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Investigation on crystallization and transformation processes in amorphous alloy $Fe_{81}B_{13.5}Si_{3.5}C_2$

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Amorphous $Fe_{81}B_{13.5}Si_{3.5}C_2$ ribbons produced by the melt spinning technique were used for the study of crystallization as a model system. Thermal treatment up to 1000 °C was performed in three media – vacuum, air and argon. Crystallization process was registered by thermal analysis, X-ray diffraction and Mössbauer spectroscopy. The thermal treatment above the crystallization temperature of the amorphous $Fe_{81}B_{13.5}Si_{3.5}C_2$ alloy results in formation of multiphase crystalline structure composed by α-Fe and iron borides and silicides. Mössbauer data show rearrangement of iron neighbors as a result of thermal treatment.

Keywords: $Fe_{81}B_{13.5}Si_{3.5}C_2$ ribbons, crystallization, *in situ* high temperature XRD, ^{57}Fe Mössbauer spectroscopy.

INTRODUCTION

Amorphous Fe-Si-B-C alloys are widely used in production of different types of transformers, sensors, medical devices [1, 2]. Elements like Ni, Co, Mo (critical raw materials) are added to iron-based amorphous alloys to improve their properties [3, 4]. The amorphous structure of thus obtained alloys is thermodynamically unstable. Alloys have an amorphous structure which is thermodynamically unstable. In the process, the materials undergo changes that lead to a stable transition and a change in the phase composition [5]. Formation of crystallite phases as a result of heating in such materials gives rise to loss of their advanced properties. The combination of several metalloids is intended much easier glass-formers, but complicates the crystallization process. We use amorphous $Fe_{81}B_{13.5}Si_{3.5}C_2$ ribbons produced by the melt spinning technique as a model system for the study of the crystallization process.

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EXPERIMENTAL

The materials were characterized by X-ray powder diffraction (X-ray diffractometer for investigation of thin films and nanostructures, Empyrean fitted with a high temperature attachment HTK 16N – Anton Paar, CuK_α radiation). TG-DSC-DTG analyses of samples were carried out on a Setsys Evolution 2400, SETARAM, France, combined with OmniStar mass-spectrometer operating in the temperature range 20–1000 °C at heating rate of 10 °C.min^{-1}. The operational characteristics of the TG–DSC system were: sample mass of 18.0±2.0 mg; ceramic sample pan; static air and inert (100% Ar) atmosphere. Mössbauer spectra were recorded by ^{57}Co/Rh source and Wissenschaftliche Elektronik GmbH electromechanical apparatus (Germany), operating at a constant acceleration mode. The parameters of hyperfine interactions of the obtained spectral components (isomer shift (IS), quadruple splitting (QS), hyperfine effective field (H_{eff}), line width (FWHM) and partial area of the spectra (A) were determined by CONFIT program. The errors for IS, QS, and FWHM are ±0.01 mm/s. The error

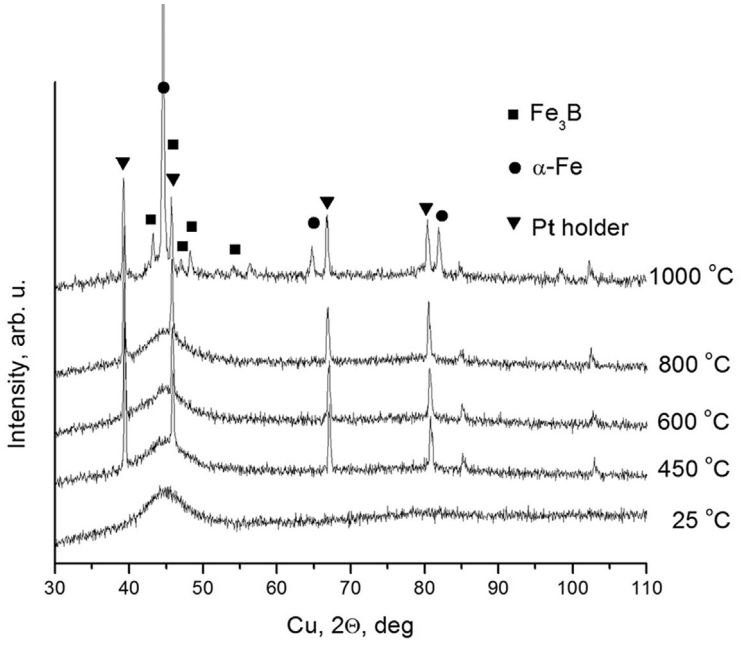

Fig. 1. X-ray diffraction pattern measured at indicated temperatures of heating ribbon.

for H_{eff} is ± 0.1T. Spectra were calibrated by α-Fe standard. The computer fitting was based on the least squares method.

