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CRYSTALLISATION OF AMORPHOUS Zr-Fe ALLOY QUENCHED BY THE LEVITATION METHOD

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The purpose of this paper is to report a study of the structure and the growth kinetics of spherical crystals which appear in the amorphous phase of eutectic Zr-Fe alloy during annealing at relatively low temperature.

$Zr_{.76}Fe_{.24}$ eutectic alloy was quenched from the melt by a levitation splat-quenching device[1]. Specimens thicker than 1-5 μm were predominantly crystalline while those thinner than 1-5 μm werw predominantly amorphous (Fig. 1.) . Bright field and dark field transmission electron microscopy and electron diffraction techniques were used to determine the structure and to study the crystallisation kinetics.

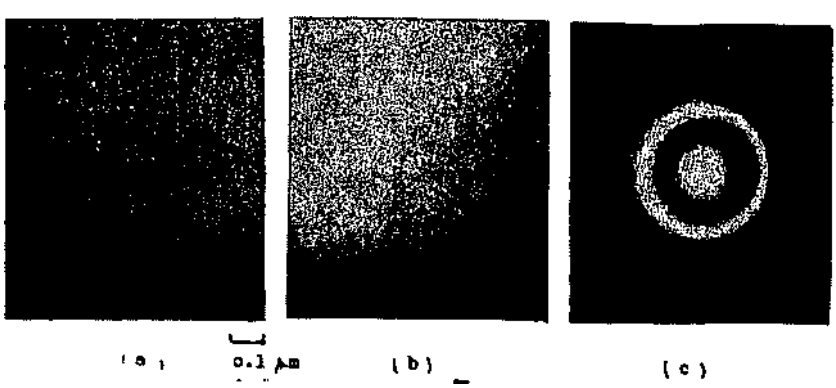

Fig. 1. Bright field (a), dark field (b) images, and electron diffraction patterns (c) of an as quenched amorphous $Zr_{.76}Fe_{.24}$ alloy.

The structure of an amorphous $Zr_{.76}Fe_{.24}$ alloy can be described by the model of a topological disordered structure, while the relaxation sequences are analogous to those of many other amorphous alloys[2] i.e.:

amorphous phase ⟶ FCC phase ⟶ low symmetry phase ⟶.

The growth kinetics of spherical crystals from the amorphous matrix were studied by hot stage electron microscopy.

Isochronal annealing of the amorphous phase gave a crystallisation temperature of about 450 °C. Annealing was performed from room temperature to 500 °C in steps of 50 °C and 10 min duration. No changes in morphology and structure were observed up to 400 °C. At 450 °C partial crystallisation of the electron beam irradiated region and complete crystallisation of the outer regions were observed. This retardation in crystallisation by electron irradiation was observed previously by other authors[3].

Crystals of about 50-100 A in size emerged in the amorphous matrix after annealing for 50 min at 400 °C , and covered the whole specimen after 60 min.

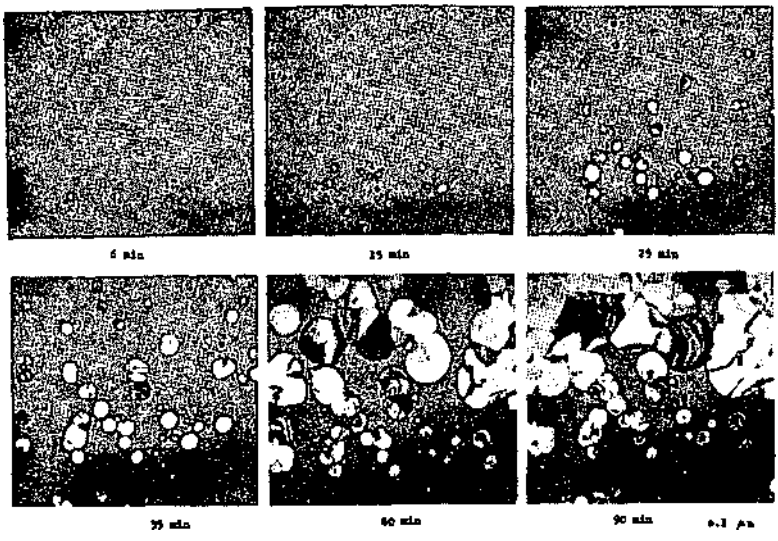

Fig. 2. Growth of spherical crystals from the amorphous matrix of $Zr_{.76}Fe_{.24}$ alloy during isothermal annealing at 350 °C.

