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GLASS-FORMING ABILITY AND CRYSTALLIZATION KINETICS OF AMORPHOUS PALLADIUM–BORON ALLOYS

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ABSTRACT

Palladium–boron alloys have been prepared to check their ability to produce metallic glasses when spun from the melt.

An amorphous alloy with 31.5 at.% boron obtained in the form of ribbon has been submitted to both isothermal and non-isothermal DSC tests. The isothermal crystallization kinetics have been analyzed according to the Avrami law for phase transformations in solids.

The *n* exponent of the law has been determined to obtain information on the geometrical features of the growing crystals. A confirmation of the calculated *n* value has been sought through an analysis of non-isothermal DSC peaks.

INTRODUCTION

The glass-forming ability of metallic systems rapidly quenched from the liquid state has been frequently related to the presence of a "deep eutectic" in the phase diagram.

An accurate analysis of such diagrams for binary systems able to produce glassy alloys led Donald and Davies [1] to put forward a rule to express this concept in a quantitative way. They stated that the technique known as "melt spinning" can produce amorphous ribbons only if the ΔT lowering of the liquidus line in the phase diagram (with respect to that of an ideal mixture) divided by the liquidus temperature of the ideal mixture (i.e. $\Delta T/T_{id}$) is $\geqslant 0.2$ at the eutectic composition.

Some efforts to obtain metallic glasses from binary systems in conflict with the rule ($\Delta T/T_{id} < 0.2$) have been unsuccessful in eutectic Be alloys containing Si, Y, B, Fe and Sc [2]. The Pd–B system that satisfies the criterion of the "deep eutectic" ($\Delta T/T_{id} = 0.45$) has been checked in the present work.

EXPERIMENTAL

Palladium alloys containing between 23 and 42 at.% boron have been prepared by melting the pure components in alumina crucibles heated to 1650°C under a

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protective atmosphere of purified argon. The alloys were then introduced into a melt spinning apparatus and quenched from the molten state at around 1100°C onto a copper wheel rotating at 6000 rev. min^{-1}.

Several partially amorphous ribbons have been obtained, but in a narrow concentration range around the eutectic composition, both X-ray diffraction and DSC tests revealed the presence of a completely amorphous structure. The transition from the amorphous to the crystalline state has been studied on a $Pd_{68.5}B_{31.5}$ metallic glass by means of both isothermal and non-isothermal tests carried out in a DuPont 1090 DSC apparatus on specimens of 1.1–1.5 mg.

Isothermal DSC runs were recorded at temperatures between 375 and 390°C. After reaching the operating temperature at a 170°C min^{-1} heating rate, the DSC baseline was unstable for about 30 s and then exothermic peaks of crystallization were detected after an induction period whose length depended on the isothermal temperature value and which ranged between 51 and 288 s.

Tests with a linear temperature increase were also performed at heating rates of between 2 and 50°C min^{-1} and non-isothermal DSC peaks of crystallization were recorded.

RESULTS AND DISCUSSION

The transformed fractions, α, during isothermal crystallization shown in Fig. 1 were determined as a function of time: they are the ratios of the partial and the total areas under the DSC peaks.

Crystallization kinetics of metallic glasses has been recognized [3–9] as following the nucleation and crystal growth process described by Avrami and Johnson–Mehl. Only two Pd-based glassy alloys containing Si [10] and Ag–Si [11] seem to follow the