RESULTS AND DISSCUSION

X-ray diffraction pattern of initial sample $Fe_{81}B_{13.5}Si_{3.5}C_2$ (Fig. 1) is characteristic of the amorphous material and consist of broad maxima without any crystalline phases registered. Mössbauer spectrum is presented in Fig. 2. It clearly shows the presence of magnetic (sextet type) components only. Calculated parameters obtained after spectrum evaluation are given in Table 1. After fitting procedure we have distinguish tree components corresponding to the different environment of Fe atoms. The three components have an isomer shift that indicates the presence of non-iron neighbors. The iron atoms in the first and second coordination sphere have many combinations of noniron neighbours and also at slightly different interatomic distances, causing the occurrence of internal magnetic fields with different values. This can be explained by the homogeneous distribution of non-iron ions in the structure of the ribbons. Registered sextet components with broad and overlapped lines are typical of amorphous alloys [4, 5].

Differential Scanning Calorimetry (DSC) was used to investigate thermal stability of studied amorphous foil in two different media – inert (100% Ar gas) and air flow (see Fig. 3). DSC curve obtained for the amorphous alloy exhibits 2 intensive exothermic peaks at 896 and 956 °C (in Air medium) and 508, 535 °C (in Ar medium) are correspond-

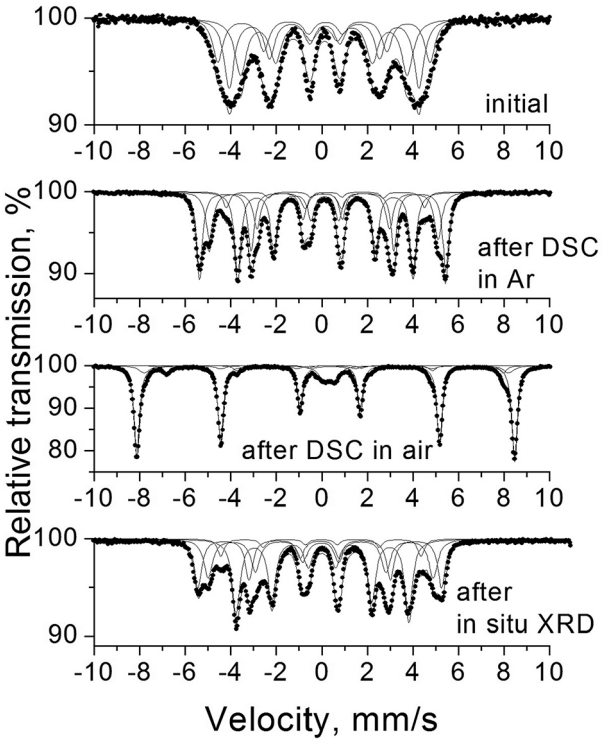

Fig. 2. Mössbauer spectra of sample $Fe_{81}B_{13.5}Si_{3.5}C_2$ after different treatment.

Table 1. Mössbauer parameters of sample $Fe_{81}B_{13.5}Si_{3.5}C_2$after different treatment

Sample	Components	IS, mm/s	QS, mm/s	H_{eff}, T	FWHM, mm/s	A, %
Initial sample	Sx1-Fe^0	0.11	0.03	28.9	0.53	26
	Sx2-Fe^0	0.10	0.01	25.9	0.61	37
	Sx3-Fe^0	0.09	0.00	22.7	0.53	37
after DSC in air	Sx1-Fe^{3+} – α-Fe_2O_3	0.36	–0.10	51.6	0.28	75
	Sx2-Fe^{3+} – $Fe_{3-x}O_4$	0.29	0.00	49.7	0.57	10
	Sx3-$Fe^{2,5}$ – $Fe_{3-x}O_4$	0.66	0.00	46.0	0.38	7
	Db-Fe^{3+}	0.38	0.48	–	0.51	8
after DSC in Ar	Sx1-Fe^0 – α-Fe	0.03	0.00	33.6	0.31	33
	Sx2-Fe^0 – α-Fe(Si,C)	0.07	0.01	31.2	0.38	25
	Sx3-Fe^0 – Fe_3B	0.16	0.01	27.0	0.32	6
	Sx4-Fe^0 – Fe_2B	0.13	0.01	23.9	0.33	36
after in situ XRD	Sx1-Fe^0 – α-Fe	0.04	0.01	33.3	0.24	25
	Sx2-Fe^0 – α-Fe(Si,C)	0.07	0.01	30.9	0.28	22
	Sx3-Fe^0 – Fe_3B	0.10	0.02	27.6	0.32	10
	Sx4-Fe^0 – Fe_2B	0.13	0.01	23.5	0.31	43

