

Kinetics of two-stage crystallization in Metglas 2826A

R. S. TIWARI

Department of Physics, Banaras Hindu University, Varanasi 221 005, India

J. C. CLAUS

DIEHL GmbH and Co. D-8500 Nurnberg 1, West Germany

S. RANGANATHAN

Department of Metallurgy, Indian Institute of Science, Bangalore 560 012, India

Crystallization kinetics of MSI and MSII stages in Metglas 2826A has been investigated by quantitative transmission electron microscopy. The volume fraction of crystallization against time curve has been found to show a plateau in the lower temperature region of annealing. It has been found that the glass transition temperature, T_g , has no effect on the sequence reversal of the crystallization reaction. It has been shown that the sequence reversal of transformation stages occurs due to the large difference in the activation energy of crystallization of MSI and MSII. In addition, the change in the morphology of the crystals obtained by annealing the amorphous alloy below and above the glass transition temperature, T_g , is reported.

1. Introduction

Earlier studies by Heimendahl and Maussner [1, 2] have shown that Metglas 2826A undergoes crystallization in two stages. This observation was missed by Chang and Sastri [3], as they carried out isothermal studies at only one temperature and adopted time intervals of treatment unfavourable for the differentiation of the two stages. It has been shown for 2826A that the crystallization of the alloy begins with the homogeneous nucleation and parabolic growth of MSI phase and the remaining amorphous matrix is enriched in metalloids (i.e. phosphorus and boron) [1, 2, 4]. Employing EDAX technique in conjunction with STEM, the primary crystallization behaviour of MSI phase has been clearly demonstrated by Heimendahl and Oppolzer [5]. The nucleation and growth behaviour of MSII phase has been investigated by earlier workers [1, 2, 4]. It has been found that there is no homogeneous nucleation of MSII phase and crystals grow at a constant rate.

In a recent study, Thorpe *et al.* [6] have further investigated the crystallization behaviour of Metglas 2826A. They found a strong dependence of crystallization behaviour on the scan rate during DSC investigation. According to their observation, at scan rates of 22.5 K min^{-1} , MSI and MSII crystallization are inseparable and at 48.7 K min^{-1} sequence reversal of crystallization stages occur. Furthermore, Bergmann and Fritsch [7] have analysed the crystallization behaviour of Fe-B metallic glasses in terms of nucleation theory for systems with more than one crystallization stage and phase. They have calculated the temperature-time-transformation curves for different types of crystallization reaction. Although DSC observations have been reported to verify the theoretic

cal curves [7], no quantitative transmission electron microscopic studies in this regard have been reported so far.

In the present work, further investigations were carried out to clarify the kinetics of MSI and MSII crystallization in this alloy. The effect of scanning rate of DSC on the concurrence or sequence reversal of crystallization stages is discussed. It has also been shown that the experimental curve for the volume fraction of crystallization is similar to the calculated curve for the two-stage crystallization.

2. Experimental details

The procedures of annealing and sample preparation for transmission electron microscopy have been reported earlier [2]. The isothermal treatments of samples obtained from Allied Chemical, USA, were carried out in a salt bath with a temperature accurate to $\pm 1^\circ \text{C}$. The samples were subsequently electropolished by a Tenupole twin-jet apparatus and observed by TEM techniques.

3. Results and discussion

3.1. TEM analysis of MSI and MSII crystallization

Fig. 1 shows the microstructures which are representative of isothermal transformation of the amorphous alloy 2826A annealed at 375 and 405°C for two different durations. Two types of crystal morphology may be noticed in the microstructure (Fig. 1a). Earlier studies by Heimendahl and Oppolzer [5] established that the composition of the small crystals was very different from that of the glassy matrix. This change in composition requires long-range diffusion and crystallization by this mode has been termed "primary