To study the kinetics of spherical crystal growth in the amorphous matrix, the specimen was aged 50 min at 400 °C, cooled to room temperature, and heated up to 350 °C. The growth of the emerging spherical crystals were followed by taking electron micrographs

at appropriate time intervals up to 90 min during the isothermal annealing in the microscope. At figure 2. the sequence of micrographs shows the growth of the crystals during annealing. The plot of the crystal diameters in time (fig.3.) were obtained from the micrographs.

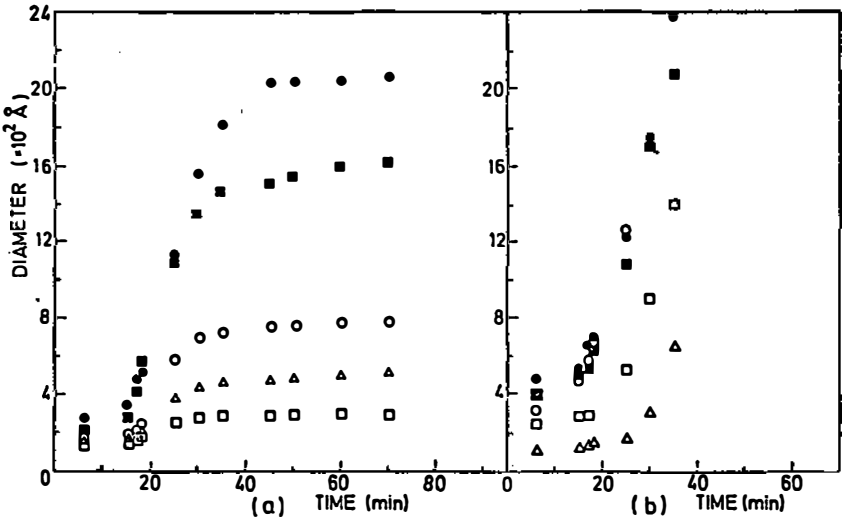

Fig. 3. Time dependence of the diameters of spherical crystals in the amorphous matrix of Zr-Fe alloy during isothermal annealing at 350 °C; crystals in the inner (a), and outher (b) part of irradiated region.

The following characteristics of growth were noticed:

(1) the distribution of crystals was fairly random;

(2) the growth rates were initially small and increased after 10-15 min;

(3) the larger crystals grew faster than the smaller ones;

(4) the growing rate rose with temperature;

(5) the amorphous matrix crystallised in one phase only by congruent crystallisation ;

(6) the coalescence of crystals occured everywhere except in the inner part of the irradiated region.

According to the above characteristics (excluding (6)) , the kinetics of crystallisation of the amorphous $Zr_{.76}Fe_{.24}$ alloy can be described by a simple model[4] based on the following hypotheses:

1° Growth is driven by the free energy reduction upon crystallisation of the amorphous matrix.

2° Growth is controlled by the thermally activated atomic transfer process at the crystal-amorphous matrix boundary.

In that case, the growth rate u can be written as[5]:

$$u = B \cdot F \quad , \tag{1}$$

where B is mobility of the boundary; F is force on the boundary.

If the following conditions are fulfilled:

- nucleation is homogenous,
- accumulation of strain energy due to the growth of crystals is negligible,
- mobility of the crystal-amorphous matrix boundary is expressed in terms of a diffusion rate over a distance comparable with atomic spacings,

then, the growth rate $u = dr/dt$ can be expressed as[5]:

$$\frac{dr}{dt} = B\left[\frac{\Delta g_o}{a^*} - \frac{2\sigma V_o}{a^* r}\right] . \tag{1'}$$

Hence, the force F is composed of two terms:

(a) the force due to the free energy reduction upon crystallisation:

$$F_1 = \frac{\Delta g_o}{a^*} \quad ,$$

where Δg_o is the free energy change upon crystallisation per atom, a^* is the boundary thickness;

(b) the force due to the boundary energy (Gibbs-Thompson effect)

$$F_2 = -\frac{2\sigma V_o}{a^* r} \quad ,$$

where σ is the boundary free energy, V_o is average volume per atom of Zr-Fe alloy, r the radius of a crystal.

From (1') one can easily obtain:

$$t - t_o = r/X + (Y/X^2) \ln\left[rX - Y\right] , \tag{2}$$

where X and Y are given in Table I, and t_o is an integration constant. Eqn (2) gives the general dependence $t(r)$. The initial condition for each particular r could be included by re-defining r as $(r_p/r_{cr})r$, where r_p is the initial radius of a particular crystal, r_{cr} is the critical radius for which $dr/dt = 0$ in (1'). This specific dependence has the form:

$$t - t_o = \frac{r}{\left(\frac{r_p}{r_{cr}}\right)X} - \frac{Y}{X^2} \ln\left[\left(\frac{r_p}{r_{cr}}\right)X\, r - \left(\frac{r_p}{r_{cr}}\right)^2 Y\right] \tag{2'}$$

The time dependence of the crystal radii obtained from (2') and the expetimental data are compared in figure 4.

