

CRYSTAL NUCLEATION IN AMORPHOUS (Au_{100-y}Cu_y)₇₇Si₉Ge₁₄ ALLOYS

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Abstract—Melt-spun alloys of the series (Au_{100-y}Cu_y)₇₇Si₉Ge₁₄ are found to be amorphous for $y \leq 37.5$ and partially or fully crystalline for $y = 50$ and $y = 75$. Because, unlike most metallic glasses, these alloys exhibit well separated glass transition and kinetic crystallization temperatures, crystallization can be studied in the fully relaxed amorphous phase. Isothermal calorimetric analysis of the devitrification kinetics of the amorphous alloys indicates sporadic nucleation and a constant growth rate. A steady state nucleation frequency is established after a transient period, except for the $y = 37.5$ alloy, where the kinetics are dominated by growth on quenched-in nuclei. In the $y \leq 25$ alloys, we find that the classical theory of homogeneous nucleation is consistent with the observations, including transient effects. The analysis of the crystallization kinetics indicates that slow crystal growth rates play an important role in glass formation in these alloys. As the copper content of the alloys is increased, the reduced glass transition temperature increases, but, surprisingly, glass formation is more difficult at high copper contents. This is interpreted to be a consequence of a different nucleus composition.

Résumé—Nous avons trouvé que des alliages centrifugés de la série (Au_{100-y}Cu_y)₇₇Si₉Ge₁₄ sont amorphes pour $y \leq 37,5$ et partiellement ou totalement cristallisés pour $y = 50$ et $y = 75$. Contrairement à la plupart des verres métalliques, ces alliages présentent des températures de transition vitreuse et de cristallisation cinétique bien séparées, de sorte que l'on peut étudier la recristallisation de la phase amorphe totalement relaxée. L'analyse calorimétrique isotherme de la cinétique de dévitrification des alliages amorphes indique une germination sporadique et une vitesse de croissance constante. Une fréquence de germination stationnaire s'établit après une période transitoire, sauf pour l'alliage $y = 37,5$ où la cinétique est dominée par la croissance de germes trempés. Dans les alliages où $y \leq 25$, la théorie classique de la germination homogène est compatible avec les observations, y compris celles des effets transitoires. L'analyse de la cinétique de cristallisation montre que les vitesses de croissance cristalline lentes jouent un rôle important dans la formation du verre dans ces alliages. Lorsqu'on augmente le teneur en cuivre des alliages, la température réduite de la transition vitreuse augmente, mais la formation du verre est plus difficile pour les fortes teneurs en cuivre, ce qui est surprenant. Nous interprétons ce fait comme la conséquence d'une composition différente du germe.

Zusammenfassung—Spritzgekühlte Legierungen der Serie (Au_{100-y}Cu_y)₇₇Si₉Ge₁₄ sind für $y \leq 37,5$ amorph und bei $y = 50$ und 75 zum Teil oder vollständig kristallin. Weil diese Legierungen entgegen den meisten Metallgläsern deutlich getrennte Temperaturen für den Glasübergang und die kinetische Kristallisation aufweisen, kann die Kristallisation in der vollständig relaxierten amorphen Phase studiert werden. Die Analyse der Entglasungskinetik der amorphen Legierung mit isothermer Kalorimetrie deutet eine sporadische Keimbildung und eine konstante Wachstumsgeschwindigkeit an. Nach einer Übergangsperiode stellt sich eine stationäre Keimbildungsfrequenz ein; Ausnahme ist die Zusammensetzung $y = 37,5$, wo die Kinetik durch Wachstum an eingeschreckten Keimen bestimmt ist. Das Verhalten der Legierungen mit $y \leq 25$ ist verträglich mit der klassischen Theorie der homogenen Keimbildung einschließlich der Übergangserscheinungen. Die Auswertung der Kristallisationskinetik zeigt, daß kleine Kristallwachstumsraten in diesen Legierungen eine große Rolle bei der Glasbildung spielen. Wird der Kupfergehalt der Legierung erhöht, dann nimmt die reduzierte Glasübergangstemperatur zu. Überraschenderweise ist bei hohen Kupfergehalten die Glasbildung jedoch schwieriger. Dieser Befund wird auf eine andere Zusammensetzung der Keime zurückgeführt.

1. INTRODUCTION

In forming metallic glasses by cooling molten alloys, it is necessary that crystal nucleation be avoided, or that the extent of crystal growth be insignificant. To gain a better understanding of glass formation, it is

useful to examine crystal nucleation in the under-cooled liquid. This can be done in two ways: (1) by observing crystallization on cooling the melt, as in small droplet experiments [1–3]; or (2) by observing crystallization on heating the glass (i.e. *devitrification*). The minimum requirement for glass formation is that *homogeneous* nucleation occur at sufficiently low rates. To observe homogeneous nucleation kinetics in small droplet experiments, it is necessary to avoid heterogeneous nucleation at the

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droplet surface; this condition is not easily met. Although heterogeneous nucleation may also occur in devitrification, the nucleation kinetics are more easily analyzed, because crystal growth rates are much slower.

A number of researchers have examined devitrification kinetics in metallic glasses [e.g. 4–7]. It is found that crystallization occurs close to the glass transition temperature, T_g . In metallic glasses it is known that structural relaxation occurs on annealing below T_g and that it causes substantial reductions in atomic transport rates (e.g. diffusion and creep) [8, 9]. This is a problem in the analysis of crystallization kinetics because nucleation and growth rates are then dependent not only on temperature but also on thermal history. Above T_g the glasses are fully relaxed, i.e. they have the equilibrium liquid structure, and the transport rates are dependent only on temperature. In calorimetric studies, when the temperature is increased linearly with time, the thermal effects of the glass transition (at T_g) and devitrification (at the kinetic crystallization temperature, T_{kc}) may overlap and be difficult to interpret. It is important, therefore, to study a system in which devitrification occurs at a temperature substantially above T_g and can be observed independently of the glass transition.

We have made alloys of composition $(\text{Au}_{100-y}\text{Cu}_y)_{77}\text{Si}_9\text{Ge}_{14}$ and have calorimetrically observed crystallization in glasses prepared by rapid quenching. We chose $\text{Au}_{77}\text{Si}_9\text{Ge}_{14}$ as the initial alloy, because its transition temperatures are in a convenient range for observation and because of the availability of thermal and viscosity data [10, 11]. Chen and Park [12] have shown that adding small amounts of Cu to $\text{Pd}_{83.4}\text{Si}_{16.6}$ increased T_g and T_{kc} , as well as $T_{kc} - T_g$. We found a similar but much stronger effect of Cu addition on $\text{Au}_{77}\text{Si}_9\text{Ge}_{14}$. After X-ray examination of the as-quenched glasses, samples were heated in a calorimeter to determine T_g and T_{kc} . From the shape of crystallization peaks, obtained both isothermally and at various scan rates, the mode of nucleation in the viscous liquid was determined.

