Classification
Physics Abstracts
78.70B

Study of transformation kinetics in the $\text{Fe}_{40}\text{Ni}_{38}\text{Mo}_4\text{B}_{18}$ metallic glass by positron annihilation methods

Mbungu-Tsumbu (*), D. Segers, M. Dorikens and L. Dorikens-Vanpraet

Laboratorium Kernfysica, Rijksuniversiteit Gent, Proeftuinstraat 86, B-9000 Gent, Belgium

(Reçu le 19 avril 1985, accepté le 3 septembre 1985)

Résumé. — Nous traitons ici des transformations induites par des traitements thermiques dans les verres métalliques $\text{Fe}_{40}\text{Ni}_{38}\text{Mo}_4\text{B}_{18}$ de l'état amorphe à l'état cristallisé, par l'observation de la variation du temps de vie de positrons et de l'élargissement Doppler de la ligne d'annihilation. Le comportement de la forme de la raie d'annihilation de positrons montre des contributions réversibles et irréversibles. Nous suggérons que la part réversible est reliée aux changements induits par l'expansion thermique. La variation irréversible marque surtout des transitions de phase. La cristallisation de l'échantillon apparaît comme un processus en trois phases. Les résultats appuient l'idée que les positrons sont piégés dans le verre métallique.

Abstract. — We report on transformations induced in the metallic glass $\text{Fe}_{40}\text{Ni}_{38}\text{Mo}_4\text{B}_{18}$ by thermal treatments from the amorphous to the crystallized state, following the variation of the positron lifetime and the Doppler broadening of the annihilation line. The behaviour of the annihilation lineshape shows reversible and non-reversible contributions. We suggest the reversible part to be related to the changes induced by thermal expansion. The non-reversible variation chiefly shows phase transitions. Crystallization of the sample appears as a three-stage process. The results support the idea that positrons are trapped in the as-received metallic glass.

1. Introduction.

A number of papers on the study of metallic glasses show that the amorphous state is altered by structural relaxation and crystallization processes. Positron annihilation behaviour in the amorphous state has been described both in terms of topological short-range ordering (TSRO) and chemical short-range ordering (CSRO) at the basis of the structural relaxation mechanisms [1]. During crystallization the positron behaviour is determined by the phase diagram of the amorphous and crystallized alloy system. This paper reports on kinetic transformations from the amorphous to the crystallized state in the Metglas 2826MB.

2. Experimental.

Positron annihilation experiments (lifetime and Doppler broadening) have been performed during heating and cooling of the sample, during isothermal heating

of the sample and at room temperature on an annealed sample. The heat treatment was performed in vacuum (10^{-3} Pa), a programmed furnace was used. The metallic glass of the present study, Metglas 2826MB : $\text{Fe}_{40}\text{Ni}_{38}\text{Mo}_4\text{B}_{18}$, was commercially obtained from Allied Chemical Corporation (New Jersey, USA) in the form of ribbons of 2.6 cm wide and 60 μm thick. Each measured specimen consisted of two stacks of five layers of the sample material, with a positron source sandwiched between them. Lifetime measurements as a function of number of layers show that the intensity of the « parasite » components in the spectrum becomes less than 1 % for 4 layers and more, so that 5 layers may be considered as thick enough. For the lifetime experiments the positron source was an aqueous solution of $^{22}\text{NaCl}$ deposited onto a layer of sample. For the Doppler broadening measurements during the isochronal annealing of the sample the source was $^{22}\text{NaCl}$ between two thin Ni foils (5 μm), while for measurements during heating and cooling and during isothermal heating of the sample a thin ^{68}Ge source (5 μm , N.E.N.) was used as positron source.

Positron lifetime spectra were measured by means of a conventional fast-slow system using Philips

(*) On leave from Université de Kinshasa, Kinshasa, Zaïre.

