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AN INVESTIGATION OF QUENCHING EFFECTS ON STRUCTURAL RELAXATION OF A METALLIC GLASS

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ABSTRACT

$Fe_{40}Ni_{40}B_{20}$ amorphous ribbons are prepared employing different quenching rates by changing peripherial velocity (V) of rotating copper drum used for melt vitrification. Cross section area was consistent and proportional to 1/V, which showed stable experimental conditions during ribbon formation. Ribbon width, although decreased with increasing V, was slow changing function of V. Ribbon thickness, as expected, played main part in cross section decrease. Differential Scanning Calorimetry measurements were used to study crystallization and low temperature relaxation. Low temperature annealing showed exothermal enthalpy relaxation being proportional with quenching rate. Activation energies and crystallization temperatures stayed virtually unchanged in the range of used quenching rates, showing abscence of quenched-in crystalline seeds (or phase). For higher quenching rates DSC traces showed presence of higher degree of disorder. However these quenching-in deffects were annealed well before crystallization started its course.

INTRODUCTION

Metallic glasses are obtained by rapid melt cooling. High cooling rates, up to 10^6 K/s, enable one to avoid crystalline seeds formation and hence subsequent crystallization virtually freezing liquid structure into solid amorphous (glassy) one [1] . These structures are metastable both with respect to its crystalline counterpart and to its hipotetically ideal glassy state which represents an amorphous state with lowest free energy [2] .
During structural relaxation in a glassy state compositional (CSRO) and topological (TSRO) short range ordering take place, having quite complicated kinetics [3] . During this structural changes,apart from free energy change, almost all physical properties like structural factor [4] , density [5] , Young's moduls [6] etc., change as well. These changes are usually measure of disorder in a glassy state being larger for higher quenching rates.

In this work DSC results on low temperature structural relaxation and crystallization of $Fe_{40}Ni_{40}B_{20}$ metallic glass obtained by different quenching rates are shown.

EXPERIMENTAL

$Fe_{40}Ni_{40}B_{20}$ glassy ribbons were obtained by using free jet melt spinning technique [7] on a single rotating copper drum. Quenching rates were varied by changing peripherial velocity of the rotating copper drum in the range of 15 to 55 m/s. Amorphous ribbons several meters long (depending on the melt quantity), 2 to 4 mm wide and 2o to 45 µm thick were produced. The nozzle orifice diameter was used constant in this work. Calorimetric measurements were taken on a Perkin-Elmer DSC in the interval of 5 to 8o deg/min with sensitivity of 4o mJ/s. Some as-quenched samples were preannealed in the DSC apparatus at 683 K for 2o minutes. Crystallization kinetics was studied using crystallization temperatures from DSC traces.

RESULTS AND DISCUSSION

Cross sectional area (A) and ribbon thickness versus substrate velocity (V) are shown in figure 1. As can be seen A and t changed almost linearly with 1/V. These results are in agreement with some theoretical mass [8] and heat [9] transfer calculations for glass formation during rapid melt quenching. Observed consistency of cross section area showed stable experimental conditions during ribbon formation. Since ribbon width was just slightly influenced by substrate speed the ribbon thickness behaved in the same manner as cross section area.

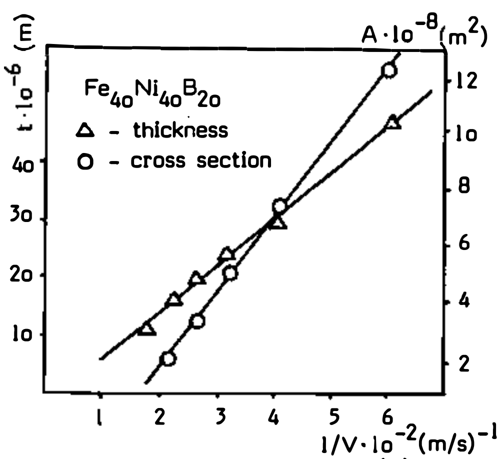

Figure 1 : Cross section area (A) and thickness (t) versus inverse substrate velocity (1/V).