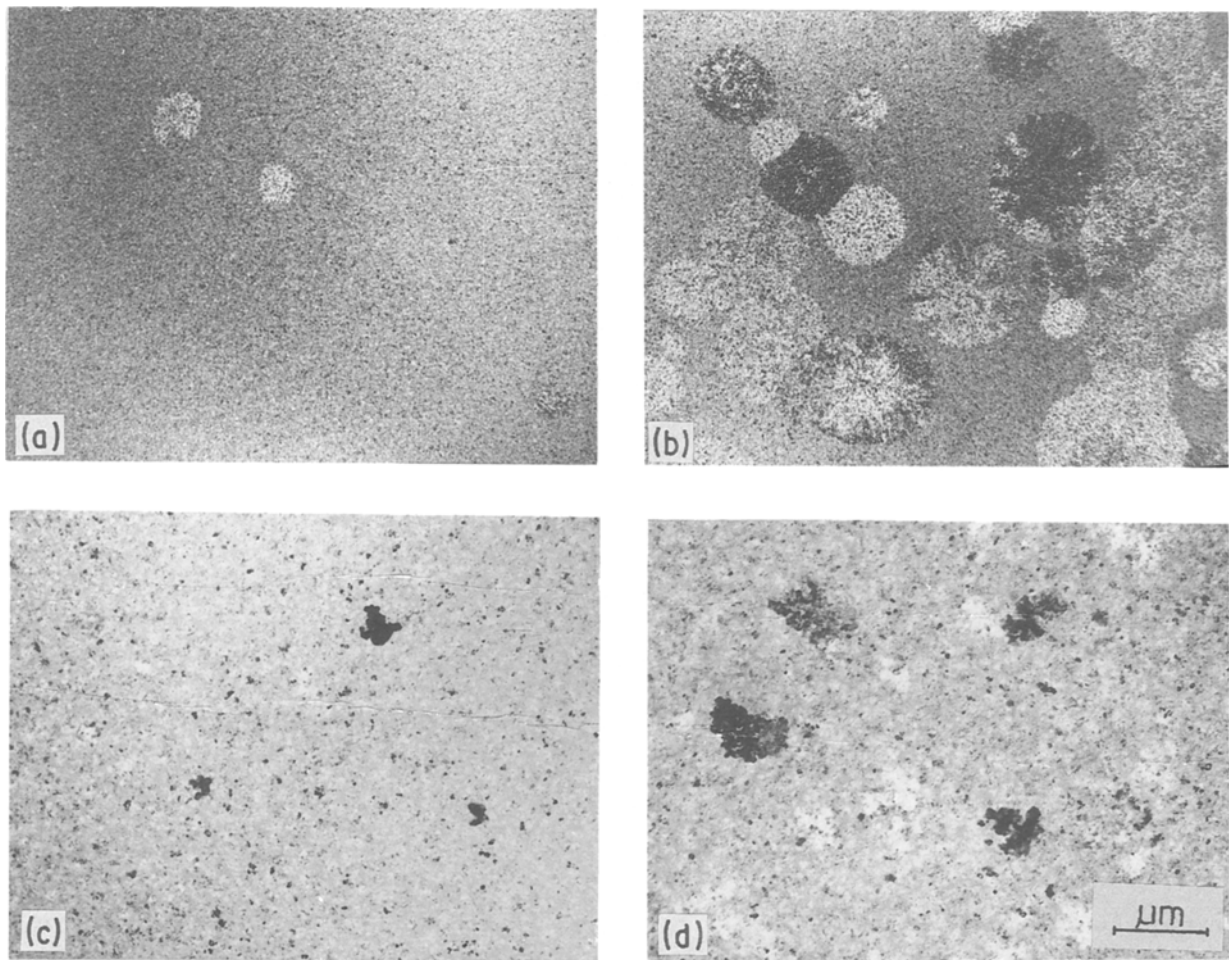


Figure 1 TEM microstructure showing isothermal crystallization at (a) 375°C for 1000 min, (b) 375°C for 3000 min, (c) 405°C for 5 min, (d) 405°C for 10 min.

crystallization" by Koster and Herold [8]. This corresponds to the MSI stage. The bigger crystals start appearing after MSI crystallization is nearly complete. This phase is formed by polymorphic crystallization and is termed MSII [1]. Fig. 1b shows the microstructure after annealing at 375°C for 3000 min. There is no change in the volume fraction of MSI phase (compare Figs 1a and b). However, MSII crystals have grown to larger size. From the size distribution and number of crystals observed after different time intervals (e.g. Figs 1a, b) it appears that there are quenched-in nuclei for the MSII phase [9]. This is in conformity with our earlier observation that the nucleation rate for MSII phase is zero [4]. Figs 1c and d show the results obtained at a higher temperature of 405°C. The same sequence of MSI and MSII has been found to occur. However, MSII phase starts appearing without completion of the crystallization of MSI phase, i.e. there is an overlap between the completion of MSI and the start of the MSII phase.

For determining the volume fraction of crystallization, a large number of microstructures obtained at different time intervals have been used. As the transmission electron microscope images are seen in projection, the volume fraction, f_v , is not equal to the area fraction, f_A . The formula

$$f_v = \frac{f_A}{1 + (3t/2d)} \quad (1)$$

has to be used, as has been discussed by Cahn and

Nutting [10]. An estimate of the thickness, t , was made by using the latex ball technique [11]. The diameter of the crystals, d , and f_A were measured from the micrographs.