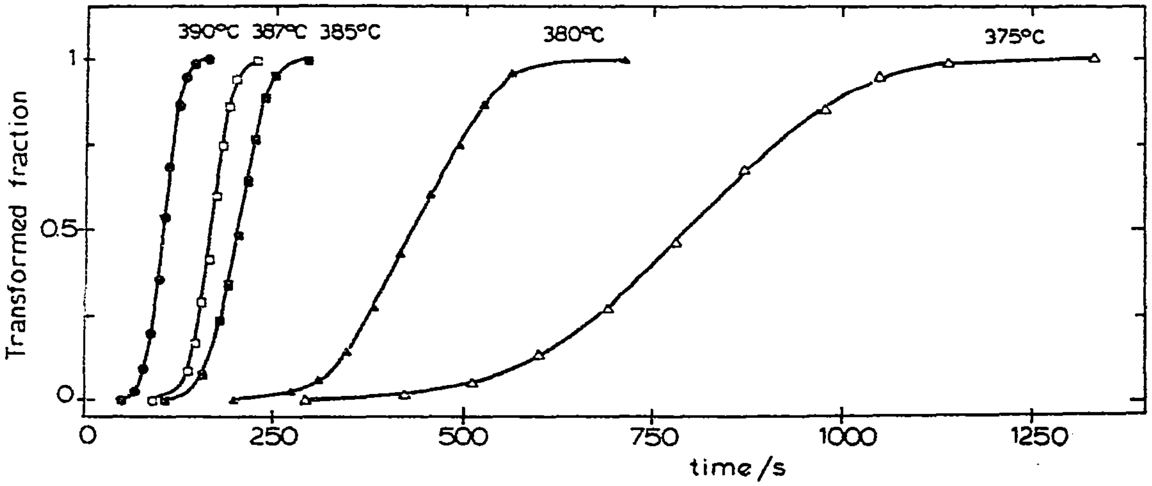


Fig. 1. Transformed fractions during isothermal crystallization of $Pd_{68.5}B_{31.5}$ metallic glass as a function of time.

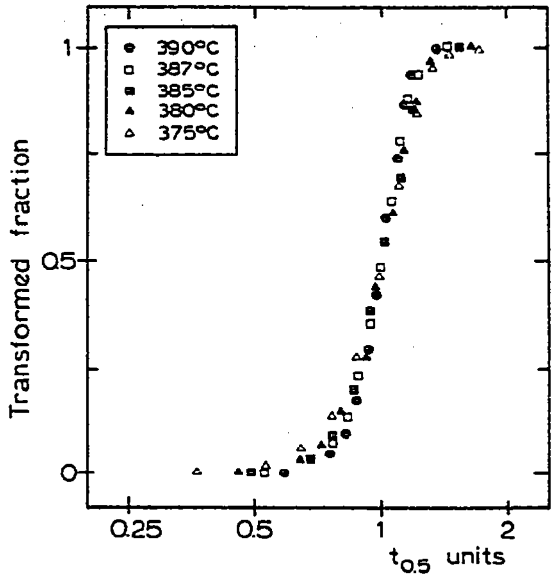


Fig. 2. Experimental points of Fig. 1 vs. log t, shifted along the log t axis to obtain superimposition of the α transformed fractions 0.5, produced at time $t_{0.5}$.

