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RELATIONSHIPS BETWEEN THE QUENCHING CONDITIONS AND THE RELAXATION ENTHALPY OF Fe–Si–B AMORPHOUS RIBBONS *

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ABSTRACT

DSC measurements of the relaxation enthalpy, ΔH_Γ, were used to investigate variations in the thermal history of Fe–Si–B amorphous ribbons as a function of the experimental conditions of planar flow casting on massive wheels. Effects of the partial pressure of the atmosphere, thermal conductivity of the substrate and the wheel diameter were investigated. Modifications of the thermal history of the ribbons are clearly shown by changes in ΔH_Γ measured by DSC. Decreasing the partial pressure of helium below 400 mbar is unfavourable for amorphization. Decreasing the thermal conductivity of the substrate leads to large variations in the thermal conditions along the ribbon. Copper is the most efficient substrate.

INTRODUCTION

Amorphous materials are produced for magnetic applications in the form of ribbons by planar flow casting from the liquid state. In this procedure, the surface conditions and the progressive increase in wheel surface temperature govern the local conditions of heat transfer [1]. During the quench, changes in these conditions result in a change of ribbon temperature, thus modifying the thermal history of the material produced.

Previous investigations [2–7] have shown that differential scanning calorimetry (DSC) was an efficient technique for determining the relaxation enthalpy, ΔH_Γ, of amorphous samples in the as-quenched and in the relaxed states. The ΔH_Γ values measured by DSC depend on the quenching rate involved during the quenching process: the higher the quenching rate, the

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* We wish to congratulate Professor W.W. Wendlandt on his 60th birthday and for his large contribution to the field of thermal analysis. Congratulations.

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less relaxed the structure of the as-quenched ribbon and, consequently, the higher the relaxation enthalpy measured by DSC.

The aim of this work was to investigate the effects of the quenching conditions on ΔH_Γ measured by DSC over the length of amorphous, soft magnetic ribbons produced by planar flow casting on different wheels under air and under different partial pressures of helium.

EXPERIMENTAL

The compositions of the Fe–Si–B master alloys are given in Table 1.

The ribbons (1 cm width, ~ 30 μm thickness) were prepared using (i) wheels of the same diameter and of different compositions and (ii) wheels of the same composition and of different diameters. The experimental conditions of the planar flow casting experiments are given in Table 2.

The as-quenched ribbons were checked by X-ray diffraction, using Co K_α radiation and a diffracted-beam graphite monochromator.

A Perkin-Elmer DSC-2C device connected to a 3500 Thermal Analysis Data Station was used for the calorimetric measurements. Each specimen

TABLE 1

Composition of the master alloys (at%)

Alloy	Fe	B	Si	C
I	79.3	11.1	9.6	–
II	81.0	13.2	3.7	2.1

TABLE 2

Experimental conditions of the planar flow casting experiments

Wheel [a]				Atmosphere	Alloy
Composition	Thermal conductivity (W cm^{-1} K^{-1})	Diameter (mm)	Width (mm)		
Mild steel	~ 0.4	300	50	air	II
Cu–Be	~ 1.96	300	50	air	II
Cu	~ 3.98	300	50	air	II
		210	30	air	II
		200	30	He (100–1000 mbar)	I

[a] Massive, linear speed = 20 m s^{-1}.

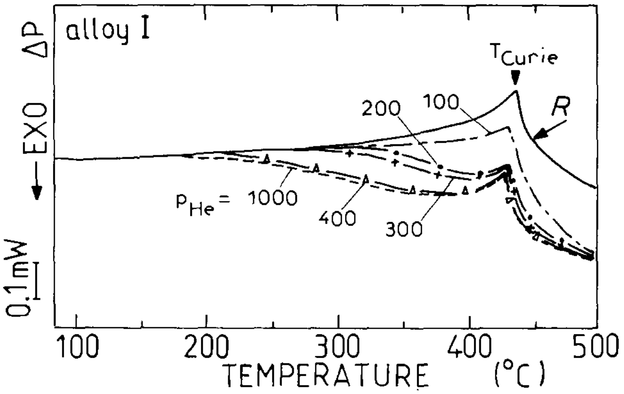

Fig. 1. DSC curves of amorphous $Fe_{79.3}B_{11.1}Si_{9.6}$ alloys quenched under different partial pressures of helium (p_{He} in mbar). R is the reference curve (see text). DSC curves are normalized to 1 mg sample weight.

($\sim$ 20 mg) was enclosed in a copper pan. Crystallized samples of the same composition were used as a reference. The relaxation enthalpy of the amorphous samples was measured by integrating the area between the curve obtained on heating the as-quenched sample for the first time (for instance, the curve "1000 mbar" in Fig. 1 and the curve obtained on heating the same sample a second time (curve R, in Fig. 1), the first heating being conventionally stopped at 500 ° C, before crystallization occurs, and immediately cooled. The curve R is a reference curve, strictly reproducible for all the amorphous alloys of the same composition; it corresponds to a relaxed and prestabilized state under the conditions of the heat treatments used (heating rate 80 ° C min^{-1}, cooling rate 320 ° C min^{-1}).