2. MATERIALS PREPARATION AND CHARACTERIZATION

Alloys of composition $(\text{Au}_{100-y}\text{Cu}_y)_{77}\text{Si}_9\text{Ge}_{14}$ (at.%) with $y = 10, 15, 20, 25, 30, 37.5, 50$ and 75 were prepared by r.f. melting in an argon atmosphere and quenched, in bulk, into ice water. Glassy ribbons were then made by melt spinning on to an aluminum disk, 20 cm in diameter, rotating at 2500 rpm. The ribbons had a width of ~ 1 mm and a thickness of ~ 20 μm . The disk speed, ejection pressure, nozzle diameter, initial liquid temperature and the distance of the nozzle from the disk were kept constant in order to minimize differences in quench rate. The alloys were usually quenched in air, but a $y = 37.5$

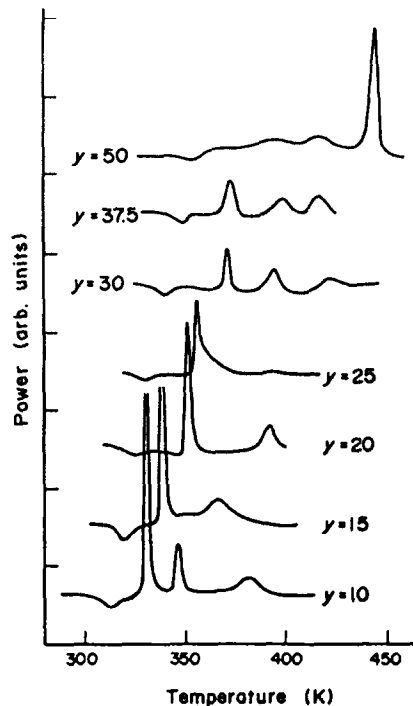


Fig. 1. Differential scanning calorimetry output on heating at 20 K min^{-1} through the glass transition and devitrification temperature ranges of $(\text{Au}_{100-y}\text{Cu}_y)_{77}\text{Si}_9\text{Ge}_{14}$ glasses.

alloy was also quenched in argon to test the effect of the presence of oxygen.

Information on the structural state of the samples was obtained by X-ray diffraction using a Debye-Scherrer camera with $\text{CuK}\alpha$ radiation. The alloys with $y \leq 37.5$ showed no evidence of crystallinity as quenched. The $y = 50$ alloy contained both crystalline and amorphous phases and the $y = 75$ alloy was fully microcrystalline as quenched. X-ray diffraction was also performed on the glasses at various stages of thermal treatment. Transmission electron microscopy was carried out in a JEM 120 operating at 80 kV.

Differential scanning calorimetry (DSC) was performed in a Perkin-Elmer DSC-II instrument. The samples, of mass ~ 2 mg, were under a flowing argon atmosphere. In addition to monitoring thermal effects the DSC was used for precise annealing treatments.

3. TRANSFORMATIONS ON HEATING

Typical DSC scans for the seven glassy compositions are shown in Fig. 1. The heating rate in each case was 20 K min^{-1} . A striking feature of these glasses is the large endothermic peak associated with the glass transition. Chen [10] has observed a similar feature in $\text{Au}_{77}\text{Si}_9\text{Ge}_{14}$. In general, the size of the endothermic peak near T_g is known to increase with the degree of structural relaxation of a glass [13]. It is customary to take the low temperature inflection

Table 1. Values for transition temperatures (in K) in $(\text{Au}_{100-y}\text{Cu}_y)_{77}\text{Si}_9\text{Ge}_{14}$ glasses, determined using DSC with a heating rate of 20 K min^{-1}

y	T_g	T_{kc}	T_p	T_s	T_l	$T_p - T_g$	$T_{r,g}$
0 [10]	300.0	—	308.0	606.0	625.0	8.0	0.480
10.0	313.0	320.0	330.5	606.0	624.0	17.5	0.502
15.0	320.0	335.0	338.5	606.0	623.0	18.5	0.514
20.0	324.0	346.8	350.9	605.0	622.0	26.9	0.521
25.0	329.5	350.5	355.3	608.0	627.0	25.8	0.526
30.0	340.5	363.1	370.9	607.0	632.0	30.4	0.539
37.5	347.5	367.0	372.5	607.0	644.0	25.0	0.540
50.0	344.5	—	424.5	634.0	682.0	80.0	0.505

point of the peak as T_p . However, this temperature will vary substantially with the degree of relaxation, especially in the glasses discussed here. Therefore, for the purpose of comparison, values of T_g were determined as the peak temperature in 20 K min^{-1} scans. These values are given in Table 1.

The crystallization behavior on heating was characterized by measuring the onset temperature of the first exothermic peak, T_{kc} and the peak maximum, T_p , which can be determined more precisely. These values, as determined in 20 K min^{-1} scans, may be found in Table 1. T_{kc} is called the *kinetic* crystallization temperature to emphasize that the temperature at which significant crystallization is measured depends on the time scale of the experiment.

Also given in Table 1 are the solidus, T_s , and liquidus, T_l , temperatures as determined from 20 K min^{-1} heating scans. Values of $T_p - T_g$ and the

reduced glass transition temperature $T_{r,g} = T_g/T_l$ are shown both in Table 1 and in Fig. 2. Note that for $y \leq 37.5$ alloys, $T_{r,g}$ continuously increases with copper content. Turnbull [14] and Spaepen and Turnbull [15] have suggested, using steady state nucleation theory, that the ease of glass formation should increase with increasing $T_{r,g}$. In agreement with this prediction, common metallic glass-formers do have unusually high $T_{r,g}$ values (0.45–0.6) [16].

It is noteworthy that in the present alloys, particularly with higher Cu contents, the glass transition and the temperature of rapid crystallization are well separated. A sample of the $y = 15$ alloy was heated to T_g at 20 K min^{-1} , held for 1 min and cooled at 320 K min^{-1} . On subsequent reheating, the first exothermic peak was unchanged in position and shape from that observed in alloys that were heated without the brief anneal at T_g . This indicates [6] that very little or no crystallization occurred during the prior heating. Therefore, the observations of crystallization are made in the fully relaxed liquid state.

In all alloy compositions, there is more than one exothermic DSC peak. In the scans of $y \geq 30$ alloys there are three distinct peaks. In the lower copper content alloys the first and second exothermic peaks overlap in a 20 K min^{-1} scan. Samples of all alloys were heated at 320 K min^{-1} to temperatures just above the first peaks. They were held at these temperatures for 1 min and then cooled to room temperature at 320 K min^{-1} . These samples were then examined by X-ray diffraction and found to be completely microcrystalline. This was confirmed by transmission electron microscopy (TEM) of a sample of the $y = 37.5$ alloy. Figure 3 shows an electron micrograph and corresponding selected area diffraction pattern, for the $y = 37.5$ alloy after heating to 380 K. Note that the diffraction pattern indicates that the microcrystals are randomly oriented, suggesting that they nucleated sporadically throughout the sample. Peak broadening due to the small grain size prevented phase identification by either electron or X-ray diffraction. Alloys heated through the higher temperature DSC peaks gave X-ray diffraction patterns indicating that retransformation to a new coarse-grained structure had occurred. In the alloys where the crystallization peak and the second exothermic peak overlap in scans, the peaks are more isolated in isothermal transformation. In all cases, the first exothermic peak is attributed to complete crystallization to a microcrystalline structure.

A glass of $(\text{Au}_{62.5}\text{Cu}_{37.5})_{77}\text{Si}_9\text{Ge}_{14}$ was made by quenching in a different apparatus under an argon atmosphere instead of air. Only small changes in transition temperatures, peak shapes or relative peak sizes were found. This result suggests that the presence of oxygen during the quench does not play an important role in the formation of the glass or in the crystallization kinetics.