XP2020 photomultiplier tubes and $1 \times 1''$ NE111 scintillators. The typical resolution of the lifetime apparatus was 300 ps. The measured lifetime spectra always contained at least 10^6 counts. Free fittings were successfully applied using Kirkegaard's POSFIT program [2]. The results of the analyses are shown in table I.

Table I. — *Results of the lifetime measurements for the metglas 2826MB.*

Sample	Lifetimes (ps)		Intensities (%)	
letter	τ_1	τ_2	I_1	I_2
A	148 ± 2	595 ± 170	99.9 ± 0.1	0.1 ± 0.1
B	144 ± 2	497 ± 22	99.4 ± 0.1	0.6 ± 0.1
C	148 ± 2	411 ± 12	99.2 ± 0.1	0.8 ± 0.1

The Doppler broadened lineshape of the 511 keV positron annihilation radiation was measured with a hyperpure Ge detector and a measuring chain with zero and gain digital stabilization. The resolution on the 514 keV gamma ray of ^{85}Sr was 1.2 keV. The Doppler broadening lineshape was characterized by the S -parameter as defined by Mackenzie *et al.* [3] i.e. the ratio of the integration over the central part of the annihilation line to the total integration.

For the measurements on the isochronally annealed sample each stored spectrum contained at least 8×10^6 counts in the 511 keV peak. The sample remained for two hours at each step of the annealing temperature. The values of the S -parameter measured at room temperature for an isochronally annealed sample are plotted in figure 1 as function of the annealing temperature.

Fig. 1. — The S parameter obtained for an isochronally annealed sample is plotted *versus* the annealing temperature.

For the measurements during continuous heating and cooling of the sample the storage of each Doppler broadening spectrum lasted one hour. The temperature change rate was about 3°C/h . The heating program followed the sequence A-B-C-D-E, as shown in

figure 2. It consisted of heating from room temperature up to 310°C (A-B), cooling-down to room temperature from 310°C (B-C), heating from room temperature up to 390°C (C-D), and cooling-down to room temperature from 490°C (D-E). The results are shown in figure 2. The minima in the curves of figures 1 and 2 are not at exactly the same temperature; this is due to different annealing conditions.

Fig. 2. — The S parameter obtained from continued heating and cooling experiments is plotted against the sample temperature.

For the isothermal annealing experiments the sample was held in vacuum, out of the furnace by means of a magnet until the furnace had reached the desired temperature. The measured spectra were successively stored during one hour and transferred to a memory system. Some results are shown in figure 3.

3. Results and discussion.

3.1 THE POSITRON LIFETIME. — The results of the lifetime measurements (Table I) show that there exists only one kind of annihilation in all the samples, in accordance with the results of P. Moser [4] (the intensity I_2 of a second component in the lifetime spectra is less than 1 %). τ equals (148 ± 2) ps in an as-received metglas (sample A), (144 ± 2) ps in the recrystallized sample after isothermal annealing experiments have been performed at 399°C during 94 hours (sample B), and (148 ± 2) ps in the recrystallized sample after continued heating and cooling

Fig. 3. — Time variation of the S parameter during some isothermal heating treatments.

have been performed up to 490 °C (sample C). The lifetime values are always longer in the as-received amorphous state than those expected on the basis of the pure constituents of the alloy (Fe, Ni) [7, 8], but shorter than those in the metals containing vacancies. Crystallization processes only induce negligible effects on the positron lifetime. The values of the lifetime seem to support the idea that positrons are trapped by some defects in all the measured samples.

