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The Study Of Local Structure Of Amorphous Fe-Co-B-Si-Nb Alloy By Atomic Pair Distribution Function

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Abstract. The materials from Fe-Co-B-Si-Nb system have several interesting and useful properties such as high mechanical strength, abrasive and corrosion resistance and good electrical properties useful in many applications, for example: materials for sensors and precise current transformers. The aim of the presented work was to obtain Fe-based alloy in an amorphous state and examination atoms arrangement in its structure which has an influence on material properties. Multicomponent alloy with nominal composition of $Fe_{37.44}Co_{34.56}B_{19.2}Si_{4.8}Nb_4$ was obtained by pressure die casting method in form of plate with thickness of d=1mm. The structure of rapidly solidified plate was examined by X-ray diffraction. This investigation revealed that the studied sample was amorphous. Based on experimental X-ray data the pair distribution function was calculated and discussion on possible atoms arrangement was carried out.

Introduction

Bulk metallic glasses (BMG) exhibit an interesting combination of physical, chemical, mechanical and magnetic properties. During the last ten years, intensive progress occurs and a number of applications have been suggested for these materials. In order to successfully apply BMG, it is necessary to accurately characterize their structure, thermal stability and other properties [1, 2].
Nowadays, the development of Fe-based ferromagnetics with high glass forming ability is a very modern and top research trend. These materials are interesting because of the excellent soft magnetic properties and because of the high fracture strength. That is why Fe-based BMG can be applied as functional and structural materials on parts of micromotors, radio wave clock antennas, watch gears and other applications.[3, 4]
The aim of the presented work was the manufacturing of selected Fe-based bulk metallic alloy and confirmation of an amorphous solid state using atomic pair distribution function (PDF) and thermal analysis.

Material and testing methods

Fe-based master alloy ingot with specified compositions of $Fe_{37.44}Co_{34.56}B_{19.2}Si_{4.8}Nb_{4.0}$ was prepared by induction melting of the pure Fe, Co, B, Si, Nb elements in argon atmosphere by the pressure die casting method. First mixture of pure elements was melted in corundum crucible two times for better material homogeneity. Next the master alloy was melted in a quartz crucible with an induction coil and cast into a copper mould by applying an ejection pressure. The plate of bulk metallic material with dimensions 30 x 10 x 1 mm was obtained.
To reveal amorphous state the examination of exothermic reaction (heat of crystallization) and diffraction pattern were carried out. In this article the atomic pair distribution function was applied to examine atomic arrangement more closely. Several most probable starting structural models eg. high and low temperature forms of Fe-Co-B alloys were analysed.

Thermal stability associated with glass transition temperature (T_g), onset crystallization temperature (T_x), peak crystallization temperature (T_p), reduced glass transition temperature (T_{rg}) and supercooled liquid region (ΔT_x) of the as-cast alloy were examined by differential scanning calorimetry (DSC) method using DSC822 Mettler Toledo at a constant heating rate of 40K/min. The liquidus temperature (T_l) were determined by differential thermal analysis (DTA) method using NETZSCH STA 449 F3 Jupiter thermal analyser.
X-ray diffraction experiments on Philips PW1050 X'Change diffractometer equipped with graphite monochromator, scintillation detector and Mo x-ray tube were carried out. The diffraction pattern in range 5 to 140 2θ was obtained with step 0.2 2θ and 28 s per step. The atomic pair distribution function (PDF) by RAD software was calculated [5]. Local structure information was extracted by modeling in real-space via PDF Rietveld refinement using PDFGui software [6].

Results of investigations

The DSC analysis allowed to determine T_g, ΔT_x and T_x. Figure 1 shows the DSC curve of the bulk metallic plate with a thickness of 1 mm. The exothermic peak describing crystallization process of studied bulk metallic glasses is observed. The crystallization effect of plate with thickness of 1 mm has onset crystallization temperature (T_x=879K) and peak crystallization temperature (T_p=899K). Liquidus temperature of melting $Fe_{37.44}Co_{34.56}B_{19.2}Si_{4.8}Nb_{4.0}$ alloy equal to T_l=1398K was determined [2].

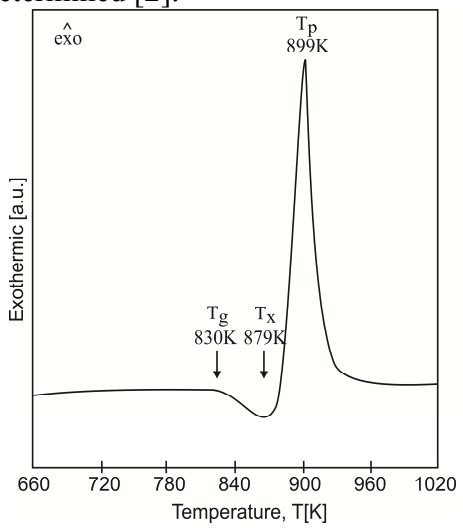

Fig. 1. DSC curve of $Fe_{37.44}Co_{34.56}B_{19.2}Si_{4.8}Nb_{4.0}$ alloy in as-cast state in form of plate with thickness of 1 mm.