In all the work previously described, the atomic percentages of silicon and germanium were kept

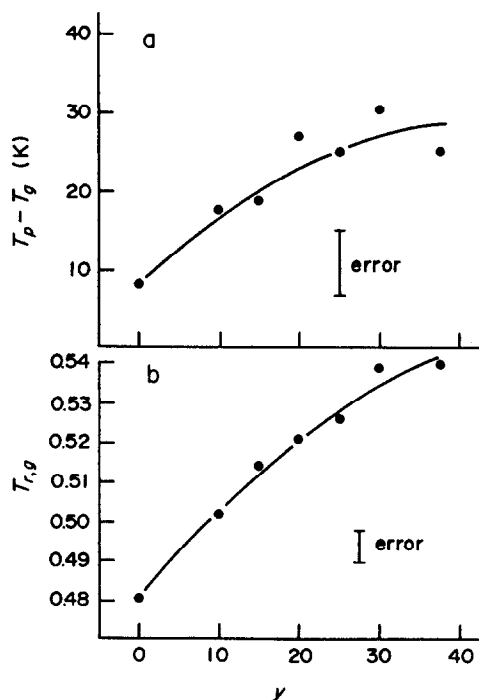


Fig. 2. (a) The difference between the temperature at the maximum in the crystallization peak, T_p , and the glass transition temperature, T_g , as a function of y for $(\text{Au}_{100-y}\text{Cu}_y)_{77}\text{Si}_9\text{Ge}_{14}$ glasses. (b) The reduced glass transition temperature, $T_{r,g}$, as a function of y .

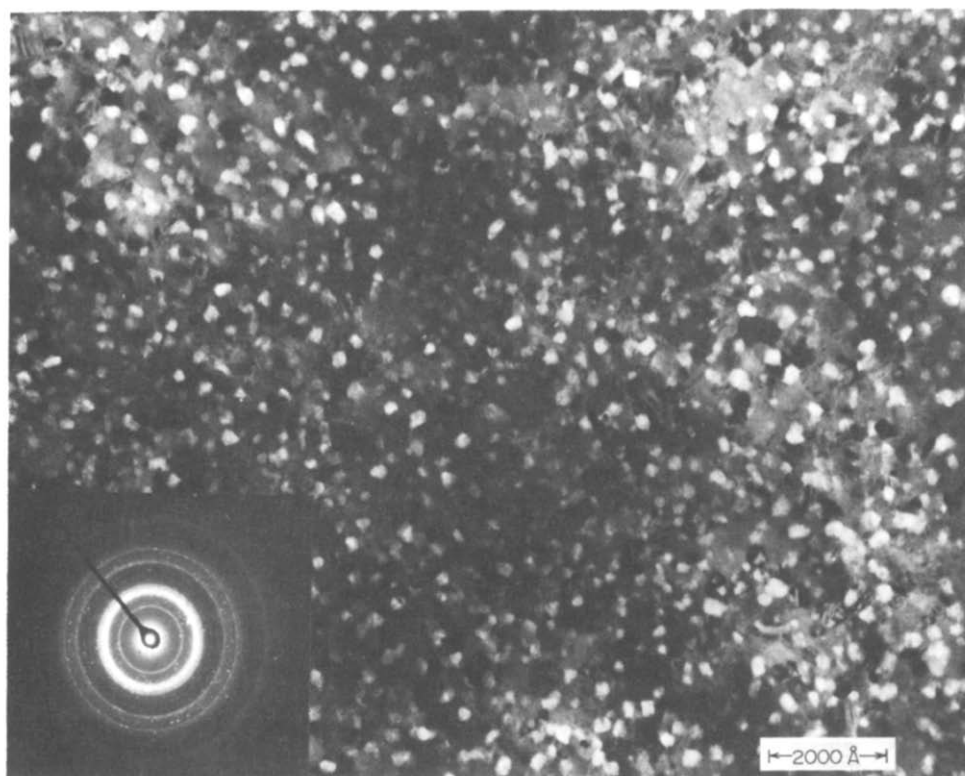


Fig. 3. A transmission electron microscopy bright field image of $(\text{Au}_{62.5}\text{Cu}_{37.5})_{77}\text{Si}_9\text{Ge}_{14}$ after heating to 380 K and the corresponding selected area diffraction pattern.

constant. A glassy alloy of $(\text{Au}_{62.5}\text{Cu}_{37.5})_{77}\text{Si}_6\text{Ge}_{17}$ was also prepared. A 20 K min^{-1} DSC scan for this alloy is shown in Fig. 4. Note that the apparent values of T_g (333 K) and $T_p - T_g$ (16 K) were significantly lower than for the $(\text{Au}_{62.5}\text{Cu}_{37.5})_{77}\text{Si}_9\text{Ge}_{14}$ glass. Chen [11] has measured T_g for glasses of composition $\text{Au}_{81.4}\text{Si}_{18.6-z}\text{Ge}_z$ for $z = 0$ to 18.6 and finds that T_g changes by no more than 12 K. This suggests that Cu-Si interactions play an important role in the stabilization of the $(\text{Au}_{100-y}\text{Cu}_y)_{77}\text{Si}_9\text{Ge}_{14}$ glasses.

4. KINETICS OF DEVITRIFICATION

4.1. Linear heating analysis

An effective activation energy for the devitrification reaction was obtained using the Kiss-

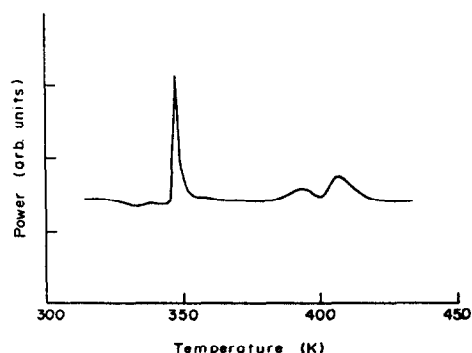


Fig. 4. Differential scanning calorimetry output on heating $(\text{Au}_{62.5}\text{Cu}_{37.5})_{77}\text{Si}_6\text{Ge}_{17}$ glass at 20 K min^{-1} .

inger technique [17]. In the DSC the crystallization peak temperature, T_p , was measured at selected heating rates, H . It should be noted that the values of T_p have to be corrected for thermal lags in the DSC. The lag increases by about 1 K for a 10 K min^{-1} increase in H [6]. A plot of $\ln(H/T_p^2)$ vs $1/T_p$ should give a straight line of gradient Q_T^*/k , where Q_T^* is the effective activation energy for the total transformation and k is Boltzmann's constant. Although the Kissinger analysis was not originally devised for solid-state transformations, Henderson [18] has shown that it is applicable. An example of a Kissinger plot is shown in Fig. 5, which is for the $y = 15$ alloy.

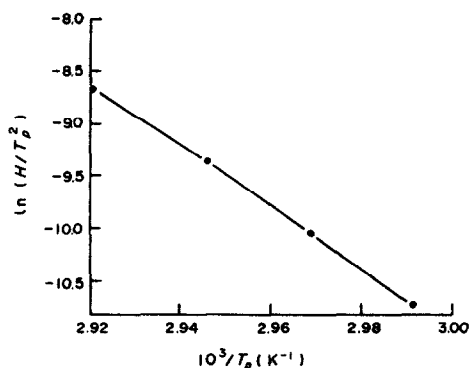


Fig. 5. A Kissinger plot from the variation of the temperature corresponding to the maximum of the crystallization peak, T_p , as a function of scan rate, H , in $(\text{Au}_{85}\text{Cu}_{15})_{77}\text{Si}_9\text{Ge}_{14}$.

Table 2. Measured crystallization peak temperatures at various scan rates, H , in $(\text{Au}_{100-y}\text{Cu}_y)_{77}\text{Si}_9\text{Ge}_{14}$

	H (K/min ⁻¹)	T_p (K)	Q_f^k (eV)		H (K/min ⁻¹)	T_p (K)	Q_f^k (eV)
$y = 10.0$	2.5	326.25	2.40	$y = 25.0$	2.5	350.65	2.99
	5.0	328.60			5.0	353.10	
	10.0	331.2			10.0	355.25	
	20.0	334.2			20.0	358.10	
$y = 15.0$	2.5	334.35	2.49	$y = 30.0$	2.5	359.05	2.35
	5.0	336.9			5.0	362.25	
	10.0	339.5			10.0	365.50	
	20.0	342.4			20.0	368.90	
$y = 20.0$	2.5	340.85	2.60	$y = 37.5$	2.5	365.75	2.71
	5.0	343.50			5.0	368.60	
	10.0	346.10			10.0	371.50	
	20.0	348.90			20.0	374.60	

For all the alloys, the values of T_p and H are given in Table 2. The activation energy, Q_f^k , varies with composition as shown in Fig. 6. The activation energy depends on the temperature dependences of the nucleation and growth rates and on any transient effects which they may exhibit. It is therefore difficult to interpret, but it is useful for comparing the stability of the glasses. It is seen in Fig. 6 that there is an abrupt change in Q_f^k between $y = 25$ and $y = 30$. This feature must arise from a change in the mode of crystallization. To obtain more information we performed isothermal experiments in the DSC.

