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APPLICATION OF THE MAGETOCALORIC EFFECT IN THE PROTECTION OF WORKS OF ART

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Abstract

This paper presents the results of investigations into the structure, microstructure and magnetic properties of $Fe_{86}Zr_7Nb_1Cu_1B_5$ amorphous alloy. Samples of the as-quenched alloy were created in the form of ribbons with approximate width and thickness of 3mm and 20 μm, respectively. The structure and microstructure of the samples were studied using spectrometry. The magnetic properties, including the low-field magnetic susceptibility and magnetisation as a function of temperature were measured. The magetocaloric effect was observed as the change in the magnetic entropy (ΔS_M), which was determined from recorded isothermal magnetic curves. The Curie temperature (T_C) was estimated, for the alloy in the as-quenched state, over a range of temperatures (303±5K). The obtained transmission Mössbauer spectra were found to be typical of those for ferromagnetic alloys, with an average hyperfine field of $(B_{hf})_{ef}$= 4.78(2) T.

***Keywords**: Amorphous Magnetic Materials; Magnetic Entropy; Magnetisation Processes, Mössbauer Spectroscopy;*

Introduction

In recent years, there has been a noticeable increase in the pollution and degradation of the environment, with concurrent development in the areas of science and technology. This development often provides new and advanced methods of damage mitigation, minimising and often eliminating the adverse effects of environmental degradation.

Modern methods, that serve to protect the environment, are used in many aspects of our everyday life. One important and significant element is the protection of our cultural heritage, where there are problems related to the storage or preservation of national works of art. An important aspect is the influence of external factors, often detrimental, during public art exhibitions. The development of new analytical methods, such as: physicochemical or microcomposition analysis, stemming from advances in science and technology, allow thorough analysis of the components of a given work of art. The most significant aspect for people involved in preservation is to select methods and analysis which will not affect negatively the work of art. The most desirable methods are those which allow for ‘non-contact’ assessment and analysis of an object - or at least reduced need for contact. In addition to the preservation, the storage and exhibition of works of art are of equal importance: they must be carried out using appropriate methods – and under conditions that avoid further degradation. Guidelines formulated by preservation officers, physicists, biologists, chemists and engineers specify optimal ways and methods of storing works of art, as well as their transport and exhibition (for example, in glass cabinets). The temperature and humidity levels in the room are important factors. In buildings where works of art are being stored, stable climatic conditions should be ensured throughout every whole day, as well as for the duration of any storage. Another significant factor is the elimination of detrimental noise. One example of the application of modern methods and technology for the protection of works of art, such as paintings, is the adoption of magnetically refrigerated cabinets for storage and transportation. Magnetic refrigeration is based on the magetocaloric effect. Magnetic cooling is the modern alternative to traditional methods of cooling, which are based on materials that are detrimental to the natural environment - for example, the emission of greenhouse gases with resulting depletion of the ozone layer. In addition to the environmental pollution resulting from the use of the cooling agents (such as freon), the traditional cooling method also requires excessive use of electricity. The main issue pertaining to the application of the modern methods of cooling is the development of materials; with Curie temperatures close to room temperature and with suitable cost (the rare earth metals, characterised by good magetocaloric parameters, are relatively expensive). Another important factor is also the bulk (size and weight) of the assembled magnetic cooler, in comparison to that of a traditional fridge.

Magnetic cooling itself was discovered a long time ago, in 1881, by *Warburg* [1]. Heating or cooling of a magnetic material, as a result of changes in the magnetic field, was described by Wiess and Piccard as the magetocaloric effect (MCE) in 1918 [2-6]. An increase in the applied magnetic field results in the magnetisation of the material, and the magnetic moments of the electrons are orientated according to the direction of the applied magnetic field. This process is thermodynamic, and ordering of the dipoles results in a decrease in the magnetic entropy S_M, which is measure of the system disorder.

