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DSC STUDY OF COLD ROLLED METALLIC GLASSES

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ABSTRACT

The effect of cold rolling on the crystallization and sub-Tg relaxation in $Fe_{40}Ni_{40}P_{14}B_6$ metallic glasses has been investigated using DSC measurements. The experimental results suggest both variations in the free volume, or configurational enthalpy and in their distribution upon cold rolling.

INTRODUCTION

Cold rolling is known to introduce a great number of metastable defects in crystalline materials. Such defects are responsible for recovery and recrystallization, accompanied by enthalpy changes, when heating up the material (ref. 1) In metallic glasses cold rolling induces great changes in the magnetic properties, but very little is known about the nature of the produced defects nor about their influence in the crystallization process. In this sense, some controversy has arisen recently because, opposite effects of cold work on the crystallization rate have been reported for the same compound. However, it is commonly believed that the induced defects will be relaxed at temperatures well below the crystallization and no influence should be noticeable in the latter (ref. 2).

In this work we report a calorimetric study of the crystallization and enthalpy relaxation, associated with the annealing out of the induced defects, in cold rolled $Fe_{40}Ni_{40}P_{14}B_6$ (METGLAS 2826). An interpretation of the induced defects in terms of the free volume is outlined on the basis of the experimental results.

EXPERIMENTAL

Sample preparation and characterization

Samples of the above mentioned composition were purchased from Allied Chem. in the form of ribbons 1.9 mm wide and 65 μm thick. They were cold rolled up to different amounts of thickness reduction. The latter was determined by measurements of the coercive force (ref. 3) which increases about 200 times for a 14%

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thickness reduction. Small pieces of about 3 mg. in weight were used for the calorimetric measurements, which were performed in a Perkin-Elmer DSC-2 apparatus.

Crystallization

Crystallization was studied by continuous heating at different rates from 1.25 to 80 K/min. The temperature lag between the sample and the sensor was corrected by using the melting point of the Zinc at each scan rate. This procedure, together with the use of a microprocessor for storing the calorimetric data at 0.1 K intervals, allows an accuracy of $\pm$ 0.2 K for the temperature of the maximum of the crystallization peak (Tx).

Avrami equations, and Arrhenius:

$$K(T) = K_{oa} \exp(-E_a/k_B T) \qquad (1)$$

or Vogel-Fulcher:

$$K(T) = K_{ov} \exp(-1/\alpha_f(T-T_o)) \qquad (2)$$

rate constants were used for fitting the evolution of Tx with the heating rate. Expression (2) is expected to hold if the crystallization involves cooperative rearrangements driven by the free volume ($v_f=\alpha_f(T-T_o)$) present in the glass. Here α_f is the expansion coefficient of the free volume and T_o the temperature at which the latter vanishes when keeping the glass at equilibrium. A set of values of the parameters in (1) and (2) were obtained by procedures described elsewhere (ref. 4,5), they are shown in table 1.

TABLE 1

Kinetic parameters for the crystallization

Thickness reduction	E_a(eV)	K_{oa}(s^{-1})	T_o(K)	α_f(K^{-1})	K_{ov}(s^{-1})
as received	4.40	$3\ 10^{30}$	500	$2.8\ 10^{-4}$	$3\ 10^{6}$
3%	4.32	$9\ 10^{29}$	479	$2.3\ 10^{-4}$	$2\ 10^{7}$
5%	4.30	$6\ 10^{29}$	545	$5.1\ 10^{-4}$	$2\ 10^{4}$
10%	4.38	$2\ 10^{30}$	526	$3.8\ 10^{-4}$	$2\ 10^{5}$

The unrealistic values of the Arrhenius preexponential factors K_{oa} suggests a better description of the rate constants in terms of expression (2), which gives reasonable values for the parameters, although they change in an arbitrary way as a function of the cold rolling. This is not surprising, because a simultaneous three parameter fitting does not allows accurate individual values to be

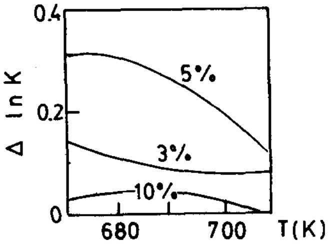

Fig. 1. Changes in the crystallization rate constant due to cold rolling.