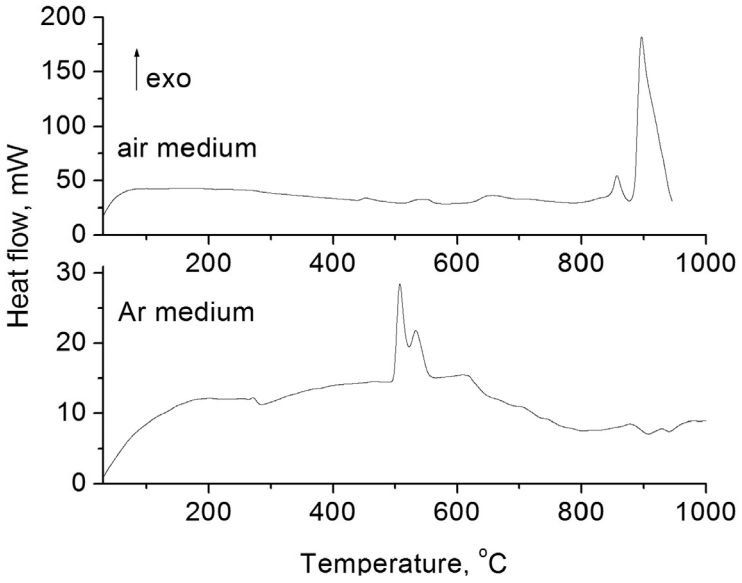

Fig. 3. DSC curves measured in the temperature range from RT to 1000 °C in different media – Ar and Air.

ing to the crystallization processes in the sample. DSC results indicate that the crystallization process occurs in two stages [6]. The different temperature maxima obtained by the thermal analysis in the two processing media could be related to different phase transitions and respectively different final phases obtained. X-ray diffraction patterns and Mössbauer spectra were measured in order to determine the phase composition of the samples after the crystallization process. Data obtained using the both methods allow the identification of the presented phases. X-ray pattern analysis has been identified the formation of α-Fe, Fe_2B, FeSi, Fe_3Si as result of thermal treatment in Ar atmosphere. Mössbauer spectrum of sample treated in Ar consist of 4 different sextets. According to the obtained Mössbauer parameters these components can be referred to the following iron-containing phases: α-Fe, α-Fe(Si,C), Fe_3B, Fe_2B [7]. On the other hand, the DSC study in air flow shows the formation of iron oxides (hematite and magnetite) and boron oxides. Metal iron phases were completely converted into oxides after DSC treatment in air. In Ar atmosphere the change from amorphous to crystalline state is associated with the formation of metallic iron and non-metallic elements included in the matrix. The similar result

was registered for *in situ* investigation of the sample in a high temperature X-ray chamber.

In situ high temperature X-Ray Diffraction analysis of studied sample was performed in vacuum up to 1000 °C. X-ray chamber allows us to investigate the crystallization process in details. Upon heating to 800 °C, there was no significant change in the XRD peaks of initial amorphous iron alloys. At a temperature of 1000 degrees, a partial transformation of the amorphous component into a crystalline form, which comprises two phases of bcc iron and iron boride tetragonal Fe_3B phase, is obtained (see Fig. 1). Mössbauer spectra analysis of sample after thermal treatment in high temperature chamber confirmed these observations. Sextet component Sx1 has parameters very similar to those of metallic iron – α-Fe. Such a component was not registered in the spectrum of initial amorphous ribbon sample. Sextet component Sx2 has parameters close to those of α-Fe, but the field values are lower and the isomer shift values are respectively higher. Sx3 and Sx4 components of the Mossbauer spectra are associated with two types of iron borides with different iron boron ratios. Lines corresponding to the Fe_3C phase were not identified, probably due to the small amount of carbon [6]. The situation is similar when the sample is heated under argon atmosphere during DSC analysis. Thus, in both cases (in inert or air media thermal treatment) the crystallization process of the amorphous $Fe_{81}B_{13.5}Si_{3.5}C_2$ alloy is associated with the formation of iron rich areas (α-Fe matrix) and the incorporated additional elements, which are improving the magnetic properties and stability of the alloy, are separating into iron-boron and iron-silicon regions. The same behavior of the investigated amorphous alloys was reported in the literature [6, 8].

CONCLUSIONS

Thermal treatment of the amorphous alloy $Fe_{81}B_{13.5}Si_{3.5}C_2$ above the crystallization temperature results in formation of multiphase crystalline structure composed by α-Fe, iron borides and silicides. These crystallization processes are responsible for the loss of primary advanced magnetic properties and for the operational stability of the studied material. Mössbauer data clearly show change of iron neighborhood and rearrangement of additive elements as a result of thermal treatment. The separation of several iron-containing components α-Fe, α-Fe(Si,C), Fe_3B, Fe_2B have been also registered. The mostly presented phase is the α-Fe, and it works as a matrix in which the other phases are embedded.

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