INFLUENCE OF THE HELIUM PARTIAL PRESSURE

Ribbons of type I alloys were prepared using a massive copper wheel (200 mm diameter and 30 mm width) in a helium atmosphere with different partial pressures. Some traces of b.c.c. α-Fe were detected by X-ray investigations on the free side of the ribbon and embrittlement was found by bending tests when the partial pressure was less than 400 mbar. The DSC results are given in Figs. 1 and 2. The relaxation enthalpy was modified when the partial pressure of helium was varied, decreasing when the partial pressures were lowered. During the planar flow casting process, the material is subjected to several stages of cooling. High-speed camera observations showed that the cooling rate was $\sim 10^7$ K s^{-1} in the melt puddle. The ribbon sticks to the wheel and its point of separation depends on the

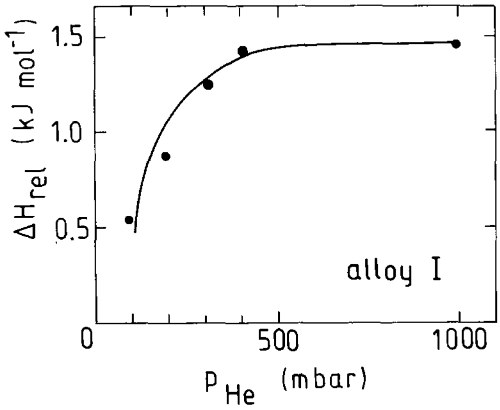

Fig. 2. Variation of the relaxation enthalpy as a function of the partial pressure of helium of the different quenches.

substrate temperature. Then the ribbon cools entirely by convection when it separates from the wheel. The sticking length was limited to half a revolution of the wheel by a mechanical procedure. The effect of the atmosphere intervenes during the last two stages of cooling. Indeed, the DSC curves of Fig. 1 show that differences in thermal behaviour between the samples mainly occurred in the temperature range below 400 ° C, except for the ribbon quenched at 100 mbar. This observation can be explained if the thermal history of the ribbons sticking to the wheel is identical to that of the melt puddle down to this temperature.

Decreasing the partial pressure of He on quenching is thus not favourable for obtaining the amorphous state.

It is worth noting that the Curie temperature of these alloys (Table 3) is not very sensitive to changes in the procedure investigated: T_c was only slightly increased (~ 3 ° C) on decreasing the helium partial pressure from 1000 to 100 mbar.

TABLE 3

Variation of the Curie temperature of amorphous ribbons of alloy I as a function of the partial pressure of helium of the different quenches

p_{He} (mbar)	100	200	300	400	1000
Curie temperature (° C) (±0.5)	422.2	421.5	421.4	420.9	419.6

INFLUENCE OF SUBSTRATE COMPOSITION

Ribbons of type II alloys were prepared on massive wheels of the same diameter in mild steel, copper–beryllium and copper. The thermal conductivity of these alloys increases from mild steel to Cu–Be to Cu (Table 2). The other experimental conditions (surface treatment, substrate speed, geometrical disposition of the nozzle) were kept constant.

High-speed photographs showed that the maximum sticking length was established during the first three revolutions for the different ribbons [8]; thereafter sticking length was kept constant at three-quarters of a revolution, the ribbon being mechanically separated from the wheel. The ribbon thickness was close to 30 μm. The ΔH_{r} values measured along each ribbon are given in Fig. 3. The surface crystallization, as qualitatively estimated by X-ray diffraction, is indicated in Fig. 4.

The copper wheel (diameter, 300 mm) allowed ribbons to be produced with a relaxation enthalpy, measured by DSC, continuously increasing with the number of revolutions of the wheel (one revolution = 0.94 m) for the ribbon length considered here (50 m). As the sticking length was kept constant (0.70 m), the temperature of the substrate was continuously increased. The temperature increase of the substrate would thus be favourable for heat transfer from the ribbon to the wheel.

For the ribbons prepared on the Cu–Be wheel, the temperature of the substrate surface increased more rapidly because of the lower thermal

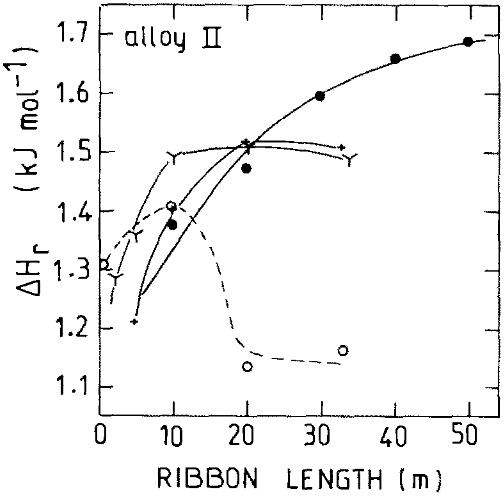

Fig. 3. Variation of the relaxation enthalpy along ribbons quenched on different substrates, at constant sticking length. Diameter = 300 mm (one revolution = 0.94 m, sticking length = 0.70 m) (●) Cu, (Y) Cu–Be, (O) mild steel. Diameter = 210 mm (one revolution = 0.66 m, sticking length = 0.50 m) (+) Cu.

