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The kinetics of crystallization of the metallic alloy Pd_4Ge

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The kinetic parameters for the crystallization of Pd_4Ge have been measured by differential scanning calorimetry (DSC). The effective activation energy was found to be 215 kJ mol^{-1} (51 kcal mol^{-1}) and the heat of reaction was determined to be 13 kJ mol^{-1} (3.1 kcal mol^{-1}). Preliminary investigation of the products of crystallization was undertaken using X-ray diffraction and electron microscope techniques. Some new phases for this alloy were observed.

1. Introduction

Many metallic glasses are of potential interest and use because of their favourable electrical, magnetic, mechanical and chemical properties. However, they are inherently unstable with respect to the crystalline phase and there is a need for a careful characterization of the crystallization process. We have studied the kinetics of crystallization of amorphous Pd_4Ge using differential scanning calorimetry and, using both isothermal and heating rate techniques, we have calculated an effective activation energy for crystallization and a heat of crystallization. Preliminary investigations have been made of the crystallized material using X-ray diffraction and electron microscope techniques and possible new phases for this alloy system are discussed.

2. Experimental procedure

Pd_4Ge was prepared by a conventional melt spinning technique [1] using a water-cooled brass wheel under an argon atmosphere. The cooling rate was estimated to be between 10^5 and 10^6 K sec^{-1}. This process produced long strips about 0.5 mm wide and 20 to 60 μm thick.

Thermal measurements were made in a Perkin-Elmer-2 differential scanning calorimeter (DSC). The strips were cut into five-millimetre lengths and about 30 to 40 of these, giving a total weight of 10 to 20 mg, were carefully weighed and then sealed into aluminium pans. A single sealed empty pan served as the reference for all the runs performed.

Both isothermal and heating-rate methods were used to determine an activation energy for crystallization. In the isothermal method, the material was heated from room temperature at a rate of 320 K sec^{-1}, until a predetermined temperature was reached, whereupon the rate of heat evolution due to crystallization was recorded as a function of time. The integrated area under this curve, from time = 0 to t, divided by the total area, gives the fraction of heat evolved as a function of time, t. It is then assumed this is equal to the volume-fraction transformed, x, which is thus determined as a function of time.

In the second method the material was heated at a constant heating rate until crystallization was complete.

The X-ray diffraction patterns were taken on a Philips X-ray diffractometer in the Department of Mineralogy and Petrology, Cambridge. A DSC was used to carry out the heat treatment and the strips of heat-treated metallic glass were glued side-by-side on a microscope cover-slip with Durafix glue. The cover-slips were mounted in the diffractometer and continuously rotated. The runs were taken at a rate 1° min^{-1}, 2θ, with one degree slits and a time constant of 10 sec, and the X-ray generator was run at 30 kV, 20 mA with a copper target. The strong peaks at about 40 degrees, 2θ, were then rescanned at 0.5° min^{-1} 2θ, with a less sensitive full-scale deflection.

The samples viewed in the electron microscope were thinned by electrochemical polishing in a solution of 23% perchloric acid and 77% acetic

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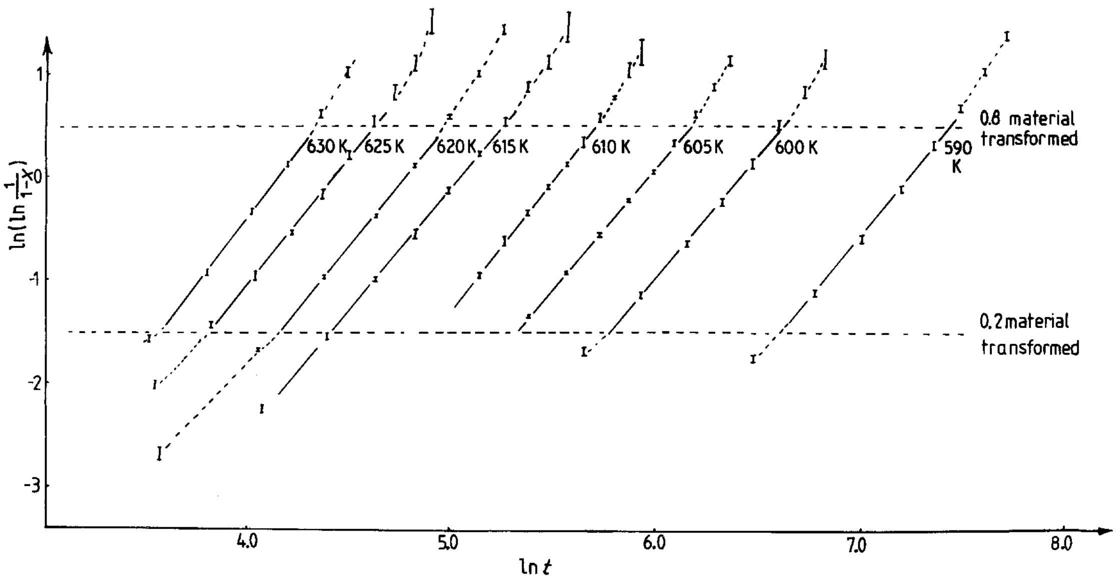

