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CRYSTALLIZATION KINETICS OF AMORPHOUS $S_{20}Se_{80}$

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The effect of temperature on the crystallization kinetics of bulk amorphous $S_{20}Se_{80}$ has been studied using differential scanning calorimetry. Using the empricial Avrami expressions, a number of kinetic parameters has been determined. The order of the reaction *n* was found to be 2.3 for the range of temperature 340-365 K and 1.6 in the range of temperature between 370-400 K. This range of *n* indicates that the crystallization process is diffusion controlled growth with decreasing nucleation rate. The activation energy was found to be 3, 1.1 ev depending on the same range of temperatures.

A time-temperature-transformation (*TTT*) curves has been plotted from isothermal results over the temperature range 340 K to 400 K showing the presence of minimum at 374 K. From the *TTT* curves the critical cooling rate required to avoid 25, 50, 75 and 100% crystallization was found to be 2.4, 1.79, 0.72 and 0.42°C/sec respectively.

The crystallization of amorphous materials can be induced by changing various parameters: temperature, optical radiation, electric field, pressure, impurities, etc., and a number of experiments have been carried out to study these effects [1-8]. A complete understanding of this type of phase transformation has been hampered, however, by its dependence on a variety of other factors including melt temperature, cooling rate, thermal history, heating rate, and amount crystallized. It has been difficult to compare the results of different experiments when all or some of these factors have been reported or taken into account.

If the kinetics of a transformation are found experimentally at a number of different constant temperatures, a complete isothermal transformation diagram may be drawn. This figure, also known as a time-temperature-transformation (*T-T-T*) diagram, gives the relation between the temperature and the time for fixed fractional amounts of transformation to be attained. Since the pioneer work of Davenport and Bain [9], (*T-T-T*) diagrams have been widely used in industry as a guide to heat treatment procedures.

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Differential scanning calorimetry is a useful technique for studying the kinetics and thermodynamics, and hence the mechanisms of crystallization, under carefully controlled conditions. It has been found that the amorphous alloy can be recycled in the calorimeter to give reproducible results. By this method time-temperature-transformation curves have been obtained for $S_{20}Se_{80}$ sample over a wide temperature range and a number of kinetic parameters has been determined.

Experimental

The glassy sample was prepared by melting weight amounts of the elements of 99.9999% purity in evacuated sealed quartz ampoule. The molten alloy was held at 500K for 6h and constantly agitated to ensure homogeneity and then quenched in ice water.

The amorphous state of the sample and its homogeneity was verified by X-ray analysis and scanning electron microscope observation.

The differential scanning calorimeter used was a Perkin Elmer DSC-2 power compensated device. About 20 mg of the sample was sealed in aluminium pan. For isothermal measurements the DSC was heated first to the desired temperature and then the amorphous sample was inserted quickly and the scan was measured at that temperature. Whilst in operation the sample chamber was continuously purged with high purity argon to prevent oxidation.

Results and discussion

An isothermal differential scanning calorimeter scan show a curve of heat evolved as a function of time at a fixed temperature. In case of crystallization the area under the curve is directly proportional to the total amount crystallized, so that any fractional area up to the time t is then proportional to the fraction α of material crystallized at time t. A plot of α *vs.* t then yields the sigmoidal shape Fig. (1) which is typical for crystallization curves obtained experimentally by other methods [10-11].

The shape of the isothermal crystallization scan of this sample is very closely approximated by the phenomelogical Avrami equation [12]

$$\alpha = 1 - \exp(-Kt^n) \qquad (1)$$

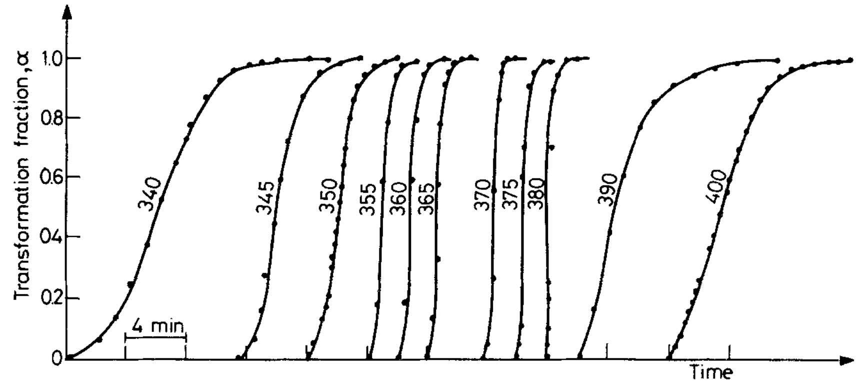

Fig. 1 Transformation fractions during isothermal crystallization of $S_{20}Se_{80}$ metallic glass as a function of time

