Journal of Thermal Analysis, Vol. 28 (1983) 413–420

ISOTHERMAL STUDY OF CRYSTALLIZATION OF Pd–Ni–Si AMORPHOUS METALLIC MATERIALS

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(Received May 30, 1983)

The isothermal crystallization of amorphous alloys of the type $(Pd_{100-x}Ni_x)_{83}Si_{17}$ has been investigated by DSC. The character of the transformation depends upon the content of Ni. If $x > 30$, material crystallizes probably without nucleation in a very narrow temperature range. If $x \leqslant 30$, the crystallization process is controlled by a nucleation-growth mechanism. The initial stages of transformation are characterized by a relatively short incubation period with an Arrhenius temperature-dependence. Afterwards, the time-dependence of the degree of conversion is sigmoidal. If $\alpha < 0.1$, then $p \sim 1$ characterizes a homogeneous nucleation. If $0.1 < \alpha < 0.9$ than the Avrami exponent is $p(\alpha) \sim 3$–4. At $\alpha > 0.9$ so-called tails are observed.

Two kinds of unseparable non-stationarities of the nucleation-growth process at the beginning of crystallization of the amorphous material are discussed.

In previous papers [1–4] the crystallization of amorphous binary and ternary (Ni, Co, Fe) alloys of the Pd–Si system has been studied. The kinetic parameters of crystallization were investigated. Our study was mainly concerned with the activation energy of crystallization, which (similarly as for other amorphous alloys) has an anomalously high absolute value [5] and in the case of the Pd–Si system exhibits a strong temperature-dependence [6]. We believe that the transport in these alloys within the temperature range of crystallization of the amorphous material can not be performed by long-range diffusion. A cooperative motion of larger regions of volume is considered here.

The aim of this work is to determine the isothermal kinetic parameters of crystallization of amorphous alloys in the Pd–Ni–Si system by DSC methods.

Experimental

On the basis of our previous results [4], three amorphous metallic materials were chosen: $(Pd_{90}Ni_{10})_{83}Si_{17}$, as a material with an unambiguous model course of the non-isothermal crystallization exotherm and the corresponding Piloyan dependence;

$(Pd_{85}Ni_{15})_{83}Si_{17}$, as a comparison material; and $(Pd_{60}Ni_{40})_{83}Si_{17}$, as a material representing the group of over-critical amorphous metallic materials. The amorphous alloys were 20 μm thick, prepared by the roller-quenching technique and tested by X-ray diffraction and electron microscopy.

Amorphous foils cut into small slices (total weight 5–13 mg) were calorimetrically studied, using a Perkin–Elmer DSC-1B apparatus in a nitrogen atmosphere. The reference aluminium pan was empty.

Results and discussion

Analysis of $(Pd_{90}Ni_{10})_{83}Si_{17}$ *and* $(Pd_{85}Ni_{15})_{83}Si_{17}$ *amorphous alloys*

The samples were annealed at temperature T_a within the interval 13–24 K below the spontaneous crystallization temperature maximum T_M. In all cases the crystallization was observable after an incubation period τ. The exponential temperature-dependence of the incubation period

$$\tau = \tau_0 \exp\left[(\Delta E^*_{A\tau})/(RT)\right] \tag{1}$$

determined the temperature coefficients $\Delta E^*_{A\tau}$, representing the earliest stages of the transformation.

The extent of crystallization α increased with time sigmoidally. The dependences

$$-\ln(1-\alpha) = (Kt)^p \tag{2}$$

for all temperatures T_a for a $(Pd_{90}Ni_{10})_{83}Si_{17}$ samples are shown in Fig. 1. For $0.1 < \alpha < 0.9$, a linear least-squares fit was used, which provided the Avrami exponent $p(\alpha)$ and the integral rate constant $K(\alpha)$. Deviations from linearity for $\alpha \ll 0.1$ are probably caused by the sensitivity threshold of the employed apparatus and by the method of mathematical evaluation. Afterwards, the exponent, $p \sim 1$ characterizes the homogeneous nucleation; it gradually increases up to the value $p \sim 4$. At $\alpha > 0.9$, so-called tails are observed, i.e. the slope of the logarithm of the investigated dependence (2) declines. Such an effect is typical for amorphous metallic materials [7], and for Pd–Si alloys it is especially marked [8]. At this stage nucleation is probably finished and volume crystallization dies away.

