THERMAL PARAMETERS OF METALLIC GLASSES OF THE Pd—Si AND THE Fe—B TYPE

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In the paper presented the amorphous-crystalline transformation of the amorphous alloys PdSi and FeB is studied by measuring thermophysical parameters. The direct measurement of thermal diffusivity and specific heat by the pulse method is carried out. Noticeable is mainly the thermal diffusivity, which enables us to follow the whole course of the phase transition in great detail. The analysis of experimental results is performed. All experimental results were obtained in 1978—1979.

ТЕРМОФИЗИЧЕСКИЕ ПАРАМЕТРЫ МЕТАЛЛИЧЕСКИХ СТЕКОЛ НА БАЗЕ Pd—Si И Fe—B

В статье приведены результаты исследования аморфных сплавов Pd—Si и Fe—B при их переходах из аморфного состояния в кристаллическое. Эти результаты получены на основе прямых термофизических измерений температуропроводности и удельной теплоемкости при помощи импульсного метода. Особый интерес представляет измерение температуропроводности, при помощи которого можно детально изучит ход фазового перехода. Проводится анализ всех экспериментальных данных, полученных в 1978—1979 гг.

I. INTRODUCTION

Several physical quantities can be used to identify phase changes of amorphous materials but it seems that the thermophysical quantities are the most sensitive. Until recently only little attention has been paid to them. Thus, for instance, only a few values of thermal diffusivity which have been obtained from internal friction measurements can be found in literature [1, 2]. Thermal capacity data of these measurements are more frequent [3, 4, 5]. This article reports direct measurements of thermal diffusivity and specific heat of amorphous metallic glasses through transformation regions.

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II. SHORT ACCOUNT OF THERMAL RELATIONSHIP OF PHASE CHANGES IN METALLIC GLASSES

Glasses generally exhibit two instability regions: a glass transition region and a crystallization region. The glass transition region is characterized by a large increase in specific heat. Simon [6] was the first who explained this increase in specific heat. Under the glass transition temperature (T_g) the undercooled liquid is frozen in one of its instantaneous configurations. Only the changes of the motion modes (vibrations and rotations) of atoms or greater complexes correspond to the temperature changes. Above T_g a very fast configurational reordering is present, causing an increase in specific heat. For the metallic glasses Au—Ge—Si this increase is about 23 Joule/g at K near the T_g temperature. Approximately the same increase of specific heat have been reported for other amorphous alloys [7, 8].

Convenient thermal fluctuations of atoms help to form crystallization centres. The region above T_g is just such a convenient region and the glass transition, in fact, stimulates crystallization. The difference $\Delta T = T_{cr} - T_g$, where T_{cr} is the temperature of crystallization, can be observed experimentally or not. For many binary alloys which are not very stable the difference ΔT is negative and crystallization is energetically more distinct, as the glass transition is the only observable phase change. The activation energies of crystallization for stable amorphous metallic glasses (i.e. ΔT is large and positive) are of the order 400 kJ/mole [8]. Thus, for example Ni—P—B—Al, Pd—Ni—Si, Fe—Ni—P—B are among the stable metallic alloys, as well as other mostly many-component ones. The activation energies for crystallization of unstable metallic glasses or of glasses of poor stability (Au—Si, Cu—Ag and others) are about 80 kJ/mole or less. The driving process of crystallization is diffusion, or phase boundary reaction.

There is no relationship between the glass stability and the enthalpy of crystallization. The value H_{cr} of the majority of metallic glasses is about 4 kJ/mole [3].

III. THERMAL CONDUCTIVITY AND THERMAL DIFFUSIVITY OF METALLIC GLASSES

No discussion about thermal conductivity of disordered structures can be complete, since the conventional theory of heat conductivity by lattice waves is applicable only to perfect crystals. A theory of thermal conductivity of amorphous materials can be made only in the case of the low temperature region where only long waves are predominant, for which the solid is an elastic continuum and for which the detailed atom structure is of less importance. The first to give a semiempirical description of the thermal conductivity of glasses at medium and

elevated temperatures was Kittel [9]. The glass in his model is considered as an extreme case of disordered crystals. He modified the equation of thermal conductivity of crystals $\lambda = \frac{1}{3} c_v v \bar{l}$, where c_v is specific heat at constant volume, v is the mean velocity of phonons and $\bar{l}$ is the mean free path of phonons. He substituted the classical mean free path l by $\bar{l}_0$ as a limit of structure geometry. $\bar{l}_0$ does not depend on phonon density nor on the phonon wave length. Then we have for the thermal conductivity the equation $\lambda = \frac{1}{3} c_v \bar{l}_0$. λ / c is approximately constant and therefore the thermal conductivity changes in the same way as the specific heat.