The higher value of glass transition temperature and crystallization temperature may extend the application temperature region of the bulk metallic glasses as engineering materials.
The large reduce glass transition temperature means excellent glass-forming ability (GFA), when T_{rg} is larger than 0.6, the nucleation and growth of crystalline phase in supercooled liquid are strong suppressed. The width of the supercooled liquid region is an important parameter of amorphous alloys and corresponds to the stability of the supercooled liquid, too. The glass-forming ability and in the consequence of this, a production possibility of amorphous structure is higher if values of reduce glass transition temperature and supercooled liquid region are as large as possible.
The width of ΔT_x is 49 K for tested plate, indicating that the alloy possesses a sufficient stability of the supercooled liquid. Whereas, the T_{rg} is going to achieve a value of 0.6 and equals 0.5937. The calculated GFA parameters indicate that the $Fe_{37.44}Co_{34.56}B_{19.2}Si_{4.8}Nb_4$ alloy exhibits satisfactory glass-forming ability in form of studied plate. The thermal stability temperatures (T_g, T_x, T_p) and calculated elementary glass-forming ability parameters (T_{rg}, ΔT_x) of studied alloy in form of plate are listed in Table 1.

Table 1. Thermal properties and chosen glass-forming ability parameters of $Fe_{37.44}Co_{34.56}B_{19.2}Si_{4.8}Nb_4$ glassy alloy.

amorphous alloy	T_g [K]	T_x [K]	T_p [K]	T_l [K]	T_{rg} [K]	ΔT_x [K]
$Fe_{37.44}Co_{34.56}B_{19.2}Si_{4.8}Nb_4$	830	879	899	1398	0.5937	49

The raw x-ray pattern of tested sample and corresponding PDF are presented in Figures 2-3.

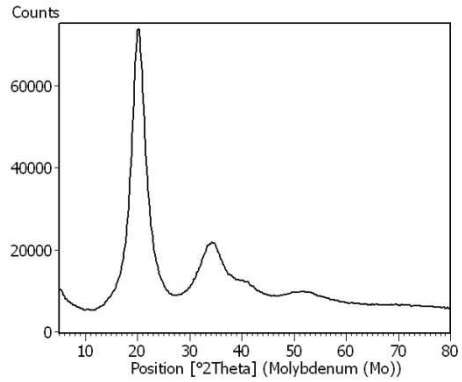

Fig. 2. X-ray pattern (a, shortened range to 80° 2Θ) of $Fe_{37.44}Co_{34.56}B_{19.2}Si_{4.8}Nb_{4.0}$ alloy in as-cast state in form of plate with thickness of 1 mm.

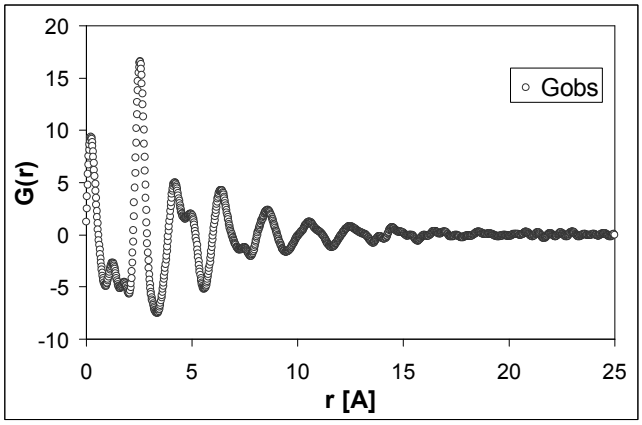

Fig. 3. PDF of $Fe_{37.44}Co_{34.56}B_{19.2}Si_{4.8}Nb_{4.0}$ alloy in as-cast state in form of plate with thickness of 1 mm.

Only diffuse scattered x-ray were observed. The amorphous sample shows short range order up to 15 Å. The PDF presented in Figure 3 shows unphysical ripple close to 0 Å.
Table 2 presents tested starting structural models of high and low temperature forms of Fe-Co-B based alloys and results of refinement eg. R_{wp} value.

During PDF Rietveld refinement to simulate structure distortions unite cell parameters, atomic coordinates, atomic displacement parameters and site occupation were fitted. Fe, Co, B, Si and Nb atoms in tested models were proportionally distributed in each site in amount fulfilling general composition $Fe_{37.44}Co_{34.56}B_{19.2}Si_{4.8}Nb_{4.0}$.

