MICROSTRUCTURE ANALYSIS OF COFEBSINB METALLIC GLASSES WITH A VARIOUS GEOMETRY PREPARED BY PLANAR FLOW CASTING AND SUCTION CASTING METHODS

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1. Introduction

Development of bulk metallic glasses (BMGs) is progressing from point of view of their different chemical composition and therefrom resulting properties. A key role in the development of various metallic glasses including BMGs is the stabilization of the amorphous structure and suppression of crystallization in undercooled melts. Conventional metallic glasses were limited to thicknesses of less than 50 μm because they usually needed high cooling rates, up to 10^6 K/s. However, current research deals with new alloys with high glass forming ability (GFA). High GFA allows to prepare metallic glasses with larger thicknesses and variuos shape (plates, rods, wires and pipes) allowing the expansion of areas of application in practice. These alloys are multicomponent alloy systems consisting mainly of common metallic and metalloid elements with lower critical cooling rates, in bulk form and with a wide supercooled liquid region. The first synthesis of Fe and Co-based metallic glasses with wide supercooled liquid region before crystallization and with ferromagnetism at room temperature was made in 1995 and 1996 [1,2]. Since then, Fe and Co-based BMGs, which have been produced by casting methods, were studied. CoFeBSiNb BMGs show high GFA, excellent soft magnetic properties, superhigh strength, making them a promising system for industry applications [3-5]. Our effort was to assess the feasibility of preparation of amorphous CoFeBSiNb based alloys in various shapes and with different thickness. We have concentrated on the preparation of alloys in form of BMGs, bilayer and single-layer ribbons, focusing on the effect of different preparation techniques on amorphous state of various samples in as-cast state.

2. Experiment

Co-based master ingots with nominal composition $Co_{46}Fe_{20}B_{23}Si_5Nb_6$ have been prepared in a vacuum furnace Leybold-Heraeus IS01/III. The as-prepared master alloy was then purified by fluxing. The ingot was put together with small pieces of anhydrous boron oxide in a quartz crucible. The mixture was heated by induction in Argon atmosphere up to 1300 °C, temperature at which both the master alloy and the boron oxide are molten. This temperature was held for 5 minutes and then the system was cooled down to 1000 °C where boron oxide was still molten. Such thermal cycles with the duration of 10 minutes were carried out 5 times. Chemical composition of the purified master alloy, $Co_{47}Fe_{20.9}B_{21.2}Si_{4.6}Nb_{6.3}$, was determined by inductively coupled plasma spectroscopy. Ribbon 6 mm wide and 25 μm thick and bilayer 6 mm wide and 60 μm thick were prepared by subsequent planar flow casting (PFC) and modified PFC techniques [6], respectively, in air. Bulk samples in form of rods with 4 mm and 5 mm diameter were prepared by suction casting method. The ribbons and rods in form of discs and powders were investigated by X-ray diffraction (XRD) using CuKα radiation and graphite monochromator in the diffracted path with the step of 0.02 degrees (2 theta) and acquisition time 40 s/step. Microstructure of the as-

cast rods with diameters 4 and 5 mm was investigated by transmission electron microscopy (TEM) using JEOL 2000 FX. Thin foils for TEM analysis from the edge and the center of the 4 and 5 mm discs were prepared by ion-beam milling after previous mechanical grinding.

3. Results

X-ray diffraction patterns in Fig. 1 show that as-cast ribbons and bilayer prepared by PFC contain only amorphous phase. However, X-ray diffraction patterns of bulk samples prepared by suction casting method, Fig. 2, exhibit small crystalline peaks. In order to facilitate visualization and identification of eventual crystalline phases present in the amorphous matrix, rod samples were ground into powder and subjected to additional XRD analysis. Using these results it was possible to identify the major crystalline phase as fcc $(Co-Fe)_{23}B_6$ with lattice parameter a=1.060 nm and with the content of Co/Fe ~ 4, as estimated from the value of lattice parameter compared to the results in [7]. Smaller amounts of orthorhombic boride Fe_3B with lattice parameters a=0.6737 nm, b=0.4364 nm and c=0.5482 nm were observed as well. The values of lattice parameters were determined using the Bruker TOPAS software.