3.2 ISOCHRONAL ANNEALING EXPERIMENTS. — The main goal of the isochronal annealing experiments is to point out the non-reversible transformations resulting from the heat treatments. The temperature dependence of the Doppler broadened lineshape shows several positron annihilation states during the transformation from the amorphous to the fully crystallized state (Fig. 1). The behaviour of the S parameter determines temperature ranges which can be related to the different phases. The S parameter slightly decreases till 400 °C, and drastically goes down between 400 °C and 500 °C. It recovers at 500 °C. The same results have been obtained by Schiltz *et al.* [7]. On the X-ray diffraction patterns the first sign of the crystallization onset only appears at 470 °C [8]. However Cumbrera *et al.* [9] showed that rings of an fcc structure (MSI structure) were already present in the electron micrographs taken for samples annealed at about 300 °C. These authors also showed that crystallization takes place through a two-stages process to give metastable MSI and MSII structures,

as termed by the authors. The MSI structure was ascribed to the iron-nickel fcc solid solution, the MSII crystals also are fcc type and were identified as the $\text{Fe}_x\text{Ni}_{23-x}\text{B}_6$ solid solution. The appearance of the MSII phase was observed for samples annealed between 380 °C and 430 °C. In spite of the observation of MSI and MSII structures an important portion of amorphous state still existed in a large temperature range above 430 °C. A new phase transition was observed at about 550 °C. The corresponding diffraction patterns were observed to be complex. A stable phase SIII was expected.

3.3 CONTINUED HEATING AND COOLING EXPERIMENTS. — The behaviour of the S parameter during heating and cooling experiments is compatible with the results obtained for an isochronally annealed sample (Fig. 2). The curve of the S parameter as plotted *versus* the sample temperature increases until saturation below 200 °C. It suddenly decreases to show several phase transitions, the main of which occurring at 295 °C, at 395 °C, and at 480 °C. The positron annihilation behaviour is in good agreement with the results of Cumbrera *et al.* [9]. In conformity with the electron diffraction patterns measured by Cumbrera *et al.* [9] the behaviour of the S parameter at 295 °C can be related to the formation of MSI crystallites. The feature of the curve between 385 °C and 480 °C can be related to the appearance of MSII crystallites. The drastic recovering at 480 °C can be ascribed to the appearance of the SIII structure. Both the positron

annihilation behaviour and X-ray diffraction patterns obtained for samples annealed above 490 °C are complex. The X-ray diffraction patterns showed [8] that several phase transitions still occur in a large temperature range above 500 °C.

The branches B-C and D-E of figure 2 resulting from cooling-down show linear tendencies. The variation of the annihilation lineshape is caused both by reversible and non-reversible effects. The superposition of reversible and non-reversible variations has been reported by many authors for metallic glasses. Balanzat *et al.* [10] detected reversible and non-reversible quenched-in resistivities for the Cu₅₀Ti₅₀ metallic glass. The reversible effect was ascribed to CSRO, while the non-reversible effect was assigned to TSRO. The TSRO is usually related to the loss of excess free volume in the as-quenched amorphous alloy [11]. The origin of the CSRO ordering is not clear. Cartier *et al.* [12] suggest that reversible effects in as-quenched metal-metal glasses are due to thermal detrapping of positrons from shallow traps. A further explanation is that the CSRO processes occur by atomic jumping [12]. Since the thermal expansion coefficient is positive in most metals the branches B-C and D-E of figure 2 can also be related to the changes induced by thermal expansion.

3.4 ISOTHERMAL ANNEALING EXPERIMENTS. — During phase transformation it is often observed in solids that some physical properties are modified following the Arrhenius law. In the case of metallic glasses the Arrhenius rate equation may involve heterogeneous reactions, since transformation from the amorphous to the crystallized state is rather complex in such material. One can write for the positron annihilation sites :

$$dC/dt = f(C) \cdot \exp(-E_a/kT), \quad (1)$$

where C represents the concentration of positron annihilation sites. E_a is the apparent activation enthalpy, k Boltzmann's constant, T the absolute temperature, and t the time. Because the positron annihilation characteristics are function of C , the S parameter also can be described following the Arrhenius rate equation for heterogeneous reactions :

