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COMMUNICATIONS

EVOLUTION OF FREE VOLUME IN ANNEALED Fe–Mo–Cu–B–TYPE ALLOY STUDIED BY POSITRON ANNIHILATION

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Positron annihilation lifetime spectroscopy (PALS) has been applied to study the microstructural changes in NANOPERM-type metallic $Fe_{76}Mo_8Cu_1B_{15}$ alloy after heat treatment. Samples in as-quenched state were isothermally annealed at five chosen temperatures in the range between 330 and 700 °C for 1 hour annealing time. The decrease of excess free volume in the as-quenched structure upon annealing is well observed by a decrease of positron lifetime. The combination of PALS with other experimental methods (in particular magnetic measurements) have shown that minimum of free volume found in sample annealed at 550 °C coincides with the temperature at which superior magnetic properties are observed.

K e y w o r d s: PALS, positron annihilation, nanocrystalline alloys, amorphous alloys, excess free volume

1 INTRODUCTION

Metallic glasses are materials in frozen metastable state. After an appropriate heat treatment performed upon as-cast amorphous ribbons, nanosize grains are formed which are embedded in the remaining amorphous matrix [1]. Cu content in these alloys causes a decrease of the crystallization temperature and increase of the nucleation rate. Boron enhances the thermal stability of the amorphous phase and affects the homogeneity of the Fe precipitates [2]. The nanocrystalline alloys exhibit unique structural and magnetic properties, which are different from those of the conventional coarse-grained polycrystalline materials. Their excellent soft magnetic response is mainly correlated with the averaging out of the magnetocrystalline anisotropy via the magnetic interactions between the two constituent magnetic phases [3]. Such magnetic properties are very favorable for technical applications in power transformers, data communication components, pulsed transformers, choke coils, magnetic heads, sensors and magnetic shielding [4]. In order to benefit from the advantageous and unique properties of nanocrystalline materials, their structure as well as magnetic arrangement should be known. For this purpose, investigations with variety of microscopic and/or nuclear-based techniques are performed [5] in addition to conventional magnetic measurements [6].

Positron annihilation spectroscopy has previously been applied in a number of studies of defect creation, interaction, and recovery in metals and alloys [7, 8]. Due to the complexity of data interpretation most of the earlier positron annihilation studies on defects were limited to simple metals and alloys rather than complex nanocrystalline materials. Recently, several researchers have used this technique to obtain a more detailed picture of the distribution of open volume in metallic glasses [9–11].

The physical basis for the use of positrons in defect studies is the fact that positrons injected into a material fall into localized states in regions of lower-than-average electron density. Positrons tend to occupy open-volume regions due to their Coulomb repulsion with the atomic nuclei. Because the amorphous metallic glasses are structurally disordered, the concept of vacancies has no significance in these systems [11]. Analysis of the resulting radiation provides information about the free volume on an atomic scale or a vacancy-like open volume (small subvacancy-sized free volume or excess free volume) inside the structure.

In this paper, positron annihilation measurements have been applied to investigate more closely the changes in microstructure induced by thermal treatment of the $Fe_{76}Mo_8Cu_1B_{15}$ alloy. The results presented here clearly demonstrate that the positron annihilation lifetime spectroscopy (PALS) is a useful tool also for nanostructured materials. However, numerous subjects such as the determination of defect type in complex alloys, and the utility of PALS in relation to other techniques, should be investigated further.

2 EXPERIMENTAL DETAILS

The amorphous $Fe_{76}Mo_8Cu_1B_{15}$ alloy was prepared in a form of ribbon by standard melt-spinning method. The produced ribbon is 6 mm wide and 22 μm thick. Samples were annealed at 330, 490, 550, 600, and 700 °C for 1 hour in vacuum better than 10^{-3} Pa. Annealing temperatures were chosen according to the results from differential scanning calorimetry.