The change in volume fraction as a function of time is plotted in Fig. 2. This clearly shows that the MSI reaction is complete around 30% volume fraction and is followed by the transformation of the remaining glassy matrix to MSII. It should be pointed out that Bergmann and Fritsch [7] have theoretically calculated the curves for crystallized volume fraction as a function of time for primary, polymorphic and eutectic crystallization. The plateau of the curve in Fig. 2 observed at 375°C is quite similar to the curve predicted by Bergmann and Fritsch for the two-stage crystallization [7]. It would be difficult to observe the plateau at higher temperatures because of the experimental error involved in the accurate determination of f_v .

Fig. 3 shows the times to start and finish the reactions leading to MSI and MSII, plotted against reciprocal temperature. The slopes of these curves yield the activation energies for crystallization, E_c , of MSI and MSII as 270 ± 30 and 470 ± 50 kJ mol⁻¹, respectively. These values are in agreement with those reported by several previous workers [2, 4, 6, 12-14].

3.2. Sequence of MSI and MSII crystallization and influence of T_g

If there is no change in the activation energies at

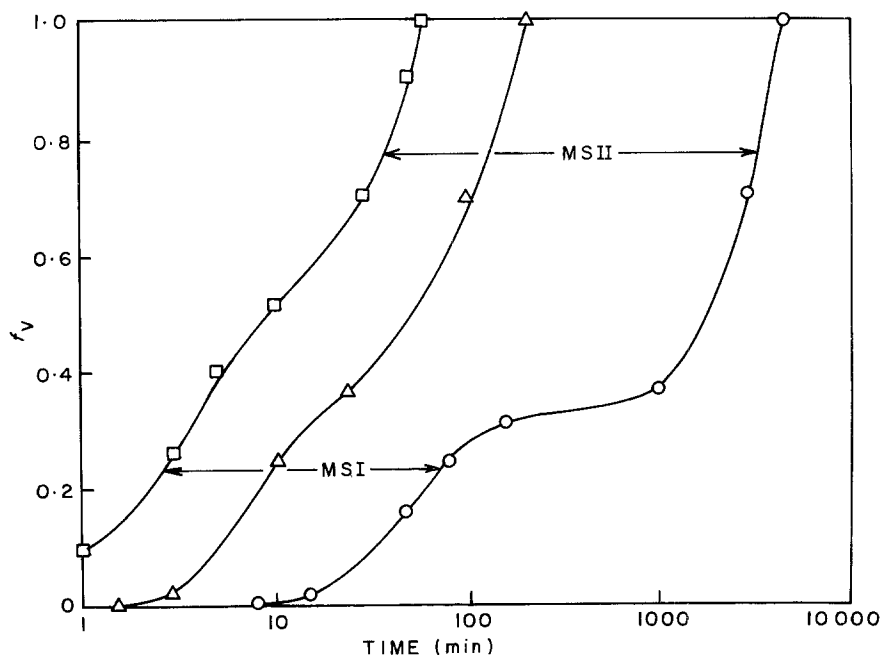


Figure 2 Change in crystallized volume fraction, f_v , as a function of time, in Metglas 2826A: (□) 405°C, (Δ) 396°C, (○) 375°C.

higher temperatures, the lines in Fig. 3 may be extrapolated. Then the lines for MSI and MSII would cross, indicating simultaneous occurrence of these phases. At still higher temperatures, a reversal of sequence could take place, i.e. MSII would occur first and would be followed by MSI. Experiments in the temperature range 405 to 430°C show that such an overlap occurs. However, a possible sequence reversal could not be observed; experimental limitation existed arising from very short heat-treatment periods of a few seconds and the possibility that the reactions occur as the sample heats up to the test temperature. A pulse annealing experiment would be more appropriate to detect reversal of sequence [15].

Freed and Vander Sande [16] have reported such a sequence reversal in CuZn alloys above T_g , the glass transition temperature. Their experimental evidence is tenuous, because they did not carry out an isothermal experiment below and above the glass transition temperature. In support of their observation they quote the work of Chang and Sastri [3] on Metglas 2826A. It is pertinent to point out that Chang and Sastri did not distinguish between the two stages (i.e. MSI and MSII) of devitrification of thin alloys. This has been done by Heimendahl and Maussner [1, 2]. In Metglas 2826A, T_g is around 380°C for a heating rate of 10 K min⁻¹, as determined recently in DTA experiments by Thorpe *et al.* [6]. T_g will show a dependence

