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ORIGINAL PAPER

Microstructure and magnetic properties of amorphous $Fe_{51}Co_{12}Si_{16}B_8Mo_5P_8$ alloy

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Abstract. Microstructure and thermomagnetic characteristics of the amorphous $Fe_{51}Co_{12}Si_{16}B_8Mo_5P_8$ alloy in the as-quenched state and after 1 h of annealing at 573 K and 773 K are studied. The structural investigations performed by Mössbauer spectroscopy and X-ray diffractometry confirmed the amorphous structure of the analysed materials. An increase in the annealing temperature up to 773 K does not lead to crystallization of the amorphous alloy. Only structural rearrangement that causes changes in the topological short-range order and annealing out of free volume is observed. This behaviour was confirmed by modifications of the shapes of hyperfine field distributions derived from the corresponding Mössbauer spectra of the investigated alloys. The Curie temperatures of the as-quenched and annealed $Fe_{51}Co_{12}Si_{16}B_8Mo_5P_8$ alloy at 573 and 773 K are 400, 405 and 421 K, respectively.

Keywords: microstructure • Mössbauer spectroscopy • magnetic properties • Curie point

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Introduction

Fe-based metallic glasses such as FINEMET, NANOPERM and HITPERM usually produced from amorphous precursors in various forms have been intensively studied over the past thirty years, because these materials exhibit a unique combination of soft magnetic properties [1], which is very interesting from a scientific point of view. The application of these materials at elevated temperatures is determined by their appropriate magnetic parameters, e.g. Curie point, coercive field, saturation magnetization, etc. The latter can be enhanced by partially replacing Fe atoms by Co in the master alloy [2, 3]. Their excellent magnetic properties make them ideal for the electrical industry, e.g. as transformers and magnetic chokes [4].

A new group of NANOMET (Fe-Si-B-P-Cu) soft magnetic materials was developed by Makino [5, 6] as a suitable candidate for energy saving. It is currently a focus of many research groups that are struggling to explain and understand the consequences of structural changes upon their magnetic properties.

The aim of this paper is to study the evolution of the microstructure and soft magnetic properties of a novel $Fe_{51}Co_{12}Si_{16}B_8Mo_5P_8$ alloy in as-quenched and annealed (below the crystallization temperature) states.

Experimental procedure

Amorphous $Fe_{51}Co_{12}Si_{16}B_8Mo_5P_8$ alloy was produced by planar flow casting method (PFC) on a quenching wheel in a form of 6 mm wide and ~0.025 mm thick ribbons. Its exact chemical composition was determined by inductively coupled plasma mass spectrometry (ICP-MS) and atomic absorption spectrometry (AAS) used for the determination of the contents of B, P, Fe, Co, Si, and Mo, respectively. The structure of the as-quenched precursor and samples annealed for 1 h at 573 K and 773 K was examined at room temperature by Mössbauer spectroscopy and X-ray diffractometry. The annealing temperatures selected were well below the primary crystallization temperature that was measured to be 839 K by a differential scanning calorimeter (DSC).

Mössbauer spectra were recorded in transmission geometry using a constant acceleration driver equipped with a $^{57}Co(Rh)$ radioactive source. Analysis of the obtained spectra was performed by the NORMOS software package [7]. Velocity calibration was accomplished by a 12.5 μm thick bcc-Fe foil. Isomer shift values are quoted in terms of the centre of its Mössbauer spectrum taken at room temperature.

X-ray diffraction patterns were collected in reflection mode using a PANalytical X'Pert PRO diffractometer equipped with a conventional X-ray tube using CoK_α radiation. X-ray patterns were measured between 20 and 150° 2Θ with a step of 0.0167° and 700 s per step.

The temperature and DC external magnetic field soft magnetic characteristics of the $Fe_{51}Co_{12}Si_{16}B_8Mo_5P_8$ alloy were carried out by a VersaLab (Quantum Design) system over a temperature range of 50–400 K (equipment limitation) and magnetic fields up to 50 mT.

