MODEL OF MASS TRANSPORT IN Pd—Si LIKE AMORPHOUS METALLIC MATERIALS

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The temperature dependence of the activation energy of crystallization ΔE^* of amorphous metallic alloys $(Pd_{80}Ni_{10})_{83}Si_{17}$ and $(Pd_{48}Ni_{13})_{83}Si_{17}$ is shown. Reorganization of the structural units is explained by means of the motion of the cooperative rearranging of regions during crystallization — the so-called viscous flow of the undercooled liquid. The temperature dependence of viscosity η of the undercooled liquid around the crystallization temperatures is determined from the viscous flow model.

The generalized model of mechanism of crystallization of metallic glasses of the type Pd—Si is proposed.

МОДЕЛЬ ПЕРЕНОСА МАССЫ В АМОРФНЫХ МЕТАЛЛИЧЕСКИХ МАТЕРИАЛАХ НА БАЗЕ Pd—Si

В работе приведены результаты измерений температурной зависимости энергии активации кристаллизации аморфных металлических материалов $(Pd_{80}Ni_{10})_{83}Si_{17}$ и $(Pd_{48}Ni_{13}Si_{17}$. Перераспределение структурных единиц в ходе кристаллизации об-ъясняется с помощью перемещения кооперативно-перегруппированных областей, т. е. на основе так называемого вязкого потока переохлажденной жидкости. Из этой модели определена температурная зависимость вязкости переохлажденной жидкости в области температур кристаллизации. На основе полученных экспериментальных данных предложено обобщение модели механизма кристал-лизации металлических стекол на базе Pd—Si.

I. INTRODUCTION

The transport properties of amorphous metallic materials are not fully known yet. The standard eperimental techniques (where the diffusion profile is deter-mined by a gradual grinding of radioactive layers) cannot be applied here due to a very small thickness (20 μm), unsuitable mechanical properties, and a too low diffusion rate in comparison with the kinetics of crystallization processes of these materials. The only published direct data which characterize diffusion of non-metal

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(boron) into an amorphous alloy [1] give abnormally low values of the diffusion coefficient, namely $D < 10^{-18}$ m²s⁻¹. The empirical fact that the diffusion coefficient is a function of viscosity ($D \sim \eta^{-1}$) and temperature within a wide temperature range can be explained on the basis of the molecular-kinetic approach to the viscous relaxation processes in amorphous material using the mechanisms of the viscous flow.

II. EXPERIMENTAL

According to the viscous flow model [2, 3] the rheological behaviour of amorphous material is essentially based on the cooperative motion of certain regions — subsystems of the material which, due to a sufficient fluctuation energy (free enthalpy to be exact), can be rearranged or displaced to a new arrangement with no relation to their surroundings. The size of these associated regions and its temperature dependence is limited by the tightness of the amorphous ordering.

The entropic model [2] yields the activation energy of viscous flow ΔE_η^* as a function of temperature T

$$\Delta E_\eta^*(T) \sim R \partial (\ln \eta)/\partial (T^{-1}) = CRT^2/(T-T_0).$$ (1)

The free-volume model [3] gives the activation energy ΔE_η^* as an exponential function of temperature T, namely

$$\Delta E_\eta^*(T) = D \exp [W/(RT)]$$ (2)

where C, D, T_0, W are material parameters (temperature independent) and R is the gas constant.

The temperature dependence of the activation energy of viscous flow is not surprising. In fact (1) (obeys an expectation which) follows from a general assumption that the viscosity of amorphous materials fulfills within the temperature range between melt (T_{top}) and glass-forming (T_g) temperatures the Fogel-Fullcher law, i.e.

$$\eta = A \exp [B/\{R(T-T_0)\}]$$ (3)

where the parameters A, B, T_0 do not depend on temperature.

We have studied the crystallization of $(Pd_{90}Ni_{10})_{83}Si_{17}$ and $(Pd_{85}Ni_{15})_{83}Si_{17}$ amorphous alloys using the DSC thermal analysis methods [4—6]. The apparent activation energy of the crystalline phase growth ΔE_K^* for the degree of conversion $\alpha \sim 0.5$ was determined in two ways: In the case of isothermal annealing of samples the analysis of the temperature dependence of the period required for the crystallization of 50 % of the material, $t_{0.5}(T_a)$ was performed. In the case of the linear heating of samples the Kissinger method was used. In both cases the determined value was in fact an average thermal coefficient corresponding to

a non-zero temperature interval. For the activation energy determined by the isothermal method, $\Delta E^{*i}_{0.5}$ corresponds to the temperature interval $T \in (671—679)$ K for $(Pd_{90}Ni_{10})_{83}Si_{17}$ and $T \in (678—684)$ K for $(Pd_{85}Ni_{15})_{83}Si_{17}$, respectively. In the second case the activation energy ΔE^*_{Kiss} corresponds to the temperature interval $T \in (689—705)$ K for $(Pd_{90}Ni_{10})_{83}Si_{17}$ and $T \in (692—708)$ K

