JOURNAL OF MATERIALS SCIENCE 22 (1987) 3011–3016

Kinetics of thermal devitrification of some titanium amorphous alloys

MILENKO V. ŠUŠIĆ
Institute of Physical Chemistry, Faculty of Sciences, 11000 Belgrade, Studentski trg 16, Yugoslavia

A thermal investigation concerning the behaviour of amorphous alloys of 51% Cu, 10% Ni and 39 wt% Ti (denoted by A) and of 13% Cu, 27% Ni and 60 wt% Ti (denoted by B) was performed using the differential scanning calorimetric method, alternatively in hydrogen and nitrogen atmosphere. It was shown that the crystallization (devitrification) is carried through in two and three different steps for alloy A and alloy B, respectively, within the temperature interval 573 to 823 K (300–550° C). Activation energies of each individual crystallization step, as well as frequency factors, rate constants, half-times and enthalpies of the crystallization reactions were determined.

1. Introduction

Recently glassy metals have been classified into a new group of materials which are of scientific and technological importance. Metallic glasses show some properties which are similar to those of metals and alloys, but at the same time they are characterized by glass-like properties resulting from the amorphous structure. The structure of these materials proves that the atoms are interconnected by oriented metal bonds, without showing long range order, which causes their izotropical behaviour. They are opaque and ductile materials characterized by unusual magnetic and electric properties when compared to the corresponding crystalline materials. Glassy metals are chemically homogeneous at a scale exceeding several atomic diameters. They are deprived of a grain structure and hence of grain boundaries which makes them very corrosion resistant [1, 2].

Three important models, the dense random packing model [3], the microcrystalline model and the random packing of atomic clusters [4] have been accepted in describing the structure of metallic glasses. The microcrystalline model assumes that tiny crystallites are randomly distributed throughout the amorphous matrix, while the random packing cluster model presumes mutual packing of the clusters into a series but without crystallinity. The dense random packing model considers the structure of fluids. Metallic glasses are mainly obtained by the method of rapid cooling of liquid metals and alloys [5–8]. This method has been quite well developed so that the obtained products can have the form of powders, ribbons or wires, and are commercially available.

According to the chemical classification (four groups) [9] metallic glasses are two or multicomponent systems containing in many cases nonmetallic components i.e. silicon, carbon, beryllium, boron, germanium, phosphorus. When exposed to heating the glassy metals become crystallized and this procedure can be followed by phase separation. In the majority of cases the crystallization reactions that occur are classified into three types: polymorphic, priority and eutectic crystallization [10].

Numerous chemical, physical and physico-chemical methods have been utilized for the investigation of amorphous materials including metallic glasses. Various forms of differential thermal analyses [11] are frequency used for thermal, as well as for kinetic investigations. A method [12] based on the change of the heating rate, which has been adapted for investigations of industrial materials [13], excels among differential scanning calorimetric methods (DSC). This method has been particularly recommended by the DuPont Company when working with a DuPont Thermal Analyser [14], and hence it was applied in this research.

There is very limited data available in the literature on titanium-based metallic glasses. Some results demonstrate the interesting properties of amorphous Ti–Cu [15] and Ti–Ni–Cu–Si [16] alloys, whilst Ti–Zr is shown to have two glass transitions and two glassy phases [17]. The four different compositions of the amorphous alloy, $Ti_{0.35}Cu_{0.65}$, TiCu, $Ti_{0.60}Cu_{0.40}$ and $Ti_{0.65}Cu_{0.35}$, two of which correspond to intermetallic compounds (TiCu and Ti_2Cu), show considerable hydrogen adsorption at room temperature and in hydrogen atmosphere, thus forming hydrides that each contain a different amount of hydrogen. Thermal and X-ray analyses show that the crystallization process in hydrogen atmosphere takes place in two steps at 430 and 470° C respectively, while amorphous hydride, $TiCu_{1.33}$, formed in hydrogen atmosphere at room temperature decomposes during heating at 160° C [18, 19]. The results we have obtained during the investigation of crystallization of the amorphous alloys 62Ti–25Ni–9Cu–4Si and 52Ti–8Ni–39Cu–1Si show that this process takes place in three [16] and four steps, respectively [20].