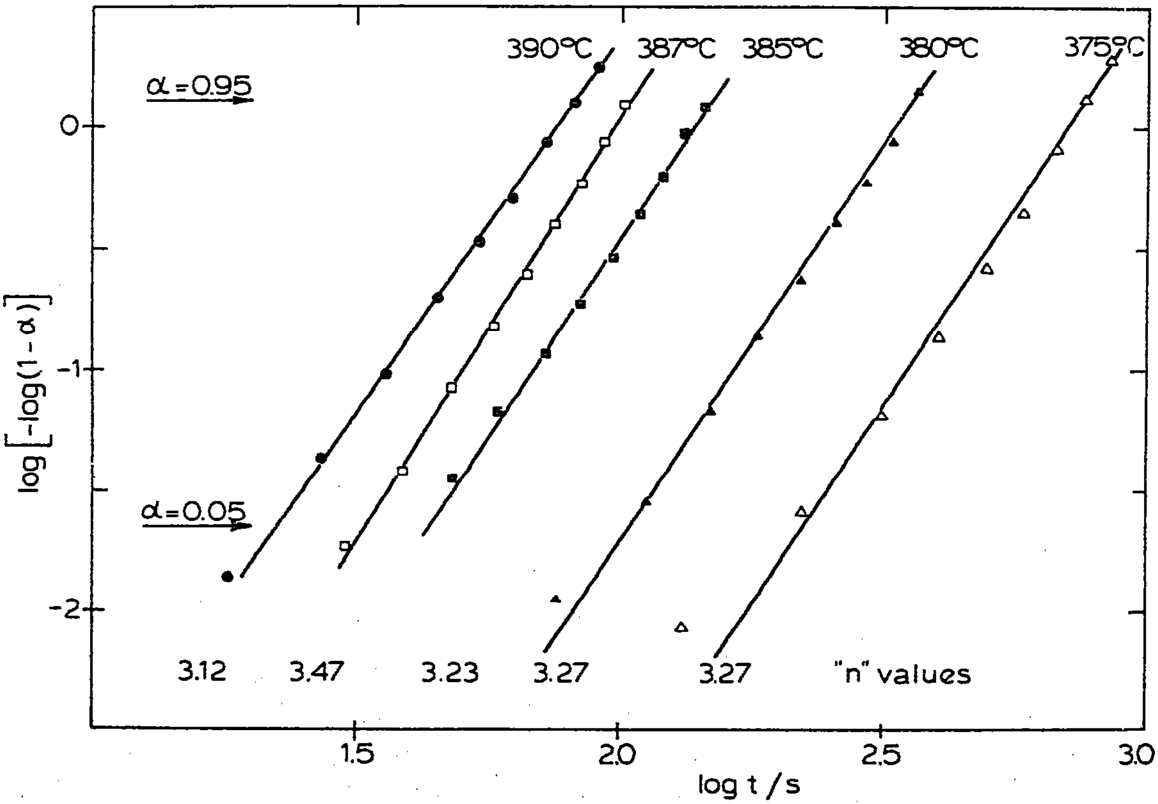


Fig. 3. Avrami plot of log{$-$log(1$-\alpha$)} as a function of log time for various isotherms. The exponent, n, of the Avrami law resulting from the slope of the straight lines is indicated.

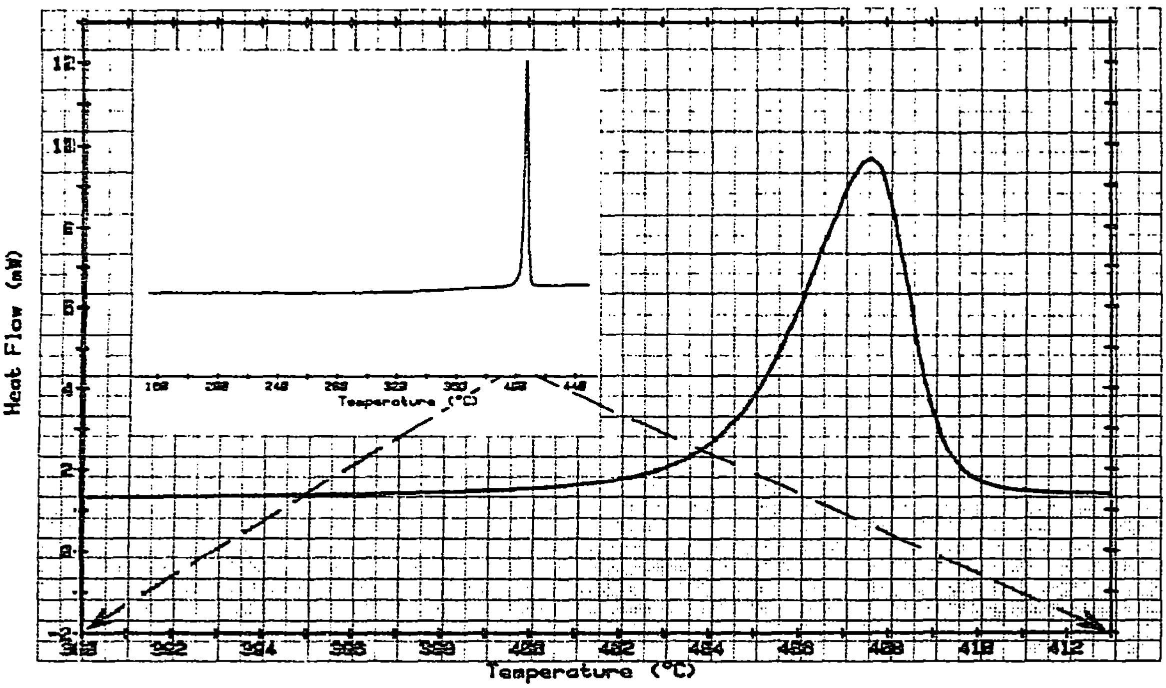


Fig. 4. Original DSC traces at 20°C min^{-1} for 1.5 mg of the $Pd_{68.5}B_{31.5}$ glassy alloy. A strong expansion of the temperature scale of the inset curve (see arrows) is used in the other record.

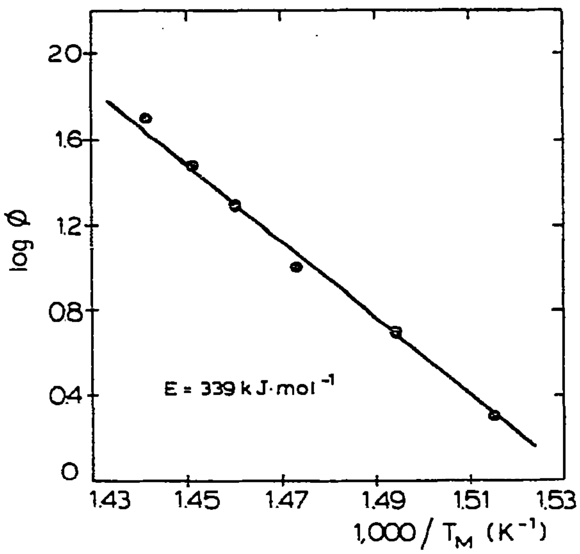
law for autocatalyzed reactions, thus differing from the well known $1-\alpha = \exp(-kt^n)$ Avrami isothermal rate equation.

