CRYSTALLIZATION SIZE EFFECTS STUDY OF $Fe_{40}Ni_{38}Mo_4B_{18}$ METALLIC GLASS FROM HIGH VOLTAGE (1 MeV) ELECTRON MICROSCOPY (*)

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ABSTRACT — A size effect study of the intermediate phases MSI and MSII, on the crystallization of $Fe_{40}Ni_{38}Mo_4B_{18}$ (2826 MB) metallic glass has been carried out. Time evolution of morphological parameters for both grain classes are analysed in the border and inner parts of the wedge-shaped samples observed in a H.V. electron microscope. The transformation rate is accelerated in thinner regions until a saturation is reached.

1 — INTRODUCTION

In the last few years great attention has been paid [1]-[3] to the morphological description of polycrystalline materials and their time evolution. The development of sophisticated automated data systems permitting more reliable results and a better knowledge of physical mechanisms involved in grain growth processes allows the study of some complex problems like textures [4], recrystallization dynamics [5], plastic deformation [6], 'abnormal' grain growth [7], etc. However, to the best of our knowledge, these methods have not been applied to study the nucleation and the grain growth processes during the crystallization of amorphous systems.

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The crystallization process of the metallic glass $Fe_{40}Ni_{38}Mo_4B_{18}$ (2826 MB) [8] takes place in two stages, the second one presenting a close analogy with the recrystallization in cold-rolled metals. In this work the image analysis techniques are applied to elucidate the effects of thickness on the crystallization kinetics of the above metallic glass.

2 — EXPERIMENTAL

Samples prepared as described elsewhere [8] were examined in a high voltage electron microscope (1 MeV) at ONERA (Paris). The samples were heated inside the microscope up to 775 K - above the second stage of the crystallization process - and annealed for 20 minutes at this temperature prior to a dynamic heating to reach the high temperature stable phase.

Images of structural evolution were recorded on a magnetoscopic band. Morphological parameters were measured using a Kontron MOPO2 image analyser. This instrument uses a magnetic cross-grid table with a sensor pen under operator control. By detecting pulses propagating along the X and Y wires and measuring their time of flight to the pen it is possible to determine the x-y coordinates of points on the grain perimeter. These coordinates are fed to a microprocessor which calculates both the perimeter and the area of each grain cross section.

3 — RESULTS

An observed feature on the electron microscope images is that crystallization starts at the border of the wedge-shaped sample, showing a higher nucleation rate than the thicker areas. The crystallite surface density determined in these two areas of the sample are plotted against time in Fig. 1, showing a good linear dependence in both cases. However, it is noteworthy that a saturation of the nucleation mechanism takes place at the border region after about ten minutes.

The nucleation rates calculated by a least-squares fit of data in Fig. 1 are 18.9 s^{-1} and 16.2 s^{-1}, respectively. This observed

difference has been considered significative, from statistical considerations, at a confidence level of 5 %.

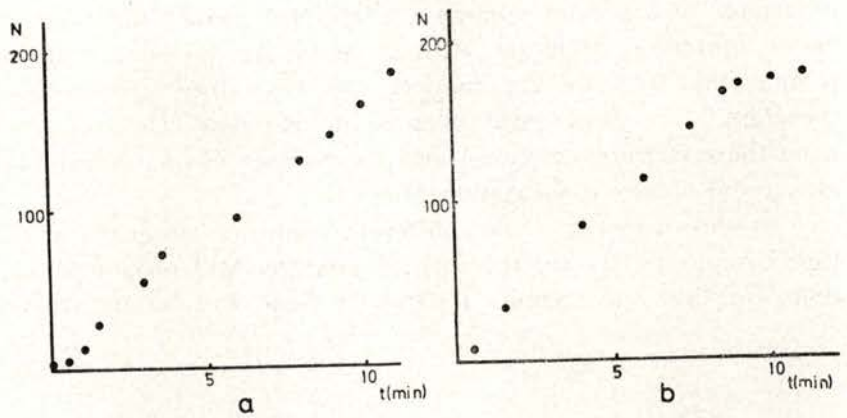

Fig. 1 — Time evolution of nuclei number surface density: a) inside the sample b) at the border.