0022–2461/87 $03.00 + .12

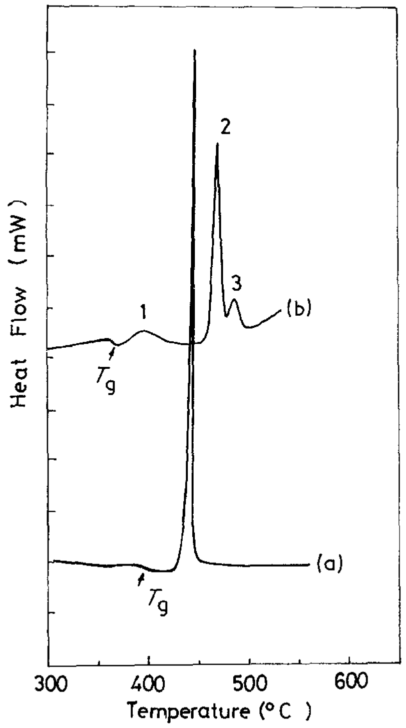

Figure 1 DSC thermograms: (a) Alloy A in hydrogen 15 K min^{-1}., (b) Alloy B in nitrogen, 15 K min^{-1}.

2. Experimental procedure

The amorphous titanium alloys 51% Cu, 10% Ni and 39 wt % Ti (denoted by A) and 13% Cu, 27% Ni and 60 wt % Ti (denoted by B) in ribbon-like form of 50 μm thickness were investigated. These were produced in the Baykov Institute of Metallurgy, Academy of Sciences of the Soviet Union, Moscow. The samples, several milligrams in weight, were cut from these ribbons and then thermally investigated by DSC (DuPont Thermal Analyser 1090) within a temperature range from room temperature up to 920 K with a heating rate of 5 to 30 K min^{-1} in (A) hydrogen and (B) nitrogen atmosphere. The amorphous, partly and completely crystallized samples, previously heated to a particular crystallization degree were then examined by X-ray analysis with a Cu$K\alpha$ and graphite monochromator.

3. Results and discussion

In both A and B alloys the process of crystallization occurs in several steps. Fig. 1 presents characteristic DSC thermograms in which two and three exothermal maxima for A and B, respectively, corresponding to the crystallization steps with rather different enthalpies can be seen.

Some important thermodynamic and kinetic parameters were determined from the change in peak temperature of the exothermal maximum, following the change in the heating rate. On the basis of the following relation

$$\Delta \log \beta/\Delta(1/T) = -E/R \qquad (1)$$

TABLE I Thermal devitrification of alloy A in hydrogen atmosphere

E(kJ mol^{-1})	Z(min^{-1})	$-\Delta H$(J g^{-1})
247.441	9.627×10^{17}	83

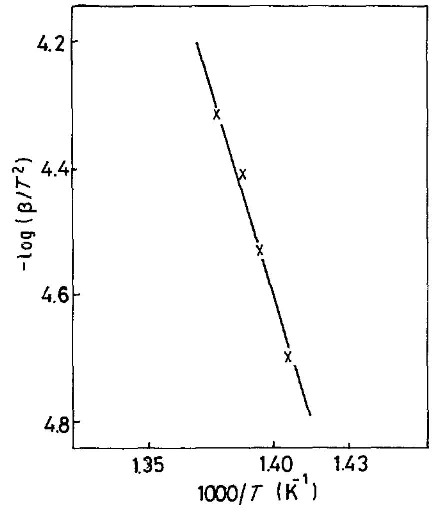

Figure 2 The plot of log (β/T^2) against $1/T$ for alloy A.

where β is the heating rate in degrees per minute, E is the activation energy, T is the absolute temperature at the exothermal maximum, with the appropriate corrections, or according to the relation

$$\Delta \log (\beta/T^2)/\Delta(1/T) = -E/R \qquad (2)$$

without corrections, the activation energy was determined. Furthermore, according to the relation

$$Z = [\beta E \exp (E/RT)]/RT^2 \qquad (3)$$

the pre-exponential (frequency) factor Z in the Arrhenius equation was determined.

The crystallization rate constant k was calculated according to the relation

$$k = Z \exp(-E/RT), \quad \text{i.e.} \ln k = \ln Z - E/RT \qquad (4)$$

from which the reaction half-time $t_{1/2} = 0.693/k$ was determined.