Figure 1 Plots of ln (ln 1/1 $-x$) against ln t. Values for n are obtained from the slopes of these lines.

acid. Polishing occurred rapidly at a potential of $7\frac{1}{2}$V. The specimens were imaged on JEM 200A and JEX 120CX electron microscopes.

3. Results

3.1. Calorimetric results

The isothermal runs and the constant heating rate experiments both showed two maxima in the rate of heat evolution. The second of these maxima was always much smaller and broader than the first. However, since only the first peak was concerned with crystallization from the amorphous alloy, only the kinetics of that peak are considered here.

The data were analysed using the generalized empirical Avrami relation for nucleation and growth (Christian [2]):

$$x = 1 - \exp(-At^n), \qquad (1)$$

where x is the volume-fraction transformed, A is related to the rates of nucleation and growth, t is the time and the exponent n depends on the details of the nucleation and growth mechanisms. The parameter n was obtained by measuring the slope of a graph of $\ln[-\ln(1-x)]$ plotted against $\ln t$. The plots in Fig. 1 show a good linear relationship in the region $x = 0.2$ to 0.8. (This is the area between the dashed lines.) Outside these limits the inaccuracies involved in measuring the areas make the plots considerably less meaningful. In particular, $\ln[-\ln(1-x)]$ will tend to infinity at the arbitrary time chosen when the reaction is considered to have gone to completion. The values of n are tabulated in Table I. There was no significant change of n over the temperature range 590 to 630 K, and n was determined to be 2.5 ± 0.2 (one standard deviation).

Under certain experimental conditions [3, 4] A can be expressed in the form

$$A = A_0 \exp(-E_c/RT), \qquad (2)$$

where A_0 is a constant, E_c is an apparent activation energy, R is the universal gas constant and T is the temperature. If a plot of $\ln(t_m)$ against T^{-1} is a straight line, where t_m is the time to reach the maximum in the crystallization curve, then an effective activation energy E_c/n can be obtained from the slope [5]. This is plotted in Fig. 2. The

TABLE I The values of n derived from the graphs of $\ln[-\ln(1-x)]$ against $\ln t$

Temperature (K)	n
630	2.56
625	2.7
625	2.48
625	2.56
620	2.44
615	2.36
610	2.40
610	2.54
605	2.34
600	2.36
590	2.44

Mean value = 2.5 ± 0.2.

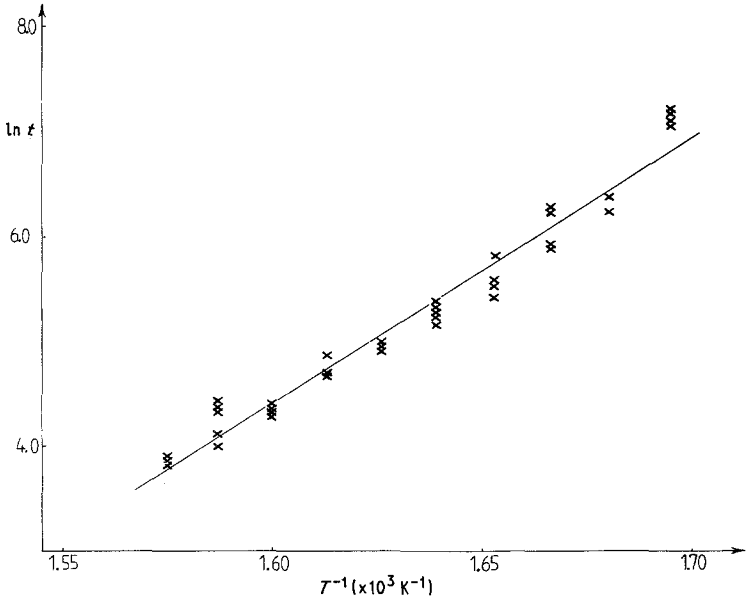

Figure 2 Plot of ln (t_m) against T^{-1}.

best-fit straight line was found by a least-squares analysis which gave an effective activation energy E_c/n of 212 ± 7 kJ mol^{-1} (50.5 ± 1.7 kcal mol^{-1}). (The errors quoted are one standard deviation.)