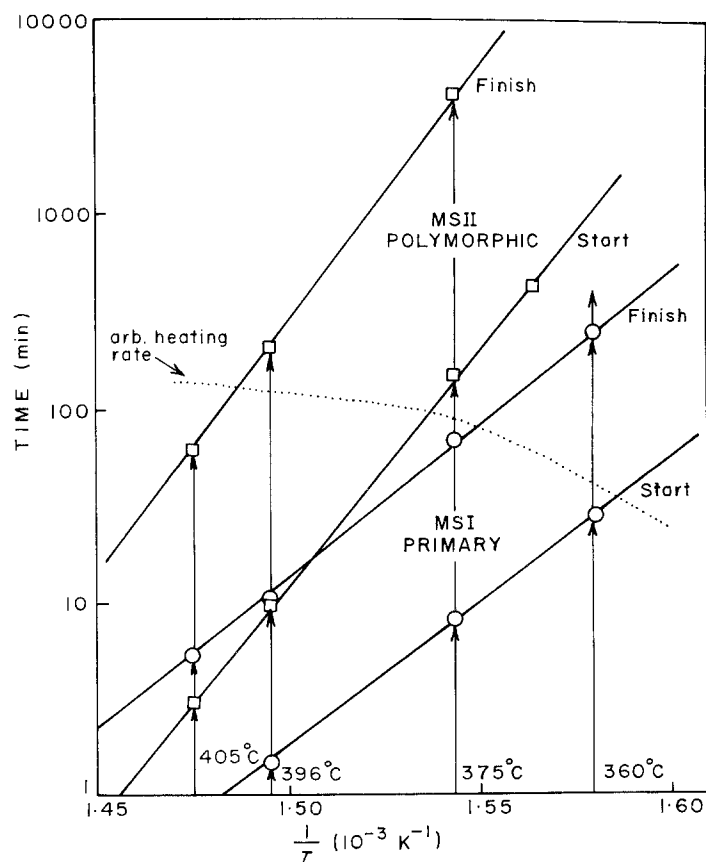


Figure 3 Time to start and finish of the crystallization of (○) MSI and (□) MSII Metglas 2826A as a function of reciprocal of temperature.

on heating rate [6]. Even if we take a range for T_g around 380°C, it is clear from the present work (Fig. 3) that both below and above the glass transition temperature, no sequence reversal has occurred. It has been recently demonstrated by the work of Thorpe *et al.* [6] that the extremely high heating rates used in DTA experiments lead to peak overlap and sequence reversal of MSI and MSII crystalline phases in 2826A. Although these results are obtained from non-isothermal experiments, they are explicable with the help of Fig. 3. Different paths to reach "start" and "finish" lines for MSI and MSII would correspond to different heating rates. One such heating rate is indicated by the dotted line in Fig. 3. For example, if the heating rate is extremely slow, MSI crystallization would start after a long time and MSII stage would be absent for the duration of the experiment. At an intermediate heating rate, both MSI and MSII would appear after a certain interval of time. Fig. 3 suggests that peak overlap and sequence reversal would occur at higher heating rates. Although we have considered the possible sequence reversal of MSI and MSII, it is important to recognize, however, that such an overlap and sequence reversal are not sharply differentiated by T_g . It may be pointed out that the sequence of crystallization reaction would depend upon the activation energies of MSI and MSII reactions which, in turn, would depend upon the nucleation and growth mechanisms of the respective reactions [17]. For example, in the present case the activation energies of MSI and MSII reactions are quite different (270 and 470 kJ mol⁻¹) and consequently overlapping and cross-over regions occur below 390°C in Fig. 3. Therefore, we may conclude that the sequence reversal or overlapping of reactions is governed by the crystallization kinetics of MSI and MSII, and not by the glass transition temperature.

In Fig. 1, it is interesting to note that the morphology of MSII crystals grown at 405 and 375°C, is different. While the shape of the crystals at 375°C is spherulitic, it is dendritic at 405°C. A similar morphological difference has also been reported by Dong *et al.* [18] in the case of Ni₅₆Zr₄₂. The cause of such morphological differences in crystals obtained either by annealing the amorphous alloy at different temperature or by rapid quenching of the liquid is not yet known. From the present observation it appears that above T_g , amorphous phase behaves like a liquid phase, in which case the dendritic morphology of the crystal is very common [19]. It may be mentioned here that the effect of T_g on the lamellar structure of crystallization product of Metglas 2826 has also been reported [20]. However, more investigations are required to establish this correlation.

4. Conclusions

On the basis of our present investigation on the crystallization kinetics of Metglas 2826A, the following conclusions may be drawn.

1. The volume fraction of crystallization against time curve shows a plateau instead of a simple s-shape behaviour.
2. No effect of T_g on the sequence reversal has been found in the present investigation.
3. The effect of scanning rate on the overlapping and sequence reversal of MSI and MSII as observed by Thorpe *et al.* [6] is explicable in terms of the kinetics of crystallization of two stages with a large difference in the activation energy of crystallization.
4. A change in the morphology of MSII crystal below and above T_g has been observed.

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