Journal of Thermal Analysis, Vol. 38 (1992) 409-420

THERMOMECHANICAL ANALYSIS (TMA) CORRELATED TO DIFFERENTIAL SCANNING CALORIMETRY (DSC) FOR AGEING STUDY OF SOME METALLIC GLASSES

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To characterize the ageing of some metallic glasses, a correlated study of the differential scanning calorimetry method (DSC) and of the thermomechanical analysis (TMA) emphasizes the specificity of the latter. We analyzed metallic glasses which have been produced either by chemical methods or by melt spinning techniques. Using TMA and DSC, we have established that the relaxation of metallic glasses is strongly dependent on treatment applied: either thermal or mechanical history. Conversely, we do not observe large differences between DSC and TMA analysis for the crystallisation. From experimental data, we try to modelize the behaviour of this type of materials under operating conditions.

Keywords: metallic glasses, DSC, TMA

Introduction

Metallic glasses can be obtained by several techniques: vapor deposition, electrodeposition, chemical deposition, liquid quenching at rates greater than 10^5 deg·s^{-1} and more recently mechanical alloying. Such non-crystalline alloys possess a number of unusual properties including high tensile strength, high corrosion resistance, high electrical resistivity and often good soft ferromagnetic properties. Knowledge of the ageing of metallic glasses is crucial from a point of view of industrial applications. The amorphous metallic alloys are thermodynamically unstable not only with respect to the crystalline state but also with respect to a fully relaxed amorphous state. These types of non equilibrium alloys show spontaneous evolution toward an equilibrium either stable or metastable after a certain time lapse without thermal treatment. Hence the study of the ageing and especially of the relaxation is essential for investigation of product stability to promote their industrial use. Structural relaxation induced considerable variations in

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macroscopic measured properties. Even if the atomistic processes occurring during configurational relaxation are not completely understood according to Egami [1], the relaxation is attributed to chemical short range order (CSRO) which involves changes of kinds of neighbouring atoms and topological short range order (TSRO) which involves changes in the geometrical packing of atoms (free volume). However both ordering processes seem to be closely interlinked. The physical properties of metallic glasses may depend in part on the large excess free volume quenched into the glass. Changes in magnetic, electrical, thermodynamical or mechanical properties are a consequence of elimination or redistribution of excess free volume and a consequence of evolution in neighbouring bonds during appropriate annealings below T_g (glass transition temperature).

Among the possible techniques for the ageing study of various metallic glasses, we choose two techniques with a high sensitivity to structural changes: differential scanning calorimetry (DSC) and thermomechanical analysis (TMA). Enthalpy directly obtained from calorimetry reflects structural changes very well because the enthalpy changes correspond to the mean value of bond energy evolution. Dilatometry has become a sensitive method to detect free volume changes which are equivalent to length changes if the material is isotropic.

Experimental

Preparation of the samples

Two types of metallic glasses in sheets or ribbons (10–40 μ thick) are investigated:

– Electrodeposited amorphous alloys obtained in laboratory with different non metal concentrations such as $Ni_{1-x}P_x$, $Co_{1-x}P_x$.

– Rapidly quenched amorphous alloys obtained either in laboratory or in industry such as $Fe_{85-x}Co_xB_{15}$, $(CoFeNi)_{78}(SiB)_{22}$, $(FeCoMo)_{73}(SiB)_{27}$.

Microprobe analysis and X-ray diffraction are used as complementary methods to determine the composition of the samples and to confirm their amorphous state.

Differential scanning calorimetry DSC

The calorimetric experiments were performed in a Perkin Elmer DSC7 or a Setaram DSC111 apparatus under a pure nitrogen or argon atmosphere.

Thermomechanical analysis TMA

The dilatometric study was performed either with a Mettler TMA 40 or a Perkin Elmer TMA 7 apparatus. During the heating we observe the deformation of the sample under load: the system measures the length of the sample as a function of a uniaxial stress and temperature. With the Mettler dilatometer two types of experiment can be carried out either with a static or dynamic load. In all cases very small loads (σ <3.5 N/mm^2) are applied, the strain on the sample remains in the elastic range at room temperature. The tensile stress prevents the bending of the sample during heat treatment.