Crystallization kinetics was studied by dynamic annealing using different heating rates. Temperatures of different crystallization stages were taken from the DSC traces. Corresponding activation energies were calculated by Kissinger method [10] from Arrhenius plots using:

$$\ln(T^2/a) = E/RT + \text{const}$$

where T represents absolute temperature, a- heating rate, R- gas constant and E- activation energy for crystallization. Arrhenius plots for crystallization are shown in figure 2. Activation energy for onset of crystallization was about E_x = 260 kJ/mol. Crystallization temperatures and activation energies were not influenced by changing quenching rates in the range of corresponding substrate velocities from 15 to 55 m/s. This showed first that there were no quenched-in crystalline phase or seeds for lower substrate velocities, which would greatly influence onset of crystallization and probably activation energy to same extent. On the other hand samples quenched at higher velocities showed same crystallization behavior indicating full low temperature relaxation taking place before start of crystallization.

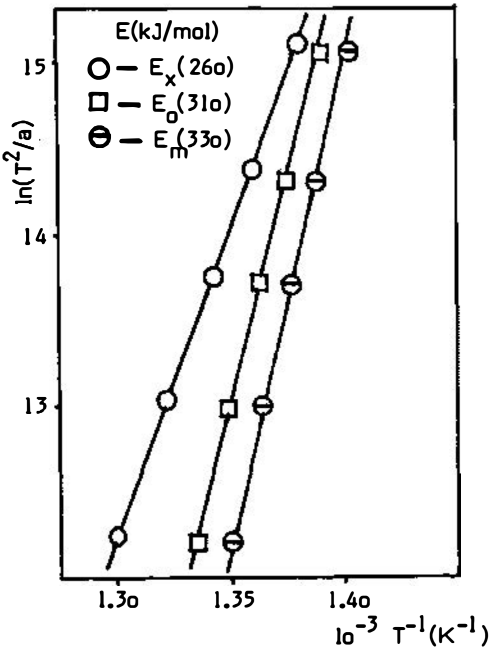

Figure 2 : Arrhenius plots of $Fe_{40}Ni_{40}B_{20}$ crystallization temperatures.

Low temperature relaxation was carried out up to 683 K by measuring enthalpy relaxation of as-quenched samples and preannealed ones. The DSC low temperature relaxation traces are shown in figure 3. As can be seen samples prepared by higher substrate velocities ($V_a > V_b > V_c$) showed additional exotermal enthalpy relaxation with respect to those obtained at lower quenching rates ($\Delta H_a > \Delta H_b > \Delta H_c$). This clearly showed that higher quenching rates introduced more "defects" in amorphous structure. These defects are usually explained as a frozen-in free volume [11]. It is noted that apparent temperature for start of low temperature relaxation was lower for higher quenching rates ($T_a < T_b < T_c$) which was connected with logaritmic relaxation kinetics. This logaritmic behavior came from superposition

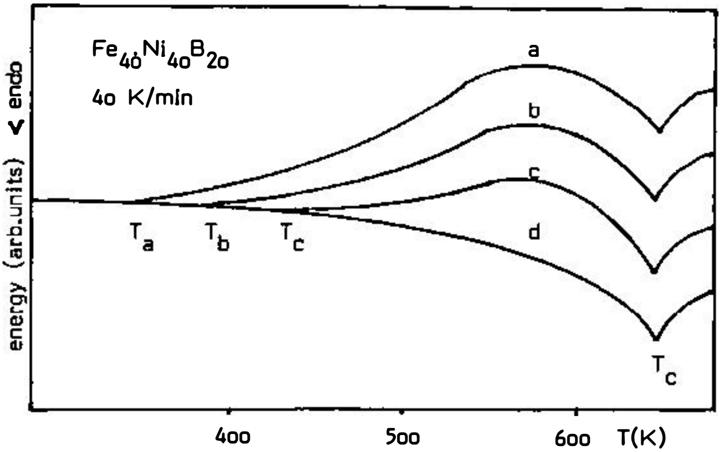

Figure 3 : Differential thermograms obtained during constant heating rate(4o K/min) for $Fe_{40}Ni_{40}B_{20}$ glass.
a- as-quenched sample (V=55 m/s), b- as-quenched sample (V=35 m/s), c- as-quenched sample(V=15 m/s), d- preannealed sample (683 K, 2o mins)

of many different relaxation times resulting in apparently step by step relaxation during initial quenching (due to different quenching speed) and/or during subsequent relaxation. Deffects with shorter relaxation times are being relaxed first and so on.

In conclusion it sould be noted that in $Fe_{40}Ni_{40}B_{20}$ metallic glass low relaxation and crystallization mechanisma could be well separated in a wide range of usable quenching rates expected to give ribbons with desired properties.

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