Physical and Technological Aspects Concerning the Heat Treatment of Glassy Metals by means of a Laser

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ABSTRACT

In this paper the previous results concerning the effect of continuous laser annealing on amorphous metal properties (magnetic, mechanical and structural) are reviewed. Many improvements are discussed in the experimental methods, in the thermal model and in the correlation of a large series of results.

An explanation of the laser heating effects is given and further developments are indicated.

1. INTRODUCTION

Metallic glasses are obtaining increasing importance in basic and applied research [1, 2]. Although they have exceptional properties (soft ferromagnetism, resistance to mechanical stress and corrosion, large spectrum of magnetoelastic responses), the amorphous metals present some problems concerning their structural stability. Therefore the thermal treatment is necessary for improving the above mentioned qualities. The main purpose is to relax the amorphous structure, which is "out of equilibrium", to a more stable state, removing the internal stresses and distributing the free volume. We attempt to obtain this result by processing the glassy metal ribbons with a laser.

After five years of research, resulting investigations have made it possible to furnish a coherent picture of laser annealing effects.

Before reporting this, we need to give some information about metallic glasses and the change in their properties with thermal treatment.

2. PECULARITIES OF AMORPHOUS METALS

The amorphous alloys to which we refer in the following are those obtained by rapid quenching from the melt. The typical composition is (Metal)₈₀(Non-metal)₂₀. Cooling from the liquid phase very quickly (10^6 K/s), the solid state is obtained without nucleation and growth of crystalline nuclei. For example, let us consider the specific volume; the rapid decrease of the temperature below the fusion value T_f , produces in the first stage a supercooled liquid and subsequently for $T = T_G$ (Fig. 1) one obtains the solidification of a structure which does not represent topological and chemical order, while its volume is larger than in the crystalline phase (Fig. 1). The T_G value approaches T_f if the velocity of cooling increases.

The phase transition from "super-cooled" liquid to amorphous solid occurs with a high increase of

Fig. 1. Specific volume versus temperature for an alloy submitted to the transition cycle. (A) liquid- (B) amorphous- (C) relaxed amorphous- (D) crystal.

the viscosity, which obeys (in the liquid) the Vogel law $\eta = \exp C(V_0/V_f)$, where V_0 is the atomic volume in the stable state, and V_f is the free-volume (i.e. the volume frozen in the amorphous matrix and superabundant in respect of the crystalline state (Fig. 1)).

An increase in the percentage of non-metallic components reduces the cooling rate necessary to form the amorphous material; but a higher amount of metalloids produces the disappearance of the ferromagnetic properties (the atomic moment is reduced for the electron transfer from non-metal to metal (Fig. 2)).

Fig. 2. Reduction of atomic moment due to the increase of the 3d+4s electrons when metals are alloyed with non-metals.

Generally, the eutectic composition at the temperature T_f , is the best one for obtaining an amorphous structure accompanied by ferromagnetism. The more common alloys are listed in Table 1 with a set of data on their relevant characteristics.

TABLE 1. Relevant Properties of Investigated Amorphous Alloys.

R.M.Q. rapid melt quenching; E.D. electro-deposition; C.H. conventional heat treatment; L.A. laser annealing; M.A. magnetic annealing; H_c coercive force; H_k anisotropy field; B_s saturation induction; $\mu_{\max}$ permeability maximum; E Young's modulus; λ_s saturation magnetostriction; $\sigma_{\max}$ maximum tensile stress; Q density; Q_e electrical resistivity; δ internal friction (log-decrement magnetoelastic waves); $\Delta B/\Delta \sigma$ stress sensitivity maximum; K factor of magnetoelastic coupling; σ_i internal stress; K_U magnetic anisotropy; * our measurements results; ** our production; ° Allied Chemical; °° Vacuumschmelze.