Table 1 gives the mean morphological parameters determined for the two sample areas studied. For the grain area a, one defines an equivalent planar diameter $D_a = (4a/\pi)^{1/2}$, and for the perimeter s of the grain, an equivalent planar diameter $D_s = s/\pi$: D_{max} is the maximum diameter of the grain, D_x and D_y are the Feret's diameters [9] and F is a shape factor given by $F = 4\pi a/s^2$.

TABLE 1

	D_a	D_s	D_{max}	D_x	D_y	F
Border	99	115	113	110	103	0.68
Inside	148	180	180	167	156	0.62

Diameters are expressed in nm.

At this stage, two intermediate phases, MSI and MSII, are present in the sample; the first one is formed by small finely

dispersed crystallites and the second one by coarse particles. Data in Table 1 refer to the whole population of the two grain classes.

The higher mean diameter in the thicker region could be associated to a greater volume available for growth, allowing an easier formation of larger MSII crystals. At the border of the sample the free surface hinders the crystallite growth and, therefore, the smaller MSI crystals predominate. On the other hand these steric restrictions limit the number of nucleation sites giving the observed saturation effect.

As shown in Fig. 2, two different zones are observed in the time evolution of D_a for the small crystallite (MSI phase) population. The first one exhibits a parabolic form and can be related

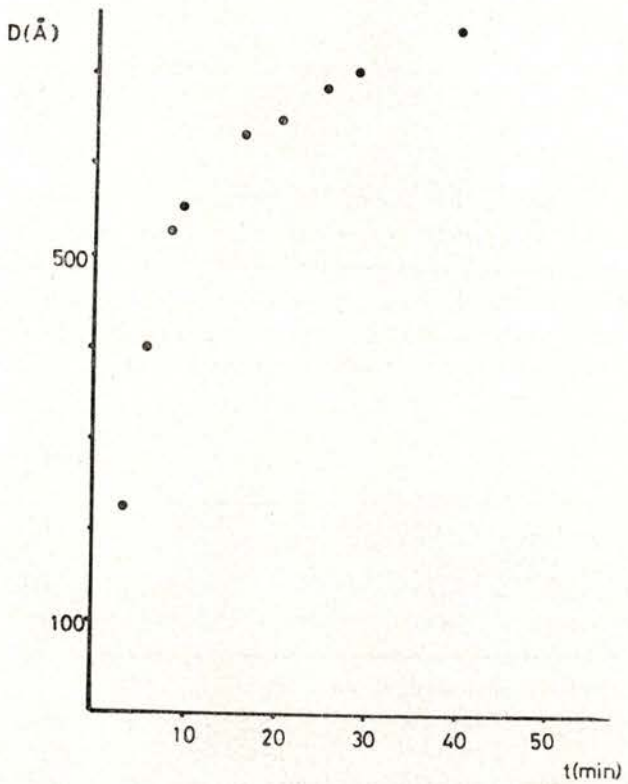

Fig. 2 — Time evolution of equivalent planar diameter for MSI phase grains.

to a diffusion controlled growth (primary nucleation), whereas the second is linear and should correspond to the overlapping of diffusion fields in a saturated situation.