Heat treatments

In all our studies ageing is accelerated by applying heat treatments. Ageing depends strongly on the thermal history: we applied either an isothermal or anisothermal programmed thermal treatment or combination of both.

Results and discussion

Amorphous crystalline transformation

It seems very interesting to compare results obtained both for anisothermal calorimetric and dilatometric measurements [2–4]. Such an anisothermal procedure provides a lot of information on ageing behaviour. But actually it is not easy to clearly separate the portion of the temperature change effect from the portion of spontaneous changes occuring during the treatment. Therefore to characterize more completely the ageing behaviour it is necessary to carry out isothermal studies which take a lot of time.

For the electrodeposited alloy $Ni_{76}P_{24}$ as for melt spinned ribbons (Co Fe Ni)$_{78}$ (Si B)$_{22}$ [5, 6] after a broad exothermic peak in the relaxation range, sudden changes occur in the apparent specific heat C_p and in the apparent thermal expansion coefficient (TEC) α (Figs 1, 2).

In an isotropic material hypothesis, length changes are directly related to volume evolution ($\Delta V/V=3\,\Delta L/L$) [7–9]. Length expansion evolution (Fig. 3) gives the image of the excess free volume evolution: during structural relaxation, the reduction and redistribution of quenched-in excess volume occur with a small increase in density whereas during crystallisation more substantial changes occur. Even if this hypothesis is often verifed, several authors have mentioned the anisotropy of certain metallic ribbons

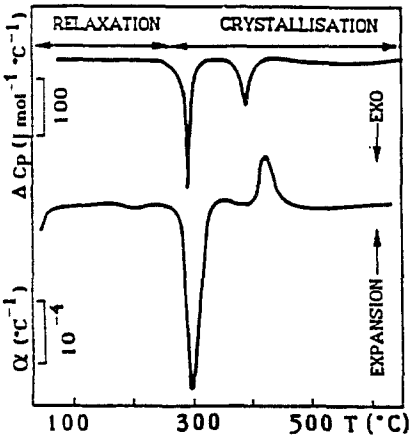

Fig. 1 Apparent specific heat (relative to crystal) ΔC_p and thermal expansion coefficient α *vs.* temperature T,(heating rate = 10 deg/min) – $(CoFeNi)_{78}(SiB)_{22}$

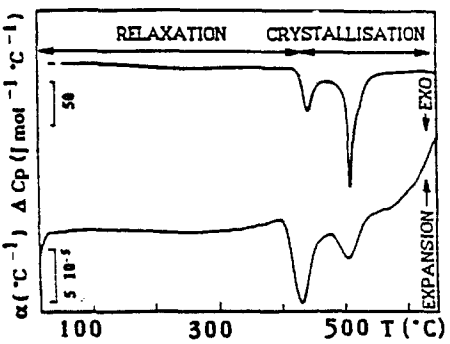

Fig. 2 Apparent specific heat (relative to crystal) ΔC_p and thermal expansion coefficient α *vs.* temperature T, (heating rate = 10 deg/min) – $Ni_{76}P_{24}$

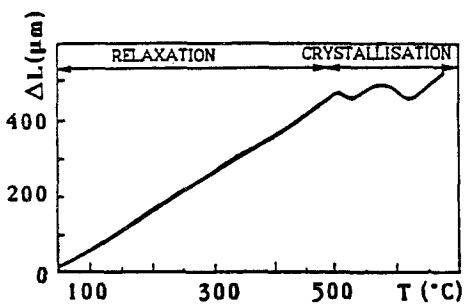

Fig. 3 Length expansion Δl *vs.* temperature$T$, (heating rate = 10 deg/min) – $(FeCoMo)_{73}(SiB)_{27}$

using the TMA technique [10–11]. Therefore we examined the possible anisotropy of some metallic glasses in the transverse (TRANS) and longitudinal (LONG) directions of the ribbon with respect to the tensile axis [6]: differences appear during amorphous crystalline transformation for the two directions of observation (Fig. 4).