Composition	Production	H_c (mA/cm)	* H_k (mA/cm)	B_s (T)	$\mu_{\max}$ 10^3	* E (GPa)	* λ_s 10^6	$\sigma_{\max}$ (GPa)	Q (mg/mm ³)	Q_e ($\mu\Omega$ mm ² /m)	Heat Treatment	* δ	* $\Delta B/\Delta \sigma$ (T/MPa)	* K	* σ_i (GPa)	* $K_U 10^{-3}$ (J/m ³)
° Fe ₄₀ Ni ₄₀ P ₁₀ B ₆	R.M.Q.	0.48	500	0.9	60	145	8		7.7	1.8	C.H.-M.A. L.A.	0.02		0.5	-0.04	0.4
° Fe ₇₅ Mo ₂ B ₂₀	R.M.Q.	0.72	3000	1.4		144	33	2.6	7.4	1.2	C.H.-M.A. L.A.	0.04	0.02	0.45	-0.04	4.1
° Fe ₆₇ Co ₁₈ B ₁₄ Si ₁	R.M.Q.	0.65		1.7	200	120		1.6	7.6	1.3	C.H.-L.A.	0.05				
° Fe ₈₁ B _{13.5} Si _{3.5} C ₂	R.M.Q.	0.64	2000	1.6				0.8	7.3	1.3	C.H.	0.03	0.025	0.55	-0.02	0.4
°° Fe ₈₁ B ₁₃ S ₄ C ₃	R.M.Q.	0.4	1000	1.3	100	150	40		7.1	1.3	C.H.-M.A.	0.02			-0.03	0.3
°° Fe ₃₉ Ni ₃₉ Mo ₂ (SiB) ₂₀	R.M.Q.	0.1	3000	0.8	250	140	8		7.4	1.4	C.H.	0.05			-0.05	0.6
° Co based	R.M.Q.	0.5		0.5	600	140	0.1		7.7	1.4	C.H.					
** Ni ₉₃ P ₇	E.D.	5	35·10 ³	0.4											0.2	0
** Co ₈₀ P ₂₀	E.D.	0.9	3500	0.7											0.09	1

With respect to structure, the amorphous metals have no long range order (L.R.O.) and short range order (S.R.O.) (among coordinate atoms) is not homogenous in the whole bulk, changing randomly from point to point. There is no consolidate model, but one, known as D.R.P.H.S. (Dense Random Packing of Hard Spheres) /3/, is effective for describing the actual situation which is of conglomerates in a state of minimum energy, distributed without correlation, not possessing free-volume.

Therefore, an amorphous metal is a solid system in which many states of equilibrium coexist, but which is overall "out of equilibrium".

While the amorphous structure does not have crystalline order, some anisotropy effects can be discussed:

i) Defects in the isotropic random distribution of components atoms, due to differences in the hydrostatic pressure and shear stresses during the rapid solidification (chemical short range order - C.S.R.O.) /4/;

ii) Lacunae due to the presence of free-volume;

iii) In the magnetostrictive alloys an important cause of magnetic anisotropy is the presence of internal stresses (compressive) which oppose the free rotation of the domains.

Therefore, it is clear that the thermal treatment is very important in order to reach a state of higher equilibrium by obtaining a uniform distribution of free-volume and a relaxation of the internal stress.

In the diagram of Fig. 3 a crystalline solid should be in position C, while an amorphous (as-produced) material would represent a coexistence among all the minima of region A. After the thermal treatment, the higher amorphization produces the translation in the states A'.

Fig. 3. Schematic representation of a metastable status for an amorphous structure (A) and the better-distributed density of state after structural relaxation (B).

Conventional heat treatment is performed, for a period of hours, in a furnace at a temperature (T_F) below both the crystallization temperature (T_{cr}) and the Curie temperature (T_C). An inert gas is used in

order to prevent oxidation. A magnetic field in the direction of the ribbon axis is imposed on the amorphous samples during the annealing, if the longitudinal magnetic anisotropy is to be reduced. A transverse field is superimposed if an induced anisotropy is required [5]. In Fig. 4 the scheme of our experimental arrangement for conventional heat treatment (C.H.T.) is given.

Fig. 4. Apparatus for the conventional heat treatment of ribbon-shaped sample. D = dehumidifier of the He flow; C = Pyrex tube; TA = external system for temperature control inside the tube C; TH = internal system for temperature control in furnace.

We shall describe the important differences between C.H.T. and laser heating, but it is fundamental that the latter is also able to produce the structural relaxation (S.R.).

A brief introduction follows to the effects that structural relaxation can produce.

3. DEPENDENCE OF MAGNETO-ELASTIC PROPERTIES ON THE THERMAL THEORY

Changes in the T.S.R.O. and chemical short range order, together with a decrease of internal stress, accompany the transition towards a more stable state when heating of the amorphous ribbons is performed. In magnetostrictive materials the first two effects are of minor importance in comparison with the relaxation of internal stress. This can be easily [6] related to the constant of magnetic anisotropy k_u (in the absence of crystalline order) by the equation:

$$k_u = -\frac{3}{2} \lambda_{si} \langle \sigma_i \rangle \quad (1)$$

where λ_{si} is the coefficient of isotropic magnetostriction and $\langle \sigma_i \rangle$ is the average internal stress. On the other hand, by minimizing the total energy, for the longitudinal magnetization M_L the result is:

$$M_L = H_L M_S^2 / 2k_u \quad (2)$$

where H_L is the longitudinal magnetizing field and M_S is the saturation magnetization. In this way the anisotropic magnetic field results

$$H_k = \frac{2k_u}{M_S} = -3 \frac{\lambda_{si} \langle \sigma_i \rangle}{M_S} \quad (3)$$

The relations (1) and (2) forecast the decrease of k_u and H_k , while the longitudinal saturation magnetostriction

$$\lambda_{sL} = \int_0^{H_k} \frac{\partial M}{\partial \sigma} \Big|_{H_L} \cdot dH_L,$$

should increase if the compressive internal stress does not oppose the sample deformation (Figs. 5 and 6).