In the theoretical analysis of thermal conductivity of glasses Klemens [10], using the solution of the equation of motion of the elastic continuum, has determined non-equilibrium numbers of phonons as a function of lattice waves. Thus he has obtained a formal relation for the thermal conductivity of glasses

$$\lambda = \frac{1}{3} \sum_i \int d\omega c_i(\omega) v_i \bar{l}_i(\omega)$$

where $c_i(\omega)$ is a contribution of phonons with polarization "j" and frequency "ω", $d\omega$ is specific heat of the unity volume and $\bar{l}_i(\omega)$ is the mean free path of phonons.

Thermal conductivity of glasses is considerably lower than the thermal conductivity of crystalline solids, the dispersion of thermal conductivity values for different glasses is much less than the dispersion for crystalline solids at the same temperature, the thermal conductivity of glasses decreases as the temperature decreases, while the thermal conductivity of crystalline solids increases as the temperature decreases (20).

Low temperature thermal conductivity of metallic glasses was measured by Matey and Anderson [11, 12]. They used the Wiedeman—Franz law to separate the electron and the phonon component of thermal conductivity and they came to the conclusion that the phonon component of metallic glasses has the same absolute magnitude and exhibits the same temperature dependence as the phonon component of λ of non-metallic amorphous materials. Krempasky [13] analysing experimental data of thermal conductivity of both chalcogenide and metallic glasses, showed that the Lorentz number in many cases is a function of temperature. The calculation of the electron component of thermal conductivity is thus loaded with a considerable error. In the case of metallic glasses this dependence $L = L(T)$ is made for the samples of the composition $Pd_{80}Si_{20}$.

Direct measurements of the temperature dependence of thermal diffusivity of metallic glasses so far not been made. The only data about thermal diffusivity of metallic glasses have been obtained from internal friction measurements. In the following we

explain the temperature dependence of thermal diffusivity which we have measured. According to Debye the thermal diffusivity is

$$k = \frac{1}{3} v \bar{l}$$

where v is the sound waves velocity, $\bar{l}$ the mean free path of phonons. $\bar{l}$ in the case of glasses is equal to the value of the characteristic structure unit and it does not change during the glass transition. Substantial changes appear, however, in the manner of the sound waves propagation in an amorphous material near the T_g. In a general case, three components of elastic waves velocity exist in solids — two transversal ones (v_t) and a longitudinal one (v_l). The total velocity of elastic waves propagations is then

$$v = v_l \left(\frac{1}{3} + \frac{2}{3} \frac{v_t}{v_l} \right).$$

Contrary, in liquids only the longitudinal component v_l can be realized (this case can be extended to the case of undercooled liquids). The characteristic thermal diffusivity decrease of ordinary nonmetallic glasses at the glass transition has been ascribed unambiguously to the changes of sound waves velocity in the material. In the case of metallic glasses the situation is more complicated since it is not possible to neglect the contribution of electrons.

During crystallization of amorphous metallic glasses more factors effect the increase of thermal diffusivity "κ"; the mean free path of electrons and phonons gets larger as a consequence of structure ordering and at the same time all three components of sound waves velocity propagation appear in the crystal.

As can be seen from both table (1) and the experimental results [2, 15, 16], thermal conductivity and diffusivity of many-component metallic glasses are considerably lower than thermal conductivity and diffusivity λ increase fivefold for the alloy Pd—Si, while for the alloy Fe—B only 1.7-fold. It is therefore possible to assume that the metallic glasses of the type Fe—B are worse thermal conductors than the metallic glasses Pd—Si.

During crystallization the values of thermal conductivity and diffusivity of pure Pd and Fe.

IV. EXPERIMENTAL

A pulse method [17] has been used for measurements of specific heat and thermal diffusivity versus temperature. The samples of measured metallic glasses had the made at the Institute of Physic of the Slovak Academy of Sciences had the dimensions 0.3 cm×0.8 cm×0.002 cm. The placement of samples between ceramic blocks is shown in Fig. 1.

All the systems of the sample-ceramic blocks-heated wire-differential thermocouple was placed in an evacuated quarts tube. The rate of temperature increase was about 1 °C/min in all experiments. Vacuum was maintained by a rotational oil gauge.