The free volume changes associated with annealing of the $Fe_{76}Mo_8Cu_1B_{15}$ ribbon was examined using PALS at the Department of Nuclear Physics and Technology FEI STU Bratislava. Details of this technique are described elsewhere [12, 13]. The lifetime distributions were obtained using a conventional lifetime spectrometer by means of a pair of BaF_2 scintillation detectors and resolution of 200 ps full width at half-maximum (FWHM). The

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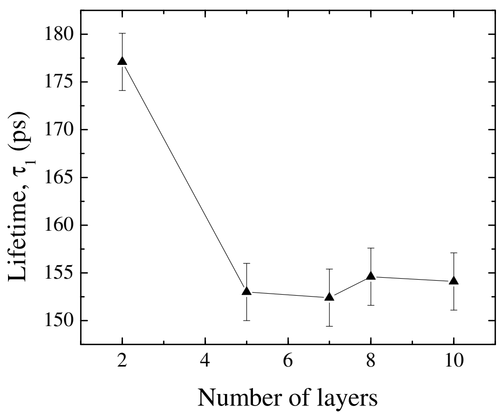

Fig. 1. Dependence of the positron lifetime τ_1 on the number of layers of $Fe_{76}Mo_8Cu_1B_{15}$ alloy in the as-quenched state.

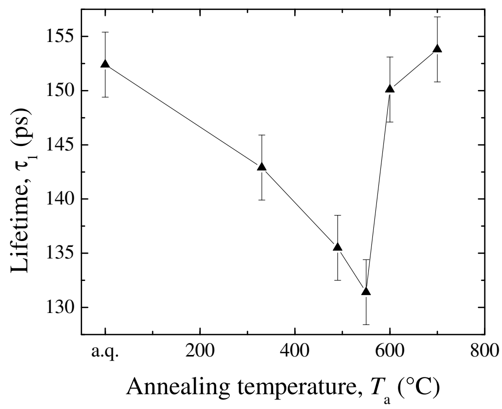

Fig. 2. Positron lifetime τ_1 as a function of annealing temperature T_a for the $Fe_{76}Mo_8Cu_1B_{15}$ alloy.

lifetime distributions were measured at constant room temperature of 19 °C. At least 1.6×10^6 counts were collected in each spectrum. The measured spectra were decomposed using the LT 9.0 fitting program [14].

The specimen consisted of two stacks of 7 layers of the sample material with the ^{22}NaCl-on-kapton foil source sandwiched between them. The outer side of the sandwich was covered with a 100 μm thick silicone plate from each side. This plate is used for the estimation of minimum sample thickness to ensure that the essential fraction of positrons annihilates in the sample pair.

3 RESULTS AND DISCUSSION

3.1 Experiment optimization

Positrons implanted in a solid from a typical radioactive source have a mean penetration depth between 10 and 100 μm. To ensure that almost all positrons annihilate in a sample pair the optimal sample thickness should be known. Using theoretical assumptions [15] we have estimated the needed thickness of the whole sample to be of 132 μm which is equal to 6 layers of the metallic glass ribbon.

Consequently, to support the empirical calculation, we have made an experiment optimization using different number of $Fe_{76}Mo_8Cu_1B_{15}$ ribbons covered by a silicone wafer. The positron lifetime variations with number of layers in the sandwich arrangement are shown in Fig. 1.

In a sandwich arrangement with two ribbons of the as-quenched $Fe_{76}Mo_8Cu_1B_{15}$ alloy, a fraction of positrons has already passed through the sample and, subsequently, some positrons have entered the outer Si. That is why the corresponding τ_1 value in Fig. 1 is significantly high. Using 10, 8, 7, and even 5 layers of the sample have no relevant influence on the value of the positron lifetime. From the results we can conclude that 5 layers are sufficient for complete stopping of positrons inside the investigated sample. However, heat treatment applied on metallic glass has significant impact on changes in its microstructure [5]. Therefore, we have decided to use 7 layers of sample from each side of the positron source for our main experiment.