4.2. Isothermal analysis

Samples of the various glasses were crystallized isothermally in the DSC. They were heated at 320 K min^{-1} to 10 K below their glass transition temperature, held for 1 min, then heated to the hold-temperature at 320 K min^{-1} . The pause at $T_g - 10 \text{ K}$ serves to reduce transient effects due to thermal lags in the DSC. The 325 K isothermal transformation curve for the $y = 15$ glass is shown in Fig. 7. The first and second exothermic peaks overlap, but they can be separated by making both peaks symmetric about their peak temperatures. Since the two symmetrical peaks add up to give the composite

trace, this procedure seems justified. The symmetrical first exothermic peak, shown by the dashed line, corresponds to crystallization. Peaks obtained at six temperatures are shown in Fig. 8. The mode of crystallization can be determined from the shape of these peaks using a technique based on the Johnson-Mehl-Avrami (JMA) analysis [19].

In the JMA analysis, which assumes a random dispersion of transformed regions, the volume fraction transformed, x , is given by

$$x = 1 - \exp(-x_{\text{ex}}) \quad (1)$$

where x_{ex} is the extended volume fraction transformed, i.e. the fraction that would be transformed if there were no impingement. If there is a fixed population of nuclei, N per unit volume and during an isothermal anneal crystals grow radially from these nuclei at a constant velocity, G , then x_{ex} is

$$x_{\text{ex}} = N \frac{4}{3} \pi G^3 t^3 \quad (2)$$

where t is the time of the anneal. If, on the other hand, there are no nuclei initially, but they appear at a constant rate, I per unit volume, then

$$x_{\text{ex}} = \int_0^t \frac{4}{3} \pi G^3 I (t - t')^3 dt' = \frac{\pi}{3} I G^3 t^4. \quad (3)$$

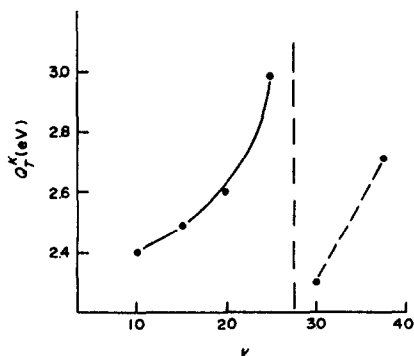


Fig. 6. Values of the total activation energy of crystallization as determined from the Kissinger analysis, Q_f^k , for $(\text{Au}_{100-y}\text{Cu}_y)_{77}\text{Si}_9\text{Ge}_{14}$ glasses.

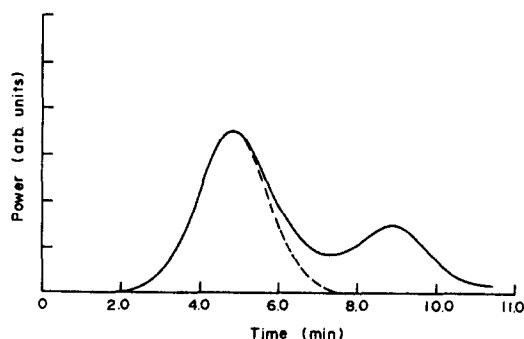


Fig. 7. Differential scanning calorimetry output for isothermal crystallization of $(\text{Au}_{85}\text{Cu}_{15})_{77}\text{Si}_9\text{Ge}_{14}$ glass at 325 K.

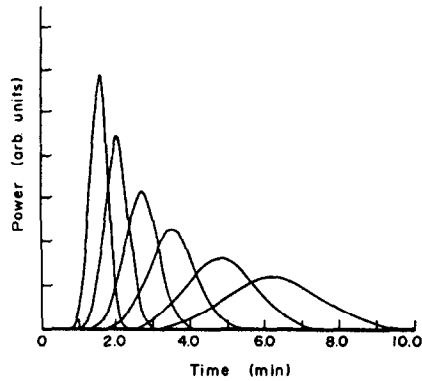


Fig. 8. Isothermal crystallization peaks for $(\text{Au}_{85}\text{Cu}_{15})_{77}\text{Si}_9\text{Ge}_{14}$ glass at the temperatures given in Table 3.

In either case, the transformation kinetics under isothermal conditions will be described by the JMA equation

$$x = 1 - \exp [-(Kt)^n] \quad (4)$$

or

$$\ln [-\ln (1-x)] = n \ln t + n \ln K \quad (5)$$

where K is a temperature-dependent kinetic parameter, and where the Avrami exponent, n , will be 3 for a constant number of nuclei and 4 for a constant nucleation rate. In devitrification, however, as found in studies on both oxide [20] and metallic [4] glasses, the nucleation rate may initially be zero and increase sigmoidally to a final, steady-state value. This transient nucleation behavior arises because it takes some time to establish the steady-state population of embryos of the product phase [19]. Once the steady-state nucleation rate, I_{ss} , is established, the concentration of nuclei, N , as a function of time, t , is given by

$$N = I_{ss}(t - \tau) \quad (6)$$

where τ is an *effective time lag* and is a measure of the "transient time" or "incubation period" [21]. The number of nuclei may be approximated by equation (6) for $t > \tau$ and $N = 0$ for $t \leq \tau$. With this approximation

$$x_{ex} = \int_{\tau}^t \frac{4}{3} \pi G^3 I_{ss} (t - t')^3 dt' = \frac{\pi}{3} G^3 I_{ss} (t - \tau)^4 \quad (7)$$

so that

$$\ln [-\ln (1-x)] = 4 \ln (t - \tau) + 4 \ln K. \quad (8)$$

Figure 9(a) shows $\ln [-\ln (1-x)]$ plotted against $\ln t$ for the 327 K isothermal crystallization peak of the $y = 15$ alloy. The resulting curve has a continuously decreasing slope. However, if an effective time lag is assumed, τ can be adjusted so that the curve becomes linear (Fig. 9b). The slope of this optimal line, as determined by a χ^2 test, is 4.0. This procedure was carried out for all the peaks in Fig. 8, yielding slopes in the range 4.0 ± 0.2 . Analysis of the

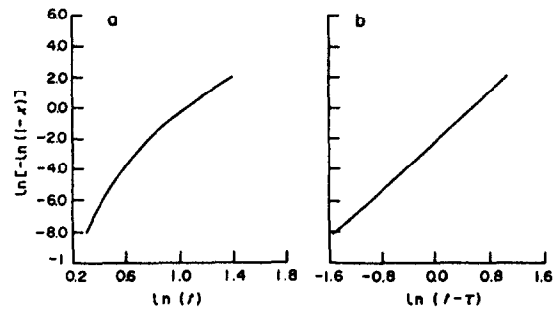


Fig. 9. Johnson-Mehl-Avrami analysis of the 327 K isothermal crystallization peak of $(\text{Au}_{85}\text{Cu}_{15})_{77}\text{Si}_9\text{Ge}_{14}$ glass. (a) The fraction crystallized, x , as a function of time, t (in minutes) (b) x as a function of $(t - \tau)$, where the effective time lag, τ , has been taken as 1.14 min.

isothermal transformation curves for the $y = 10$ alloys is complicated by a transient due to structural relaxation above T_g . However, these data also yield Avrami exponents of approx. 4 and again transient nucleation is observed. In the $y = 20$ and $y = 25$ glasses, the first and second exothermic peaks overlap substantially, but by assuming symmetrical peaks, the modified JMA analysis can again be performed, yielding exponents of approx. 4 and indicating significant effective time lags. The $y = 30$ alloy also shows this behavior.

