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Nanocrystallization of $Co_{33}Zr_{67}$ Glasses

T. SPASSOV
Department of Chemistry, University of Sofia, 1126 Sofia, Bulgaria
U. KÖSTER, J. MEINHARDT
Department of Chemical Engineering, University of Dortmund, D-44221 Dortmund, Germany

Crystallization of $Co_{33}Zr_{67}$ glasses was studied at temperatures below and above the glass transition temperature, T_g, by means of TEM and differential scanning calorimetry (DSC). Nanocrystalline cubic structure (“big” cubes; $a = 1.22$ nm) was revealed at temperatures above T_g as well as at low annealing temperatures in DSC. Systematic analysis of the overall transformation kinetics of the amorphous-to-nanocrystalline reaction leads to the conclusion that primary crystallization with time-dependent growth rates instead of polymorphic transformation, takes place. We propose that the formation of this nanostructure is provoked by oxygen contamination in the glass.

1. Introduction

The formation of nanocrystalline materials by crystallization of metallic glasses (including zirconium-based glasses) has attracted much attention in recent years. Crystallization of $Co_{33}Zr_{67}$ glasses has already been a subject of numerous investigations [1–8]. Bushow [1], Jansson and Nygren [2], Sinning *et al.* [3] and Nicolaus *et al.* [4] reported that the first crystallization reaction is a polymorphic transformation of the amorphous material to the nanocrystalline metastable cubic modification of $CoZr_2$ ($E9_3$, $NiTi_2$ type). The next reactions in this alloy are associated with the transformation from the cubic to the stable tetragonal modification of $CoZr_2$ (C16, $CuAl_2$ type). Sinning *et al.* [3] found that the crystalline microstructure depends strongly on the heating rate or on the temperature of isothermal annealing, because at temperatures higher than 400°C or at heating rates higher than 1 $K\,min^{-1}$, a nanocrystalline microstructure (with grain size of a few nanometres) could be realized. Blank-Bewersdorff and Köster [7] were able to observe by TEM the direct crystallization into the tetragonal stable phase of the $CoZr_2$ compound at temperatures far below the glass transition temperature. In our previous papers [8, 9] we reported the formation of nanocrystalline microstructure of the metastable fcc $TMZr_2$ (TM = Fe, Co, Ni) phase by polymorphic crystallization of zirconium-based transition metal glasses at temperatures above the glass transition temperature, T_g.

Altounian *et al.* [10] have studied the influence of trace impurities, especially oxygen, on the crystallization of $Ni_{33}Zr_{67}$, $Co_{33}Zr_{67}$ and $Fe_{33}Zr_{67}$ and found that oxygen leads to metastable fcc crystalline structure instead of the equilibrium tetragonal structure.

In the present work, the transformation kinetics of the amorphous-to-nanocrystalline reaction was studied in $Co_{33}Zr_{67}$ by differential scanning calorimetry (DSC) and TEM in an attempt to obtain more information about the evolution of this metastable nanocrystalline phase (structure) instead of the equilibrium phase.

2. Experimental procedure

The $Co_{33}Zr_{67}$ (at %) amorphous and microcrystalline ribbons were prepared by melt-spinning in a helium atmosphere of 300 mbar, on to a copper wheel (diameter, 250 mm) with surface velocities of up to 35 $m\,s^{-1}$. X-ray (using CuK_α radiation) and electron diffraction studies have been carried out on the as-spun, as well as on the annealed, ribbons to identify the amorphous state and to characterize the crystalline phases.

The transformation kinetics of the amorphous to (nano-)crystalline state was studied by differential scanning calorimetry (DSC, Perkin–Elmer) both at constant temperature and constant heating rates. Because of the strong tendency of the zirconium-based glasses to oxidize, for the calorimetric measurements, the samples were enclosed in aluminium pans and the experiments were carried out under an argon atmosphere. Samples subjected to heat treatment in an external oven (tin bath) were wrapped in zirconium foil. Because of the very fast crystallization at high annealing temperatures, a method for rapid heating has been applied [11], using electric current pulses with a well-controlled current intensity and duration of the pulse through the sample.