3.2 Effect of heat treatment on the microstructure

The obtained PALS spectra were decomposed into two components. The long-lived component is characterized by positron lifetime of about 2000 ps and its relative intensity is less than 1 %. It can be ascribed to positrons which annihilate in air. Because of relatively small fraction of this component we do not discuss it to more details. No evidence of a third component in the spectrum was observed. Positron lifetime of the first component τ_1 is plotted in Fig. 2 as a function of annealing temperature T_a.

After annealing at moderate temperature of 330 °C which is far below the onset of crystallization, structural relaxation takes place that leads to rearrangement of atoms into energetically more favourable positions. At the same time, stresses formed during preparation of the original precursor are released. Consequently, the observed decrease in τ_1 from 152 ps to 143 ps corresponds to annealing-out of free volume and/or stress centres introduced during the preparation of the amorphous ribbons. Similar relaxation process which removes most of the existing defects, characterized by decrease of mean positron lifetime in the bulk region, was observed in nuclear reactor pressure vessel WWER-1000 steel using pulsed low-energy positron system [8].

A steep drop in τ_1 at temperatures of 490 °C and 550 °C coincides with the progress of crystallization process [5] which leads to formation of fine bcc-Fe grains. The same mechanism as mentioned above applies. At 550 °C, the primary crystallization of the system is finished. From the PALS point of view, positron lifetime τ_1 reaches its minimum of 131 ps. We can conclude that after annealing at 550 °C, the $Fe_{76}Mo_8Cu_1B_{15}$ alloy is in a state with well developed and structurally homogeneous bcc-Fe crystallites, which is also supported by Mössbauer spectrometry, XRD, DSC, TEM, and HREM experiments [5].

A rapid increase in τ_1 beyond $T_a > 550$ °C is associated with a diffusion growth of bcc Fe crystalline grains.

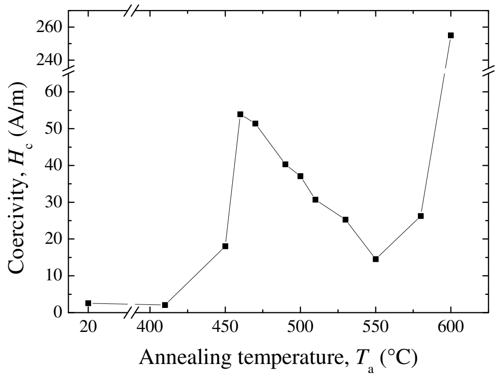

Fig. 3. Coercivity H_c as function of annealing temperature T_a [6].

At the same time, a fcc structural arrangement of Fe atoms appears and at 600 °C the second crystallization step is already well developed [5]. Consequently, the trapping centres for positrons can be related with the onset of secondary crystallization, growth of grains, and their clustering, structural change from bcc to fcc arrangement, possible distortions at interface of the grains, as well as formation of iron boride crystallites.

Magnetic measurements performed upon the same NANOPERM-type system [6] pointed out an optimal value of coercivity after annealing at $T_a = 550\,°\mathrm{C}$. Figure 3 shows the overall temperature dependence of coercivity H_c against T_a. Nanometer dimensions of crystallites ensure such magnetocrystalline anisotropy that at this stage optimal magnetic properties necessary for practical applications occur. Further increase in H_c is associated with growth of bcc-Fe crystals and appearance of other crystalline phases. Taking into consideration the results of PALS and Mössbauer spectrometry we can conclude that the optimal, from magnetic point of view, stage of this particular nanocrystalline alloy coincides with the structural arrangement which exhibits the lowest amount of free volume.

4 CONCLUSIONS

The changes in positron annihilation lifetime spectra in thermally treated $Fe_{76}Mo_8Cu_1B_{15}$ alloy confirm that annealing at moderate temperatures initiates structural relaxation and releases stresses acquired during the technological preparation of the original alloy. Minimum in positron lifetime observed in the sample annealed at 550 °C indicates that the alloy has stable though combined structure which at this stage shows optimal magnetic properties.

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