An unmodified JMA analysis of a 365 K isothermal crystallization trace for a $y = 37.5$ alloy indicates a straight line with slope 2.97 (Fig. 10). The crystallization peak for the $y = 50$ alloy is too small for analysis. However, it was already clear from the X-ray data that the as-quenched sample was partially crystalline.

In summary, analyses of the isothermal transformation kinetics of the alloys with $y \leq 30$ yield Avrami exponents of ~ 4 , indicating a constant nucleation rate and a constant growth rate. However, the nucleation rate attains a constant, steady-state value only after times on the order of minutes. Together with the large number of nucleation events (Fig. 3), this modified JMA analysis suggests that the

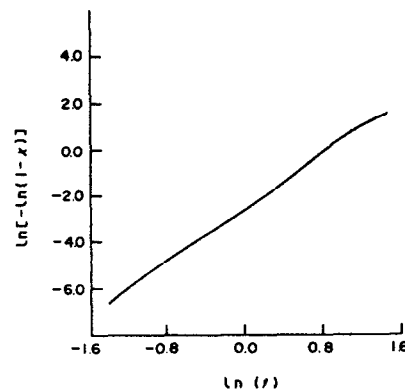


Fig. 10. Johnson-Mehl-Avrami plot derived from the fraction crystallized, x , as a function of time, t (in minutes), for isothermal crystallization (365 K) of $(\text{Au}_{62.5}\text{Cu}_{37.5})_{77}\text{Si}_9\text{Ge}_{14}$.

nucleation is occurring homogeneously. In the $y = 37.5$ alloy the JMA analysis gives an exponent of ~ 3 , indicating a zero nucleation rate and a constant growth rate. Such behavior could result from a substantial population of quenched-in nuclei. Since this alloy has a higher $T_{r,g}$ than the lower copper content alloys and therefore is expected to have a lower maximum steady-state nucleation frequency, the presence of quenched-in nuclei is somewhat surprising. The constant growth rate indicated for all of the alloys would be consistent with either polymorphic or eutectic crystallization [5].

4.3. Comparison of activation energies

It is of interest to examine how the isothermal crystallization behavior described above varies as a function of the temperature. For this study only one alloy, with $y = 15$, was used. The temperature dependence is described by an activation energy, which is most easily determined by comparing the times required for transforming a specified fraction at various temperatures. In the present case, with symmetrical crystallization peaks, it is convenient to set the fraction at $x = 0.5$, with the corresponding time, $t_{1/2}$. A plot of $\ln t_{1/2}$ vs $1/T$ for the $y = 15$ alloy gives an activation energy $Q_{1/2} = 2.59$ eV.

This overall activation energy may be divided into components using the modified JMA analysis. At each temperature the assumed time lag, τ , is adjusted so that the slope of the JMA plot becomes 4.0. Table 3 lists these time lags and, as shown in Fig. 11, they exhibit Arrhenius behavior, with an activation energy, $Q_\tau = 2.0$ eV. Equation (8), again with $n = 4$, was used to obtain the kinetic parameter K at each temperature. Its activation energy, Q_A , was found to be 2.98 eV. Note that, as expected, $Q_{1/2}$ is a weighted average of Q_τ and Q_A .

After the time lag, τ , the rates of nucleation and growth are dependent only on temperature. In a narrow temperature range, their behavior may be Arrhenius, with activation energies of Q_N and Q_G respectively. When the nucleation rate is zero, it is easily derived from equation (2) that the activation energy of K , Q_A , is given by

$$Q_A = Q_G. \quad (9)$$

When the nucleation rate is constant, K is obtained from equation (5), or from equation (8) if an effective time lag is present. From equations (3) or (7) it can

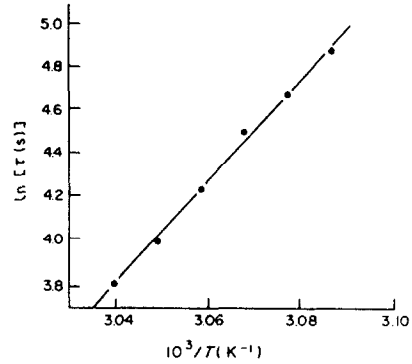


Fig. 11. Arrhenius plot of effective time lag, τ (in seconds), as a function of temperature, T , for isothermal crystallization of $(\text{Au}_{85}\text{Cu}_{15})_{77}\text{Si}_9\text{Ge}_{14}$.

be derived that the activation energy of the kinetic parameter, K , is given by

$$Q_A = \frac{1}{4}[Q_N + 3Q_G]. \quad (10)$$

It is not possible to determine Q_N and Q_G from calorimetric data alone.

In Section 4.1 the Kissinger technique was used as a convenient means for obtaining an overall activation energy. It is of interest to note that the value obtained for the $y = 15$ alloy, $Q_T^K = 2.49$ eV, is similar to the value obtained from isothermal measurements, $Q_{1/2} = 2.59$ eV. Thus, the Kissinger technique appears to average the temperature dependences of the transient nucleation period, of steady state nucleation and of growth, in a similar way to the isothermal method.

5. DISCUSSION

5.1. Effective time lag for transient nucleation

A striking feature of the analysis used for the devitrification kinetics is the effective time lag, τ , indicating transient nucleation. Transient nucleation is known to arise because of the time necessary to build up a steady-state distribution of sub-critical clusters. The kinetics of this process have recently been analyzed in detail, for a one component system, by Kelton *et al.* [21]. They obtained a full numerical solution of the cluster formation kinetics as derived from classical nucleation theory, and they assessed published approximate analytical expressions by comparison with the full solution. They showed that, in the case where there are no clusters initially, the analytical treatment of Kashchiev [22] provides a good approximation to the transient nucleation behavior. Kashchiev's expression for the time-dependent nucleation rate, $I(t)$, is

$$I(t) = I_{ss}[1 + 2 \sum_{m=1}^{\infty} (-1)^m \exp(-m^2 t/\phi)] \quad (11)$$

where I_{ss} is the steady-state nucleation rate and the characteristic time, ϕ , is given by

$$\phi = \frac{8kT}{\pi^2 \zeta_n [d^2 \Delta G_n / dn^2]_{n=n^*}}. \quad (12)$$

Table 3. Transient times at various temperatures in $(\text{Au}_{85}\text{Cu}_{15})_{77}\text{Si}_9\text{Ge}_{14}$

T (K)	τ (s)
324.0	132.0
325.0	106.8
326.0	89.4
327.0	68.4
328.0	53.7
329.0	44.7

In this expression ΔG_n is the free energy of formation of a cluster of n molecules, n^* is the number of molecules in a critical cluster, ζ_n is the rate at which molecules add to a critical cluster, k is Boltzmann's constant, and T is the absolute temperature. From equation (11) Kashchiev shows that the effective time lag, τ , as used in equation (6), is given by

$$\tau = \frac{\pi^2}{6} \phi. \quad (13)$$

Kelton *et al.* [21] have shown that the temperature dependence of τ is dominated by the temperature dependence of the molecular transport rate.