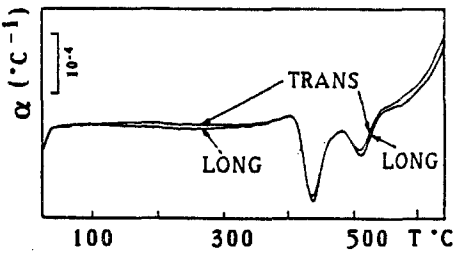

Fig. 4 Thermal expansion coefficient α *vs.* temperature T for longitudinal (LONG) and transverse (TRANS) direction of the ribon (heating rate = 10 deg/min) – $(FeCoNi)_{78}(SiB)_{22}$

Kinetic analysis of the crystallisation

The study of crystallisation temperatures T_x (maximum of the peak) from TMA and DSC measurements for various heating rates allows the activation energy E_a determination following Kissinger's method [12]. However the complexity of the phenomena studied precludes the consideration of activation energies as an intrinsic physical quantity but rather as a phenomenological comparison of parameters between materials: Fig. 5 shows a satisfactory correlation for activation energy deduced form TMA and DSC measurements for $Fe_{85-x}Co_xB_{15}$ alloys [13–14].

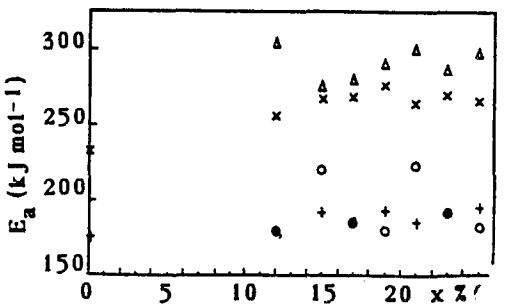

Fig. 5 Apparent activation energy E_a for each crystallisation peak - $Fe_{85-x}Co_xB_{15}$ 1st peak ...+... DSC ...o... TMA [14]; 2d peak ...x... DSC ...Δ... TMA [14]

Influence of the thermal history on relaxation

Measurements of the effects of annealing for different glassy alloys below crystallisation temperature were often reported on the basis of calorimetry and dilatometry. For an as quenched sample, a broad exothermic peak is observed up to the glass transition during the first calorimetric run which becomes smaller or disappears after successive runs [15]. Appropriate thermal history can also reveal endothermic peaks [16–18].

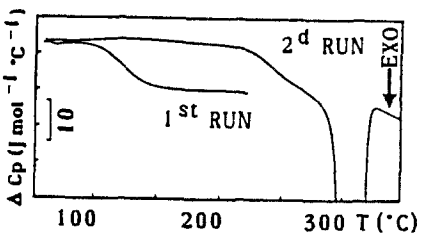

Fig. 6 Apparent specific heat ΔC_p *vs.* temperature T- $Co_{84}P_{16}$
a) 1st annealing up to 230°C (heating rate =3 deg/min); *b*) 2d annealing up to the crystallisation (heating rate =3 deg/min)

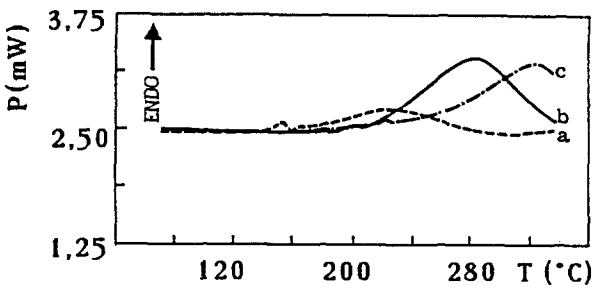

Fig. 7 Heat flow P for successive substracted runs *vs.* temperature T, (heating rate=40 deg/min) for preannealed $Fe_{73}Co_{12}B_{15}$ samples (t_a =180 min); *a*) T_a =150°C; *b*) T_a = 200°C; *c*) T_a =250°C

