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Kinetics of thermal devitrification (crystallization) of a titanium amorphous alloy

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Thermal investigation, by differential scanning calorimetry, of the behaviour of an amorphous alloy (39 Cu, 8 Ni, 1 Si and 52 Ti, wt%) was undertaken in a hydrogen atmosphere. It was shown that crystallization (devitrification) proceeds through four different stages within the temperature range 673 to 853 K (400 to 580° C) and consequently four exothermal maxima at temperatures which depend on the heating programme are registered on the thermograms. The activation energies of each cyrstallization stage, the frequency factor, rate constant, half-time of the reaction and crystallization enthalpy, were determined. Particular attention is paid to a discussion of the crystallization process of each stage in correlation with the results obtained by X-ray analysis.

1. Introduction

Metallic glasses have recently been classified into a new group of materials that are of particular theoretical and practical importance. It was noticed that metallic glasses show some properties similar to those of metals and alloys but, at the same time, they are also characterized by glass-like properties resulting from their amorphous structure. The structure of the relative materials proves that the atoms are mutually connected by oriented metal bonds without showing long-range order; this causes their isotropic behaviour. They are opaque and ductile materials characterized by unusual magnetic properties and much higher electrical conductivity when compared to the corresponding crystal materials. Metallic glasses are chemically homogeneous at a scale exceeding several atomic diameters. They are deprived of a grain structure and hence of grain boundaries, and this makes them be very corrosion-resistant. This was particularly proved in cases where metallic glasses formed of a transition metal–metalloid alloy containing chromium [1] are concerned.

Three important models, the dense random packing model [2], the microcrystalline model, and the random packing of atomic clusters [3], have been adopted in the description of metallic glass structure. The microcrystalline model presupposes tiny crystallites to be distributed randomly throughout the amorphous matrix, while the random packing of clusters model presumes a mutual packing of clusters into series, but without crystallinity. The dense random packing model considers the structure of fluids on the basis of groups consisting of tetrahedral units which are arranged in a regular and continuous fashion. Metallic glasses are mainly obtained by methods of rapid cooling of both liquid metals and alloys [4–7]. This method has been quite well developed, so that the products obtained may have the form of powders, ribbons or wires, or can be assigned for commercial purpose ($Fe_{0.81}B_{0.135}C_{0.02}$, $Fe_{0.40}Ni_{0.38}Mo_{0.04}B_{0.18}$), etc.

According to the chemical classification (four groups) [8], metallic glasses are two or more component systems containing, in more cases, nonmetallic components (silicon, oxygen, beryllium, germanium, phosphorus). When exposed to the heating process, metallic glasses become crystallized and this procedure can be followed by phase separation.

Numerous chemical, physico-chemical and physical methods have been utilized for investigation of the properties of amorphous materials, including metallic glasses. Various forms of differential thermal analyses [9] are frequently used for thermal, as well as kinetic investigations. A method [10, 11] based on a change in the heating rate, which has been adjusted for use where investigations of industrial materials [12] are concerned, is a particularly good form of the differential scanning calorimetric methods. This method has been particularly recommended by the DuPont Company when working with DuPont Thermal Analyser [13] and thus it has been adopted for use in this paper.

Literature data on metallic glasses based on titanium are very poor. Some results demonstrate rather interesting properties of amorphous titanium and copper alloys [14]. The four diverse compositions of 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 a considerable hydrogen adsorption at room temperature and in a hydrogen atmosphere, thus forming hydrides which contain different quantities of hydrogen.

X-ray analysis shows that hydrogen adsorption causes no crystallization at all, but gives rise to a slight

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increase in volume. Thermal investigations (differential thermal analysis, DTA, thermogravimetric analysis, TGA, and differential scanning calormetry, DSC) prove that the crystallization (devitrification) process in a hydrogen atmosphere takes place in two stages (430 and 470° C), while the amorphous hydride $TiCuH_{1.33}$ formed in a hydrogen atmosphere at room temperature decomposes during heating (at 160° C) when a crystal titanium hydride (TiH_{2-x}) is formed (exothermaly at 235° C). Thus the hydride formed reacts with copper at 535° C in endothermal process, to produce TiCu and H_2 [15, 16]. The results obtained duing the investigation of crystallization of the amorphous alloy 62Ti25Ni9Cu4Si, show that this process proceeds in three stages [17].

2. Experimental details

The amorphous titanium alloy (39% Cu, 8% Ni, 1% Si and 52% Ti) in a ribbon-like form, and several centimetres thick, produced by the Baykov Institute of Metallurgy, Academy of Science, SU Moscow [18], has been examined. The samples, of several milligrams, were first cut from this ribbon and then thermally investigated by differential scanning callorimetry (DuPont 1090 Thermal Analyser) within the temperature range from room temperature to 900 K at a heating rate of 5 to 30 K min^{-1} in a hydrogen (and nitrogen) atmosphere. The amorphous, partly and completely crystallized samples, previously heated to a particular crystallized degree, were then examined by X-ray analysis with Cu*Kα* and a graphite monochromator.