Results and discussion

Microstructure investigations

The amorphicity of the as-quenched and annealed samples of the $Fe_{51}Co_{12}Si_{16}B_8Mo_5P_8$ metallic glass (MG) ribbons was confirmed by X-ray diffraction. As demonstrated in Fig. 1, only broad reflections are observed. The possible occurrence of crystalline phases would be indicated by narrow peaks after annealing which is, however not the present case. The obtained Mössbauer spectra presented in Fig. 2a were recorded at room temperature in transmission geometry. They show broadened absorption lines which are highly overlapped. Such line shapes are also characteristic of a disordered (amorphous) structure. Consequently, they were refined by distributions of hyperfine magnetic fields $P(B)$ that are plotted in Fig. 2b.

In the as-quenched state, the investigated MG exhibits a bell-like $P(B)$ distribution that extends over a broad range of B values (see Fig. 2b above). After annealing at 573 K and 773 K structural rearrangement in the amorphous matrix takes place. This is demonstrated namely by a tendency of the corresponding $P(B)$ distributions to separate into

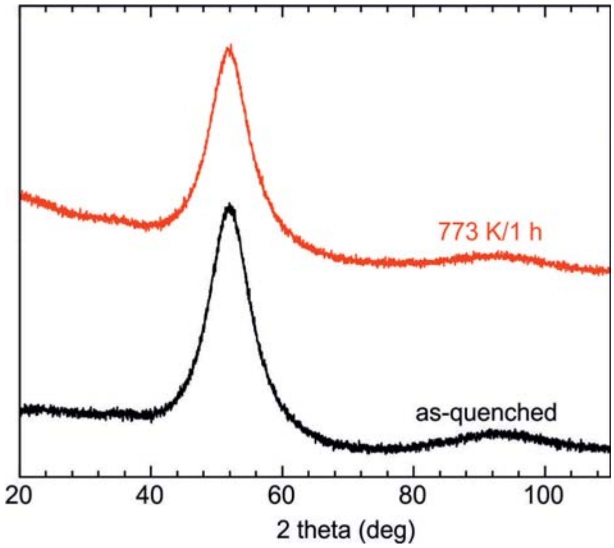

Fig. 1. X-ray diffraction patterns of the $Fe_{51}Co_{12}Si_{16}B_8Mo_5P_8$ alloy in the as-quenched state and after annealing at 773 K for 1 h.

well resolved bimodal shapes with clearly observed low- and high-field humps. They represent magnetically distinct regions inside the amorphous structure.

While the low hyperfine magnetic fields indicate the presence of areas in the amorphous matrix with diminishing magnetic interactions, on the other hand high hyperfine magnetic fields suggest enhanced magnetic interactions. The contribution of the latter gradually increases as the annealing temperature increases. As a result, two magnetically distinct regions develop in the studied MG after annealing. Because the system is still amorphous, as confirmed by both Mössbauer and XRD data, the observed changes in the magnetic microstructure are caused exclusively by the rearrangement of the constituent elements, i.e. by changes in the short-range order.

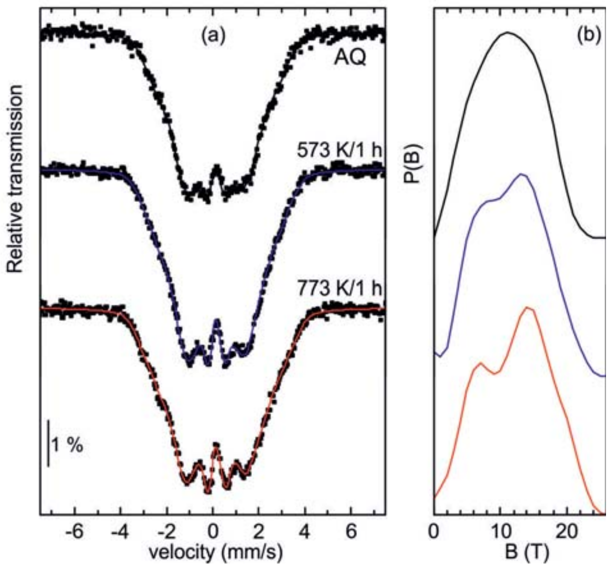

Fig. 2. Room-temperature Mössbauer spectra (a) and corresponding distributions of hyperfine magnetic fields $P(B)$ (b) of the $Fe_{51}Co_{12}Si_{16}B_8Mo_5P_8$ alloy in the as-quenched state (AQ) and after the indicated annealing.