If rates of nucleation and crystal growth are constant during the process, the Avrami law requires that the sigmoidal curves of Fig. 1 become parallel when plotted against time on a log scale. Johnson and Mehl showed that the rates of nucleation and growth either increase or decrease in the cases in which the shift of these curves along the log t axis (to make the 0.5 transformed fraction to coincide) does not give a superimposition of all the curves.

A good parallelism of the sigmoidal curves on a log t scale has been found in the present case and superimposition by shifting is reported in Fig. 2. The low spread displayed by the experimental points allows one to state that (a) the Avrami rate equation is followed and (b) the rates of nucleation and crystal growth are practically constant.

According to the $1-\alpha = \exp(-kt^n)$ equation, plots of $\log\{-\log(1-\alpha)\}$ vs. $\log t$ should give straight lines of slope n. Such plots for the DSC isotherms are reported in Fig. 3 where the incubation period has been subtracted (see ref. 3) in the $\log t$ scale. Straight lines have been obtained (coefficients of linear correlation between 0.9978 and 0.9994) at least for α crystallized fractions between 5 and 95%. A mean value of 3.27 has been determined for the Avrami coefficient n; such a figure indicates that crystal growth should occur in three dimensions, i.e. in spherulitic form.

It has been shown recently [12] that the exponent n can also be calculated from a single DSC run at a constant heating rate, provided the activation energy, E, of the



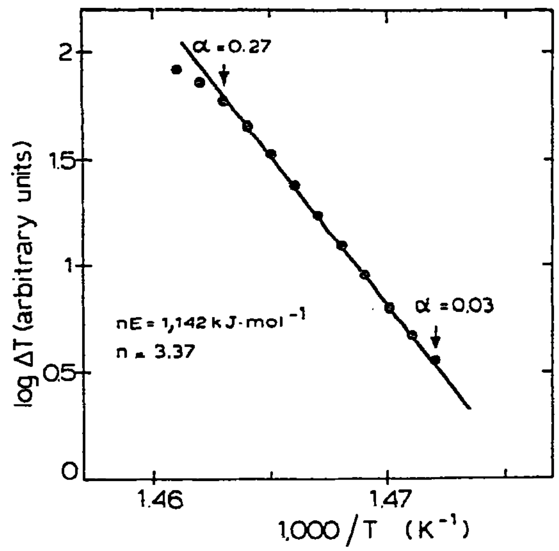


Fig. 5. Ozawa plot of the logarithm of heating rate vs. the reciprocal of the peak absolute temperature for $Pd_{68.5}B_{31.5}$ alloy.

Fig. 6. Logarithm of the DSC deflection in Fig. 4 as a function of the reciprocal of the absolute temperature.

process is known. A plot of log ΔT (differential temperature) vs. $1/T$, first introduced by Piloyan et al. [13], in fact gives a slope of nE/R instead of E/R when the Avrami rate equation is followed [12,14].

The ΔT evaluation on the sharp DSC peak of the $Pd_{68.5}B_{31.5}$ glassy alloy was made possible through the strong expansion of the T axis shown in Fig. 4. The apparent activation energy, E, has been determined by the Ozawa peak shift method [15], the correctness of which has been proved by theoretical transformation laws [16]. The Ozawa plot of log Φ (heating rate) vs. $1/T_M$ (reciprocal of the peak absolute temperature) for the metallic glass is reported in Fig. 5.

From the 0.4567 E/R slope of the straight line, a value of 339 kJ mole^{-1} for the activation energy of crystallization is obtained. The Piloyan et al. plot is given in Fig. 6: from the slope of the straight line and the predetermined E value, a value of 3.37 for the Avrami exponent, n, is calculated.

The agreement with the isothermal evaluation reported above (n between 3.12 and 3.47) confirms the hypothesis of a spherulitic form for the crystals produced by the transformation.

CONCLUSIONS

(1) Palladium–boron alloys are able to produce amorphous ribbons by melt spinning.

(2) The crystallization kinetics of $Pd_{68.5}B_{31.5}$ metallic glass follow the Avrami rate equation over a wide range of transformed fractions (5–95%).

(3) The Avrami coefficient, *n*, determined both in isothermal conditions (values of 3.12–3.47) and at constant heating (3.37) indicates that the crystals grow in a spherulitic form.

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