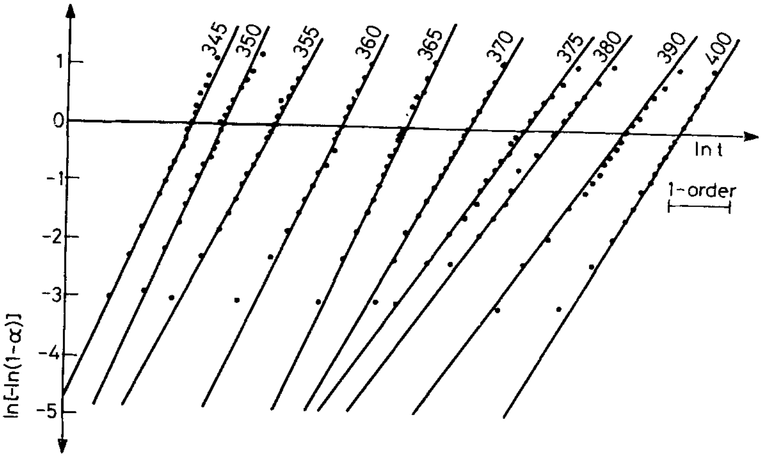

Fig. 2 Avrami plot of ln [-ln(1-α)] as a function of ln time for various isotherms

where α is the fraction of material crystallzsed after time t, n is a constant depends on the details of the nucleation mechanism, and K, sometimes called the rate constant, is related to the rates of nucleation and growth. The Avrami equation can be rearranged to give

$$\ln[-\ln(1-\alpha)] = \ln K + n \ln t \tag{2}$$

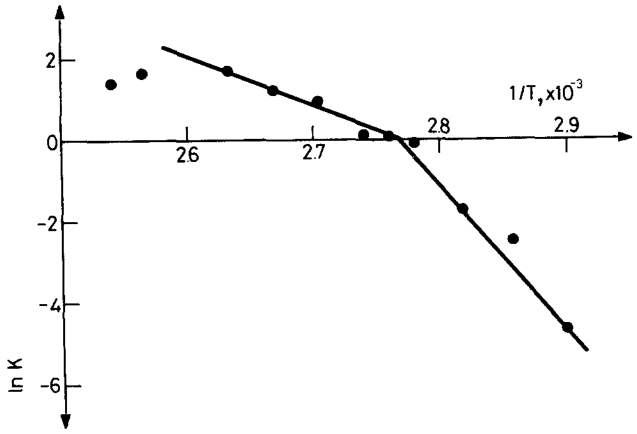

Fig. 3 Dependence of ln K on 1/T for $S_{20}Se_{80}$

and, under isothermal conditions, a plot of the left-hand side of this expression against lnt can be used to find n and K. Typical plots are shown in Fig. 2. Table 1 shows the variation of n with temperature, it is evident from this Table that n decreases from 2.3 in the range of temperature 340-365 K to 1.6 in the range 370-400 K. Cristian [13] discussed the nucleation behaviour expected for values of n between 1.5-2.5 if we were to follow this scheme we would conclude that in $S_{20}Se_{80}$ transformation are taken to imply that the process is diffusion controlled growth with decreasing nucleation rate.