If the magnetisation process is isothermic, then an increase in the magnetic field occurs; dipoles are arranged, parallel to the direction of the external magnetic field, and the entropy decreases. Conversely, if the demagnetisation process is adiabatic, then the value of the entropy is constant, and the temperature changes from the initial state to an end state.

The change in the magnetic entropy (ΔS_M) can be calculated from the equation [7]:

$$\Delta S_M = \mu_0 \int_0^{H_{\max}} \left(\frac{\partial \sigma(T,H)}{\partial T} \right)_H dH = \int_0^{B_{\max}} \left(\frac{\partial \sigma(T,B)}{\partial T} \right)_B dB \qquad (1)$$

The largest change in the value of the entropy is observed during the magnetisation of a ferromagnetic material in the vicinity of its Curie temperature; therefore, it is important to find a suitable magnetic material which has its Curie temperature close to room temperature [8,9]. Alloys of materials exhibiting a second-order phase transition are of particular research interest. An example of this type of phase transition is the ferromagnetic to paramagnetic transition, at the Curie temperature.

Measurement of the temperature difference during the adiabatic demagnetisation of a ferromagnetic alloy is a direct measurement of the magetocaloric effect [10]. In order to perform these measurements, a temperature probe can be used (by contact or non-contact methods). Another way of measuring the MCE is the indirect method, in which the changes of temperature $\Delta T(T)_{\Delta H}$ and entropy $\Delta S_M(T)_{\Delta H}$ are derived from magnetisation process measurements [10] -according to Equation (1). The accuracy of the measurements of magnetisation, temperature and the magnetic field affect the accuracy of the entropy values. Despite the fact that the magetocaloric effect was discovered over 100 years ago, there are no effective solutions used on an industrial scale. However, there have been many attempts at, and prototypes built, of magnetic fridges - mostly using materials exhibiting the gigantic magetocaloric effect. Alloys of the rare-earth metals are materials which exhibit a relatively substantial magetocaloric effect near room temperature [11,12]. However, these materials require a large change in the magnetic field value, and are relatively expensive, which makes them less attractive in comparison with transition metal alloys. In the latter, the magetocaloric effect can be achieved within a much lower magnitude of magnetic field.

This paper presents the results of an investigation involving magnetic measurements and the evaluation of the magetocaloric effect for the alloy $Fe_{86}Zr_7Nb_1Cu_1B_5$ in the as-quenched state. The soft magnetic properties exhibited by this alloy are partcularly interesting; making it a promising candidate for industrial applications, as well as for the protection of works of art.

Experimental

Materials

The material used in the investigations was an alloy with the nominal composition of $Fe_{86}Zr_7Nb_1Cu_1B_5$. Ingots of the alloy were produced by arc-melting of high purity (99.99 at %) component elements. The single-cylinder rapid-quenching method (melt-spinning) allowed the production of samples in the form of amorphous ribbons with approximate thickness and width of 20μm and 3mm, respectively. The stability of the production process was preserved by using a protective argon atmosphere.

Methods

The structure of samples, cut out from the ribbons, was studied by means of Mössbauer spectrometry. The Mössbauer spectra were recorded in the transmission geometry; the source was a ^{57}Co isotope, in a Rh matrix, with an activity of 20mCi. The transmission Mössbauer spectra were analysed utilising NORMOS software [13]. The studies were performed at room temperature.

The magnetic susceptibility was measured for toroidal samples, with an approximate external diameter of 2.5cm. The magnetic properties of the samples were measured over the temperature range of 130 to 310K. A Faraday magnetic balance was used to record isothermal magnetisation curves; this allowed calculation of the change in magnetic entropy, ΔS_M, which is a measure of the magetocaloric effect [10, 14].

Results and discussion

Fig. 1 presents the transmission Mössbauer spectrum and, derived from this, the hyperfine field distribution, for the samples of the $Fe_{86}Zr_7Nb_1Cu_1B_5$ alloy, in the as-quenched state.