The results from the non-isothermal method were analysed by plotting $\ln \phi/T_c$ against T_c^{-1}, where ϕ is the heating rate and T_c is the temperature at which the maximum rate of heat evolution due to crystallization occurs. The slope of the plot yields a value for E_c/n, the same effective activation energy that was defined above [4]. The best straight line fitted by a least-squares analysis gave an energy E_c/n of 218 ± 7 kJ mol^{-1} (51 ± 1.7 kcal mol^{-1}) (see Fig. 3).

The heat of reaction was obtained by measuring the total area under the peaks and was found to be 13 ± 1.5 kJ mol^{-1} (3.1 ± 0.4 kcal mol^{-1}).

3.2. Structural investigation

X-ray diffraction patterns were recorded of samples "quenched" in the calorimeter at the maximum cooling rate of 320 K sec^{-1}, after less than 10% of the material had transformed. It was found that peaks corresponding to a distorted pseudo-body-centered cubic phase (b c c) were superimposed on the diffraction pattern of the amorphous phase. The true symmetry of this crystalline phase is probably body-centred tetra-

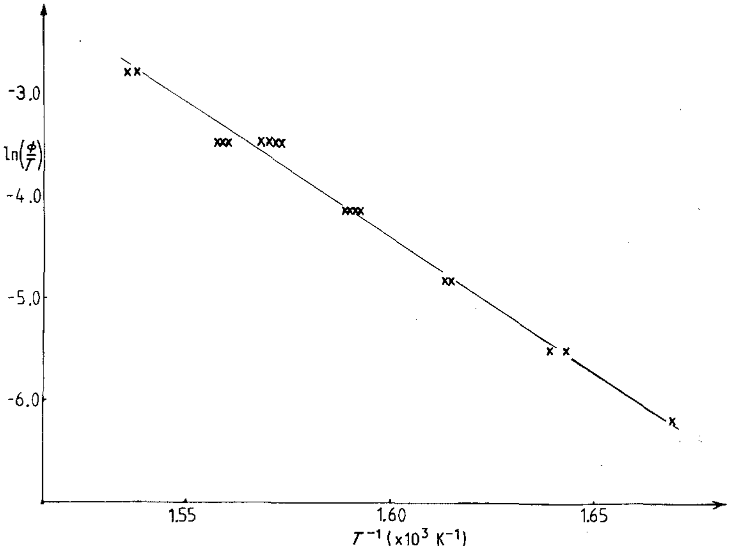

Figure 3 Plot of ln (ϕ/T_c) against T_c^{-1}.

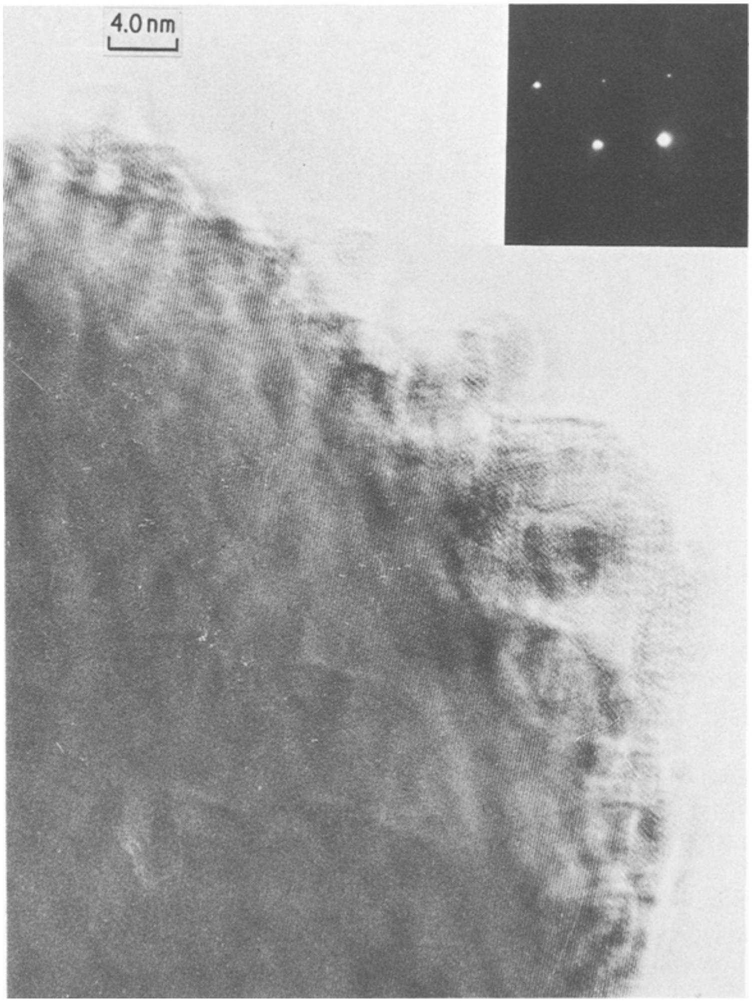

Figure 4 Electron micrograph and diffraction patterns of a hexagonal close-packed crystallite formed upon crystallisation of amorphous Pd_4Ge.