The microstructure at various stages of the crystallization was studied by TEM, Philips CM 200, operating at 200 kV. Specimens were thinned by electrolytic jet polishing using an electrolyte of 3 parts methanol, 1 part glycerine and 1 part HNO_3.

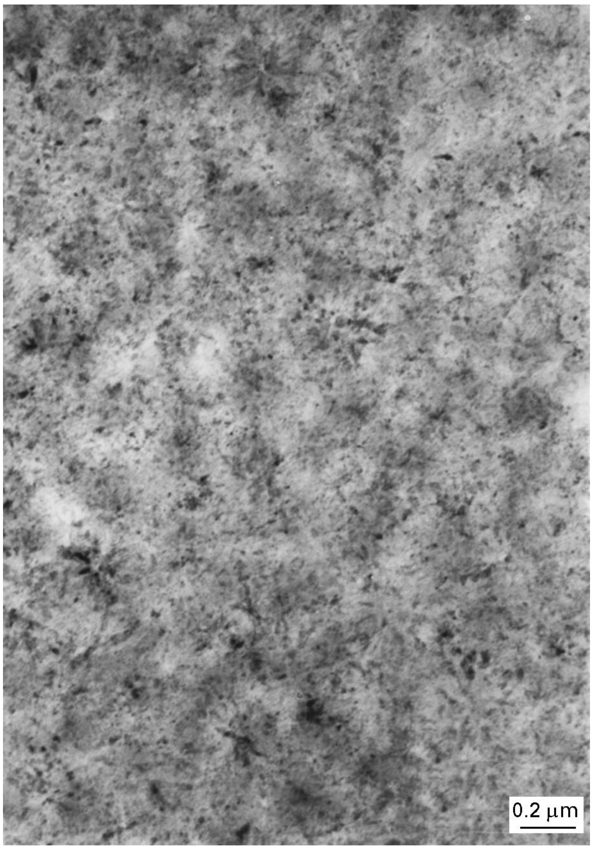

Figure 1 Transmission electron micrograph of $Co_{33}Zr_{67}$ as-cast with a 12 m s^{-1} surface velocity.

3. Results and discussion

X-ray and electron diffraction studies have been carried out with $Co_{33}Zr_{67}$ alloys melt-spun with different quenching rates (different surface velocities of the quenching disc 6, 12 and 35 m s^{-1}) as well as after annealings. X-ray and electron diffractograms taken from both sides of the as-quenched with 35 m s^{-1} surface velocity alloy were typical for an amorphous structure. TEM and electron diffraction taken from the contact side and from the volume of the ribbon as-cast at 12 m s^{-1}, revealed a nanocrystalline $CoZr_2$ cubic structure (f c c, $a = 1.22$ nm), Fig. 1, while from the free surface, mainly the stable tetragonal $CoZr_2$ phase was detected. The ribbon quenched at 6 m s^{-1} surface velocity consists of fine-grained $CoZr_2$ cubic crystals at the contact side and larger tetragonal crystals at the free surface.

The crystallization of $Co_{33}Zr_{67}$ glasses was studied below and above the glass transition temperature, T_g. This amorphous alloy crystallizes first into a metastable f c c $CoZr_2$ phase, the so-called “big cubic” phase [9]. Fig. 2 shows the nanocrystalline microstructure of f c c $CoZr_2$ formed after annealing above T_g (0.4 s at 828 K, by the rapid heating technique). During further annealing, the nanocrystalline cubic phase becomes more coarse-grained and starts to transform into the stable tetragonal $CoZr_2$ phase through a second metastable phase, which could be indexed assuming a hexagonal structure [9]. A similar phase transformation sequence was reported by several investigators [4, 5, 9], but it should be noticed that at temperatures below T_g under slightly different conditions (metals with different purity), direct crystallization into large spherical crystals of the stable tetragonal phase was also observed [7]. Altounian *et al.* [10] also found a strong influence of the purity of zirconium on the crystallization behaviour. These authors assumed that the formation of the nanocrystalline f c c $CoZr_2$ phase is stabilized by the oxygen contamination.