In order to evaluate τ from equations (13) and (12) and compare it with experiment, the following material parameters must be known: the interfacial free energy between the amorphous and crystalline phases, σ ; the volume free energy difference between the bulk phases, ΔG_v ; and the molecular mobility, which is governed by the viscosity, η , of the amorphous phase.

For the crystal-liquid interface in pure metals, Spaepen [15, 23, 24] has argued that

$$\sigma = \frac{\Delta S_f \alpha_m}{(N_A \bar{V}^2)^{1/3}} T \quad (14)$$

where N_A is Avogadro's number, $\bar{V}$ is the molar volume of the crystal, ΔS_f is the molar entropy of fusion, and $\alpha_m = 0.86$ for f.c.c. crystals. In evaluating σ for the present alloys, ΔS_f was given the value for pure gold ($9.393 \text{ JK}^{-1} \text{ mol}^{-1}$ [25]) and $\bar{V}$ was taken to be $1.086 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}$ (from the density of liquid $\text{Au}_{77}\text{Si}_9\text{Ge}_{14}$ [26]).

The difference in free energy per unit volume, ΔG_v , can be calculated simply for pure metals, since the difference in specific heat between the liquid and crystalline phases is small

$$\Delta G_v = \Delta T \Delta S_f / \bar{V} \quad (15)$$

where ΔT is the undercooling $T_M - T$ [27]. For binary alloys, we have shown elsewhere, using regular solution models for the liquid and solid phases, that the dependence of the homogeneous nucleation frequency on the reduced temperature T/T_i (T_i : liquidus temperature) is similar to that for pure metals using a reduced temperature T/T_M [28]. In multi-component systems, a precise calculation of ΔG_v from solution models becomes cumbersome. Therefore, the following simple approximation, based on the scaling relation between T_i and T_M , will be used in the calculations

$$\Delta G_v \approx (T_i - T) \Delta S_f / \bar{V} \quad (16)$$

where ΔS_f is the entropy of fusion of pure gold, which is also very close to that for pure copper.

This approximation results in an underestimate of ΔG_v , as can be seen from a consideration of the binary system with zero solubility in the crystalline phase. Using a regular solution model for the liquid,

one obtains [28]

$$\Delta G_v = (T_i - T)(\Delta S_f - R \ln x_i) / \bar{V} \quad (17)$$

where x_i is the atom fraction of the nucleating component in the liquid. For Au-Si alloys in the range of interest here, equation (17) gives values of ΔG_v that are about 20% higher than those obtained from equation (16). In the quaternary system, AuCu-SiGe, Au and Cu are continuously soluble in the solid state, whereas the metalloids (Si, Ge) have only very limited solubility in Au. The crystal nucleus that is most likely to form from the melt is therefore probably a disordered, low metalloid, Au-Cu alloy. The difference in configurational entropy between this alloy and the original melt is less than that between a binary melt with a similar metalloid content and the pure metal crystal. As a result, equation (16) does not underestimate ΔG_v as much as equation (17) would indicate.

Chen and Turnbull [11] have determined that near T_g , the viscosity of amorphous $\text{Au}_{77}\text{Si}_9\text{Ge}_{14}$ displays Vogel-Fulcher behavior

$$\eta = \eta_0 \exp \left(\frac{\gamma}{T - T_0} \right) \quad (18)$$

where $\eta_0 = 0.052 \text{ Nsm}^{-2}$, $\gamma = 1360 \text{ K}$ and $T_0 = 241.3 \text{ K}$. Polk and Turnbull [29] found that at the liquidus, 671 K , $\text{Au}_{77}\text{Si}_9\text{Ge}_{14}$ has a viscosity of 0.0115 Nsm^{-2} . This value is lower than the viscosity predicted by the extrapolation of Chen and Turnbull's data. We estimate the viscosity of the $(\text{Au}_{85}\text{Cu}_{15})_{77}\text{Si}_9\text{Ge}_{14}$ alloy by assuming:

- (1) that the viscosity at the liquidus temperature is 0.0115 Nsm^{-2} ,
- (2) that the viscosity at the glass transition temperature is $6 \times 10^8 \text{ Nsm}^{-2}$, derived from Chen and Turnbull's data,
- (3) that the activation energy of the viscosity at T_g is 2.0 eV , the value for the activation energy of τ , determined near T_g .

The apparent activation energy for viscosity, Q_η , at a temperature T' is given by

$$\left(\frac{Q_\eta}{k} \right)_T = \left[\frac{\partial (\ln \eta)}{\partial (1/T)} \right]_T = \frac{\gamma (T')^2}{(T' - T_0)^2}. \quad (19)$$

In estimating η_0 , γ and T_0 , we set

$$\eta_0 \exp \left(\frac{\gamma}{T_i - T_0} \right) = 0.0115 \quad (20)$$

$$\eta_0 \exp \left(\frac{\gamma}{T_g - T_0} \right) = 6 \times 10^8 \quad (21)$$

and

$$\left(\frac{Q_\eta}{k} \right)_{T_g} = \frac{\gamma T_g^2}{(T_g - T_0)^2} = 2.32 \times 10^4. \quad (22)$$

Solving equations (19) to (22) for the $\gamma = 15$ alloy ($T_i = 623 \text{ K}$, $T_g = 320 \text{ K}$) we find that $\eta_0 =$

$1.121 \times 10^{-8} \text{ Nsm}^{-2}$, $\gamma = 6546 \text{ K}$ and $T_0 = 150 \text{ K}$. Using these values in equation (18) allows interpolation of η between T_f and T_g . The diffusivity, D , is obtained from the viscosity using the Stokes-Einstein relation

$$D = \frac{kT}{3\pi a_0 \eta} \quad (23)$$

in which a_0 is a molecular diameter. In accordance with standard practice for metals [30], a_0 was taken to be in ionic diameter, $1.70 \text{ \AA}$ for Au^{3+} . The validity of the Stokes-Einstein relation has been confirmed (to within two orders of magnitude) over a large range of viscosity values [9]. It has, however, not been demonstrated directly for these glass-forming melts. The molecular jump rate, ν , can be estimated from D using

$$\nu = 6D/\lambda^2 \quad (24)$$

where λ is the jump distance. We took λ to be the interatomic distance in crystalline gold, $2.884 \text{ \AA}$. The rate constant ζ_n in equation (12) is ν times the number of atoms on the surface of a critical cluster.

We are now able, using equations (12) and (13), to predict the effective time lag, τ , for the $y = 15$ alloy. The calculation is outlined in the Appendix. At 326 K the calculated value of τ is 2.36 s . This value is very large in comparison with the expected values for pure metals, where the time lags are immeasurably short [31]. In agreement with the prediction of large and measurable time lags in the Au-Cu-Si-Ge system, the experimental value at 326 K was found to be 89.4 s . Although the experimental and calculated values of τ disagree by two orders of magnitude, the errors in estimating the viscosity, and from it the atomic jump rate, could easily account for this. It appears that the experimentally observed time lags are consistent with classical nucleation theory.

5.2. Glass formation and quenched-in nuclei

Turnbull [14] has shown that for typical metals, using the assumption discussed above for the atomic mobility, the steady-state nucleation frequency, I_{ss} , is given by

$$I_{ss} (\text{m}^{-3} \text{ s}^{-1}) \approx \frac{10^{35}}{\eta} \exp\left(\frac{-\Delta G^*}{kT}\right), \quad (25)$$

where η is the viscosity of the liquid (in Nsm^{-2}) and ΔG^* is the free energy of formation of a critical nucleus. For spherical nuclei

$$\Delta G^* = \frac{16\pi\sigma^3}{3(\Delta G_v)^2}. \quad (26)$$

Using the material parameters estimated in the previous section, and equations (25) and (26), we can calculate I_{ss} for the nucleation of a gold-copper phase in $(\text{Au}_{85}\text{Cu}_{15})_{77}\text{Si}_{10}\text{Ge}_{14}$ as a function of reduced temperature, $T_r = T/T_f$. The maximum steady state nucleation frequency is $3.3 \times 10^{20} \text{ m}^{-3} \text{ s}^{-1}$, occurring at $T_r = 0.531$.