The rate constant K for both materials increases with temperature according to the Arrhenius law and determines the temperature coefficient ΔE^*_{AK}. In the case of the exponent p no temperature-dependence was observed and average values $\bar{p} = 4.23 \pm 0.096$ for $(Pd_{90}Ni_{10})_{83}Si_{17}$ and $\bar{p} = 4.45 \pm 0.075$ for $(Pd_{85}Ni_{15})_{83}Si_{17}$ were found. However, when a larger temperature interval is taken into account (using the electrical resistivity method [9, 10]), the Avrami exponent decreases to $\bar{p} = 3.5 \pm 0.14$ with the decrease of temperature T_a to ~ 660 K for $(Pd_{90}Ni_{10})_{83}Si_{17}$.

At every annealing temperature T_a interpolation was used to determine the time of 50% and 100% crystallization of the materials $t_{0.5}$ and ϑ. From the experimental

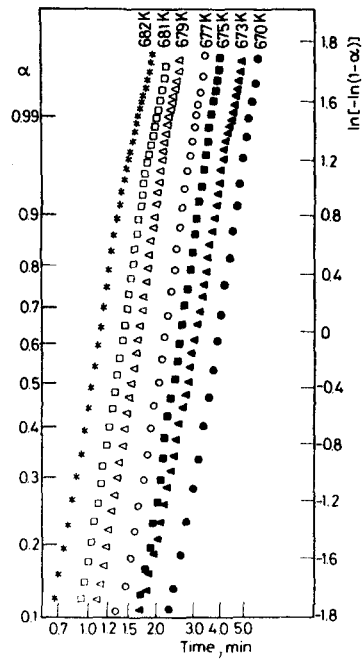

Fig. 1 Avrami dependences of isothermal crystallization of amorphous alloy $(Pd_{90}Ni_{10})_{83}Si_{17}$ for $\alpha > 0.1$ for various temperatures

temperature-dependences of $t_{0.5}(T_a)$ and $\vartheta(T_a)$, the temperature coefficients $\Delta E^*_{A0.5}$ and $\Delta E^*_{A\vartheta}$ were determined. These coefficients represent the complex activation energy of crystallization $\Delta E^*_A(\alpha)$ [5].

Annealing temperatures T_a, experimental incubation periods $\tau(T_a)$, time values $t_{0.5}(T_a)$ and $\vartheta(T_a)$, and parameters $p(T_a)$ and $K(T_a)$ for the amorphous metallic materials $(Pd_{90}Ni_{10})_{83}Si_{17}$ and $(Pd_{85}Ni_{15})_{83}Si_{17}$ are listed in Table 1. The magnitudes of the crystallization activation energies determined by isothermal methods of kinetic analysis are given in Table 2.

Discussion

If the start of nucleation-growth transformation $t = 0$ is taken at the beginning of annealing instead of the end of the incubation period τ in the kinetic analysis of isothermal crystallization of amorphous metallic material, a smaller error ($r'^2 \sim 0.99$) but an inconsistently large Avrami exponent p' (for $(Pd_{90}Ni_{10})_{83}Si_{17}$, $p' \sim 4.55$) will be obtained. For example, the value $p' \sim 11$ from [8] is criticized in [7]. Our approach is supported by the fact that, after preheating of samples at $T < T_a$,

Table 1 Incubation periods, τ, periods of 50% and 100% conversion, $t_{0.5}$, and ϑ (without incubation periods), Avrami exponents, p, and time constants, K, of isothermally annealed amorphous alloys $(Pd_{90}Ni_{10})_{83}Si_{17}$ and $(Pd_{85}Ni_{15})_{83}Si_{17}$; δ and δ_{rel} – absolute and relative mean quadratic fluctuations

$(Pd_{90}Ni_{10})_{83}Si_{17}$						$(Pd_{85}Ni_{15})_{83}Si_{17}$					
T_a, K	τ, min	$t_{0.5}$, min	ϑ, min	p	K, min^{-1}	T_a, K	τ, min	$t_{0.5}$, min	ϑ, min	p	K, min^{-1}
671	6.5	4.2	6.9	4.2	0.94	678	4.36	4.72	7.5	4.7	0.9
673	5.0	3.1	5.2	4.1	1.21	680	3.36	3.43	5.7	4.5	1.3
675	3.4	2.5	4.2	4.2	1.58	681	2.92	2.97	4.9	4.6	1.4
677	2.6	2.1	3.6	4.4	1.96	682	2.60	2.69	4.5	4.4	1.5
679	2.2	1.5	2.8	4.2	2.55	683	2.43	2.14	3.7	4.2	1.8
						684	2.13	1.92	3.4	4.4	2.1
δ	±0.22	±0.22	±0.23	±0.180	±0.030	δ	±0.06	±0.05	±0.14	±0.14	±0.12
δ_{rel}	±4.60%	±7.22%	±4.39%	±4.52%	±2.38%	δ_{rel}	±2.68%	±2.42%	±3.90%	±3.33%	±6.42%