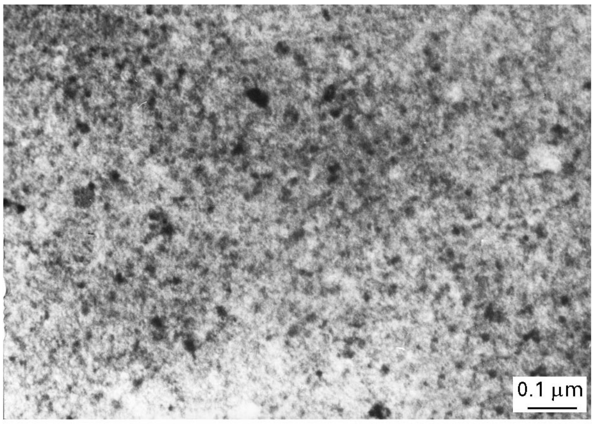

Figure 2 Microstructure of f c c $CoZr_2$ after the first crystallization reaction during a rapid heating experiment (0.4 s, 828 K).

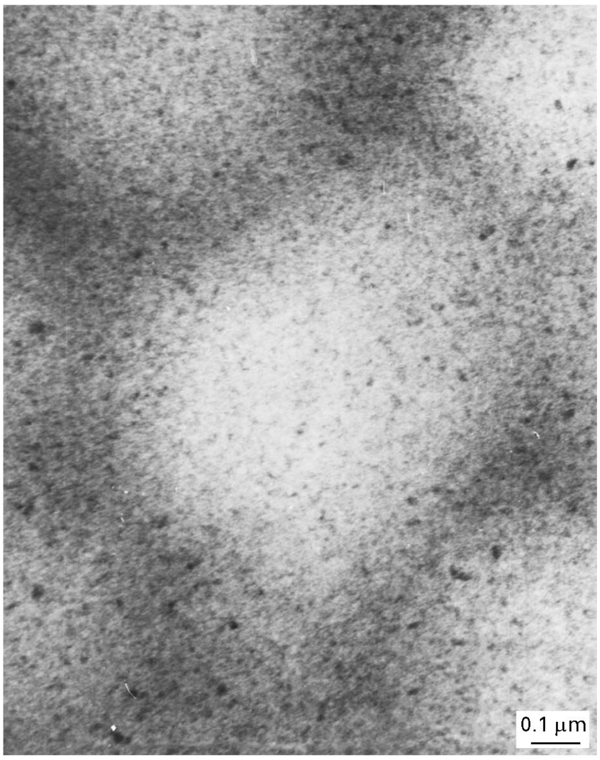

Figure 3 Transmission electron micrograph of a sample annealed up to 730 K in the DSC.

Microcalorimetric measurements of $Co_{33}Zr_{67}$ in the temperature range 300–900 K, with 40 K min^{-1} scanning rate showed clear exothermic peaks, which correspond to the phase transformations thus described. TEM and electron diffraction taken on or after the first DSC peak, Fig. 3, showed similar nanostructure compared to the microstructure after pulse-heating experiments (see Fig. 2). It is not clear whether this glass crystallizes totally (completely) by