One might assume that such a high nucleation

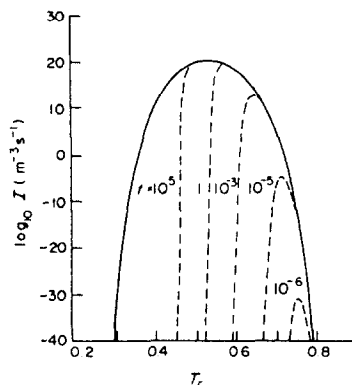


Fig. 12. Calculated values of the homogeneous nucleation frequency, I , as a function of reduced temperature, T_r , in $(\text{Au}_{85}\text{Cu}_{15})_{77}\text{Si}_{10}\text{Ge}_{14}$. The solid line indicates the steady-state nucleation frequency, while the dashed lines show the frequency obtained at the indicated times (in seconds) after the start of an isothermal anneal. The nucleating phase is assumed to be a disordered gold-copper alloy.

frequency would be incompatible with glass formation, even at high quench rates. The total number of nuclei produced during a quench can be estimated by integrating the solid curve in Fig. 12. It is found that the number is the same as that which would be produced if the maximum nucleation frequency were to operate for a temperature range of $\sim 50 \text{ K}$. In melt-spinning the quench rate is approx. 10^6 Ks^{-1} . Thus, if steady-state nucleation operates during the quench, we expect 10^{16} m^{-3} nuclei. Evidently, nucleation is not bypassed by melt-spinning. It is known, however, that in some systems [6], glasses are formed with substantial populations of quenched-in nuclei. In such cases, glass formation is due more to suppression of growth than to suppression of nucleation. If the number of quenched-in nuclei is sufficiently high, growth from them dominates the devitrification kinetics and equation (2) applies. This was found to be the case for the $y = 37.5$ alloy, but the analysis of the kinetics for the lower copper content alloys indicated that the crystallization was dominated by nucleation during the anneal. It is important to know what population of pre-existing nuclei would be detectable in this kinetic analysis (Section 4.2).

We will consider the devitrification of the $y = 15$ alloy at 326 K . It was found that equation (8) is valid with $K = 7.02 \times 10^{-3} \text{ s}^{-1}$. Since $K^4 = \pi I_{ss} G^3/3$ and calculating I_{ss} at 326 K to be $3.11 \times 10^{20} \text{ m}^{-3} \text{ s}^{-1}$, we derive that $G \approx 2 \times 10^{-10} \text{ ms}^{-1}$. This value for the growth rate is very reasonable. (At high undercoolings, a good estimate for G is $\nu\lambda$, which at 326 K is $3.6 \times 10^{10} \text{ ms}^{-1}$.) Given this growth velocity one can calculate the effect of a population, N per unit volume, of quenched-in nuclei. Assuming that the distribution of nuclei is random, the devitrification kinetics are described by

$$x = 1 - \exp\left[\left(-\frac{\pi}{3} G^3\right)(I(t - \tau)^4 + 4Nt^3)\right] \quad (27)$$

where the effective time lag, τ , is in this case taken to be 89.4 s. The kinetics derived from equation (27) were then analyzed as in Section 4.2 by plotting $\ln[-\ln(1-x)]$ vs $\ln(t-\tau')$ where τ' is adjusted to obtain the best straight line plot. It is found that when N is zero, $\tau' = \tau$ and the gradient of the line $n = 4$. As N is increased, τ' decreases and n increases. It was found experimentally that n was 4.0 ± 0.2 for the $y \leq 30$ alloys. In the present calculation, the value of N for which $n = 4.2$ is $\sim 9 \times 10^{19} \text{ m}^{-3}$. That is, this population of quenched-in nuclei could exist without being detected in the analysis.

The conclusion is that, if steady-state nucleation were to operate throughout the quench, the resultant number of nuclei would not be detectable. This surprising result is due to the very low growth rate in this system. The main uncertainty in estimating the number of quenched-in nuclei and the minimum number which would be detectable is in the evaluation of I_{ss} . Since both quantities are proportional to I_{ss} , however, the conclusion remains unaffected. It is interesting to note that, given the estimated growth rate in this system, quenched-in nuclei which appeared at the peak nucleation temperature would grow by less than 1 Å during the rest of the quench.

For the $y = 15$ alloy, the variation of the effective time lag, τ , with reduced temperature, T_r , is shown in Fig. 13. It can be shown from equations (12–14, 16, 23 and 24) and from the derivation in the Appendix that

$$\tau \propto \frac{T\eta}{(T_l - T)^2}. \quad (28)$$

In calculating the curve in Fig. 13, the expression for η derived in the previous section was used and the constant of proportionality was chosen to match the experimentally determined τ at 326 K. With the values of τ from Fig. 13 and using equation (11), it is possible to calculate $I(t)$ after a given time at any temperature. The dashed curves in Fig. 12 show $I(t)$

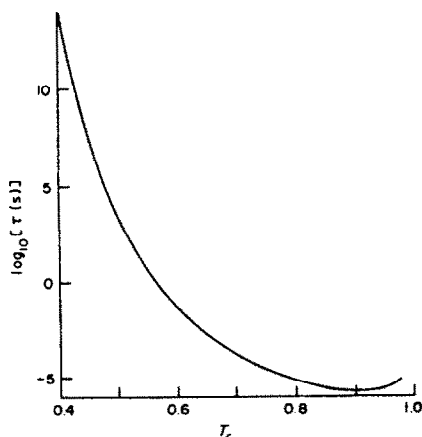


Fig. 13. Calculated values of the effective time lag, τ , as a function of reduced temperature, T_r , for $(\text{Au}_{85}\text{Cu}_{15})_{77}\text{Si}_9\text{Ge}_{14}$.

vs T_r for a selection of times. Although such plots of the isothermal behavior offer only a qualitative analysis of the behavior during a quench, it is evident that transient phenomena will reduce nucleation frequencies substantially. This effect will be especially strong in rapid quenches, such as in melt-spinning and will enhance glass formability.

The presence of effective time lags in the devitrification kinetics is direct experimental evidence that, during the quench, deviations from the steady state occurred at a temperature above the devitrification temperature. The number of quenched-in nuclei should therefore be less than that predicted from steady-state nucleation frequencies. Since that predicted number is too small to be detected, one would not expect to find evidence for quenched-in nuclei in any of the alloys. However, quenched-in nuclei were detected in the $y = 37.5$ alloy and crystallinity was evident in the higher copper content alloys. This suggests a change in the devitrification mechanism for $y \geq 37.5$, and will be considered further in the next section.

5.3. Mode of crystallization

The overall activation energy for the crystallization reaction as given by the Kissinger analysis, Q_T^k , is plotted as a function of copper content, y , in Fig. 6. Superimposed on a general rise in Q_T^k with copper content, there is a sharp drop between $y = 25$ and $y = 30$. The sharp change in the devitrification behavior is manifested also in the DSC scans of Fig. 1. In this section, we consider this change and its origins.

First, the discontinuity in Fig. 6 does *not* occur at the composition where quenched-in nuclei begin to dominate the devitrification kinetics. All the alloys with $y \leq 30$ exhibit Avrami exponents of 4. The activation energy, Q_A , of the kinetic parameter, K , in the Avrami analysis is then a function of the activation energies of nucleation and growth, Q_N and Q_G , as given by equation (10). As pointed out in Section 4.3, Q_T^k is a weighted average of Q_N , the activation energy for the time lag and Q_A .