Fig. 5. Magnetization curves of $\text{Fe}_{40}\text{Ni}_{40}\text{P}_{14}\text{B}_6$ (metglas 2826) obtained before (b) and after (a) the thermal treatment (C.H.T. for 1h in inert atmosphere at $T = 600$ K).

Fig. 6. Increase of longitudinal magnetostriction λ_s due to C.H.T. at a temperature below T_{cryst} value. When the temperature of treatment rises over T_{cryst} , the incoming phase transition produces an evident decrease of λ_s (--- curve).

If magnetic annealing is performed, the behaviour of k_u is more complicated as a consequence of a decrease or increase in magnetisation which can be produced by the magnetizing field according to its direction (Fig. 7). A large effect is revealed in λ_s by taking into

Fig. 7. Hysteresis cycle (---) and magnetization curve of an amorphous ribbon (2605A Metglas) after C.H.T. and effects of a magnetizing field application during the treatment. The magnetizing field is either transversal to the ribbon plane (H_T) or parallel to the ribbon axis (H_L). It is clear the induced anisotropy influence in the two different cases.

account its dependence on the easy magnetization direction /7/:

$$\lambda_s = \lambda_{sL} \frac{3}{2} \left[\langle \cos^2 \theta \rangle - \frac{1}{3} \right] \quad (4)$$

The combined effects of λ_s and $\langle \sigma_i \rangle$ give a very high increase of the magneto-elastic coupling factor /8/ (giant - ΔE /9/) (Fig. 8):

$$K = (\Delta E / E_s)^{1/2} \propto (\lambda_s / \langle \sigma_i \rangle)^{1/2} \quad (5)$$

The decrease of $\langle \sigma_i \rangle$, which is a compressive stress (from eq. 1, the value of σ_i is less than zero), also produces an approach of the atomic moment to the ribbon plane /10/.

Concerning the T.S.R.O. the decrement both of $\langle \sigma_i \rangle$ and of the free-volume produces a typical configuration of the domain distribution /11/ and a decrease of the mean atomic volume /12/.

When, during heat treatment, too high temperature can cause crystallization, and with it an inversion in the behaviour of all the magnetoelastic properties.

$\langle \sigma_i \rangle$ and k_u increase while λ_{sL} and K decrease (Figs. 5 to 8). The crystalline order modifies the short range order and introduces a long range order progressively.

Fig. 8. Behaviour of the magnetoelastic coupling factor as a function of the temperature of C.H.T. for several alloys:

- ○ Fe₄₀Ni₄₀P₁₄B₆ ▲ ▲ Fe₇₈Mo₂B₂₀
- △ △ Fe₈₁B_{13.5}Si_{3.9}C₂ ■ ■ Fe₆₇Co₁₈B₁₄Si₁
- ● Fe₈₁B₁₃Si₄C₂ ◇ ◇ Fe₃₉Ni₃₉Mo₄Sn₆B₁₂

The higher the temperature the less time is needed for total crystallization /12/. However these times are very short ($\cong 1$ s) when 500°C, temperature is reached and it is very difficult to control the percentage of produced crystalline phase in the constricted heart treatment. For this purpose controlled lesser treatment appears more suitable, as it enables control of the interaction time to 10^{-2} s.

4. HEAT TREATMENT BY MEANS OF LASER BEAM: PROCEDURES AND THERMAL MODEL

Fig. 9(a) is the diagram of a typical laser system of low-medium power (25–100 W) to be used in operations of surface heat treatment on small transverse dimension samples (≤ 2 mm). The laser beam, with Gaussian distribution of energy, is defocused in order to use only the central zone in which the distribution of energy is sufficiently uniform in the transverse direction and sufficiently Gaussian longitudinally to obtain a homogeneous treatment of the material (Fig. 10). Obviously the defocussing cannot be such

Fig. 9. Scheme of the arrangement for continuous laser heating of ribbon-shaped samples.

Fig. 10. Profile of intensity distribution during C.L.A. Geometrical and thermal parameters are indicated.

as to reduce the specific energy below the minimum value sufficient to reach predetermined conditions (temperature vs. time). In the following pages, with the discussion of the thermal model, it will be seen that both the typical geometry of the test pieces in question, with small thicknesses, and the low treatment temperature allow use of a low power laser, and effect with a high defocusing utilizing only 12.5% of the beam power.