Figures 6, 7 evidence the role of the thermal history in the evolution of relaxation for DSC measurements, both for the electrodeposited $Co_{1-x}P_x$ [19] and for the melt spinned $Fe_{85-x}Co_xB_{15}$ [20] alloys. We confirmed the irreversibility of the relaxation by dynamic TMA measurements for the $Ni_{76}P_{24}$ electrodeposited alloy [5]: Fig. 8 shows the anisothermal length changes for a particular thermal history; the preliminary heating stabilized the sample, in the second run no consolidation is observed in the relaxation range. Dietz *et al.* [21] observe a similar behaviour for different $Ni_{1-x}P_x$ electrodeposited alloys by static TMA measurements. Komatsu *et al* [22] have showed also

that after a pre-annealing no measurable volume changes were found during the subsequent annealing for rapidly quenched $Fe_{40}Ni_{38}Si_8B_{14}$.

During adapted heatings at temperature which avoids crystallisation, the glass structure relaxes towards a more stable state with lower free enthalpy and higher density.

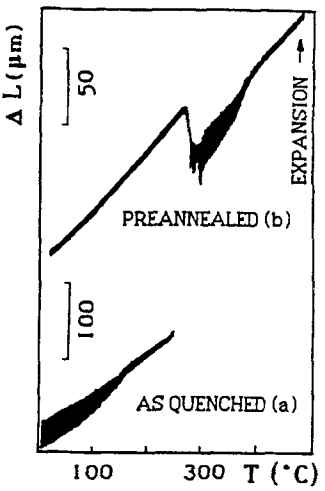

Fig. 8 Dynamic dilatometry ($F = 0.25 \pm 0.2$N): Length expansion Δl *vs.* temperature (heating rate = 10 deg/min); *a*) as quenched sample $Ni_{76}P_{24}$; *b*) pre-annealed sample $Ni_{76}P_{24}$ up to 200°C (heating rate = 2 deg/min)

Isothermal relaxation analysis

Measurement of a physical property $P(t)$ during isothermal experiments allows the study of relaxation kinetics from the rate of progress of the relaxation or reduced property P_r which is deduced from the length expansion in this study:

$$P_r = \frac{P(t) - P(t=0)}{P(t \to \infty) - P(t=0)} \quad \text{or} \quad P_r = \frac{L(t) - L(t=0)}{L(t \to \infty) - L(t=0)}$$

An investigation of the role of different parameters on the relaxation kinetics is carried out:

– Influence of the annealing temperature: we plot P_r *vs.* log (t) for $Ni_{75}P_{25}$ electrodeposited (Fig. 9) and discuss these curves: we observe a classical shift of the curves towards shorter annealing times qualitatively in accordance with Arrhenius' law.

– Role of the stress level: The relaxation is related to the intensity of the applied load in tension; the reduced property is a sensitive parameter of the stress effect [6]: for different loads the evolution began after the same time but the kinetics are accelerated for the highest load (Fig. 10). Claus [23] also mentioned the crystallisation of amorphous metallic glasses was influenced by superimposed tensile stress but the load used was up to 400 N/mm^2.

– Influence of the sample orientation: An investigation of the anisotropic behaviour of the ribbons has been attempted with TMA measurements during isothermal heating [6]. For annealings at 300°C we compare P_r for $(Co\ Fe\ Ni)_{78}\ (Si\ B)_{22}$ alloys plotted *vs.* log (t) for longitudinal and transverse direction of the samples (Fig. 11): a delay clearly appears for the longitudinal direction, the relaxation kinetics depend on direction. From a mechanical point of view we observe that for these rapidly quenched alloys