Table 1 The temperature dependence of the crystallization parameter n for the sample $S_{20}Se_{80}$

T, K	340	345	350	355	360	365	370	375	380	390	400
n	2.3	2.25	2.3	2.2	2.2	2.3	1.66	1.5	1.5	1.5	1.7

The rate constant, K, is related to the absolute temperature, T, by an Arhenious-type equation

$$K = A\exp(-E/RT) \tag{3}$$

where R is the universal gas constant, E is an apparent activation energy for crystallization and A most often called the frequency factor, is a measure of the probability that a molecule having energy E will participate in a reaction. Figure 3 shows the relation between ln k $vs.$ 1/T. The activation energy for crystallization which calculated from the slope of the line was 3.0 and

1.1ev depending on the temperature range. These two values for the activation energy indicate that the crystallization process occurs in two steps. The second step is much easier than the first one. These observations may be explained by the fact that in the first step the addition of S reduces the no. of Se rings and forms mixed rings and copolymer chains. These mixed rings with this high percentage of S may act as shallow trap with the result that the drift mobility is decreased and the activation energy of crystallization increased. In the second step the chains may start to break as a result of thermal degradation such that the viscosity in this range decreased with the consequential result that the crystallization process become much easier.

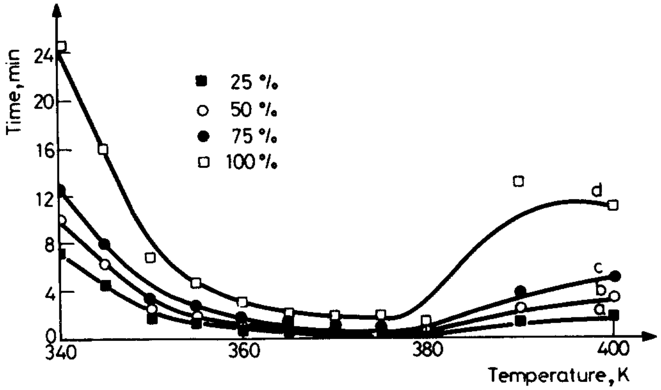

Fig. 4 Time - Temperature - Transformation (TTT) diagrames for $S_{20}Se_{80}$

In constructing the Time-Temperature-Transformation curves; 25, 50, 75 and 100% fractions were selected, the time required for each volume fraction to form at a given temperature is calculated and the calculation is repeated for other temperature. The *TTT* curves retained for the alloy under study is shown in Fig. 4.

The cooling rate required to avoid a given volume fraction crystallized can be estimated from the equation

$$Rc = Tm\text{-}Tn/tn$$

where Tm is the melting temperature, Tn and tn are the temperature and time at the nose of the *TTT* curve respectively.

The nose in a *TTT* curve, corresponding to the least time for the given volume fraction to crystallise, results from a competition between the driving force for crystallization, which increase with decreasing temperature, and the atomic mobility, which decrease with decreasing temperature. It is clear from Fig. 4 and Table 1 that the nose occurs at the same temperature range where the *n* is changed.

From the equation above and Fig. 4 R_c was calculated to be 2.4, 1.7, 0.7 and 0.42 deg/sec for the volume fraction 25, 50, 75 and 100% respectively.

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Zusammenfassung — Mittels DSC wurde der Einfluß der Temperatur auf die Kristallisierungskinetik von amorphem $S_{20}Se_{80}$ untersucht. Unter Verwendung der empirischen Avrami Gleichungen wurde eine Anzahl kinetischer Größen ermittelt. Danach ergab sich die Reaktionsordnung n für den Temperaturbereich 340-365 K mit 2.3 und für den Temperaturbereich 370-400 K mit 1.6. Dieses Intervall für *n* zeigt, daß es sich beim Kristallisationsprozeß um ein diffusionsbestimmtes Wachstum mit sinkender Kristallkeimbildungsgeschwindigkeit handelt. Für die Aktivierungsenergie wurde für die gleichen Temperaturbereiche ein Wert von 3 bzw. 1.1 eV gefunden.

Ausgehend von den isothermen Ergebnissen im Temperaturbereich 340-400 K wurde eine Zeit-Temperatur-Transformationskurve (*TTT*) dargestellt, die bei 374 K die Gegenwart eines Minimum aufweist. Auf der Basis der *TTT*-Kurven konnte für eine 25-, 50-, 75- bzw. 100-prozentige Kristallisation eine kritische Kühlgeschwindigkeit von 2.4, 1.79, 0.72 bzw. 0.42°C/s ermittelt werden.