Table 1. Average hyperfine magnetic field <*B*>, average standard deviation σ, and average isomer shift <IS> as derived from Mössbauer spectrometry data of the $Fe_{51}Co_{12}Si_{16}B_8Mo_5P_8$ alloy

Sample	<*B*> [T] ±0.15 T	σ [T] ±0.2 T	<IS> [mm/s] ±0.02 mm/s
As-quenched	10.97	4.7	0.14
573 K/1 h	11.53	5.0	0.13
773 K/1 h	12.18	5.3	0.14

The obtained spectral parameters comprising the average hyperfine magnetic field <*B*>, standard deviation σ and average isomer shift <IS>, as obtained from the $P(B)$ distributions are listed in Table 1. It is noteworthy that while <*B*> and σ increase after annealing, <IS> remains practically unchanged. The almost constant <IS> indicates that the chemical environment of the resonant nuclei is not altered which means that changes in the short-range order are of a topological and not of a chemical origin. In this respect, σ can be considered as a measure of the degree of structural arrangement. As σ increases the amorphous structure becomes more disordered. This can be understood in terms of the topological redistribution of the constituent elements in the local environment of the resonant ^{57}Fe nuclei. In this way, hyperfine interactions and hence the corresponding hyperfine magnetic fields are altered. Consequently, this results in modifications of the microstructure towards a more ferromagnetic arrangement. Thus, a rise in Curie temperature is expected. These observations are confirmed by magnetic measurements as discussed below.

Magnetic measurements

It is well known that good magnetic properties of MGs depend not only on the chemical composition of the alloys but also on their microstructure. The temperature dependence of normalized magnetization M/M_{max} for the $Fe_{51}Co_{12}Si_{16}B_8Mo_5P_8$ MG measured in zero-field-cooled (ZFC) mode under an external DC magnetic field of 25 mT is presented in Fig. 3. Typical ferromagnetic behaviour is observed for the as-quenched state as well as after annealing at 573 K and 773 K. With increasing the temperature of measurement, magnetization decreases. It is noteworthy, however, that after annealing the values of magnetization increase in the whole measured temperature range. The higher is the temperature of annealing the more pronounced the increase in normalized magnetization is observed. This behaviour is related to structural rearrangement which was unveiled by the results of Mössbauer spectrometry.

One of the most important parameters which determines the application potential of MGs is the Curie temperature T_C. Because of experimental limitations that do not allow measurements of magnetic parameters at temperatures higher than 400 K, T_C values had to be extrapolated according to the temperature dependence of magnetization expressed using the following formula [8]:

$$M(T) = M_s(0)\cdot(1 - T/T_C)^{\beta}$$

where $M(T)$ is the magnetization at temperature T, $M_s(0)$ is the saturation magnetization at $T = 0$ K, and β is a critical exponent which for the Heisenberg model is 0.36.

The Curie temperatures for the $Fe_{51}Co_{12}Si_{16}B_8Mo_5P_8$ alloy in the as-quenched state and after annealing at 573 K and 773 K which were derived according to the above formula from the data presented in Fig. 3 are 403, 405 and 421 K, respectively.