The laser system is made up of the source, a focusing system and a nozzle coaxial with the beam, for a flow of inert gas to protect the surface of the material from oxidation and to equalize the cooling. Measurement of energy acting upon the material can be made by using a system consisting of a copper mask and an optical pyrometer, as shown in Fig. 9(b). A numerical control table permits consulting with a variable speed of the specimen relative to the laser beam. The para-

TABLE 2. Average Values of Laser Heat Treatment Parameters and Amorphous Metals' Thermal Properties

Incident Power	P	30–60 W
Translation velocity	V	5–60 × 10 ⁻³ m/s
Spot diameter	b	8–15 × 10 ⁻³ m
Gas flow	f	1.3 l/min
Nozzle diameter	d	2.2 × 10 ⁻³ m
Permanence time	t _p	0.1–2 s
Theoretical absorbed power	P _a	2.5–25 W
Skin depth at 10.6 μm	δ	1.2–1.6 μm
Reflectivity on the rugose side	R _s	0.2–0.3
Reflectivity on the smooth side	R _s '	0.4–0.5
Thermal diffusivity	k	2.5–3.5 × 10 ⁻⁶ m ² /s
Specific heat	C _s	450–550 J/KgK

meters influencing the thermal treatment are: the power of the beam; the reflection coefficient of the surface at the wave length of the laser emission; the relative translation speed (beam-material) and therefore the interaction time; the geometry of the treated material; the defocusing; the thermal properties of the material; the protecting gas.

Our experimental tests were performed with the parameters indicated in Table 2 on the amorphous metals indicated in Table 1. Given the large number of variables influencing the treatment, it was found necessary to develop a thermal model able to evaluate the thermal cycle (temperature vs. time) to which the zones of irradiated amorphous metal are submitted, as a function of the treatment parameters. By choosing a system of reference as indicated in Fig. 10, it is possible to calculate the temperature in the generic point P(x, y) by means of a numerical operation of double integration. In an initial phase of study /13, 14/ the hypotheses made can be presented as follows:

a) the thickness of the material "e" is small when compared with the depth of the thermal diffusion defined as $2\sqrt{k^*t_p}$, where k^* is the thermal diffusivity of the material and t_p is the length of time the beam remains on a generic point P of material (interaction time);

b) the energy distribution of the beam is Gaussian;

c) the thermal properties of the material do not vary substantially with the temperature;

d) there is a flow of incident gas in the treatment zone which rapidly cools to room temperature the material not directly submitted to the action of the beam.

The assumption "c" will appear (Sect. 6) as a simplifying hypothesis, while "a", "b", and "d" were actually obtained during the experimental tests with the parameters indicated in Table 2.

In fact, results show that:

— the depth of thermal diffusion for the materials submitted to treatment is around fifty times more than the thickness of the materials, which is between 30 and 60 μm;

— cooling of the surface occurs by means of the transfer of heat that is established between the jet of cover gas and the material.

Power lost due to cooling can be evaluated by the relation proposed by Gordon /15/ concerning the heat transferred between a plate and a jet of incident gas:

$$Nu = 0.1810(Re)^{0.5}(Pr)^{0.33d/B} \quad (6)$$

where:

Nu = Nusselt number = hd/k^*

h = coefficient of heat transfer

d = diameter of nozzle

k^* = thermal conductivity of the gas

Re = Reynolds number = $\rho Vd/\mu$

Pr = Prandtl number = $c\mu/K$

ρ = gas density

V = velocity

μ = viscosity

C = thermal capacity

B = distance from nozzle to plate

A_s = surface area.

Substituting in (6) the values relative to helium

/16/, used as a covering gas, we calculate the coefficient of heat transfer and then the power lost:

$$q = A_s h(T_s - T_0) \quad (7)$$

Therefore, in the experimental conditions adopted, the power lost in the treatment zone below the beam of the Laser power.

However, beyond that zone the action of the jet of gas is found to determine a minimum value of the cooling times /15, 17/.