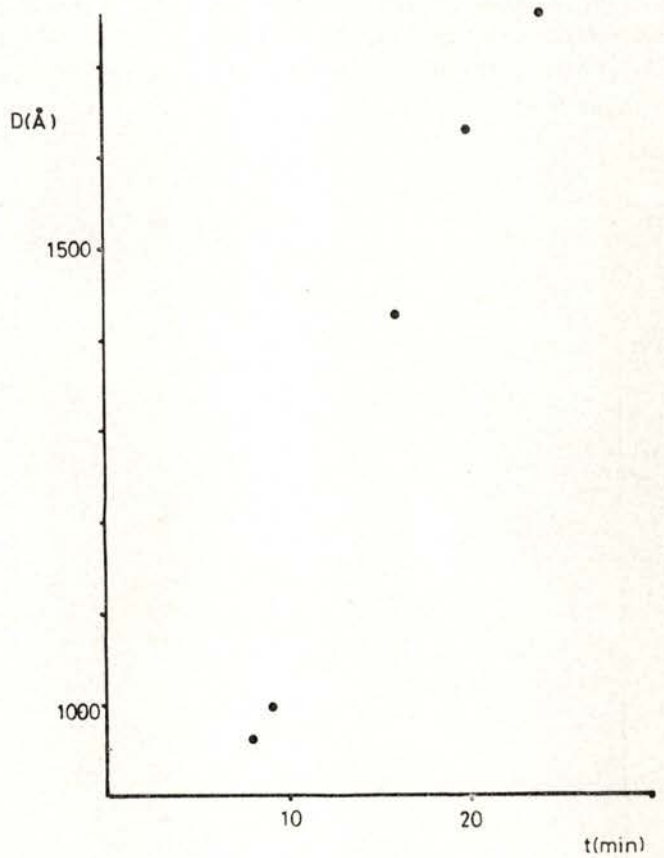

Fig. 3 — Time evolution of equivalent planar diameter for MSII phase grains.

For the other crystallites (MSII phase) the time evolution of D_a (Fig. 3) is linear in all the time range; this behaviour could be assigned to an interfase controlled growth. The growth rate of MSII crystals is higher than the MSI one and, as a consequence, the initial overlapping of the two grain class populations vanishes: MSII phase predominates, exhausting the remaining amorphous matrix.

Standard deviations versus time for lognormal distributions of D_a are show in Fig. 4 for both grain classes. As observed, the standard deviation is higher for MSI crystals and this could be explained from the primary character of crystallization reaction, the time-extended homogeneous nucleation giving a more dispersed distribution. MSII crystals are formed by a peritectic process, therefore the size distribution of crystals is more homogeneous.

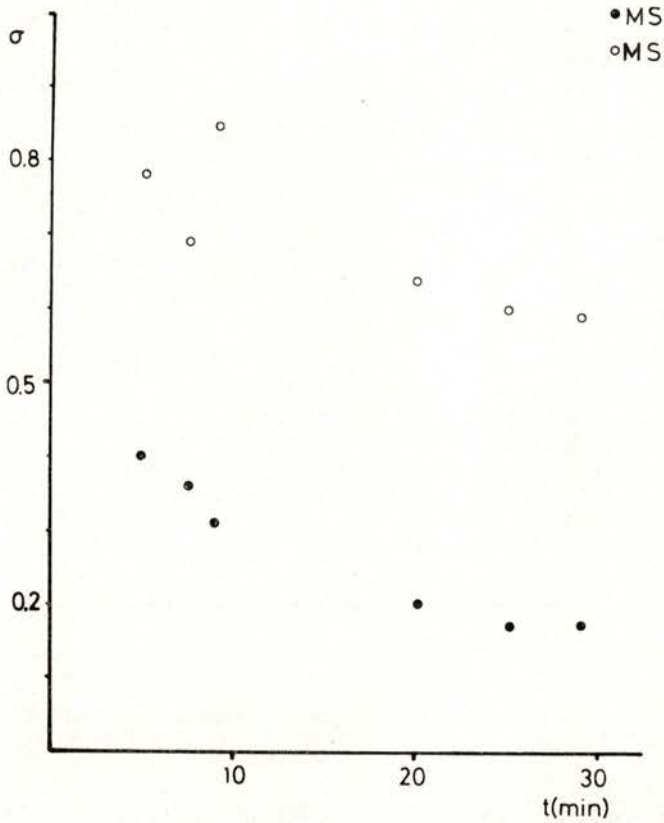

Fig. 4 — Time dependence of standard deviation for both grain populations.

An additional comment to Fig. 4 is relative to the time variation of the standard deviation at the first period of time. In fact, the theory of Kurtz & Carpay [10] predicts that the

standard deviation of equivalent Gaussian distributions of the size parameters for a lognormal population are independent of time. However, this conclusion is based on the hypothesis that no new grains are nucleated during normal grain growth ($\dot{N} \leqslant 0$) and this condition is fullfilled only after the amorphous matrix is exhausted. At this moment the growth of individual grains occurs by the collapse of adjacent grains together with a discontinuous transfer between topological classes.

We can conclude that crystallization has a very local character and the sample thickness may affect significantly the kinetics of crystallization phenomena. Therefore, the sampling for statistic studies must be restricted to small areas in order to obtain homogeneous populations. On the other hand, crystallization begins in the thinnest regions: the onset of the crystallization shows a strong thickness dependence and, thus, this parameter is not suitable for bulk values comparisons or activation energy estimates.

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