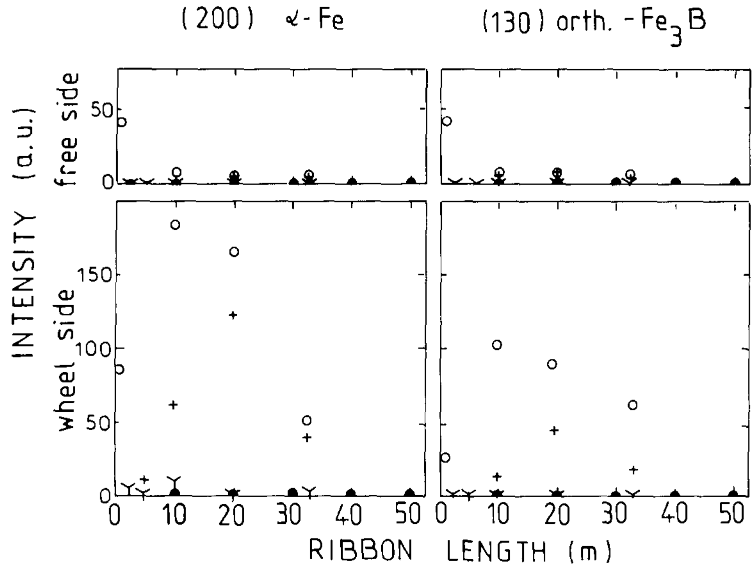

Fig. 4. Influence of substrate composition on surface crystallization (symbols as in Fig. 3).

conductivity of the wheel. ΔH_{Γ} also varied more rapidly than in the case of the copper wheel but the final value was smaller. X-ray investigations of the different specimens corresponding to quenches on copper and Cu–Be wheels, respectively, showed that the ribbons were almost completely amorphous. Only traces of b.c.c. α-Fe were detected on the wheel side, and the ribbons were ductile.

When the ribbons were quenched on a mild steel wheel, the relaxation enthalpy measured by DSC attained a maximum after approximately ten revolutions of the wheel and then decreased to a steady value. Ribbons always showed crystallization traces (Fe_3B and α-Fe) on the wheel side and only some traces of α-Fe on the free side. They were brittle. These results may be interpreted by considering that the substrate temperature continuously increased during the quench until an optimum temperature was attained corresponding to the most favourable conditions of the quench. Above that critical temperature, the efficiency of the quench would decrease and the substrate surface temperature would be high enough to significantly relax the amorphous material.

Results obtained on a copper wheel with a smaller diameter (diameter, 210 mm; length, 30 mm) showed that the most favourable amorphous state was rapidly attained, but that the corresponding ΔH_{Γ} measured by DSC was smaller than that for the copper wheel of 300 mm diameter, with the same linear speed. X-ray diffraction results show that Fe_3B and α-Fe begin to be detected on the wheel side of the ribbon and α-Fe on the free side, beyond the first 5 m of the ribbon. As previously, the increase in substrate temperature is favourable until a certain value, after which the efficiency of the quench decreases. This is in agreement with Sato et al.'s results [9].

CONCLUSIONS

In this paper it is shown that the thermal history of amorphous Fe–Si–B ribbons during quenching depends on the experimental conditions chosen for planar flow casting. Modifications of the thermal history are clearly shown by the changes in the relaxation enthalpy measured by DSC: the higher the quenching rate, the less relaxed the structure of the as-quenched ribbon and, consequently, the higher the relaxation enthalpy measured by DSC. This investigation reveals the following points.

(1) Decreasing the helium partial pressure below 400 mbar is unfavourable for amorphization.

(2) Decreasing the substrate thermal conductivity, all the other quenching conditions remaining identical, leads to large variations in the thermal conditions along the ribbon. When the thermal conductivity or the diameter of the wheel are decreased, the surface temperature of the wheel increases continuously during quenching. The wheel surface attains a maximum temperature after which the efficiency of the quench decreases. The material obtained is highly relaxed or even partly crystallized.

(3) Copper is the most efficient substrate. When short ribbons are required, quenching on a small copper wheel is suitable for obtaining well-quenched, amorphous ribbons. When long ribbons are required, the surface wheel temperature needs to be carefully controlled in order to obtain high, constant ΔH_r values.

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