Fig. 1. The principal arrangement for the pulse measurement: K = ceramic blocks, V = sample, DT = diferential thermocouple, ZT = source of heat pulses.
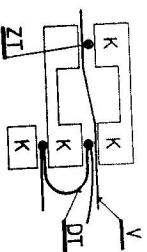
For samples of weak thermal conductivity and plane source of thermal pulse Kubičár [18] has derived the relative errors vor one measurement for

k : 4—8 %
c : 5.5—6.6 %
λ : 6.8—10 %.

In the case of these samples of metallic glasses the requirements for the determination of absolute values of "κ", "c", "λ" are very strict. A number of factors has to be introduced since the correction for the contact thermal resistance of the sample and its surrounding, the intrinsic thermal capacity of the pulse source, sample geometry, heat drain from the sample and thermal sample stability are necessary. The relative error in the case of samples from metallic glasses is naturally higher than those given above for non-conducting materials. The present state of the experiment does not permit us to determine which factor influences the precision of the measurement more and which less.

For these reasons only the relative values of parameters are shown in the figures. The "κ" and "c" are related to the temperature of 200 °C. No phase transformation up to this temperature is present in these samples of metallic glasses.

V. ANALYSIS OF EXPERIMENTAL RESULTS

The relative values of thermal diffusivity and specific heat of the measured samples versus temperature are shown in Figs. 2, 3, 4, 5. The influence of the amount of Ni on the change of "κ" and "c" was investigated in the region of the glass transition and crystallization.

As can be seen from the figures the samples of metallic glasses not containing Ni do not exhibit the region of glass transition characterized by a typical specific heat increase and thermal diffusivity decrease. The region of glass transition could not

be observed because the temperature interval $\Delta T = T_{cr} - T_g$ was very narrow. According to Chen [7] for the Pd83Si17 alloy the interval ΔT is only 7 K. For the binary alloys this temperature interval does not exceed 10 K. In the case of Pd83Si17 the only observable phase change is crystallization. The recording of the glass transition region depends, however, on precision and sensitivity of the experiment.
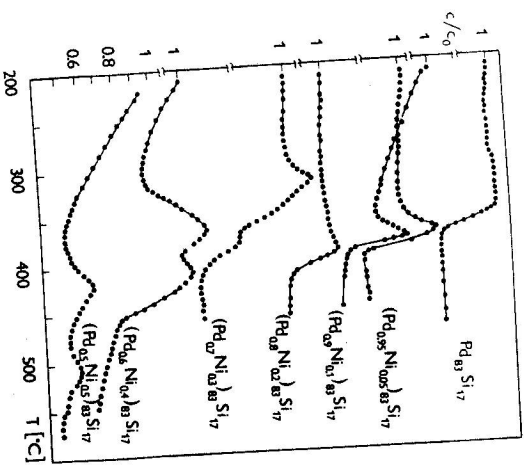

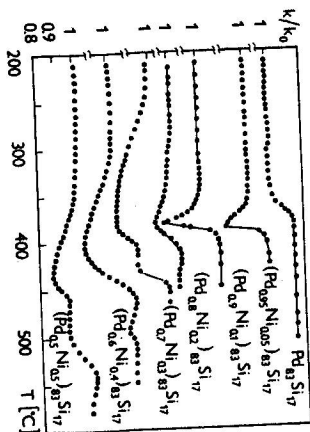Fig. 2. Temperature dependences of specific heat for samples of PdNiSi.

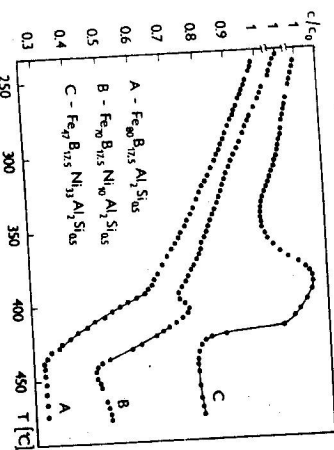Fig. 3. Temperature dependences of relative values of thermal diffusivity for samples of PdNiSi.

Fig. 4. Temperature dependences of specific heat for various values of concentrations of Ni: A = 0 at % Ni, B = 10 at % Ni, C = 33 at % Ni.
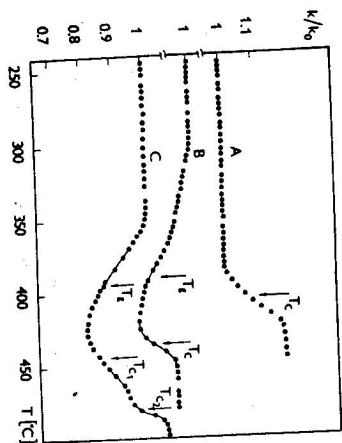

Fig. 5. Temperature dependences of relative values of thermal diffusivity for various concentrations of Ni: A = 0 at % Ni, B = 10 at % Ni, C = 33 at % Ni.