Table 2 Activation energies of crystallization of amorphous alloys $(Pd_{90}Ni_{10})_{83}Si_{17}$ and $(Pd_{85}Ni_{15})_{83}Si_{17}$; ΔE_A^* – if incubation period $\tau \neq 0$; $\Delta E_A^{*\prime}$ – if incubation period $\tau = 0$; r – correlation coefficients of linear approximation

Studied relation	$(Pd_{90}Ni_{10})_{83}Si_{17}$				$(Pd_{85}Ni_{15})_{83}Si_{17}$			
	ΔE_A^*, kJ · mol^{-1}	r^2	$\Delta E_A^{*\prime}$, kJ · mol^{-1}	r^2	ΔE_A^*, kJ · mol^{-1}	r^2	$\Delta E_A^{*\prime}$, kJ · mol^{-1}	r^2
$\tau = \tau_0 \exp[(\Delta E_{A\tau}^*)/(RT)]$	537	0.95	–	–	450	0.94	–	–
$\tau \sim 1/(\Delta T)^2 \exp[(\Delta E_{A\tau}^*)/(RT)]$	557	0.95	–	–	470	0.94	–	–
$t_{0.5} = t_0 \exp[(\Delta E_{A0.5}^*)/(RT)]$	455	0.96	504	0.99	573	0.94	515	0.99
$\vartheta = \vartheta_0 \exp[(\Delta E_{A\vartheta}^*)/(RT)]$	411	0.96	470	0.99	509	0.95	489	0.99
$K = K_0 \exp[(-\Delta E_{AK}^*)/(RT)]$	470	0.98	–	–	501	0.97	–	–

τ – incubation period, $t_{0.5}$ – time to reach the degree of conversion $\alpha = 0.5$, ϑ – time to reach $\alpha = 1$, K – integral rate constant, T – temperature, $\Delta T = T_{melt} - T$, T_{melt} – melting point, τ_0, t_0, ϑ_0, K_0, R, ΔE_A^* – constants

$p \sim (3–4)$. The preheating is equivalent to substracting the duration of the incubation period τ.

The incubation period is a common characteristic of an isothermal phase transformation and may be conceived as the time required for the creation of a uniform statistical distribution of the sizes and concentrations of the subcritical nuclei corresponding to the annealing temperature T_a. The incubation period represents the transition effect of the nucleation rate I_t, i.e. the period of its increase from $I_t = 0$ to the steady value $I_t = I_0$ [5]. Incubation periods serve as a measure of the stability of amorphous metallic materials in practice too.

On the other hand, the classical definition gives the induction or incubation period as the duration of non-sensitivity of the experimental equipment, i.e. the time during which the smallest detectable amount of new phase is created. In this case, however, the induction period is already a part of the transformation.

The real reason for a non-steady nucleation-growth process at the beginning of isothermal crystallization of amorphous metallic material is not known. In Pd–Si materials, incubation periods for the same temperature difference $(T_M - T_a)$ are shorter than in other common amorphous alloys [8] and they have little influence on the magnitude of the Avrami exponent p. The magnitudes of the activation energies are more favourable in the event of inclusion of the incubation period.

Therefore, it is probable that the real transition effect at the beginning of isothermal crystallization of the investigated amorphous metallic materials of the Pd–Si system consists of both mentioned incubation processes. It was not possible either to separate them or to determine their ratio. Thus, we assume that the real absolute values of parameters p'' and $\Delta E_A^{*''}$ lie between the determined values p and p', and ΔE_A^* and $\Delta E_A^{*'}$, respectively. The behaviour does not change with varying $3d$ metal content.

Analysis of over-critical amorphous alloy $(Pd_{60}Ni_{40})_{83}Si_{17}$

Over-critical amorphous samples (more than 30% Ni [3]) were investigated isothermally in the same way as the subcritical materials. Although we enlarged the range of annealing temperatures to $3\ K < T_M - T_a < 38\ K$, and the observation time t_a up to 60 minutes, no thermal effect of the low-temperature stage of crystallization transformation (which was realized during the experiment) was observed.

The samples annealed at temperature $T_a < 677$ K for time t_a further exhibited crystallization transformation, the enthalpy of which quantified the non-crystallized fraction. It seems that the amorphous alloy $(Pd_{60}Ni_{40})_{83}Si_{17}$ is stable below 677 K, or in the cycle of linear heating of the sample following immediately after the isothermal treatment the temperature of the beginning of the first non-isothermal crystallization exotherm, T_{x1}, falls, and the temperature of its maximum, T_{M1}, rises.