$$dS/dt = g(S) \cdot \exp(-E_a/kT). \quad (2)$$

$g(S)$ is a function of S . The isothermal curves obtained with the S -parameter plotted as function of the annealing time were analysed using a « simplex » fitting technique [13] with appropriate functions. The values of the time t_{s_i} corresponding to a horizontal cross cut through the isothermal curves (Fig. 4) can be used to determine the activation enthalpy [14, 15]. From the integration of (2) between two well defined states of $S(t)$ ($S_0 = S(t_{s_0} = 0)$ and $S_i = S(t_{s_i})$),

$$\int_{S_0}^{S_i} \frac{dS}{g(S)} = \int_{t_{s_0}}^{t_{s_i}} dt \cdot \exp(-E_{ai}/kT), \quad (3)$$

one can write :

$$\ln(t_{s_i}) = C_1 + C_2/T, \quad (4)$$

Fig. 4. — A cross cut through some fitted isothermal curves $S(t)$.

where C_1 and $C_2 = E_{ai}/k$ are constants. Plotting the $\ln(t_{s_i})$ as a function of $1/T$ one finds a linear relationship. The values of C_1 and C_2 can be evaluated using a simple least-squares fitting. Several horizontal cross cuts S_i have been made through the measured isothermal curves $S(t)$. The values of t_{s_i} corresponding to each S_i are given in table II. Least-squares fittings were used to evaluate the C_1 and C_2 parameters at each cross cut S_i (Fig. 5). The corresponding values for the activation enthalpy E_{ai} are also given in the same table II. For the cross cuts S_i between 0.4885 and 0.4870 one can observe that the E_{ai} values are comparable. We conclude that the corresponding crystalliza-

Table II. — The time t_{s_i} values at a cross cut S_i through some isothermal curves.

cross cut at S_i	t_{s_i} (in hours) at temperature T (°C) =						apparent act. enthalpy E_{ai} (eV)
	371	386	396	399	409	418	
0.4885	17.65	0.99	2.85	- -	0.51	0.15	3.4 ± 0.3
0.4880	49.51	7.99	4.97	- -	1.18	0.48	3.69 ± 0.07
0.4875	85.08	13.44	8.24	1.48	2.21	0.99	3.64 ± 0.08
0.4870	128.62	66.88	13.66	3.26	3.20	1.80	3.85 ± 0.17

Fig. 5. — The cross cut time t_{si} plotted as a function of $1/T$. The slope is proportional to the activation enthalpy.

tion process of metglas 2826MB consists of only one activation enthalpy. The mean value obtained for E_{a_i} is :

$$E_{am} = (3.65 \pm 0.3) \text{ eV}.$$

4. Conclusion.

The phase transitions in the metallic glass $\text{Fe}_{40}\text{Ni}_{38}\text{Mo}_4\text{B}_{18}$ remain complex. From the continued heating and cooling experiments, crystallization of the sample appears as a three-stage process. The results of the isochronal annealing experiments only clearly show two steps of crystallization. Crystallization of samples induces small effects on the positron lifetime. The S -parameter behaves in the same way from both results of the isochronal experiments and of the continued heating and cooling experiments. Nevertheless, the continued heating and cooling experiments which were performed at a very low temperature change rate ($\pm 3^\circ\text{C/h}$) allow a better observation of phase transitions.

The behaviour of the lifetime and the S -parameter supports the idea that positrons are trapped by defects and inhomogeneities inherently present in the as-received metallic glass $\text{Fe}_{40}\text{Ni}_{38}\text{Mo}_4\text{B}_{18}$. The annihilation characteristics of positrons are very sensitive

to phase transitions. The variation of the annihilation lineshape shows reversible and non-reversible contributions. The reversible behaviour can be related to the changes induced by thermal expansion. The non-reversible variation is due chiefly to phase transitions.

The first and the second phase transitions show up by the lowering of the S -parameter values at 295°C and at 395°C , indicating densification mechanisms. The third stage of crystallization which is marked by an increasing of the S -parameter at 480°C can be ascribed to an introduction of more attractive traps for positrons. The temperature range in which isothermal curves have been measured corresponds to that of the second stage of the crystallization process. The value of the apparent activation enthalpy is high when compared to that of pure metals but comparable to that obtained for alloys similar to the present ones by Lucci *et al.* [16].