3. Results and discussion

The crystallization procedure occurring in a hydrogen atmosphere is similar to that taking place in a nitrogen atmosphere. The only difference noted reflects the fact that the crystallization enthalpies of the single stages in hydrogen are somewhat lower compared to those in nitrogen. Fig. 1 presents a characteristic DSC thermogram, obtained in a hydrogen atmosphere, on which four exothermal maxima corresponding to four crystallization stages with rather different enthalpies can be noticed.

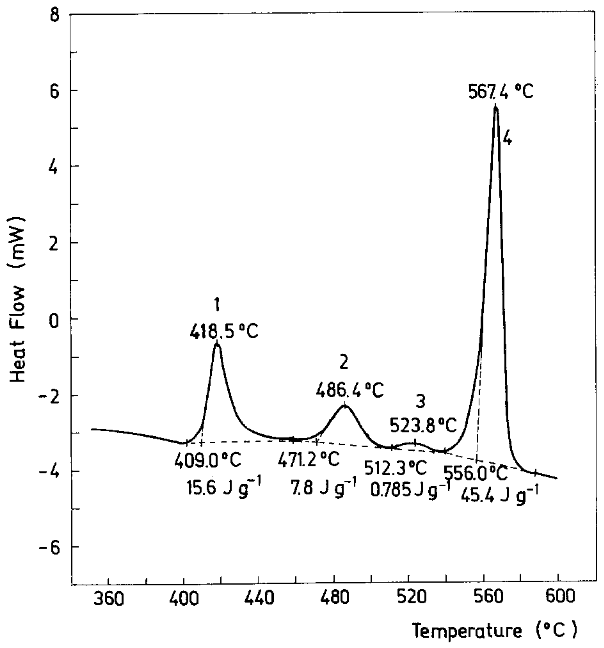

Figure 1 DSC thermogram of an amorphous sample in hydrogen, $\beta = 20\,K\,min^{-1}$.

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

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

where β is the heating rate (K min^{-1}), E is the activation energy, T the absolute temperature, together with the appropriate corrections, or according to the relation below:

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

where no corrections were made, the activation energy was determined.

According to the relation

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

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

The crystallization rate constant, k, was defined according to the relation

$$\begin{aligned} k \;&=\; Z \exp\,(-E/RT) \\ \text{i.e. } \ln k \;&=\; \ln Z \,-\, E/RT \qquad (4) \end{aligned}$$

from which the reaction half-time

$$t_{1/2} \;=\; 0.693/k \qquad (5)$$

was determined.

The exothermal maxima according to the increasing maximum peak temperature were marked by numbers 1 to 4; these also denote crystallization stages. Distinct thermal and kinetic values are marked by indexes from 1 to 4. By plotting log (β/T^2) against $1/T$ for each thermal (crystallization) stage, straight lines are obtained (Fig. 2). The slopes Δ log $(\beta/T^2)/\Delta\,(1/T)$, -17.07×10^3 for the first, -15.55×10^3 for the second, -19.23×10^3 for the third and 11.76×10^3 for the fourth maximum can be derived from this figure. On the basis of these slopes and according to Equations 2 to 4, the corresponding values presented in Table I can be calculated. The enthalpy can be immediately read from thermograms.

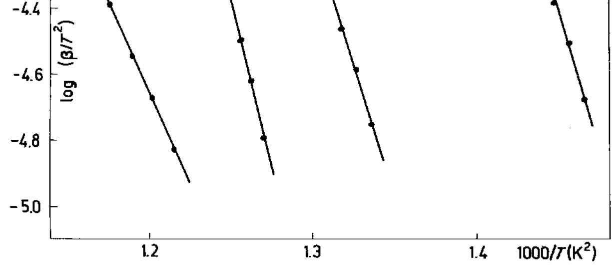

Figure 2 Plot of log (β/T^2) against $1000/T$, K^{-1}.

TABLE I Thermal devitrification in a hydrogen atmosphere

E (kJ mol^{-1})				Z (min^{-1})			
E_1	E_2	E_3	E_4	Z_1	Z_2	Z_3	Z_4
326.41	297.44	367.73	224.97	8.1×10^{24}	3.9×10^{20}	1.8×10^{23}	7.8×10^{13}

Fig. 3 shows the dependence of crystallization rate constants for all four stages on temperature. 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 maximum temperatures.

It is evident, on the basis of activation energy values, frequency factor, crystallization enthalpy and constant rate of crystallization at maximum temperature of the corresponding crystallization stage at $\beta = 15\,\text{K}\,\text{min}^{-1}$ (Fig. 3, Table I) that these values, excepted for enthalpy, behave in almost the same way as the dependence of degree of crystallization. The crystallization enthalpy decreases from the first to the third crystallization degree which is characterized by the lowest value. The fourth, i.e. the last, crystallization degree is characterized by the highest enthalpy, as can be seen from Fig. 1.