gonal with $a = 0.304$ nm and $c = 0.308$ nm, the distortion from cubic symmetry being less than 2%.

However, the electron microscope showed that the structure of the above sample was not so simple. Certainly many b c c crystallites were found with a cell dimension of about 0.304 nm but, also, a hexagonal close-packed (h c p) structure was found. Fig. 4 shows the "two-beam" image of a h c p crystallite together with its diffraction pattern, which was identified as the $(1\,2\,\bar{3}\,1)$ plane. By accurately measuring the angle between the $(1\,0\,\bar{1}\,\bar{1})$ and $(1\,\bar{1}\,0\,1)$ reciprocal lattice points, the c/a ratio was determined to be 1.63 which is the exact ratio expected for a perfect h c p structure. The micrograph of this crystallite, which was at least 85 nm x 100 nm in size, shows well-resolved lattice fringes corresponding to the diffracted beam, especially at the edge of the crystallite where it was thinner and visibility was improved. The fringe spacing was measured using a travelling microscope and was found to be 0.20 nm, as expected from the diffraction pattern. This gives $a = 0.262$ nm and $c = 0.427$ nm. The lattice fringes are very regular with few faults except in the interface between the crystalline phase and the matrix, where there is an unidentified structure which extends for about 4.0 nm.

Two further microcrystalline diffraction patterns were also observed from the same specimen. The first could be indexed as having a face-centred cubic (f c c) lattice with $a = 0.40$ nm, which is the same lattice as pure palladium. It is possible, therefore, that these crystallites were pure palladium which had evolved from the amorphous matrix, or perhaps it is a palladium–germanium alloy with the f c c lattice sites being statistically

TABLE II Comparison of kinetic parameters for Pd_4Ge and Pd_4Si

Material	E_{act} (kJ)	n	ΔH (kJ)	Reference
Pd_4Ge	213 ± 7	2.5 ± 0.2	1.3 ± 1.5	See text
Pd_4Si	320 to 340	2.8 to 2.9	–	[7]

occupied by either palladium or germanium. Dark-field microscopy showed the size of these crystallites to be about 80 nm in diameter. The second diffraction pattern had rings corresponding to lattice spacings of 0.34, 0.20, 0.17, 0.12, 0.112 nm, which correspond to the lattice spacings for germanium, although the predicted weak ring at 0.1414 nm was not observable in the pattern.

A crystallized sample held for 24 h at 750 K was found to contain the equilibrium phase Pd_5Ge [6] which occurs on one side of the eutectic. Further peaks visible on the diffraction trace could not be indexed as any known phase and it is assumed that they correspond to the equilibrium compound Pd_3Ge, the structure of which is currently being investigated.

4. Discussion

The kinetic parameters of Pd_4Ge are listed in Table II together with those of Pd_4Si [7]. Both of these materials have a low value for the exponent n, which according to Christian [2] may suggest nucleation only occurs on preferred sites if the reaction is controlled by the nucleation rate or there is a decreasing nucleation rate with the transformed regions growing from negligibly small dimensions if the transformation is diffusion controlled.

Table II also shows that Pd_4Si and Pd_4Ge have similar effective activation energies, the replacement of Ge by Si giving a slightly higher energy. However, Duhaj *et al.* [7] found a single stage transformation from amorphous to crystalline products with no intermediate metastable products, whereas Pd_4Ge went through a number of metastable phases during its transformation; because of this, it is not entirely clear that a direct comparison between activation energies can be made.

The X-ray analysis showed that the main initial product of crystallization has a pseudo-bcc lattice, in contrast with Pd_4Si which initially crystallized out with the same lattice (fcc) as the parent metal, palladium [8]. However, electron microscopy showed that other phases were present. Specifically, unidentified phases with hcp and fcc lattices and crystallites of Ge were observed. The production of all three types of close-packed structures in the same sample is a clear indication of the similarity of the energies of formation of these structures, and indicates that the formation of these phases is governed by kinetic rather than equilibrium considerations.

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