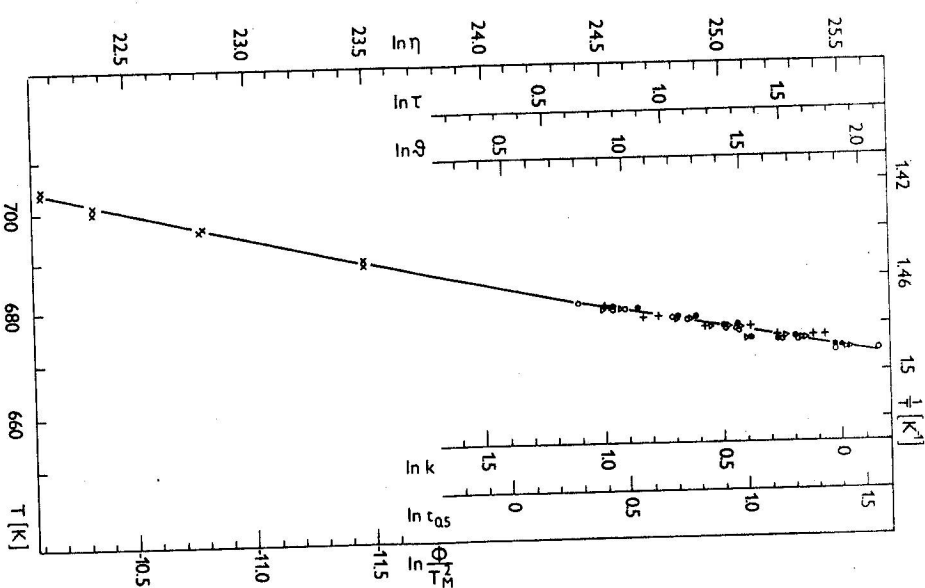

Fig. 1. Comparison between the calculated viscosity and the experimental rates of transformation of the amorphous $(Pd_{90}Ni_{10})_{83}Si_{17}$ [4]. The activation energies ΔE_K^* are in kJ mol⁻¹. Methods used for the kinetic analysis: + — isothermal incubation time analysis; · — isothermal Avrami analysis of time of a 50 % conversion; △ — isothermal Avrami analysis of time of a 100 % conversion; × — Kissinger non-isothermal analysis; Solid line is extrapolated viscosity described by expression (4).

for $(Pd_{85}Ni_{15})_{83}Si_{17}$, respectively. The apparent activation energy of crystalline growth for $(Pd_{90}Ni_{10})_{83}Si_{17}$ decreases from $\Delta E^*_{0.5} \sim 455$ kJ mol⁻¹ at $T \sim 675$ K to $\Delta E^*_{kss} \sim 364$ kJ mol⁻¹ at $T \sim 695.5$ K, and for $(Pd_{85}Ni_{15})_{83}Si_{17}$ it decreases from $\Delta E^*_{0.5} \sim 573$ kJ mol⁻¹ at $T \sim 681$ K to $\Delta E^*_{kss} \sim 372$ kJ mol⁻¹ at $T \sim 702.5$ K.

Due to a short temperature interval the theoretically predicted curvature in temperature dependence $\ln(t_{0s})$ versus T_a^{-1} and $\ln(\Phi/T_M^2)$ versus T_M^{-1} caused by the temperature dependences of $\Delta E^*_R(T)$ were not observed (Φ denotes the heating rate and T_M is the temperature of the crystallization exotherm peak).

Assuming that temperature dependences (1), (3) are valid and at the softening temperature T_a the amorphous material is in a isoviscous state, i.e. $\eta(T_a) = 10^{12}$ Pa s, the following values have been determined:

for $(Pd_{90}Ni_{10})_{83}Si_{17}$

$$\Delta E^*_\eta = \frac{18.17\, T^2}{(T-540.12)^2}$$

$$\eta = 6837 \exp\left(\frac{2184}{T-540.12}\right)$$

for $(Pd_{85}Ni_{15})_{83}Si_{17}$

$$\Delta E^*_\eta = \frac{7.27\, T^2}{(T-604.29)^2}$$

$$\eta = 755 \times 10^3 \exp\left(\frac{874}{T-604.29}\right) \qquad (4)$$

Fig. 1 shows the comparison between the calculated viscosity and the experimental rates of transformation of the amorphous $(Pd_{90}Ni_{10})_{83}Si_{17}$ [4].

III. DISCUSSION

The model of the viscous flow and the postulation of crystallization of investigated amorphous materials (i.e. $\Delta E^*_R =$ mechanism of crystallization of investigated amorphous materials (i.e. ΔE^*_R) can be applied when there is a difference by an order between alternative activation energies, i.e. the activation energy ΔE^*_η of the viscous flow and the activation energy ΔE^*_D of the diffusion of moving units. Generally in crystalline metallic alloys it is $\Delta E^*_D \sim (40-130)$ kJ mol⁻¹. In the case of Pd—Si-like alloys the diffusion coefficient of Si⁺ ions are not known. Usually the activation energy of the viscous flow is higher. The activation energy of the viscous flow in a pure silicon melt within the temperature range $T \in (1983-2173)$ K is $\Delta E^*_\eta \in (735-568)$ kJ mol⁻¹ [7]. On the basis of the relatively high value of activation energy of transport through the phase boundary in the crystallizing amorphous alloy $\Delta E^*_\eta \sim (350-550)$ kJ mol⁻¹ and its pronounced temperature dependence (4) (Fig. 1) one may assume that the nucleation and growth of the crystalline phase in the studied type of amorphous material is controlled more probably by the motion of spatially associated regions than by migration of individual ions occurring in the amorphous material. There can be several reasons for long range diffusion not being decisive in the process of transport although it has a lower activation energy than the viscous flow (e.g. a too low preexponential factor in the dependence of the diffusion coefficient on temperature).