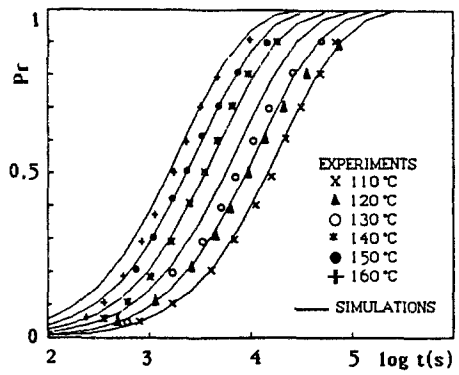

Fig.9 Reduced property P_r *vs.* log (t) for different isotherm scans. Comparison between isothermal experiments and theoretical predictions obtained using the DNLR model for $Ni_{75}P_{25}$

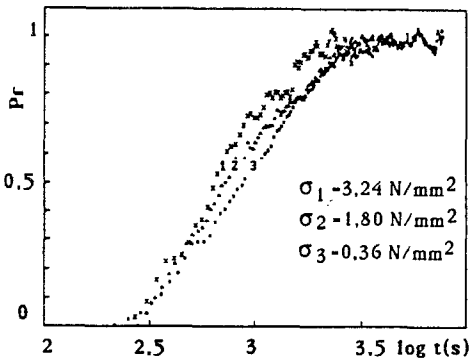

Fig. 10 Reduced property P_r *vs.* log (t) for different stresses σ.$(CoFeNi)_{78}(SiB)_{22}$

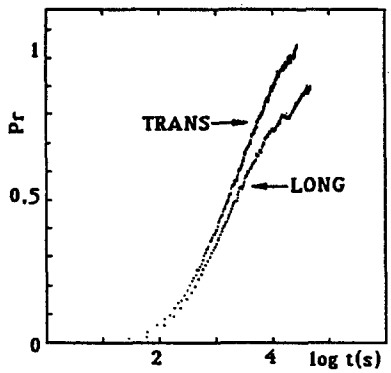

Fig. 11 Reduced property P_r *vs.* log (t) for samples in longitudinal (LONG) and transverse (TRANS) direction of the ribbon $(CoFeNi)_{78}(SiB)_{22}$

relaxation i anisotropic. Therefore depending on the parallel or perpendicular direction of the ribbon length, we observe different rheological behaviour. Sinning *et al.* [10] showed that for Fe_{40} Ni_{40} B_{20} the anisotropy between the irreversible contractions in the longitudinal and transverse dimensions could be gradually but completely removed by annealing. For the same alloy Yavari [24] has interpreted the anisotropy from small-angle neutron scattering study: the anisotropy is of magnetic origin and caused by longitudinal tensile stress present during freezing of the ribbon. Friedrich *et al.* [11] mentioned also anisotropy for specimens cut in the center or at the edge along the ribbon axis for Ni_{72} Si_8 B_{20}. The anisotropy of the density exists in the as quenched material as a consequence of highly directional processes.

Ageing modelisation of the relaxation

The modelisation developed in the laboratory [25] permits simulations to be compared with experimental P_r results (Fig. 9): From the non linear relaxation distribution (DNLR) model we characterize the evolution of the material by the following kinetic law:

$$\frac{d\delta}{dt} = \Delta\alpha \frac{dT}{dt} - \delta \sum_j \frac{g_j(t)}{\tau_j(t)} \quad \text{or} \quad \frac{d\delta}{dt} = \Delta\alpha \frac{dT}{dt} - \frac{\delta}{\exp\frac{K\delta}{RT}} \sum_j \frac{g_j(t)}{\frac{h}{kT}\exp\left(\frac{\Delta H^+}{RT} - \frac{\Delta S_j^+}{R}\right)}$$

δ : instantaneous departure from equilibrium; $\delta = 1\,(t) - 1\,(\infty)$ for the present study,

$\tau_j(t)$: relaxation time,

$\Delta\alpha$: difference of the thermal expansion coefficient between metastable liquid and glass,
dT/d : rate of temperature change,
ΔH^+ : activation enthalpy,
ΔS^+j : activation entropy for the j^{th} process,
K : characteristic parameter of non linearity,
$g_j(t)$: instantaneous weight of the j^{th} process involved in the relaxation.