Alloying a binary alloy with a small amount of a third element causes that the temperature T_g shifts towards higher values, the interval ΔT gets broader and it is possible to record the glass transition either by specific heat or thermal diffusivity. According to Chen the interval ΔT for the (Pd95Ni5)83Si17 sample is 30 K, we have found this interval to be 20 K.

Table 1

Samples	k (cm²s⁻¹)	c (Jg⁻¹K⁻¹)	λ (Jcm⁻¹s⁻¹K⁻¹)
Pd82Si18Am	0.051	0.269	0.1428
Pd82Si18 Kryst.	0.26	—	0.714
Fe75P15C10Am	0.17	0.4956	0.0588
Fe75P15C10Kryst.	0.030	—	0.105
Pd81Si19Am	0.039	—	0.1806
Pd81Si19Kryst.	0.075	—	0.84

A further concentration increase of Ni up to 20 % Ni has no effedt on the morphology of phase transformations. The temperature interval of glass transition is rather narrow and the glass transition is followed by crystallization. For the given sample the temperatures T_g and T_{cr} obtained from the course "k" and "c" correlate very well. Increasing the Ni concentration both temperatures shift towards higher values as a consequence of increased glass stability.

The crystallization mechanism of metallic glasses with a Ni content above 20 % in the amorphous matrix of PdSi is rather more complicated. Thus, there appear two regions of glass transition and two crystallization regions. The temperatures T_g and T_{cr} given from the course "k" and "c" do not show any more agreement at concentrations above 20 % Ni. Especially from the dependences of "c" it is possible to see that the crystallization onset is already in the region of glass transition and although not finished entirely crystallization is followed by another transition and another crystallization. These overlapping processes are the reason of the temperature interval increasing and the ambiguity of the temperatures T_g and T_{cr}. The detailed analysis of these several step phase transformations will be possible only if isothermal conditions of thermophysical quantities measurements are established.

All considerations about changes of thermal quantities caused by structural changes of an amorphous matrix are verified by direct microscopic observations. The mechanism of crystallization of the amorphous matrix of Pd83Si17 (undereutectic composition) is as follows: up to a critical amount of Ni, the first to crystallize between 20—30 % is the phase rich in Pd. At an above critical amount of Ni this reacts with Pd and the phase PdNi crystallizes. In the end PdNi reacts with the rest of the amorphous matrix and the phase to crystallize least is the NiSi one.

A similar crystallization mechanism was described by Spaepen [19] who introduced the so-called topological disordering at short distance and the chemical disordering at short distance. Up to a critical amount of the alloying element this is being built into the original amorphous matrix as an element which replaces the solvent, i.e. the metal (Pd, Fe). No change of chemical disorder arises which is prooved by crystallization of the same type as that the original alloy without Ni. This state is characterized by the so-called topological disorder at short distance. If the content of the alloying element exceeds the critical limit, not only topological disorder arises but, as a consequence of bond saturation, also an amorphous matrix separation into the phase rich in Ni is present. This is called the chemical disordering at short distance.

Despite of all adverse influences during measurements of thin metallic glass films we have tried to compute the absolute values of thermal diffusivity. Using relations valid for the corresponding arrangement of samples in the holder [16] we have obtained the following values of thermal diffusivity at room temperatures:

$$Pd_{83}Si_{17} \quad : k = 0.03 \text{ cm}^2\text{s}^{-1}$$
$$(Pd_{95}Ni_5)_{83}Si_{17} \quad : k = 0.027 \text{ cm}^2\text{s}^{-1}.$$

The values of thermal diffusivity for the remaining measured samples of the type Pd—Ni—Si were $0.023—0.039 \text{ cm}^2\text{s}^{-1}$. For the samples of the composition Fe—Ni—B these values were $0.015—0.0522 \text{ cm}^2\text{s}^{-1}$.

Concluding we can say that the pulse method so successful in crystalline bulk materials measurements can be used for thermal quantities measurements of thin samples of metallic glasses as well.

The temperature dependences of thermal diffusivity measured by the pulse method have been the only direct measurements of this unit so far. Together with curves of specific heat they present the existing phase changes in the material with great accuracy. When this method has been perfected and the adverse effects connected with the arrangement of the experiment are overcome, it will be possible to evaluate the absolute values of thermal conductivity, specific heat and thermal diffusivity, so far often missing in literature.

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