The temperature behaviour of a generic point P of sample, placed inside the Laser spot, is given by the two relations /14/:

$$T_G(r, t) = \frac{F_0 k (b/2)^2}{4he} \cdot \int_0^t \frac{\exp\left[-\frac{k2H}{he} t' - \frac{r^2}{4kt'} + \frac{r^2(b/2)^2}{4kt'(b^2/4 + 4kt')}\right]}{4kt' + (b^2/4)} dt' \quad (8)$$

$$T_p(t^*) = \frac{1}{t^*} \int_0^{t^*} T_G(|b/2 - Vt|; t^* - t) dt \quad (9)$$

where T_G is the temperature produced by a fixed Gaussian source at distance r and after a time t /17/, and $T_p(t^*)$ is the temperature reached in a sample point after a time t^* calculated from the entry into a moving laser beam /14/. The effect of the relative moment between the laser beam and the ribbon sample is taken into consideration by equation (9). The irradiation of a generical point P, situated in the spot, commenced at r was equal to $b/2$ ($t_0 = 0$). After a time t^* the distance of P from the beam centre is $r_p = b/2 - vt^*$. For a generic instant t ($0 < t < t^*$) the r value results as $r = b/2 - vt$. By hypothesizing that the laser beam stays a distance r during the time ($t^* - t$) required to the P position, its contribution to point temperature can be written as:

$$T_p(t) = T_G(b/2 - vt; t^* - t) \quad (10)$$

We consider that the spot remains in an intermediate position for the infinitesimal time interval dt . In order to obtain the temperature of P after t^* seconds from the beginning of its irradiation, it is necessary to calculate an average which takes into account all the contributions $T_p(t)$, obtaining the relation (9). The behaviour of $T_p(t^*)$ can be calculated by evaluating $T_G(b/2 - vt; t^* - t)$, for $t = (n/100)t^*$ and successively, using the T_G value calculated by obtaining T_p from

the relation (9) by means of a computer programme. This process is repeated for t^* included between 0 and $t = b/v$ which is the length of time that the beam is on the same spot. When P leaves the laser spot, relations (8) and (9) are no longer valid, the temperature follows the cooling curve under the action of the flow of the gas. The development of the thermal model demonstrates how the heating of the material is closely bound to the relative position of the material with respect to the laser beam.

Some experimental tests of the thermal model have been carried out by means of the measurement of the surface temperature of the material during treatment. An optical pyrometer was used, as well as thermocouples placed on the test piece. A moderate correlation was seen between the temperature-time diagrams obtained experimentally and the theoretical calculation, taking into account the limitations of the two measuring systems adopted. The limitations were the presence of protecting gas for the optical pyrometer and the very low thermal inertia of the test pieces, compared to that of the thermocouple.

As an example, Fig. 11 shows the typical thermal

Fig. 11. Theoretical behaviour of the average temperature $\langle T_a \rangle$ evaluated from the equation (9) ($\langle T_a \rangle = T_p$) when the following parameters values are fixed: laser power = 35 W (absorbed power = 0.4 W); beam diameter = 12 mm; translation velocities = 5 mm/s (1); 8 mm/s (2); 10 mm/s (3); 20 mm/s (4); 35 mm/s (5).

cycles to which the amorphous metals have been submitted, treated with a maximum theoretical absorbed power of 0.4 W and with velocity of 5 mm/s. It is possible to observe how the material has exceeded the crystallization temperature for approximately 0.6 s.

Several authors have examined the process of isothermal crystallization of one of the amorphous metals which we have submitted to treatment ($\text{Fe}_{40}\text{Ni}_{40}\text{P}_{14}\text{B}_6$).

Fig. 12. (a) T.E.M. picture of fractured Fe₄₀Ni₄₀P₁₄B₆ amorphous ribbon after the thermal cycle (a) reported in Fig. 11; X-ray diffraction patterns of the front surface (A) and the rear surface (B).

(b) T.E.M. fractography pattern of the same alloy but after the cycle (b) reported in Fig. 11.

(b) TEM fractography pattern of the same alloy but after the cycle (b) reported in fig. 11.

The process develops by means of nucleation and growth of the crystal in a radial lamellar structure. This mechanism was also observed by Morris [18], who proposed a temperature-time transformation curve for the alloy. An analysis of this curve allows for the hypothesis that in the thermal treatment the action times of the laser beam do not permit complete crystallization of the material but only nucleation and partial growth. Fig. 12 (a and b) shows a fractograph of amorphous metals, submitted to thermal

treatment by laser under different operative conditions, fractured by means of shearing stress. The sample (b) of amorphous metal treated with 0.4 W power and a velocity of 10 mm/s presents a morphology of the fracture surfaces which is totally different from the one (a) treated at 0.4 W and 20 mm/s. As the thermal cycle a and b demonstrate, Fig. 11, the average bulk temperature has not exceeded the temperature of crystallization in either sample; but sample (a) represents a crystallized surface, which demonstrates a non-homogeneous treatment of the material probably related to a longer interaction time (we shall return to this subject in section 6). As a matter of fact Fig. 12a shows a complex fracture morphology characterized by three zones: one zone in the laser affected surface, where the fracture assumes typical aspects of crystalline fracture; a smooth and uniform zone which is typical of the fracture of vitreous material in the surface opposite the treated one; and a zone between these two in which a longitudinal fracture is evident and could be ascribed to the heterogeneity of the structure.

