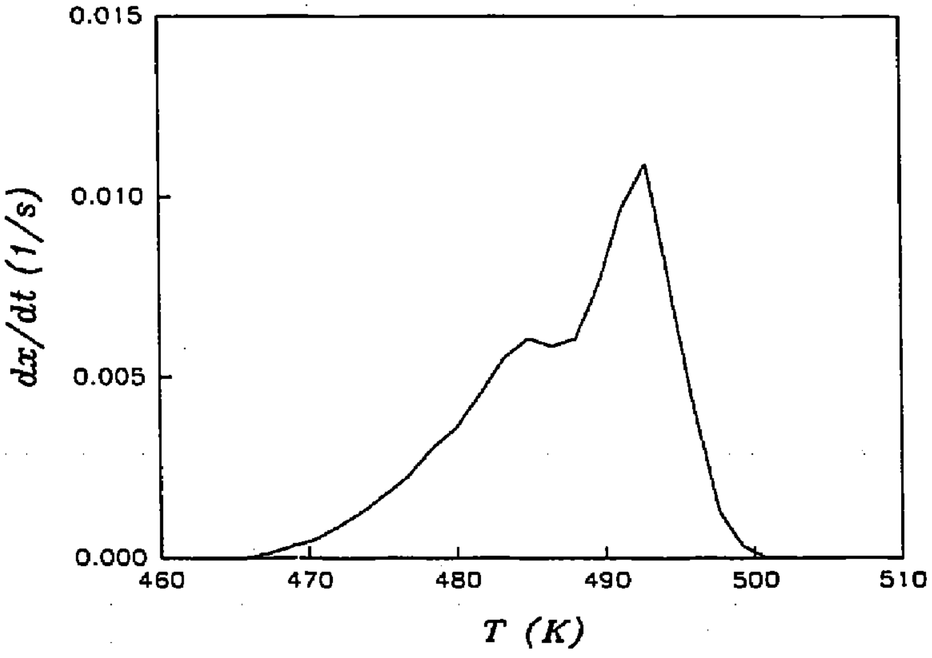

Fig. 1. DSC record, at a heating rate of 8 K min^{-1}, showing the two unresolved exotherms.

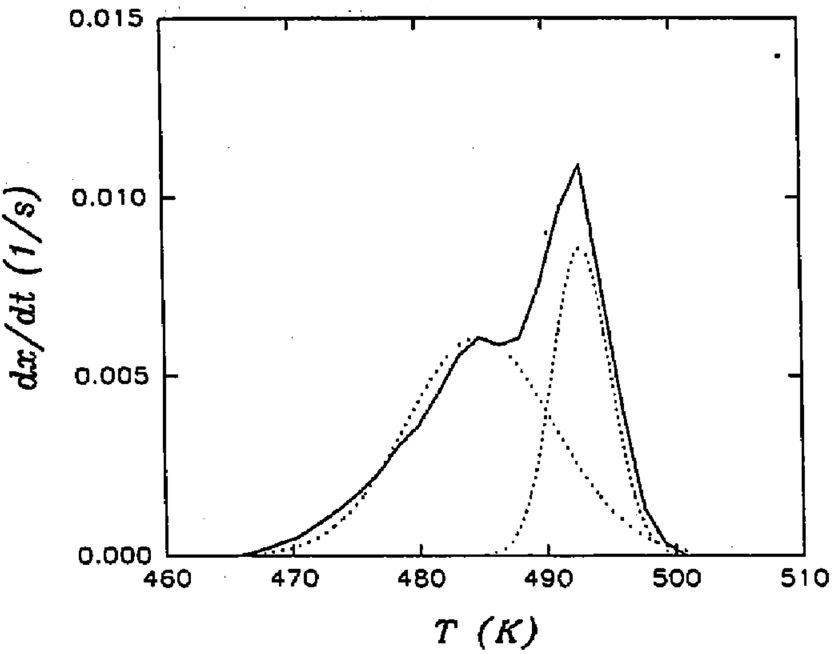

Fig. 2. Theoretical overlapping peaks resolution at a heating rate of 8 K min^{-1}.

as-quenched alloy. The DSC record exhibits two unresolved exotherms. In order to resolve the overlapping peaks, a numerical method developed by Ligero et al. [14] was used that provides two associated theoretical functions (ATF) which satisfactorily describe both crystallization reactions. Figure 2 shows the experimental DSC curves superimposed on the ATF given by the said method for a heating rate of 8 K min^{-1}. The crystallization kinetics are studied taking the data derived from the mentioned ATF as the experimental data.