3.1. Alloy A

The crystallization process of this alloy is carried through in two steps occurring at very close temperatures, which is observed from the asymmetry of the maximum in the thermogram. Thus, the measurements were carried out assuming a one step process. By

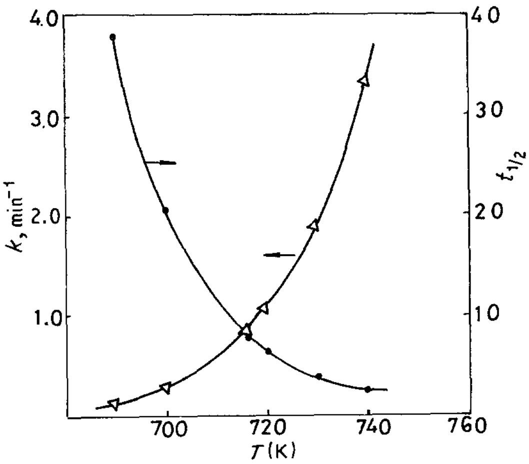

Figure 3 The crystallization rate constant and half-time dependence on temperature for alloy A.

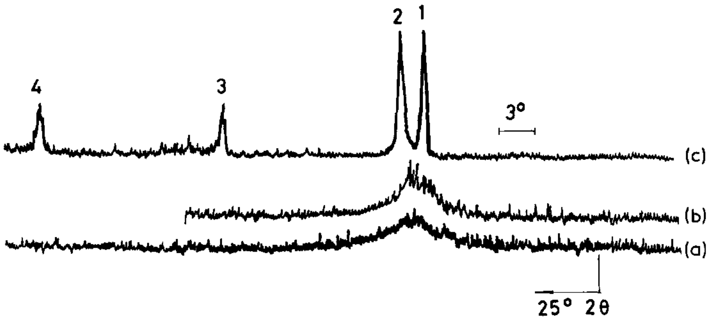

Figure 4 X-ray diffractograms of alloy A: (a) non-heated, (b) amorphous heated up to 673 K and (c) 758 K. Numbers on diffractogram correspond to: 1. (1 1 0) TiCu, (1 1 0) TiCuNi, 2. (1 0 1) TiCuNi, 3. (2 0 0) TiCu, (2 0 0) TiCuNi, 4. (1 2 2) TiCu, (1 2 1) TiCuNi.

plotting log (β/T^2) against $1/T$, a straight line was obtained (Fig. 2). The slope $\Delta \log(\beta/T^2)/\Delta(1/T)$ equal to -12.94×10^3 was derived from this plot, and according to Equations 2 to 4 the corresponding values of the crystallization process, the activation energy, the rate constant and the frequency factor were calculated, Table I. The enthalpy, ΔH, is directly read from the thermograms. Fig. 3 shows the temperature dependence of the crystallization rate constant k and of the reaction half-time $t/2$. The glass transition, T_g, occurs at a temperature approximately 40 degrees below the temperature of the maximum of the crystallization process, Fig. 1a.

The crystallization process was investigated by X-ray analysis of a partially and a completely crystallized sample. Fig. 4 shows X-ray diffractograms of a sample (amorphous) before (a) and after heating up to 673 K (400° C) (b) and 758 K (458° C) (c). It is evident that an untreated sample gives a diffractogram characteristic for a completely amorphous state (a low and broad maximum). When the sample is exposed to the heating process (673 K) the diffractogram shows only initiation of crystallization, which is completed by heating above 723 K. According to the analysis of X-ray diffractograms, the crystallized sample contains polycrystallites of the intermetallic compound TiCu and TiCuNi.

3.2. Alloy B.

The crystallization of this amorphous alloy occurs in three steps. The exothermal maxima, according to the increasing peak temperature of the maximum, were denoted by numbers 1 to 3 which at the same time denote the crystallization steps. Distinct thermal and kinetic values are marked by indices 1 to 3. By plotting log (β/T^2) against $1/T$ in the same way as was done in the case of alloy A, straight lines were obtained for each crystallization step (Fig. 5). The slopes Δ log $(\beta/T^2)/\Delta(1/T)$ equal to -12941 for the first, -12500 for the second and -8333 for the third crystallization step were derived. From these data the corresponding kinetic parameters were calculated (Table II). The enthalpies were read off directly from the thermograms. The crystallization rate constants depend on the temperature as shown in Fig. 6. It is obvious that the relative constants are rather high, although they differ from each other by a factor of 2 at the most, at the temperatures of the maxima. The enthalpies are found to be equal to $-\Delta H_1 = 7.6\,\mathrm{J\,g^{-1}}$ for the first