The crystallization process was investigated using X-ray analysis (Cu$K\alpha$, graphite monochromator) of partly and completely crystallized samples. Fig. 4 shows X-ray diffractograms of samples before (amorphous), curve a, and after heating up to 433° C, curve b, 505° C, curve c, and 580° C, curve d. It is obvious that the untreated sample (amorphous) gives a diffractogram that is characteristic for a completely amorphous state (a low and widely extended maximum). When the sample is exposed to the heating process until the completion of the first crystallization stage (433° C), the diffractogram shows the rise in height of a widely extended maximum, only. When the sample is heated to 530° C until completion of the second and third crystallization stages, the diffractogram shows a further rise of the extended maximum with the occurrence of a few low peaks that are characteristic of the formation of particular crystal structures. A diffractogram of the sample heated to 580° C, i.e. to the end of the complete crystallization, shows numerous peaks that are characteristic of the former crystal phases.

Having summarized the above results, a conclusion that the first two exothermal maxima on the thermogram do not characterize the first and the second stages of crystallization, can be made. However, bearing in mind the considerable enthalpy of the relative processes, as well as theoretical models of crystallization of amorphous metals, we are of the opinion that in this case, the crystallization process does occur, i.e. the process of nucleation up to microcrystallites that are not big enough to cause the corresponding reflections of X-rays, as the model [3] predicts. When the sample is exposed to temperatures exceeding 600° C, its diffractogram is identical to that of a completely crystallized sample. A low crystallization enthalpy in the third stage indicates crystallization at the nucleation level to occur in it, while the real crystallization process takes place during the last stage of crystallization with the highest enthalpy. It was also noticed that some other titanium alloy [17] behaves in the same manner.

4. Conclusions

Amorphous titanium alloy (39% Cu, 8% Ni, 1% Si and 52% Ti) when heated in a hydrogen or nitrogen atomsphere, transforms to the crstal state. The crystallization process takes place in four distinct stages, at corresponding temperatures and with corresponding kinetic and thermal values. The crystallization process, both in hydrogen and nitrogen, occurs in an identical manner. The activation energies for all the stages are considerable (225 to $368\,\text{kJ}\,\text{mol}^{-1}$). It was also noticed that the crystallization rates constants (0.6 at $1.2\,\text{min}^{-1}$) and the frequency factors (7.8×10^{13} ot $8.0 \times 10^{24}\,\text{min}^{-1}$) are also high. In the first three stages of crystallization, polycrystallites and clusters producing no important X-ray reflections are formed, while the real crystallization occurs in the fourth, i.e. the last, stage when crystals giving characteristic X-ray diffractograms are formed. The enthalpy

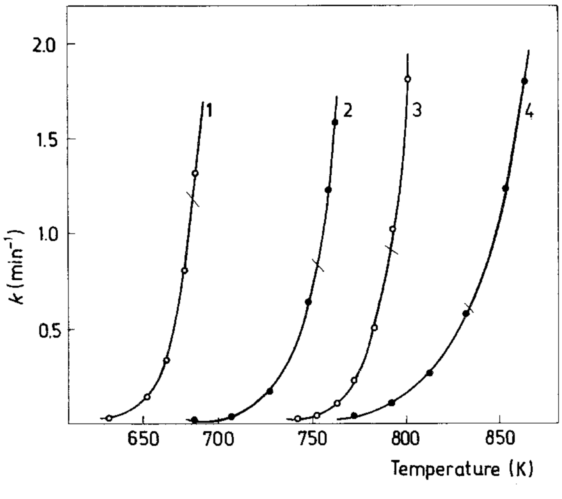

Figure 3 Crystallization rate constants as a function of temperature.

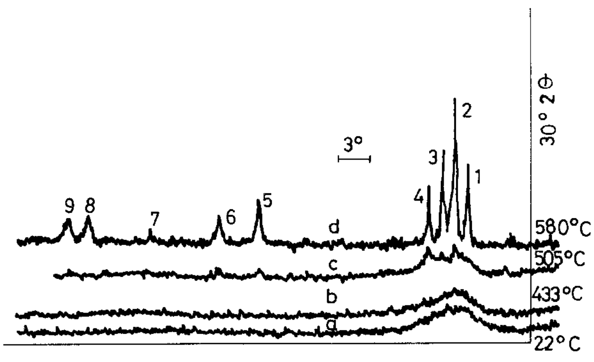

Figure 4 X-ray diffractograms (Cu$K\alpha$) of the sample: (a) before heating, and after heating to (b) 706 K, (c) 803 K and (d) 853 K. The numbers on the diffractogram correspond to: 1. (1 0 3) Ti_2Cu, 2. (1 1 0) TiCu, 3. (0 1 2) TiCu, 4. (1 1 0) Ti_2Cu, 5. (0 2 0) TiCu, 6. (2 0 0) Ti_2Cu, 7. (1 1 6) Ti_2Cu, 8. (1 2 2) TiCu, 9. (2 1 3) Ti_2Cu.

TABLE II Thermal devitrification in a hydrogen atmosphere

β	ΔH_1 (J g^{-1})	ΔH_2 (J g^{-1})	ΔH_3 (J g^{-1})	ΔH_4 (J g^{-1})
10	13.0	7.0	0.61	42.2
15	14.6	7.2	0.76	42.9
20	15.6	7.8	0.78	45.4
30	17.6	7.8	0.57	48.5

of this process is considerably higher when compared with that of the previous stages of crystallization.

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