Crystallization proceeds by at least two steps as revealed by the two exotherms occurring at peak temperatures as shown in Table 2 for the different heating rates. The averaged enthalpies of transformation derived from the areas under the exotherm are 0.19 and 0.10 kJ mol^{-1} respectively.

Figure 3 shows the relation between $\ln[-\ln(1-x)]$ and $\ln\beta$ for

TABLE 2

Peak temperature T_p (K) at different heating rates

β (K min^{-1})	Stage 1	Stage 2
2	477.5	485.5
4	480.9	487.7
8	484.8	492.8
16	490.0	496.4
32	496.2	502.6

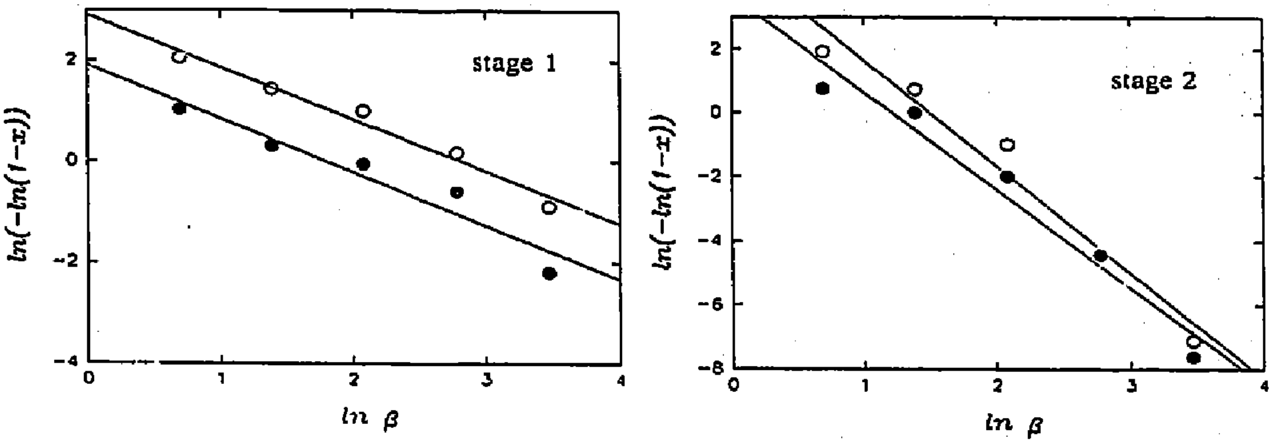

Fig. 3. Plot of $\ln[-\ln(1-x)]$ versus $\ln\beta$ for as-quenched (○) and reheated (●) samples.

as-quenched glass and reheated glass at 453 K during 20 minutes. According to eqn. (1), the slope of these lines gives the n value. The values of n are found to be about one for the first stage and about four for the second (see Table 3). It can be observed that the heat treatment only affects the second stage, therefore n can be taken to be equal to $m+1$ [13, 15], giving m a value of about three for the second stage. The values of m and n are shown in Table 4. From the results, it can be concluded that for the first stage, surface nucleation dominates, while for second stage, bulk nucleation with three-dimensional growth of crystals is very likely.

TABLE 3

Data on n for as-quenched and reheated samples

	As-quenched	Reheated at 453 K
Stage 1	1.03	1.07
Stage 2	4.16	3.21

Figure 4 shows the relation between $\ln\beta$ and the reciprocal temperature; the slope of these lines should give the activation energies for crystal growth in each stage. The activation energies thus obtained are shown in Table 4.