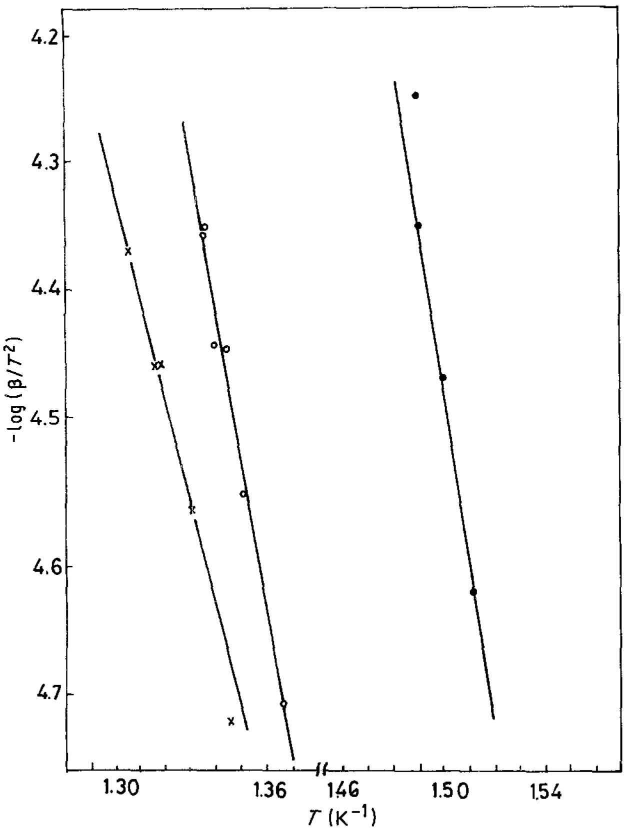

Figure 5 The plot of log (β/T^2) against $1/T$ for alloy B. Crystallization steps: (●) 1, (○) 2, (×) 3.

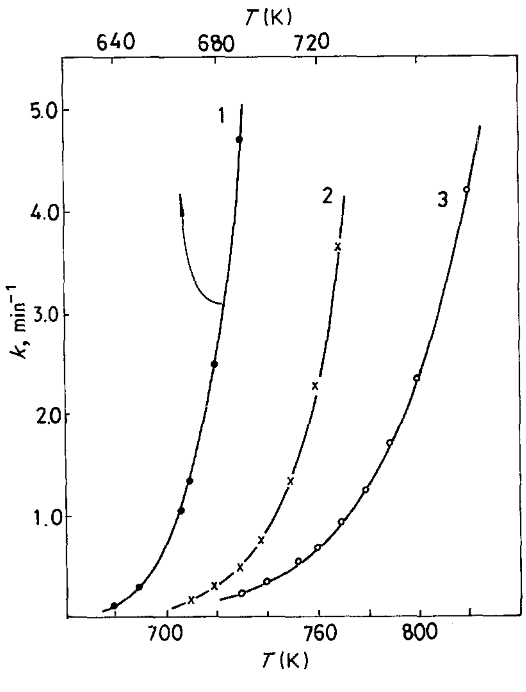

Figure 6 The crystallization rate constant dependence on temperature for alloy B. (●) 1, (×) 2, (○) 3.

TABLE II Thermal devitrification of alloy B in nitrogen atmosphere

E(kJ mol^{-1})			Z(min^{-1})		
E_1	E_2	E_3	Z_1	Z_2	Z_3
247.517	239.027	159.351	2.59×10^{19}	6.04×10^{16}	5.96×10^{10}

and $-(\Delta H_2 + \Delta H_3) = 32.3\,\text{J g}^{-1}$ for the second and the third crystallization step.

The X-ray analysis of the crystallization process shows, Fig. 7, that true crystallization takes place in the second crystallization step, when the polycrystallites of intermetallic compounds Ti_2Ni, Ti_2Cu and TiCu are formed. In the third step it is most likely that partial recrystallization occurs, together with the formation of small quantities of a new phase, which is observed as the appearance of small new peaks between the existing maxima 2 to 3 and 3 to 4 (not shown) when the sample is heated above 813 K. The glass transition, T_g, occurs at a temperature approximately 40° below the temperature of the first crystallization step. From these results and from results presented in [16, 20] it can be seen that, beside a number of common properties, the crystallization mechanism depends on the composition of the amorphous alloy shown in Table III.