Hysteresis loops $M(H)$ recorded at 50 K and 300 K for the as-quenched and annealed $Fe_{51}Co_{12}Si_{16}B_8Mo_5P_8$ alloy are plotted in Fig. 4. As can be seen, hysteresis loops corresponding to the as-quenched state of the alloy and to the sample annealed at 573 K exhibit almost identical magnetic behaviour both at 50 K and 300 K for magnetic field strengths higher than 10 mT. Small deviations in the shapes of the $M(H)$ under weak magnetic fields are connected with only minor structural rearrangements imposed at this moderate

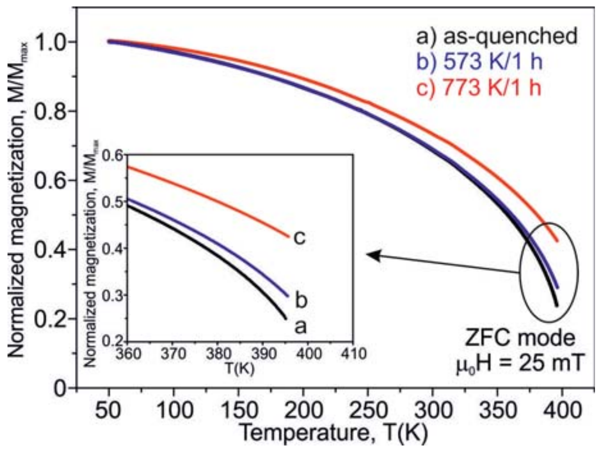

Fig. 3. Normalized magnetization curves vs. temperature for the as-quenched (a), and annealed for 1 h at 573 K (b) and 773 K (c) $Fe_{51}Co_{12}Si_{16}B_8Mo_5P_8$ alloy recorded in zero-field-cooled (ZFC) mode under an external magnetic field of 25 mT.

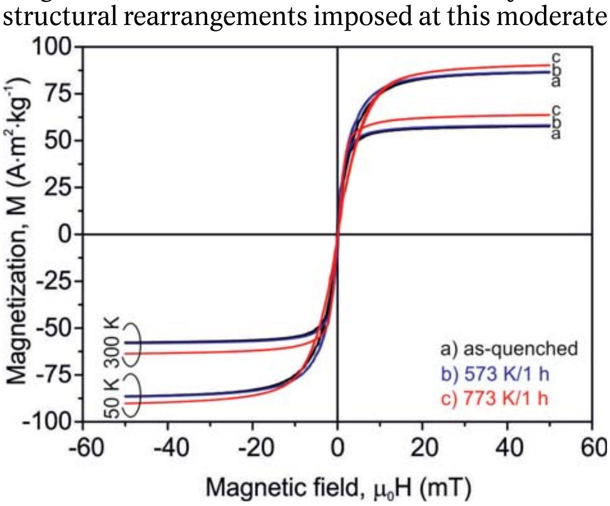

Fig. 4. Hysteresis loops for the $Fe_{51}Co_{12}Si_{16}B_8Mo_5P_8$ alloy in the as-quenched state (a) and after annealing at 573 K (b) and 773 K (c) recorded at 50 K and 300 K.

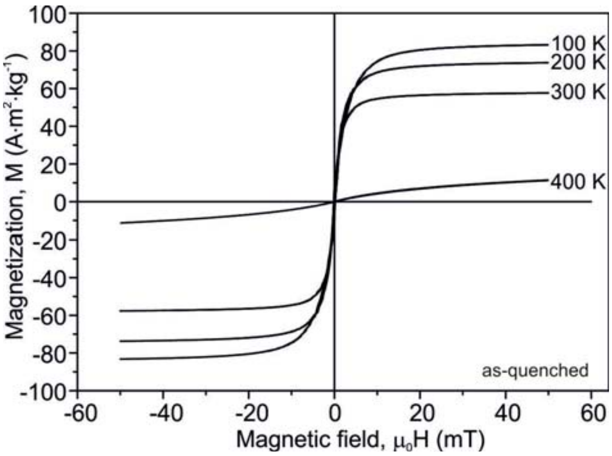

Fig. 5. Hysteresis loops of the as-quenched $Fe_{51}Co_{12}Si_{16}B_8Mo_5P_8$ alloy recorded from 100 K to 400 K with a step of 100 K.