The possibility of checking the crystallization of the amorphous structure by selecting the laser beam-material interaction time is also confirmed by the X-ray diffraction pattern of the two surfaces of the amorphous metal already described, as seen in Fig. 12a. The treated surface (A) shows a crystalline phase

TABLE 3. Techniques of Investigation and Treatments Performed; results and effects, which can be obtained.

- * in collaboration with R.T.M. Institute (TO)
 ** in collaboration with Institute of Industrial Chemistry (PD)
 *** in collaboration with C.N.R. Laboratory (NA).

Experimental Techniques	Results
Fluxometry	B-H curves Magnetostriction constants Magnetic anisotropy constant Average internal stress
Magnetoelastic Wave Resonance	Magnetoelastic coupling coefficients and constants
Heat Treatment in Furnace	Structural relaxation
Heat Treatment by laser*	Crystallization Partial phase transition
Heat Treatment in Magnetic Field	Induced anisotropy
Mossbauer Spectroscopy**	Microscopic inspection of the heat treatment effects
X-ray***	Changes in S.R.O.
Electron Microscopy	

dispersed in an amorphous matrix. The crystalline phase can be evaluated by integration of the diffraction peaks to be in 15% of the analyzed material. The opposite surface (B) shows a typical diffraction pattern of the amorphous structure with the presence of non-quantifiable peaks of crystallinity.

5. EFFECTS OF THE C.L.A. AND COMPARISON WITH THE C.H.T.

In Table 3, both the experimental techniques and the main results deriving from them are summarized, with references either to our laboratory or to those of the other collaborators. In Fig. 13 the experimental arrangements are shown.

The measurement data furnish a picture of the macroscopic magnetoelastic properties and their variations under different heat treatment and in regard to their mechanical history, together with important information on microstructural changes.

All the predictions made in Section 3 can be verified by the experimental results which we discussed in references /12, 13, 14, 19, 20/ and reported in Figures 14 to 19.

In Fig. 14 the hyperfine field distributions of the Fe atoms show relaxation towards a better isotropic structure when the laser energy density is low. Both the deviation from the Gaussian behaviour in the virgin sample (a) and the improvement obtained by means

of the laser treatment, are obvious [(b) and (c)]. The more relevant effects of the structural relaxation are evident in the internal stress (Fig. 15), the magnetic anisotropy (Fig. 16) and the magnetoelastic coupling factor (Fig. 17). In this figure the double line refers to the improvement in the amorphous properties due to laser treatment, while the single line refers to measurements obtained after the C.H.T. at the same average temperature value. The experimental results show that, when the average temperature is equal to $2/3 T_{\text{CT}}$, some structural anisotropy is initiated in the laser annealed samples.

Here T_{CT} is the temperature at which crystallization is obtained for a 1 h isothermal treatment in the furnace.

The above mentioned cause of anisotropy can be recognized in the formation of crystalline phases as the spectroscopic results of Fig. 18 show.

This partial crystallization probably occurs on the surface where the temperature is higher than in bulk. This hypothesis is valid by several results such as those in Fig. 19, where one can see that for $t_p > t_p^*$ (interaction time which produces average temperatures above the threshold $T^* \cong 2/3 T_{\text{CT}}$) the axis of easy magnetization shifts from the sample plane.

The last effect is clearly due to the magnetostrictive action of a surface layer with a density higher than in bulk.

On the other hand the pictures obtained by means

Fig. 13. Scheme of the experimental apparatus for the quasi-static measurements (a), dynamic magnetoelastic measurements (b) Mössbauer Spectroscopy.

Fig. 14. Hyperfine Field Distribution (H.F.D.) in 2826 Metglas as produced (a) and after the C.L.A. at $T_{a\max} = 390$ K (b) and $T_{a\max} = 490$ K (c).

Fig. 15. Curves of the average internal stress $\langle \sigma_i \rangle$ as a function of the maximum temperature reached in the C.L.A. ($T_{\max} = \langle T_a \rangle_{\max}$) and as a function of the fixed temperature in C.H.T. (T ; for 1 h). The results are referred to the same alloy of Figs. 14, 12, 6 and 5.

of the TEM (Fig. 12) confirm the improvements in the structure, in the case of $\langle T_a \rangle_{\max} < T^*$, and the production of a crystalline surface layer, when $\langle T_a \rangle_{\max} > T^*$, as discussed in Section 4.