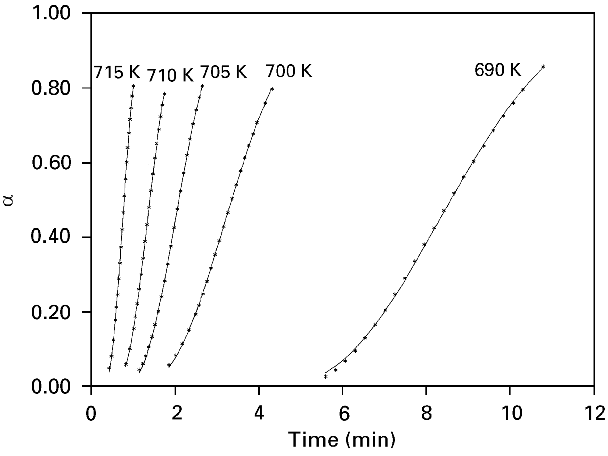

Figure 4 Isothermal transformation kinetic curves (the fit is to the JMA model with the parameters listed in Table I).

a polymorphic reaction into a metastable nanocrystalline material, or only partially by a primary crystallization of $CoZr_2$ in an oxygen-enriched matrix, but there is evidence for the primary reaction, i.e. after the first crystallization reaction the sample consists of f c c $CoZr_2$ nanocrystals and amorphous residual phase in between them. This result was confirmed from the electron diffraction, where several diffraction rings are observed, as the first one is rather broad.

TEM study of a sample annealed in the DSC up to 740 K and then thinned only from one side, showed also the nanocrystalline structure of f c c $CoZr_2$, i.e. probably at high annealing temperatures the volume crystallization is faster than the surface crystallization. Surface crystallization of this glass was observed only at low annealing temperatures by Köster and Meinhardt [12]. Therefore we concluded that the first DSC effect ($\Delta H \approx 4$ cal g^{-1}) is due only to the transformation "amorphous ⇒ metastable f c c" $CoZr_2$. X-ray diffraction also did not show traces of surface crystallization (except for some surface oxidation), i.e. sharp diffraction peaks were not observed from both sides of the ribbon heat treated up to temperatures above the first DSC peak.

Because of the difficulties in distinguishing such a primary crystallization of the metastable f c c $CoZr_2$ phase in $Co_{33}Zr_{67}$ glass from polymorphic crystallization only by TEM, a detailed kinetic analysis of this reaction was carried out in order to obtain additional information about the mechanism of this transformation. Furthermore, because of the extremely fine-grained structure, it was not possible to study the crystal growth and nucleation separately in partially crystalline samples. The isothermal kinetics of the first crystallization reaction was followed by DSC in the temperature range 690–715 K, Fig. 4. Several isothermal DSC runs have been carried out at each temperature with the aim to obtain fully reproducible and reliable experimental kinetic curves, $\alpha(t)$, independent of the way of heating up to the isothermal annealing temperature and of the possible inhomogeneities along the length of the amorphous ribbon. TEM and electron diffraction after the isothermal experiments showed the same nanostructure of f c c $CoZr_2$ phase.

TABLE I Parameters from the JMA analysis of the amorphous to nanocrystalline transformation in $Co_{33}Zr_{67}$ (k and t_0 are evaluated at fixed $n = 2.5$ for degrees of transformation 0.05–0.80)

T (K)	n	k ($\min^{-2.5}$)	t_0 (min)
690	2.25	0.0175	4.220
700	2.55	0.0826	0.992
705	2.70	0.3274	0.701
710	2.55	0.9810	0.484
715	2.65	4.121	0.253

All isothermal annealing temperatures in this study are above the threshold temperature (as defined from Nicolaus *et al.* [4]) for the production of the nanocrystalline material state from the amorphous $Co_{33}Zr_{67}$. The experimental transformation curves, $\alpha(t)$, obtained from the isothermal DSC curves, are presented in Fig. 4. At all isothermal annealing temperatures, incubation periods of the overall crystallization, t_0, were clearly seen. Applying Johnson–Mehl–Avrami (JMA) formalism [13–15]