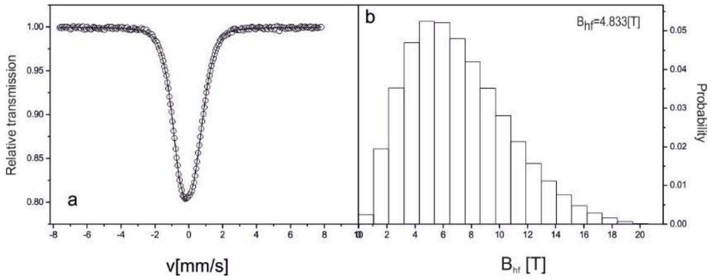

Fig. 1. Transmission Mössbauer spectrum at room temperature:
(a) and the hyperfine field distribution (b) for the $Fe_{86}Zr_7Nb_1Cu_1B_5$ alloy in the as-quenched state

The observed Mössbauer spectrum is typical of those for soft ferromagnetic materials [15-17]. In the hyperfine field distribution, derived from this spectrum, two components can be observed: low- and high-field. The presence of these two components is related to the existence of regions with different iron concentrations in the volume of the sample. Based on the hyperfine field distribution, it can be concluded that the alloy is relatively homogeneous.

Figure 2 presents the magnetic susceptibility of the $Fe_{86}Zr_7Nb_1Cu_1B_5$ alloy - measured as a function of temperature, in a magnetic field of amplitude 0.26A/m and frequency 2kHz.

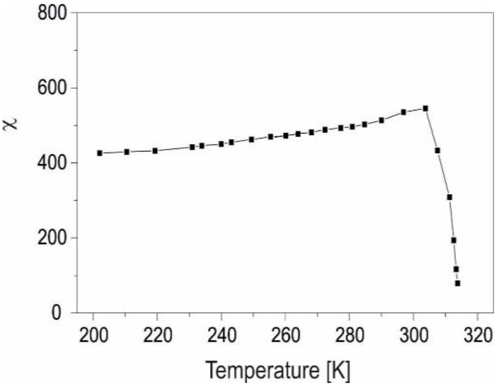

Fig. 2. The magnetic susceptibility, as a function of temperature, for the $Fe_{86}Zr_7Nb_1Cu_1B_5$ amorphous alloy in the as-quenched state

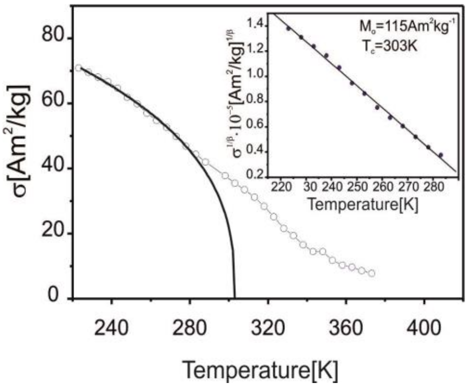

Fig. 3. The relationship of the specific magnetisation (σ) with temperature, for the investigated amorphous alloy in the as-quenched state

From the figure, it can be observed that the magnetic susceptibility increases linearly with increasing temperature, and near room temperature the peak value of χ(T) can be observed. Above the temperature of 300K, a rapid decrease in magnetic susceptibility is observed. The presence of the maximum on the χ(T) curve is related to decreases in the effective anisotropy and the magnetisation saturation with increasing temperature; the rapid decrease in the magnetic susceptibility is the result of the transition from the ferro- to paramagnetic state. From the trajectory of the curve, it can be claimed that the Curie temperature (T_C) for the alloy is in the temperature region between 303-305K; this has been confirmed by measurements of the magnetisation as a function of temperature.

Figure 3 shows the corresponding magnetisation curves (σ) for the studied alloy, as a function of temperature in a constant magnetic field of 0.75T.

The specific magnetisation decreases with increasing temperature, but does not reach zero at one, clearly specified, temperature. In the amorphous alloys, the determination of an exact value of the Curie temperature T_C presents considerable difficulty and the value is usually given as approximate. This is due to fluctuations in the alloy composition [18-20]. The Curie temperature was determined by analysing the critical behaviour of the magnetisation in the temperature range close to the Curie temperature for the studied alloy, from the linear relationship of $\sigma^{1/\beta}(T)$ [21].