In conclusion we can point out the following:

i) the C.L.A. both for low energy density and t_p values ($\langle T_a \rangle_{\max} \leq 400$ K and $t_p < 1$ s) is ef-

Fig. 16. Behaviour of magnetic anisotropy in the same conditions as Fig. 15.

fective in producing the structural relaxation (Fig. 14) and the related decrease of the internal stress, the magnetic anisotropy and the magnetoelastic coupling (Figs. 15, 16, 17);

ii) the laser annealing at a fixed specific energy ($\geq 3 \times 10^4$ W/m²) for increasing interaction time (> 1 s) gives rise to a partial crystallization, first on the surface and subsequently in the bulk as well. To this phenomenon are related: a) the observation of phase transition by means of the behaviour of the

Fig. 17. Improvement of the magnetoelastic coupling factor due to C.L.A. when $\langle T_a \rangle_{\max}$ is below 400–500 K, and evidence of its decrease for increasing temperature values.

angle, φ (Fig. 19), between the Fe atomic moment and the ribbon plane as a function of t_p ; b) the occurrence of a transverse anisotropy due to the magnetostrictive action of a crystalline surface layer /23/; c) the possibility of analysing the amorphous-crystalline transition by means of structural techniques, e.g. Mössbauer and X-ray diffraction (Figs. 18 and 12).

6. DISCUSSION AND IMPROVED THERMAL MODEL

In the previous section we have shown that significant changes in the behaviour of many physical

parameters are produced by C.L.A. when the interaction time is approximately more than 0.5 s. The observed effects can be explained by the occurrence of a structural anisotropy which might be produced by heat treatment in a magnetic field /21/, stress annealing /22/, oxidation /23/ and crystallization /24/. The first cause can be discounted: the electromagnetic radiation is polarized, but it cannot orient the domains owing to its skin depth which is only a few microns. Care was taken to avoid external stresses during heat treatment, so that stress annealing in a first phase can also be excluded. Surface oxidation did not occur because the helium flow prevented it, as has been observed with X-ray diffraction pattern.

The discussion then requires some new consideration of the thermal interaction of laser with material. The thermal model previously described stems from the consideration that $\delta < e < 2\sqrt{k \cdot t_p}$. A two dimensional case for the thermal conduction was considered to evaluate the average temperature $\langle T_a \rangle$ in the sample, as explained in Section 4, where $\langle T_a \rangle = T_p$. The theoretical values of $\langle T_a \rangle$ were found to be lower than those required for the start of crystallization but in the following we will show that the surface temperature is higher than the evaluated average temperature in the bulk. Let us consider that for any metal the surface absorption "A" is not constant. Generally a linear dependence is noted: $A(T) = A_i + A_t(T - T_0)$ where A_i is the initial absorption at $T = T_0$ and A_t

Fig. 18. H.F.D. of 2826 Metglas after C.L.A. for $\langle T_a \rangle_{\max} \cong 600$ K (a) and 700 K (b): first stages of crystallization.

Fig. 19. The angle φ (between the ribbon plane and the magnetic moment of the Fe atoms) versus the interaction time of C.L.A. φ was evaluated from the area ratios of the Mössbauer spectrum peaks.

is the increment of absorption per degree Kelvin. The A_t value can be calculated by comparing the $A(T)$ values at 300 K and 450 K, measured by means of the reflected energy in the whole solid angle.

The measurements gave: $A(300\text{ K}) = 0.56$ and $A(450\text{ K}) = 0.66$ in Metglass 2826 and $A(300\text{ K}) = 0.58$ and $A(450\text{ K}) = 0.66$ in Metglass 2605 A. This gives $A_t = [A(T) - A_i]/T \approx 6.6 \times 10^{-4} \text{ K}^{-1}$ (an average value).

If W_o is the power irradiated on the ribbon while h is the average heat transfer coefficient, obtained by considering the sum of the front rear surface and the rim of the beamed area, we have:

$$\Delta m C_s \langle \Delta T \rangle = W_o - h \Delta S \langle \Delta T \rangle \quad (11)$$

See Fig. 10 for meaning of the symbols. From the experimental values one obtains $h = 395 \text{ J/m}^2 \text{ sK}$. The average temperature increment $\langle \Delta T \rangle$ was calculated by making the average of the point temperature T_p on the surface $s \cdot b$ (Fig. 10). Since the thermal conduction in the sample bulk is much lower than the above evaluated h value ($h_{\text{bulk}} \approx 5 \text{ W/m}^2 \text{ }^\circ\text{C}$) and the rim area is much smaller than the front and the rear area, one deduces that the calculated value is the sum of the heat transfer coefficient only on the front and the rear surfaces, h_s and h_l respectively. By taking into account the different dynamic conditions, due to the He flow, the classical heat transfer

models /15/ give $h_s = 3/2 h_l$. Thereby we can obtain $h_s \approx 237 \text{ Jm}^{-2} \text{ s}^{-1} \text{ K}^{-1}$, $h_l \approx 158 \text{ Jm}^{-2} \text{ s}^{-1} \text{ K}^{-1}$, and, for the normalized heat transfer coefficients $H_l = h_l/k = 0.66 \times 10^{-3}$ and $H_s = h_s/k = 0.99 \times 10^{-3}$. It is known /25/ that where the irradiance is higher than a threshold value $I_{hl} = I_l [H_s + H_l/(1 + H_l)]$ [where $I_l = k/(lA_t)$] the surface temperature increases exponentially until the melting temperature is reached.