$$\alpha(t) = 1 - \exp[-k(t - t_0)^n]$$

an adequate description for the isothermal kinetics of this transformation was obtained. Fig. 4 shows the kinetic curves, $\alpha(t)$, calculated according to the JMA model. The kinetic parameters evaluated from the JMA equation are listed in Table I. An important result here is the practically constant value of the Avrami exponent $n \approx 2.5$ at all temperatures studied. It should be pointed out that, in contrast with our result, several authors found a mean value for the Avrami exponent, n, about 3, which they interpret in terms of the Avrami theory as a growth of pre-existing nuclei. It is difficult, however, to compare directly the results of the overall crystallization kinetics, obtained by different investigators, especially when the values for the incubation times are not shown and different techniques for the evaluation of the kinetic parameters are used. Nicolaus *et al.* [4] found a mean Avrami exponent $n \approx 2.44$, using the differentiated JMA equation to describe the anisothermal crystallization of $Co_{33}Zr_{67}$, which could be connected with the temperature interval in this study, 390–440 °C.

This value of $n = 2.5 \pm 0.2$ most probably must be connected with nucleation and crystal growth controlled by diffusion. In other words, primary crystallization of $CoZr_2$ in an oxygen-enriched matrix instead of the polymorphic reaction assumed for this glass (composition), was observed. An additional fact in agreement with the mechanism thus proposed, is the kinetic analysis at $T = 670$ K of a sample previously partially crystallized at $T = 710$ K to $\alpha \approx 0.05$. The Avrami exponent found in this case was about 1.5, i.e. only diffusion-controlled crystal growth in three dimensions was observed. Although the kinetic analysis is an indirect way for studying the crystallization mechanism, this is an important result, especially when taking into account the difficulties for distinguishing such a primary reaction from polymorphic crystallization only from microscopic observations.

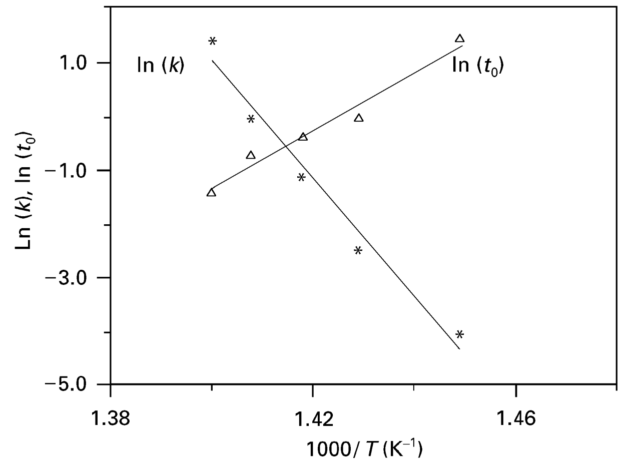

Figure 5 Arrhenius temperature dependencies of the rate constant and incubation time.

The nearly constant value of the Avrami exponent, *n*, allowed us to fix it and to determine the activation energy for the amorphous to nanocrystalline transformation from the Arrhenius temperature dependence of the incubation time, t_0, and of the constant k in the JMA equation, 105 and 215 kcal mol^{-1}, respectively, Fig. 5. While the activation energy derived from t_0 is exactly in the range of the values determined by other investigators [4], the activation energy derived from k was found to be rather high, and is obviously connected with the nanocrystalline microstructure revealed during this reaction.

4. Conclusion

The transformation of the amorphous to the nanocrystalline state in $Co_{33}Zr_{67}$ alloy was studied by TEM and DSC. The kinetic analysis of the crystallization, carried out at isothermal conditions by DSC in combination with TEM observations on the microstructure after the first reaction, showed that instead of polymorphic crystallization of stable tetragonal $CoZr_2$, which is assumed for this composition, a primary crystallization takes place. The Avrami exponent, *n*, for all temperatures of isothermal annealing, is practically equal to 2.5, which reveals that the mechanism of this transformation is nucleation and diffusion-controlled growth in three dimensions. The most probable reason for this change in the crystallization mechanism is oxygen contamination of the zirconium-based glass absorbed during the ribbon preparation or during further annealing.

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