One glass transition is observed with each of the first three alloys (Table III), which means that one glassy phase constitutes the amorphous state of the alloys. By crystallization, each alloy produces the intermetallic compound TiCu, common for all, plus another compound which differs in each case due to different compositions. However, the crystallization mechanisms are quite different. For the alloy in [20] it has been explained that the crystallization takes place only in the fourth and final step, in accordance with the theoretical model of the amorphous state [4], while other steps represent the processes of nucleation to microcrystallites not large enough for X-ray reflection, or crystallization at the nucleation level. A similar conclusion can be associated with the first nucleation step of alloy B, while the second step corresponds to the true crystallization easily identified by X-ray analysis. It can be stated that the third step represents, as already noted, the recrystallization of already formed phases, namely, the growth of crystals not completed in the second step. For alloy A the crystallization process is carried through in two steps which are thermally very close to one another, similarly as with the alloy $Zr_{36}Ti_{24}Be_{40}$ which has two glass transitions and two glassy phases [17]. It can be hypothesized that the difference in the number of steps is the result of the different composition and structure of amorphous phases, and thus also the result of the different nature of the initial crystallization centres which, in the course of their growth into the crystallites of intermetallic compounds have to pass different paths containing different energy barriers. It seems that the presence of silicon in the alloys of [16, 20] was significant influence on these processes and, particularly on the thermal stability. Namely, the increase in titanium content does not always increase the thermal stability, i.e. the devitrification temperature, so, the observed increased stability of alloys in [16, 20] with respect to alloys A and B has to be associated with the presence of silicon.

On the basis of the formation of the presented intermetallic compounds it can be considered that the crystallization is of the eutectic type, i.e. there is simultaneous formation of two phases (three, in [16]).

4. Conclusion

The thermal behaviour of two amorphous titanium alloys having different compositions: 51% Cu, 10% Ni and 39 wt% Ti (A), and 13% Cu, 27% Ni and 60 wt% Ti (B) was investigated, and a certain correlation was drawn with the behaviour of previously investigated amorphous titanium alloys [16, 20]. It has been shown that both alloys A and B are transformed into the crystalline state by heating. The crystallization of alloy A is completed at 733 K (460° C), and of alloy B at 773 K (500° C). The true crystallization process of alloy B occurs in the second step. It has been shown that the activation energies and the rate constants of the individual crystallization steps are rather high, while the enthalpies have rather different values. Comparison of the thermodynamic and kinetic properties with the chemical composition of four alloys shows that the presence of silicon increases the crystallization activation energies. All four alloys, regardless of the number of crystallization steps, form polycrystallites of intermetallic compounds Ti_2Ni,

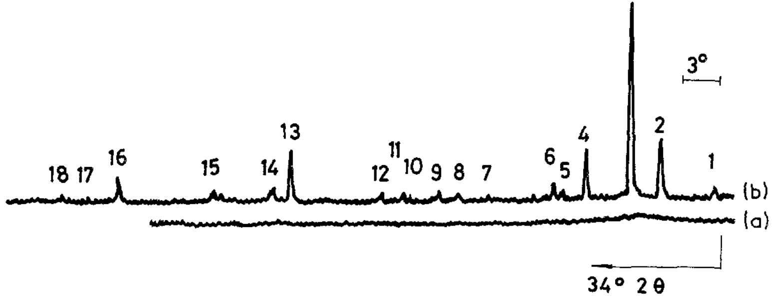

Figure 7 X-ray diffractograms of alloy B: heated up to (a) 693 K, (b) 743 K. Numbers on diffractogram correspond to: 1. (3 3 1) Ti_2Ni, 2. (4 2 2) Ti_2Ni, 3. (1 1 0) TiCu, (3 3 3) Ti_2Ni, 4. (4 4 0) Ti_2Ni, 5. (5 3 1) Ti_2Ni, 6. (4 4 2) Ti_2Ni, 7. (6 2 2) Ti_2Ni, 8. (4 4 4) Ti_2Ni, 9. (5 5 1) Ti_2Ni, 10. (0 2 0) TiCu, 11. (0 4 2) Ti_2Ni, 12. (2 0 0) Ti_2Cu, 13. (1 1 6) Ti_2Cu, 14. (6 6 0) Ti_2Ni, 15. (2 1 3) Ti_2Cu, 16. (1 1 4) TiCu, 17. (9 3 3) Ti_2Ni, 18. (9 5 1) Ti_2Ni.

TABLE III Comparison of the crystallization characteristics, composition, thermodynamics and kinetics of some amorphous titanium alloys.