The activation energy for nucleation is determined by the temperature dependences of the interfacial attachment processes [often assumed to be governed by viscosity, as in equation (25)] and of the thermodynamic term, $\exp(-\Delta G^*/kT)$. The devitrification temperatures, T_p , of the alloys in this work lie in the range $0.53 < T_p/T_l < 0.59$ and in this range it has been shown that the thermodynamic term makes a small negative contribution to Q_N [15]. The activation energy for the viscosity is assumed to be Q_v . It follows that $Q_N \lesssim Q_v$. The overall activation energy, Q_T^k , is then a weighted average of Q_v , the activation energy for atomic attachment at the surface of a sub-critical cluster and Q_G , the activation energy for attachment to a macroscopic crystal.

Kinetically, the favored crystal composition for nucleation and growth is close to that of the glass, since this minimizes the atomic transport required for

the transformation. However, the thermodynamic driving force may not favor or even permit such a reaction. This seems to be the case for nucleation in the Au-rich alloys, where, due to the unfavorable Au-Si and Au-Ge interactions in the crystal, the nuclei are probably low metalloid disordered Au-Cu alloys. The isothermal crystal growth rate in these alloys is known, from the analysis of the devitrification kinetics, to be constant in time. This is consistent either with polymorphic growth of a phase with the same composition as the glass, or with eutectic growth. It should be noted that polymorphic growth is not inconsistent with the initial formation of a low metalloid nucleus, since the nucleation rate is much more strongly dependent on the driving force than the growth rate.

The extensive solubility of Si or Ge in Cu and the occurrence of many Cu-Si and Cu-Ge intermetallic compounds suggest that the interaction of these metalloids with Cu is more favorable than with Au. For the glasses with a higher Cu content, therefore, formation of phases with a higher metalloid content, such as ternary or quaternary compounds, may be favored. The rise in the liquidus temperature near $y = 50$ may be evidence for the existence of such a compound. Formation of crystal nuclei of this composition would be kinetically favored. The drop in Q_T^* between $y = 25$ and $y = 30$ could then be attributed, at least partially, to a decrease in Q_T^* , the activation energy for interfacial attachment. Q_T^* could become lower than the activation energy for diffusional transport in the bulk, when the composition of the compound matches that of the glass. The same factor would also lead to a decrease in the effective time lag due to transient nucleation. This, together with an increased steady-state nucleation rate, may explain the presence of quenched-in nuclei in the $y = 37.5$ alloy and the crystallinity in the higher copper content alloys.

The analysis of the devitrification kinetics shows the isothermal crystal growth rate to be independent of time in the high copper content alloys as well. The microstructure of the devitrified $y = 37.5$ alloy, shown in Fig. 3, is clearly not eutectic. Polymorphic growth is therefore indicated, which is consistent with the above interpretation of the nucleation behavior.

It should be noted that in this alloy series the reduced glass transition temperature, $T_{r,g}$, increases with copper content. While a material with higher $T_{r,g}$ is generally a better glass former, the discussion above indicates that it is essential to consider the modes of nucleation and growth. If these modes change as a function of composition in a given system, $T_{r,g}$ alone will not indicate the variation of glass formability in the system.

6. SUMMARY AND CONCLUSIONS

We have prepared a new range of metallic glasses of composition $(\text{Au}_{100-y}\text{Cu}_y)_{77}\text{Si}_9\text{Ge}_{14}$. Alloys with

$y = 10, 15, 20, 25, 30, 37.5, 50$ and 75 were melt-spun: those with $y \leq 37.5$ were amorphous as quenched, the $y = 50$ alloy was partially crystalline and the $y = 75$ alloy was completely microcrystalline. As the copper content of the alloys is increased, the reduced glass transition temperature increases and the difference between the glass transition temperature, T_g , and the kinetic crystallization temperature, T_{kc} , also increases. This latter feature is important in that a large difference between T_g and T_{kc} allows independent characterization of these phenomena. Differential scanning calorimetry shows that, on heating, the amorphous alloys undergo a series of phase transformations. The first of these is believed to be complete devitrification to a microcrystalline state. The kinetics of this devitrification were analyzed under isothermal conditions. For the $y = 37.5$ alloy, the kinetics were consistent with growth on quenched-in nuclei. For lower copper contents, the analysis indicated that a steady-state nucleation frequency was established after a transient period. The experimentally determined effective time lags for transient nucleation were consistent with predictions from the classical theory of homogeneous nucleation. It was demonstrated that the Kissinger analysis for non-isothermal kinetics gave a good estimate of the activation energy for the overall devitrification reaction. Estimates of the steady-state nucleation frequency and growth rate for the alloys suggest that, on cooling the melt, a substantial population of nuclei will develop, even in a rapid quench, such as in melt-spinning. In spite of this, a glass will be formed because of the low crystal growth rate. This population of quenched-in nuclei should be undetected in the kinetic analysis. The devitrification behavior of the lower copper content alloys shows that nucleation frequencies are reduced by transient effects; if this is considered during the quench, the expected crystallinity would be even lower. The detection of quenched-in nuclei and crystallinity in the higher copper content alloys suggests a change in the composition of the nucleating phase, from a disordered gold-copper alloy to multicomponent compound. The reduced glass transition temperature alone is not sufficient to predict the variation of glass formability with composition in this system.

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APPENDIX

Estimation of the effective time lag

As described in Section 5.1, an approximate value of the

effective time lag for transient nucleation, τ , may be obtained using the expression of Kashchiev, equations (12) and (13). The material parameters necessary to do this are: the free energy difference per unit volume between the bulk phases, ΔG_v ; the interfacial free energy between the phases, σ ; and the molecular jump rate, ν . The estimation of these parameters was described in Section 5.1, and for the $y = 15$ alloy at 326 K they have the values: $\Delta G_v = 2.57 \times 10^8 \text{ Jm}^{-3}$; $\sigma = 6.36 \times 10^{-2} \text{ Jm}^{-2}$; and $\nu = 1.26 \text{ s}^{-1}$.

The free energy of formation of a cluster of radius r , ΔG_r , is given by

$$\Delta G_r = \frac{4}{3}\pi r^3 \Delta G_v + 4\pi r^2 \sigma. \quad (\text{A1})$$

In Kashchiev's approach the free energy of formation is considered as a function of the number of atoms in the cluster, not of its radius. The equivalent of equation (A1) is then

$$\Delta G_n = n\Delta g + A_n\gamma \quad (\text{A2})$$

where ΔG_r is the free energy of formation of a cluster of n atoms, Δg is the free energy difference per atom between the phases, A_n is the number of atoms on the surface of a cluster of n atoms and γ is the interfacial free energy per surface atom. We take

$$A_n = 4n^{2/3} \quad (\text{A3})$$

and

$$\Delta g = \frac{\Delta G_v V}{N_A} \quad (\text{A4})$$

where V is the molar volume of the crystal and N_A is Avogadro's number. To preserve the equivalence of equations (A1) and (A2), we then have

$$\gamma = \left(\frac{3V}{4N_A} \right)^{2/3} \pi^{1/3} \sigma. \quad (\text{A5})$$

Using equations (A2) and (A3), we can derive $(d^2\Delta G_n/dn^2)_{n=n^*}$, and with $\zeta_{n^*} = \nu A_{n^*} = 4\nu n^{2/3}$, Kashchiev's expression for τ reduces to

$$\tau = \frac{8kT\gamma}{3\nu\Delta g^2}. \quad (\text{A6})$$

Taking $V = 1.086 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}$ and using equations (A2)–(A6), τ for the $y = 15$ alloy at 326 K was calculated to be 2.36 s.