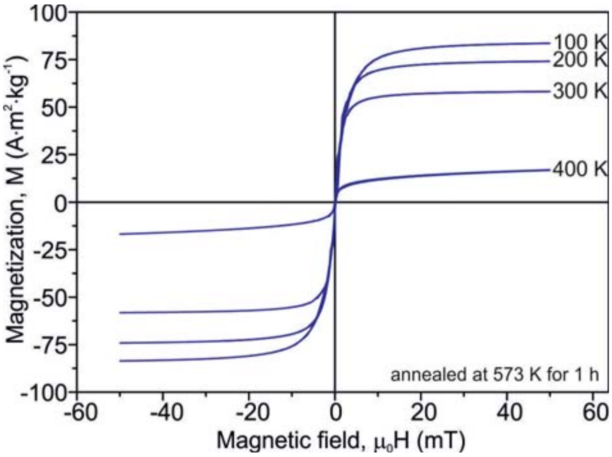

Fig. 6. Hysteresis loops of the $Fe_{51}Co_{12}Si_{16}B_8Mo_5P_8$ alloy annealed at 573 K for 1 h recorded from 100 K to 400 K with a step of 100 K.

temperature. Annealing at the higher temperature of 773 K introduces more pronounced deviations of the magnetization curves both at 50 K and 300 K in comparison with the previous ones. It can be concluded that the changes in magnetic states of the alloy are more evident because of the higher degree of modification of the short-range order after such an annealing. This is also confirmed by the results of Mössbauer spectrometry.

$M(H)$ characteristics of the as-quenched $Fe_{51}Co_{12}Si_{16}B_8Mo_5P_8$ alloy recorded at various temperatures are displayed in Fig. 5. With increasing the temperature of measurement, a decrease of magnetization is observed. The hysteresis loop acquired at 400 K exhibits almost linear behaviour. This change in its shape is caused by a vicinity of the Curie point where ferromagnetic to paramagnetic transformation takes place. Note that for the as-quenched alloy it has been determined that T_C = 403 K from the ZFC temperature dependence of normalized magnetization when $\mu_0 H$ = 25 mT.

As documented by Fig. 6, the hysteresis loop for the sample annealed at 573 K for 1 h which was recorded at 400 K looks apparently different from that of the as-quenched alloy taken at the same temperature. These changes are again connected with an increased T_C as a result of the annealing conditions. It is also worth noting that the obtained $M(H)$ characteristics presented in Figs. 5 and 6 are in good agreement with the $M(T)$ data for all investigated samples in Fig. 3.

Conclusions

A study of the relationship between microstructure and magnetic properties was presented for a novel type of $Fe_{51}Co_{12}Si_{16}B_8Mo_5P_8$ metallic glass. Its rather complex chemical composition gives rise to particular magnetic properties. The main results can be summarized as follows:

– Microstructural investigations performed by XRD and mainly by Mössbauer spectrometry for the as-quenched $Fe_{51}Co_{12}Si_{16}B_8Mo_5P_8$ alloy and after its annealing for 1 h at 573 K and 773 K show the absence of any crystallites. The whole material is completely amorphous.
– The Curie temperature of the samples increases as the temperature of annealing increases. While for the as-quenched sample T_C = 403 K, which rose to 405 K and 421 K after annealing at 573 K and 773 K, respectively.
– The observed increase in T_C is associated with modifications of a topological short-range order of the ^{57}Fe resonant nuclei as confirmed by the results of Mössbauer spectroscopy. Contribution to the microstructural modifications due to alternations in the chemical short-range order can be excluded because the average isomer shift values are practically intact by the annealing.
– The presence of magnetically distinct regions in the amorphous matrix was confirmed by distributions of hyperfine magnetic fields, $P(B)$ obtained from the deconvolution of Mössbauer spectra. They correspond to regions exhibiting diminishing magnetic interactions and to the areas where higher hyperfine magnetic fields dominate. The occurrence of both is clearly seen in $P(B)$ distributions by their bi-modal character that is well established especially after annealing the alloy at 773 K.
– For the latter sample, a more visible increase in magnetization was observed, too. Along with the aforementioned structural rearrangement this is presumably also due to stress relief and the annealing out of free volume. The last two effects might considerably contribute especially at this relatively high temperature of annealing.

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