Alloy	Composition (wt %)				T_g number	T_m^* (K)	Crystallization step	Phase after crystallization	E, (kJ mol^{-1})				$-\Delta H$ (J g^{-1})				$k^\dagger$ (min^{-1})			
	Ti	Cu	Ni	Si					E_1	E_2	E_3	E_4	$-\Delta H_1$	$-\Delta H_2$	$-\Delta H_3$	$-\Delta H_4$	k_1	k_2	k_3	k_4
A	39	51	10	–	1	715	2	TiCu, TiCuNi	247.5	–	–	–	83.0				$\underline{1.2}$	–	–	–
B	60	13	27	–	1	743	3	TiCu, Ti_2Ni	247.5	239.0	159.4	–	7.1		32.3		1.1	$\underline{1.0}$	0.55	–
[20]	52	39	8	1	1	840	4	TiCu, Ti_2Cu	326.4	297.4	367.7	224.9	15.6	7.6	0.76	45.0	1.2	0.85	0.92	$\underline{0.57}$
[16]	62	9	25	4	–	779	3	Ti_2Cu, Ti_2Ni, Ti_5Si_3	324.9	319.1	319.1	–	15.0		48.0	–	1.1	1.4	$\underline{1.1}$	–

* T_m is the temperature of the exothermal maximum at which complete crystallization occurs.

† The underlined values represent the crystallization rate constant at T_m.

Ti_2Cu, TiCu and Ti_5Si_3 (if silicon is present). Some of the other characteristics can be seen in Table III.

References

1. T. MASUMOTO and K. HASHIMOTO, *Ann. Rev. Mater. Sci.* **8** (1978) 215.
2. M. V. ŠUŠIĆ, in Proceedings of the 36th (International Society of Electrochemistry) ISE Meeting, Salamanca, Spain, (Graficas Varona, Salamanca, 1985) p. 0646.
3. J. D. BERNAL, *Nature* **185** (1960) 68.
4. S. TAKAYAMA, *J. Mater. Sci.* **11** (1976) 164.
5. W. KLEMENT, R. H. WILLENS and P. DUWEZ, *Nature* **187** (1969) 869.
6. P. DUWEZ, R. H. WILLENS and W. KLEMENT, *J. Appl. Phys.* **31** (1960) 1136.
7. N. J. GRANT and B. C. GIESSEN (eds) in "Rapidly Quenched Metals" (MIT Press, Cambridge, Massachusetts, 1976).
8. D. ADLER, *Scientific American* **236** (1977).
9. D. E. POLK and B. C. GIESSEN, in "Metallic Glasses – ASM Materials Sciences Seminar Series" edited by J. J. Gilman and H. J. Leamy (ASM, Metal Park, Ohio, 1977).
10. U. KÖSTER and U. HEROLD, in "Glassy Metals I", edited by H. J. Güntherodt and H. Beck (Moscow, "Mir", 1983) (in Russian) p. 330–333.
11. B. G. BAGLEY, in "The Nature of the Amorphous State in Amorphous and Liquid Semiconductors", edited by J. Tauc (Plenum Press, London and New York, 1974) p. 1.
12. T. OZAWA, *J. Therm. Anal.* **2** (1970) 301; **9** (1976) 369.
13. A. A. DUSWALT, *Thermochim. Acta* **8** (1974) 57.
14. K. F. BARKER, "Thermal Stability of Potentially Hazardous Materials by Differential Scanning Calorimetry (DSC)", (DuPont Com. Instr. Products, Scientific and Process Division, Wilmington), Number TA 73, DE 19898.
15. A. J. MAELAND, in "Metal Hydrides", edited by G. Bombakidis, Series B: Physics, Vol. 76, NATO Advance Study Institute (Plenum Press, New York and London, 1981) p. 177.
16. M. V. ŠUŠIĆ, *Mater. Chem. and Phys.* **12** (1985) 99.
17. L. TANNER and R. RAY, in *Scr. Metall.*, **14**, (1980) 657 in "Glassy Metal I", edited by H.-J. Güntherodt and H. Beck, (Moscow, "Mir" 1983) in Russian, p. 333.
18. A. J. MAELAND, in "Hydrogen for Energy Storage", edited by A. P. Andersen and A. J. Maeland (Pergamon, Oxford, 1978) p. 447–462.
19. A. J. MAELAND, L. E. TANNER and G. G. LIBOWITZ, *J. Less-Common Metals* **74** (1980) 279.
20. M. V. ŠUŠIĆ, P. B. BUDBERG and S. P. ALISOVA, *J. Mater. Sci.* **21** (1986) 1297.

Received 13 October 1986
and accepted 19 January 1987