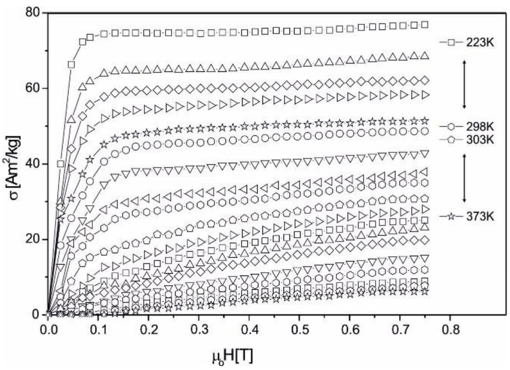

Fig. 4. Isothermal magnetisation curves at selected values of temperature and at the maximum magnetising field induction of 0.75 T, for the $Fe_{86}Zr_7Nb_1Cu_1B_5$ alloy in the as-quenched state

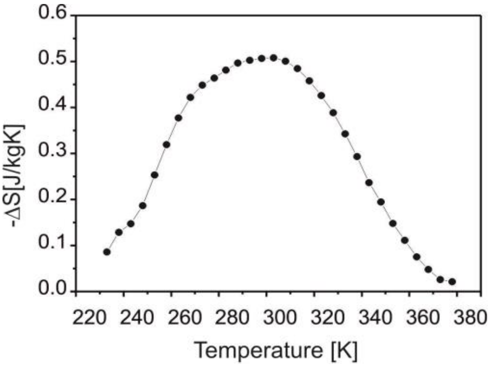

Fig. 5. Magnetic entropy changes versus temperature for $Fe_{86}Zr_7Nb_1Cu_1B_5$ alloy in the as-quenched state.

Figure 4 presents examples of isothermal curves of the specific magnetisation $\sigma(\mu_0 H)$ for the $Fe_{86}Zr_7Nb_1Cu_1B_5$ alloy, in the as-quenched state. The chosen temperatures are below and above the value of the Curie temperature for the alloy ($T_C = (303 \pm 5)$K), and the values of the magnetic field induction are between 0 and 0.75T.

The magetocaloric effect, observed as a change in the magnetic entropy, was calculated according to equation (1) from the isothermal magnetisation curves, measured over a wide temperature range. The changes in entropy values, for the $Fe_{86}Zr_7Nb_1Cu_1B_5$ alloy in the as-quenched state, were calculated and are presented as a function of temperature in figure 4. The wide maximum in the values of entropy changes can be observed in the vicinity of the Curie temperature of the alloy (303K).

Conclusions

On the basis of the performed studies, it was found that an alloy with the nominal composition of $Fe_{86}Zr_7Nb_1Cu_1B_5$ in the as-quenched state is fully amorphous and exhibits good soft-magnetic properties. Due to the low value of the Curie temperature – near room temperature – the studied alloy shows potential for applications in magnetic refrigeration. The method of “magnetic cooling” is an alternative for currently used refrigeration methods, which are harmful to environment due to the cooling agent used, as well as the high energy consumption. Increasingly stringent regulations, enforced by the European Union and worldwide organisations fighting pollution of the environment, are forcing the development of new refrigeration and air-conditioning methods. Existing equipment, filled with harmful cooling gases, will have to be gradually replaced with different, more ecologically-sound, devices. The latter group includes units based on materials in which the magetocaloric effect is observed. The magetocaloric effect, especially near room temperature, could be used in everyday life, as well as in cooling units for the protection of works of art; for example, during transportation or storage. Utilising magnetic refrigeration offers not only protection of the natural environment, due to the absence of ozone-depleting gases; but also offers lower noise emission during its operation, due to the elimination of mechanisms such as compressors. There is also the benefit of lower usage, and concomitant cost, of electricity in comparision to traditional cooling methods.

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