IV. CONCLUSION

On the basis of complex thermal analysis results [4—6] and the knowledge of the structural changes appearing during the heat treatment of amorphous samples [8], the following model can be proposed for the crystallization of Pd—Ni—Si-like amorphous alloys: The diffusion rate in amorphous alloys is very low [1]; however, the observed transport stage of this heterogeneous transformation of material is not slow enough to account for this fact. This is confirmed by the fact that kinetic equations of transformation controlled by diffusion processes are little probable in this case [4, 9]. The activation energy of transport in an amorphous alloy as well as the activation energy of transport through the phase boundary in a crystallizing amorphous alloy is $\Delta E^*_\eta \sim (350—550)$ kJ mol⁻¹ with a temperature dependence (4). Therefore, there is little probability that the formation and growth of the crystalline phase in an amorphous material at a temperature T_a could be caused by long-range diffusion. More realistic seems to be the transport by means of a cooperative motion of volume aggregates — a viscous flow mechanism.

Positron annihilation proved [10] that there are no vacancy-like defects in amorphous alloys. Structural models of amorphous metallic materials (hard sphere model and more realistic interatomic potentials) show that "holes" representing the free volume of an amorphous material cannot fulfil the transport function although their volume and activation energy of formation correspond to the properties of vacancies [3]. The main difference between vacancies and "holes" is the too short lifetime of the latter. A simulation of the defect in an amorphous material has shown [11] that practically immediately — after several elementary steps — it disappears. Its free volume is rearranged into the surrounding structural units. The free energy of the system does not increase like in a crystal but, on the contrary, due to this relaxation mechanism it decreases. This cooperative motion — the viscous flow — is caused by the amorphous state of the material, namely its non-regularity and inexpressive potential profile of the amorphous "lattice".

In the place where the crystalline structure is formed in an amorphous material, each structural unit is fixed in a new, compared with the amorphous state, much deeper potential minimum. Then, the mechanism of dissipation of the "holes" in the surrounding space is disadvantageous and practically impossible.

This is confirmed also in practice. During the crystallization of Pd—Si-like amorphous alloys the enrichment to the required stoichiometric composition does not occur. A metastable strongly supersaturated solid solution is formed in the case when the critical concentration of the metalloid is not reached. The formed crystalline phase has the lattice of the host metal with metalloid atoms being bonded up to a certain concentration. This crystalline phase further transforms by means of a growth mechanism probably due to diffusion from the closest vicinity to stable stoichiometric phases (Pd_3Si, Pd_9Si_2, ...). It results in crystallites whose sizes

represent heterogeneities existing already in the amorphous state. At a higher concentration of the metalloid a cellular decay appears and a lamellar structure is formed.

The crystallization runs similarly in ternary amorphous alloys Pd—M—Si up to a critical concentration of a $3d$ metal, M [4, 6]. The presence of impurity worsens (by geometric and force effects) the transport properties of the material. At the moment of critical supersaturation of the amorphous alloy by a $3d$ metal the heterogeneities with a high content of this impurity will reach the size of a critical nucleus thus becoming nucleation centres of the new phase (PdNi, α-PdCo, Pd$_3$Fe, ...). The stoichiometric phase of the $3d$ metal primarily crystallizes from an amorphous alloy.

REFERENCES

[1] Cahn, R. W., Ewetts, J. E., Patterson. J., Somekh, R. E., Kenway, Jackson, C.: Technical Report No. 2. School of Engineering Applied Sciences. Sussex University 1979.
[2] Adam, G., Gibbs. J. H.: J. Chem. Phys. 43 (1965), 139.
[3] Ramachandrarao, P., Cantor, B., Cahn, R. W.: J. Non-Cryst. Sol. 17 (1969), 1021.
[4] Illeková, E.: Thesis. Bratislava 1981.
[5] Illeková, E.: J. Non-Cryst. Sol. (to be published).
[6] Illeková, E., Ambrovič, P., Duhaj, P.: Thermal Analysis 28 (1983), 413.
[7] Clinton, D., Mercer, R. A., Miller, R. P.: J. Mater. Sci. 5 (1970), 171.
[8] Duhaj, P.: Metallic Glasses: Sci. Technol. Budapest 1980.
[9] Illeková, E.: Amorphous Metallic Materials. Smolenice 1978.
[10] Chen, H. S., Chuang, S. Y.: Phys. Stat. Sol. (a) 25 (1974), 581.
[11] Bennet, C. H., Chaudhari, P., Moruzzi, V., Steinhardt, P.: Philosophical Magazine A 40 (1979), 485.