To initialise the numerical treatment we require the knowledge of the initial spectrum g_j [0, $\tau_j(0)$]. In Fig. 12 we report the shape of the double spectrum deduced from theoretical considerations and used to analyse the experimental results presented on the Fig. 9. From these considerations we deduce the values of the DNLR model parameters:

$\Delta H^+ = 60.845$ J mol^{-1},
$\Delta S^+ = -180$ J mol^{-1} °C^{-1},
$K = -4.8$ J mol^{-1} °C$^{-1}\mu$m^{-1}

Moreover, the computed P_r correlates satisfactorily with experimental P_r obtained from length expansion measurements for Ni_{75} P_{25} (Fig. 9). This theoretical approach can lead to the prediction of the ageing of these types of metallic glasses for new and various thermal histories.

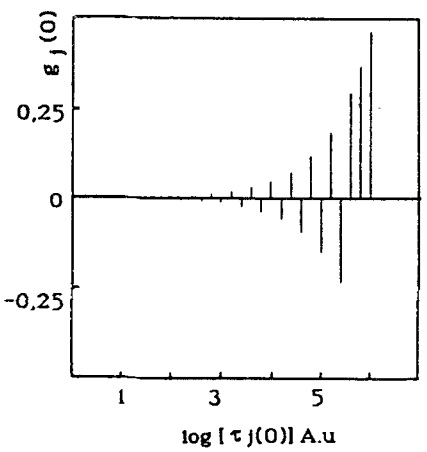

Fig. 12 Initial spectrum g_j (0) used to analyse $Ni_{75}P_{25}$ isothermal measurements

Conclusion

The combined use of calorimetry and dilatometry has given either well correlated results or results specific to each method in elucidating the ageing of some metallic glasses. Much attention has been paid to the study of thermal annealing below crystallisation temperature on the alteration of physical properties of as prepared metallic glasses. One reason for this interest is to increase stability of amorphous alloys.

The kinetic approach to crystallisation can be carried out equally successfully with TMA or DSC measurements.

The novelty of TMA firstly consists in the direct observation of the decrease for free volume from the observed shrinkage (structural relaxation of amorphous alloys is accompanied by a densification of the material ascribed to the annihilation of excess free volume or defects), secondly, evidences the anisotropy of melt spinned alloys which is related to the relief of the stresses and anisotropic configurations introduced during the quench.

From a modelisation view point we are able to reproduce various creep curves and to predict the ageing of amorphous alloys by theoretical simulation.

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The authors wish to thank Dr. H. Warlimont, Dr. Hilzinger and Dr. G. Herzer of Vaccumschmelze GmbH (Hanau F.R.G), Dr. E. Illekova and Dr. P. Duhaj of Institute of Physics (Bratislava, Tchecoslovaquie) for the scientific collaboration during which the melt spinned metallic glasses were supplied.

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Zusammenfassung — Zur Charakterisierung des Alterns einiger metallischer Gläser wird in einer Vergleichsstudie der DSC-Methode und der thermomechanischen Analyse (TMA) die Spezifität letzterer hervorgehoben. Es wurden metallische Gläser untersucht, die entweder mittels chemischer Verfahren oder durch Schmelzverdüsen hergestellt wurden. Mittels DSC und TMA wurde festgestellt, daß die Entspannung der metallischen Gläser stark von der Behandlungsweise abhängt, d.h. ob es sich um eine thermische oder mechanische Vorgeschichte handelt. Im Gegensatz dazu konnten bei der Kristallisation keine großen Unterschiede zwischen DSC und TMA gefunden werden. Anhand experimenteller Daten wurde versucht, das Verhalten derartiger Materialien unter den Betriebsbedingungen zu modellieren.