In the present case the irradiance values are:

$I_{so} \approx 2.5 \times 10^5 \text{ W/m}^2$ in the center ($1 \times 1 \text{ mm}^2$) of the Gaussian profile;

$$I_l \approx 36.4 \times 10^7 \text{ W/m}^2;$$

$$I_{hl} \approx 6 \times 10^5 \text{ W/m}^2.$$

Because $I < I_{hl}$: a steady state regime is obtained in the laser treatment. The surface temperature can be evaluated by the equation:

$$T_s = \frac{I_{so}/I_{hl}}{1 - I_{so}/I_{hl}} \frac{A_i}{A_t} \approx 730 \text{ K} \quad (12)$$

Therefore the value T_s exceeds the crystallization temperature by approximately 100 K. In our experiments the interaction time t_p was always higher than the diffusion time constant ($\tau_1 = Cl^2/k \leq 10^{-3} \text{ s}$), therefore the temperature T_s was actually reached. Naturally the t_p value influenced the percent of the produced crystalline phase /18/. In this a way of more accurate thermal analysis foresees the presence of a partial surface crystallization. The effects of this surface layer are clearly opposite to those of the internal stress relaxation as verified by all the experimental results. As an example the production of a compressive stress, which increases k_u and carries the domain magnetization out of the ribbon plane, is expected and it well explains the results of Fig. 19.

In Fig. 20 we have reported the behaviour of the temperature both in bulk and in surface (a), and the steady state regime temperature across the sample thickness (b), when $t_p \approx 0.5 \text{ s}$ and the specific absorbed energy in the central region of the Gaussian beam is approximately 250 mW/mm^2 .

7. CONCLUDING REMARKS

A great deal of scientific and technological research is being carried out on this subject, but many questions need a clearer explanation. One particular problem is given as follows:

At low energy levels, C.L.A. is effective in producing structural relaxation in a very brief period of time

Fig. 20. (a) Behaviour of surface temperature (T_s —) and bulk temperature (T_a —) in an amorphous ribbon irradiated by laser, when the specific energy absorbed in the center of the Gaussian profile is fixed at 250 mW/mm^2 . The thermal parameter values were averaged from those of the typical compositions: $\text{Fe}_{40}\text{Ni}_{40}\text{P}_{14}\text{B}_6$, $\text{Fe}_{78}\text{Mo}_2\text{B}_{20}$ and $\text{Fe}_{67}\text{Co}_{18}\text{B}_{14}\text{Si}_1$. (b) Expected temperature behaviour across the samples section from front to rear surface.

(fraction of a second), while C.H.T. takes some hours for the same purpose. How is this possible? The question requires further theoretical insight into the mechanism of interaction between laser beam and a material in the amorphous solid state. Moreover bulk relaxation must be improved without the occurrence of crystallization.

For the last purpose it is our intention to use a uniform intensity distribution in the C.L.A. In this way there is no peak of irradiance and, since T_s decreases with I_{s0} , it is possible to reach high bulk temperatures (close to T_{cr}) with surface temperatures lower than those obtained in the already performed C.L.A. experiments.

On the other hand, the results of our investigations open the way for the study of the effect related to the occurrence of a crystalline surface layer, whose thickness can be controlled by means of t_p value. The coupling of two different structures (crystalline-amorphous), in the same composition, can represent an interesting application in magnetoelasticity (delay line, stress sensors, ...).

For what concerns basic knowledge further information will be obtained by extending the experimental research to the effects of external stresses and/or of magnetizing fields applied during the laser treatment. Is C.L.A. able to produce the same results as C.H.T., in this case too?

Finally, we would point out that the results we have obtained can be useful for understanding both the phase transition from crystalline to amorphous material and the possibility to produce this by C.L.A. (developing the technique for rapid cooling suitable in this treatment). Among the possible applications we consider the production of an amorphous layer on mechanical parts which must be particularly resistant to fracture and corrosion, and so on.

Much work remains to be done, but we hope to have furnished some useful basic data for researchers who are interested in the topics discussed here.

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