Table 2. Tested starting structural models of Fe-Co-B based alloys.

Space Group	Prototype model composition	PDF R_{wp} [%]	Reference, ICDD PDF4+
Fm-3m, #225	$Co_{0.9}Fe_{0.1}$	96.49	04-004-9067
Pm-3m, #221	FeCo	68.60	04-004-9065
$P6_3mmc$, #186	$Co_2Nb_{0.8}Si_{0.2}$	64.32	04-004-9589
Im-3m, #229	FeCo	41.60	04-004-9066
I4/mcm, #140	Fe_2B	38.51	04-004-2685
Fm-3m, #225	$Nb_2Fe_{9.8}Co_{11.2}B_6$, ($Co_{23}B_6$ and $Fe_{23}B_6$ based)	28.27	04-015-0427
I-4, #82	Fe_3B	15.07	04-001-3344
Pnma, #62	$Fe_3Si_{0.4}B_{0.6}$	11.46	04-005-3276

It was found that the atomic arrangement similar to distorted model of high temperature metastable orthorombic (Pnma) form of $Fe_3Si_{0.4}B_{0.6}$ alloy fits well to experimental data giving satisfactory results. Graphic forms of results are presented in Fig. 4. Details of starting and final model are presented in Table 3.

Fig. 4. Experimental and calculated PDF's for distorted orthorhombic model of $Fe_{37.44}Co_{34.56}B_{19.2}Si_{4.8}Nb_{4.0}$ alloy in as-cast state.

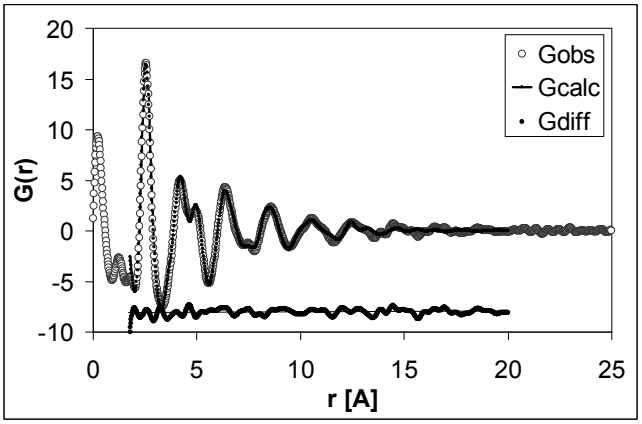

Table 3. Starting and final model of orthorombic $Fe_3Si_{0.4}B_{0.6}$ based glassy alloy.

Starting orthorombic model (Pnma), a_0: 5.41 Å b_0: 6.60 Å c_0: 4.46 Å						
Atom	Wyckoff positions	x	y	z	fractional site occupancy	atomic displacement [Å^2]
B Si	4c	0.3764	0.25	0.4426	0.6 0.4	not published
Fe	4c	0.0388	0.25	0.6578	1.0	
Fe	8d	0.1834	0.0689	0.1656	1.0	
Final orthorombic model (Pnma), a_0: 4.845 Å b_0: 7.058 Å c_0: 4.437 Å						
Atom	Wyckoff positions	x	y	z	fractional site occupancy	average atomic displacement u_{11}, u_{22}, u_{33} [Å^2]
B	4c	0.4578	0.25	0.5782	0.5	0.0342
Co Si B Nb	4c	0.0287	0.25	0.6180	0.160 0.144 0.076 0.120	0.0342
Fe Co	8d	0.2116	0.0675	0.1371	0.562 0.438	0.0342

Unit cell of final model compared to starting one is strongly distorted especially parameter a_0 and b_0 which was shortened and elongated, respectively. Parameter c_0 changed slightly. Consequently atomic coordinates changed. It is worth of notice that site occupancies in glassy alloy of both 4c Wyckoff position was reduced about half of full occupancies compared to crystalline alloy.

Summary

Exothermic reaction as well as diffraction pattern reveal that studied as-cast $Fe_{37.44}Co_{34.56}B_{19.2}Si_{4.8}Nb_4$ bulk metallic glass successfully produced by die pressure casting method was in amorphous state. The width of ΔT_x is 49 K for tested plate and T_{rg} equal 0.5937, indicating that the alloy possesses a sufficient stability of the supercooled liquid. The calculated GFA parameters show that the $Fe_{37.44}Co_{34.56}B_{19.2}Si_{4.8}Nb_4$ alloy exhibits satisfactory glass-forming ability in form of studied plate.

It was revealed by modelling in real space PDF Rietveld refinement that local structure of $Fe_{37.44}Co_{34.56}B_{19.2}Si_{4.8}Nb_4$ amorphous alloy is closed to metastable high temperature orthorhombic (Pnma) form of $(Fe,Co)_3B$ phase.

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