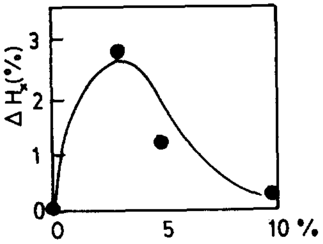

Fig. 2. Relative change in the crystallization enthalpy upon cold rolling. Measurements were performed at 20K/min.

obtained. Reproduction of the rate constants in the temperature range accesible to the experiment is much more accurate (ref. 5) and shows an initial increase, as a function of the cold rolling (Fig. 1), returning to the original values for about 10% thickness reduction. A similar behaviour was observed for the enthalpy change at the crystallization (see Fig. 2).

Sub Tg relaxation

Fig. 3 shows the differences between the apparent specific heat in two successive scans up to the glass transition (Tg). They indicate that a considerable amount of enthalpy has been released before the crystallization. The influence of the cold rolling is the same as previously found. It first increases the amount of the released enthalpy, but has the opposite effect for large values of thickness reduction.

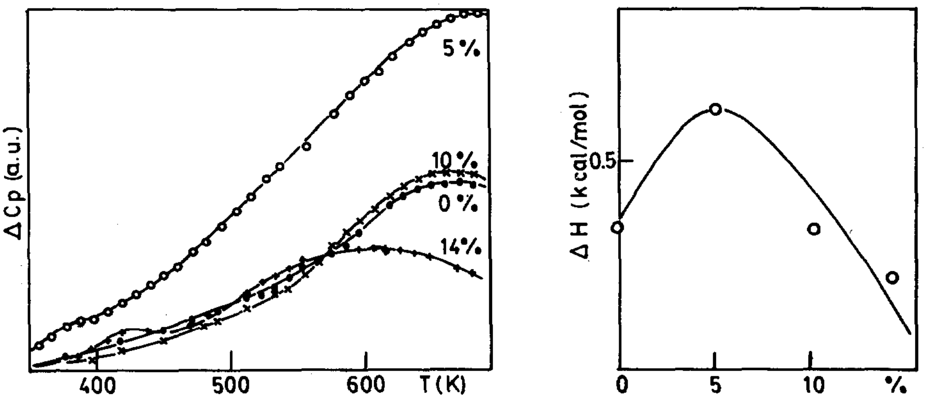

Fig. 3. Sub Tg enthalpy relaxation measured at 20 K/min. The glass transition starts at 680 K for this heating rate. Also the area under the curves (ΔH) is shown as a function of the thickness reduction.

DISCUSSION

The evolution of the crystallization enthalpy and rate constants as a function of the cold rolling, suggests that some defects are still present at the start of the crystallization. They can be associated with the free volume, appearing in expression (2) for K(T), or with the configurational enthalpy released upon crystallization. In this sense, the first stages of deformation give rise to an increase in the free volume, probably through the production of vacant-like defects in the sample. A further increase of the thickness reduction, however, decreases the number of such defects.

This behaviour is more evident in the sub-Tg relaxation results. A direct relationship between the strength of the relaxation and the cooling rate for the formation of the glass has been reported recently (ref. 6). Different cooling rates give rise to different amounts of free volume quenched in the glass, as cold rolling does. A simple model accounting for the free volume relaxation prior to the glass transition (ref. 7) supports this interpretation.

Other kinds of defects, giving rise to the variation of the magnetic properties, are also produced by cold rolling. They increase monotonously as the thickness reduction does, but relax well below the glass transition (ref. 8) and do not seem to have great influence in the total free volume of the sample.As suggested by Kronmuller (ref. 9), they can be described in terms of "quasi-dislocation" dipoles. An alternative description of these defects should relate to the inhomogeneity of the free volume distribution, which always increases on cold rolling.

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