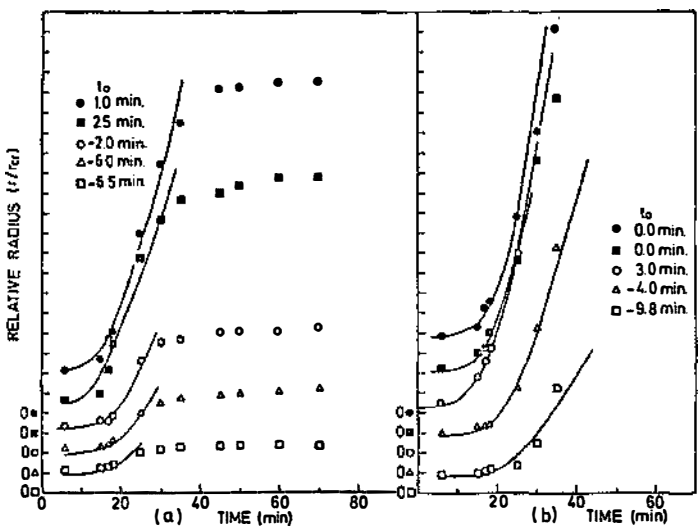

Fig. 4. Comparison of experimental and calculated (full line) time dependent curves of spherical crystal growth during isothermal annealing of Zr-Fe alloy at 350 °C; for some crystals in the inner part where coalescence were absent (a); for some crystals in the outher part where coalescence occured (b).
t_o is the translation time for each curve calculated from (2').

The following conclusions emerge from the above results:
- The model proposed for spherical crystal growth rate is acceptable up to the moment of coalescence or to 25 - 40 min annealing time, regardless initial crystal size.
- The growing rates for the non coalescing crystals decrease and probably stop after 30 ÷ 40 min of annealing. That behaviour, characteristic of the inner part of the irradiated region, is probably due to surface contamination caused by the electron beam. This contamination increases the surface diffusion barrier and, as the amorphous foil acts as thin film, may decrease the mobility of the crystal-amorphous matrix boundary. Another probable explanation for conservation in irradiated regions was given by Doi et al[3].

Table I Numerical values of the parameters used in (1') and (2').

$a^* = 6.4 \cdot 10^{-10}$ m $V_m = 12.23 \cdot 10^{-6}$ m^3 mol^{-1} $N = 6.025 \cdot 10^{23}$ mol^{-1} $T = 622$ K	$\Delta G_m^{\dagger} = \sum_i \Delta H_i + T \sum_i \Delta H_i = 7.961 \cdot 10^3$ J mol^{-1} $C^{\dagger} = \Delta H_{melt} \frac{a^*}{2V_m} = 0.423$ J m^{-2} $B = \frac{1}{a^* T} = 0.62$ s kg^{-1}	$r_{cr} = \frac{2 C V_m}{\Delta G_m} = 13.0 \cdot 10^{-10}$ m $\Sigma = \frac{B}{a^*} \frac{\Delta G_m}{2} = 0.128 \cdot 10^{-10}$ m s^{-1} $\Upsilon = \frac{B}{a^*} \frac{2 C V_m}{3} = 1.70 \cdot 10^{-20}$ m^2 s^{-1}

† ΔG_m is estimated by summing through the following equilibrium sequence:

AMORPHOUS PHASE UNDERCOOLED MELT (622 K) $\xrightarrow{1}$ MELT PHASE (1225 K) $\xrightarrow{2}$ CRYSTAL PHASE (1225 K) $\xrightarrow{3}$ CRYSTAL PHASE (622 K).

(1 heating; 2 crystallization; 3 cooling)

† C is estimated[6] with the energy of melting of a monoatomic layer of crystallised alloy at the boundary crystal amorphous matrix boundary.

- The agreement of each calculated curve with the experimental data was obtained by shifting it along the time axis. The shifting times are greater for smaller crystals. The physical meaning of this translation time t_o is not clear yet, but may be the effect of pre-aging the specimen at 400 °C for 50 min. t_o may perhaps be attributed to the time that each crystal needs to fulfil the conditions for the validity of the proposed model. Each t_o may also be correlated with the initial crystal size or with the relative experimental error which is greater for smaller crystals

The structural identification of spherical crystal phase of Zr-Fe is now in progress.

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