TABLE 4

Data on n, m and E for each crystallization stage

	Stage 1	Stage 2
n	1.03	4.16
m	1.03	3.16
E (kJ mol^{-1})	275.5	358.6

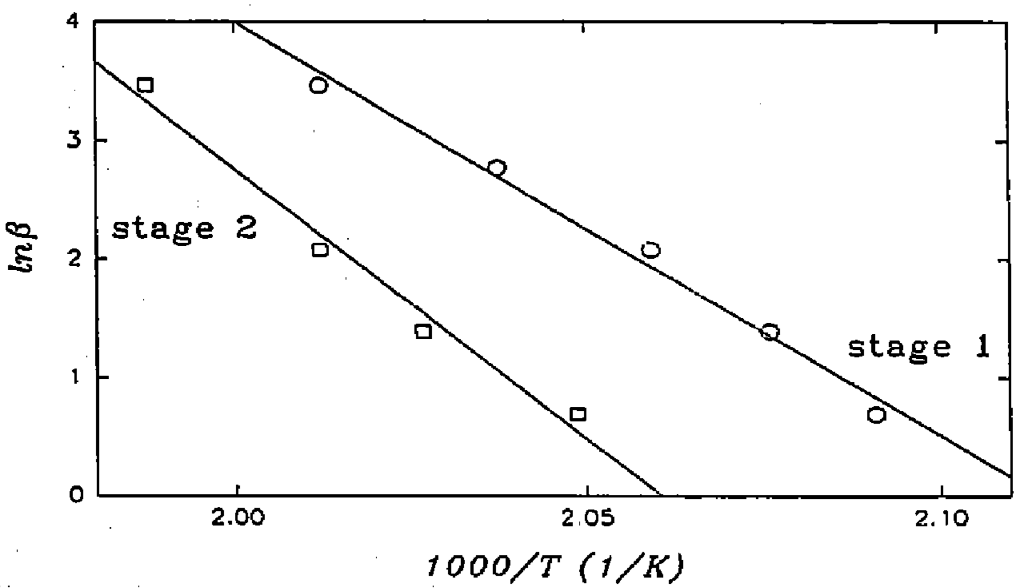

Fig. 4. Plot of ln β versus 1000/T; stage 1, ○; stage 2, □.

The activation energies of the overall crystallization events E_c where determined by Kissinger's peak shift method [7] and the values obtained were 281.3 kJ mol^{-1} for the first stage and 311.0 kJ mol^{-1} for the second crystallization stage.

It can be observed that the activation energy E_c obtained by Kissinger's method and the activation energy for crystal growth E, differ by only about 2% in the first stage of the crystallization, whereas they differ by about 13% in the second. This confirms that the activation energies obtained by methods derived from JMA equation only give reasonable results in those cases where $m/n = 1$ [13, 15].

Although it might be expected that E (activation energy for the crystal growth) would be less than E_c (activation energy for the overall crystallization process), for the purpose of this alloy, the value obtained for n corresponding to the first peak indicates that the annealing did not cause the appearance of nuclei, but that the as-quenched material already contains a sufficient number, so that both energies can be mutually identified because the crystallization process is basically a growth of the pre-existing nuclei. It is not possible to follow a similar argument for the crystallization representing the second peak because, in accordance with the reasoning outlined in the previous paragraph, it is not possible to derive a reliable value for the activation energy associated with global process, to which the value obtained for E can be compared. Taking as a basic the values obtained for the parameters m and n, it can be stated, nevertheless, that the thermal treatment has provoked, in the case of the second peak, an increase in the density of the pre-existing nuclei by which the change in the parameter n can be explained.

ACKNOWLEDGEMENTS

The authors thank Dr. A.R. Bocanegra for his generous assistance in the English translation of this study. This work is supported by CICYT (Comisión Interministerial de Ciencia y Tecnología), Project No. PB 88/0463.

REFERENCES

1 M. Avrami, J. Phys. Chem., 7 (1939) 1103.
2 M. Avrami, J. Phys. Chem., 8 (1940) 212.
3 M. Avrami, J. Phys. Chem., 9 (1941) 177.
4 W.A. Johnson and R.F. Mehl, Trans. Am. Inst. Min. Met. Eng., 135 (1939) 416.
5 B.V. Erofeev, Dokl. Akad. Nauk USSR, 52 (1946) 515.
6 D.W. Henderson, J. Non-Cryst. Solids, 30 (1979) 301.
7 H.E. Kissinger, J. Res. Natl. Bur. Stand., 57 (1956) 217.
8 Y.Q. Gao and W. Wang, J. Non-Cryst. Solids, 81 (1986) 129.
9 Y.Q. Gao, W. Wang, F.Q. Zheng and X. Liu, J. Non-Cryst. Solids, 81 (1986) 135.
10 E.I. Marseglia, J. Non-Cryst. Solids, 41 (1980) 31.
11 J.A. Augis and J.E. Bennet, J. Therm. Anal., 13 (1978) 283.
12 R.A. Ligero, J. Vázquez, P. Villares and R. Jiménez-Garay, Mater. Lett., 8 (1989) 6.
13 K. Matusita, K. Komatsu and R. Yokota, J. Mater. Sci., 19 (1984) 291.
14 R.A. Ligero, J. Vázquez, P. Villares and R. Jiménez-Garay, J. Non-Cryst. Solids, 124 (1990) 63.
15 S. Mahadevan, A. Giridhar and A.K. Singh, J. Non-Cryst. Solids, 88 (1986) 11.