Acknowledgments. — This work is part of the research programme of the IIKW, Brussels, Belgium. Financial support is acknowledged. One of the authors (M-T) is indebted to the Ministry of Development Cooperation (ABOS-AGCD) for a grant. The authors thank Professor Dr. L. M. Stals for providing the samples.

References

- [1] CARTIER, E., HEINRICH, F., KUNG, M. and GUNTHERODT, H.-J., *Nucl. Instrum. Meth.* **199** (1982) 147.
- [2] KIRKEGAARD, P. and ELDRUP, M., *Comput. Phys. Commun.* **3** (1972) 200.
- [3] MACKENZIE, I. K., EADY, J. A. and GINGERICH, R. R., *Phys. Lett.* **33A** (1970) 279.
- [4] MOSER, P., HAUTOJÄRVI, P., YLI-KAUPPILA, J. and CORBEL, C., *Rad. Effects* **62** (1982) 153.
- [5] SHIOTANI, N., in : *Positron Annihilation*, p. 561 ; Proc. of the 6th Int. Conf. on Positron Annihilation, Texas (Arlington, 1982), eds : P. G. Coleman, S. C. Sharma and L. M. Diana.
- [6] DAUWE, Ch., SEGERS, D., DORIKENS-VANPRAET, L. and DORIKENS, M., *Phys. Status Solidi a* **17** (1973) 443.
- [7] SCHILTZ, A., LIOLIOS, A., ELEFTERIADES, C., CHARDALAS, M., DEDOUSSIS, S. and CHARALAMBOUS, S., in : *Positron Annihilation*, Proc. of the 7th Int. Conf. on Positron Annihilation (New Delhi, 1985), to be published.
- [8] MBUNGU-TSUMBU, SEGERS, D., DORIKENS-VANPRAET, L. and DORIKENS, M., in : *Positron Annihilation*, p. 578 ; Proc. of the 6th Int. Conf. on Positron Annihilation, Texas (Arlington, 1982); eds : P. G. Coleman, S. C. Sharma and L. M. Diana.
- [9] CUMBRERA, F. L., MILLAN, M., CONDE, A., MARQUEZ, R. and VIGIER, P., *J. Mater. Sci.* **17** (1982) 861.
- [10] BALANZAT, E., MAIRY, C. and HILLAIRET, J., *J. Physique Colloq.* **41** (1980) C8-871.
- [11] HILLAIRET, J., BALANZAT, E., DERRADJI, N. E. and CHAMBEROD, A., *J. Non-Cryst. Sol.* **61** (1984) 781.
- [12] BALANZAT, E., STANLEY, J. T., MAIRY, C. and HILLAIRET, J., *Acta Metall.* **33** (1985) 785.
- [13] MIHARA, T., OTAKE, S., FUKUSHIMA, H. and DOYAMA, M., *J. Phys. F : Metal Phys.* **11** (1981) 727.
- [14] CARTIER, E., HEINRICH, F. and GUNTHERODT, H.-J., *Phys. Lett.* **81A** (1981) 393.
- [15] DAUWE, C., DORIKENS, M. and DORIKENS-VANPRAET, L., *Appl. Phys.* **5** (1974) 45.
- [16] THOMPSON, M. W., *Defects and Radiation Damage in Metals* (Cambridge Univ. Press, London) 1969.
- [17] LEMAHIEU, I., SEGERS, D., DORIKENS-VANPRAET, L. and DORIKENS, M., *Phys. Lett.* **102A** (1984) 269.
- [18] LUCCI, A., BATTEZZATI, L., ANTONIONE, C. and RIONTINO, G., *J. Non-Cryst. Sol.* **44** (1981) 287.