The isothermal crystallization of this amorphous material is observable only at the temperature $T_a \sim 677$ K, and it probably occurs with a velocity such that the

transformation is completed after a time interval shorter than the dead-time of the calorimeter, $t \sim 15$ s.

Conclusion

Due to the limited stability of the calorimeter, the kinetics of crystallization of amorphous Pd–Ni–Si alloys has been studied isothermally only within a narrow temperature range. Electron microscopy and diffraction patterns of samples obtained at these temperatures at various times [9] have shown that, in the case of subcritical samples, the dynamic DSC exotherm and also the isothermal crystallization anomaly represent the crystallization of amorphous matrix into supersaturated solid Ni-contaminated PdSi solution, which gradually becomes ordered in a fcc Pd-like crystalline phase, identified as M_1 superlattice. For over-critical samples, the low-temperature DSC exotherm corresponds to the primary crystallization of the PdNi phase, while the high-temperature exotherm corresponds to the crystallization of remaining amorphous matrix.

Within the experimental errors, the value of the Avrami exponent of subcritical amorphous metallic materials is $p \sim 4$ (in a larger temperature range $p \sim 3$–4). This value is consistent with the results of similar kinetic analyses of rapidly-cooled amorphous metallic materials. This value may represent either three-dimensional growth of crystallites with a decreasing nucleation rate controlled by reaction at the phase boundary crystal undercooled liquid, or diffusion-limited cellular growth of crystalline product [11]. Long-range diffusion is hardly probable in amorphous materials [6]. In the case of Pd–Si materials, cellular decomposition was observed by electron microscope in advanced stages of recrystallization of the metaphase [12]. In both subcritical materials, the observed growth of parameter p with temperature T_a indicates that the fall of the nucleation rate decreases during transformation.

When the critical concentration of the third atom is reached (e.g. $(Pd_{60}Ni_{40})_{83}Si_{17}$), the new Ni-rich surroundings attain the critical nucleus dimensions and begin to serve as the nucleation centres for the new PdNi phase.

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Zusammenfassung — Die isotherme Kristallisation amorpher Legierungen des Types $(Pd_{100-x}Ni_x)_{83}Si_{17}$ wurde durch DSC untersucht. Der Charakter der Umwandlung hängt vom Nickelgehalt ab. Ist $x > 30$, so kristallisiert die Substanz wahrscheinlich ohne Keimbildung in einem sehr engen Temperaturbereich. Ist $x \leqslant 30$, so ist der Kristallisationsprozess durch einen Keimwachstumsmechanismus bestimmt. Die Anfangsstadien der Umformung sind durch eine relativ kurze Inkubationsperiode gekennzeichnet und weisen eine Arrhenius-Abhängigkeit von der Temperatur auf. Später ist die Zeitanhängigkeit des Konversionsgrades sigmoidal. Wenn $\alpha < 0.1$, dann charakterisiert $p \sim 1$ eine homogene Keimbildung. Gilt $0.1 < \alpha < 0.9$, so ist der Avrami-Exponent $p(\alpha) \sim 3$–4. Bei $\alpha > 0.9$ werden sogenannte Schweife beobachtet.

Zwei nicht separierbare Arten der Nicht-Stationarität des Keimwachstumsprozesses zu Beginn der Kristallisation des amorphen Materials werden diskutiert.

Резюме — Методом ДСК изучена изотермическая кристаллизация аморфных сплавов типа $(Pd_{100-x}Ni_x)_{83}Si_{17}$. Характер превращений зависит от содержания никеля. При содержании никеля $x > 30$, сплав кристаллизуется в очень узком температурном интервале и, повидимому, без образования центров кристаллизации. При $x \leqslant 30$, процесс кристаллизации опредуляется процессом образование центров кристаллизации-рост. Начальные стадии превращения характеризуются относительно коротким инкубационным периодом с аррениусовской температурной зависимостью. Впоследствии, временная зависимость степени превращения (α) становится сигмоидальной. Если $\alpha < 0.1$, тогда $p \sim 1$ характеризует гомогенное образование центров кристаллизации. При $0.1 < \alpha < 0.9$ экспонента Аврами становится равной $p(\alpha) \sim 3$–4. При $\alpha > 0.9$ наблюдались так называемые "хвосты". Обсуждены два типа нераздельных нестационарных процессов образование центров кристаллизации-рост в начале кристаллизации аморфного сплава.