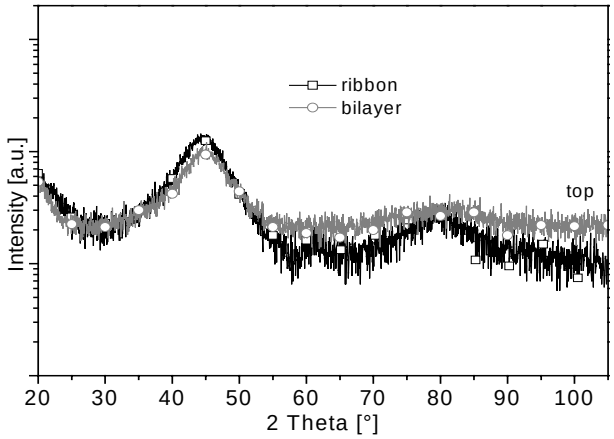

Fig. 1: *XRD patterns of the as-cast ribbons and bilayer*

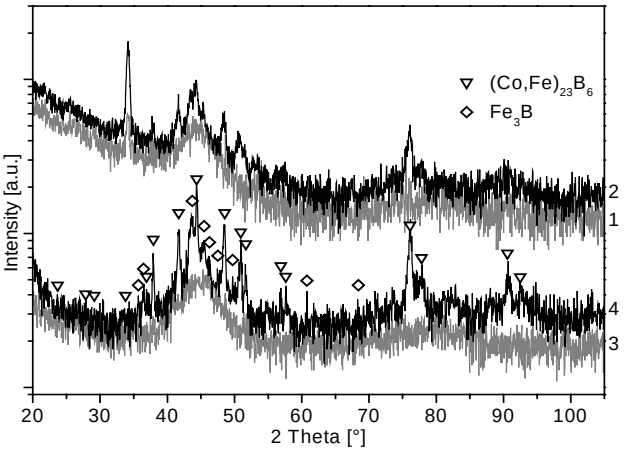

Fig. 2: *XRD patterns of the as-cast $Co_{47}Fe_{20.9}B_{21.2}Si_{4.6}Nb_{6.3}$ samples from rods with diameter 4 and 5 mm in form of disc (curves 1 and 2) and powder (curves 3 and 4), respectively*

4. Discussion

The intensity of the diffracting peaks identified in the rod with 4 mm diameter is significantly smaller than in that one with 5 mm diameter. This indicates that the average content of crystalline phases in the 4 mm rod is very low. TEM analysis of the bulk sample with 4 mm diameter shows that the edge of $Co_{47}Fe_{20.9}B_{21.2}Si_{4.6}Nb_{6.3}$ rod contains amorphous phase with no presence of crystalline particles (Fig. 3a). The center part of bulk sample (Fig. 3b) contains spherulitic-like microcrystalline phases dispersed in the amorphous matrix. The internal morphology of the crystalline phases is dendritic, suggesting that they are formed directly from the melt. This implies the emergence of BMG as in-situ composite. Rod with 5 mm diameter contains composite crystalline grains with fine structure without any amorphous matrix, in accord with the XRD trace from this sample shown in Fig. 2. Fully crystalline structure of this rod is shown in Fig. 5.

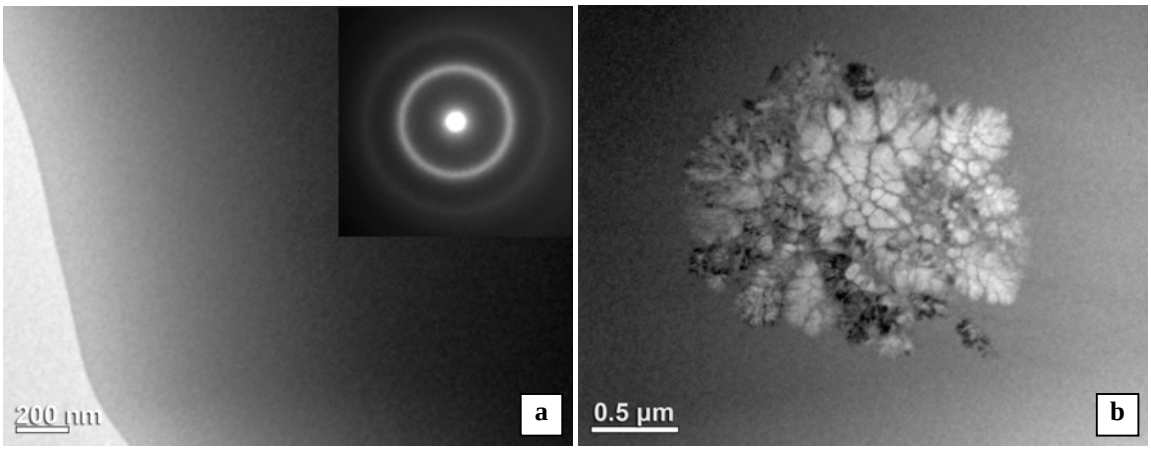

Fig. 3: *a-Bright field TEM image and corresponding selected area electron diffraction pattern obtained from the edge of the as-cast $Co_{47}Fe_{20.9}B_{21.2}Si_{4.6}Nb_{6.3}$ rod with 4 mm diameter, b-TEM micrograph of the center of $Co_{47}Fe_{20.9}B_{21.2}Si_{4.6}Nb_{6.3}$ as-cast rod with 4 mm diameter*

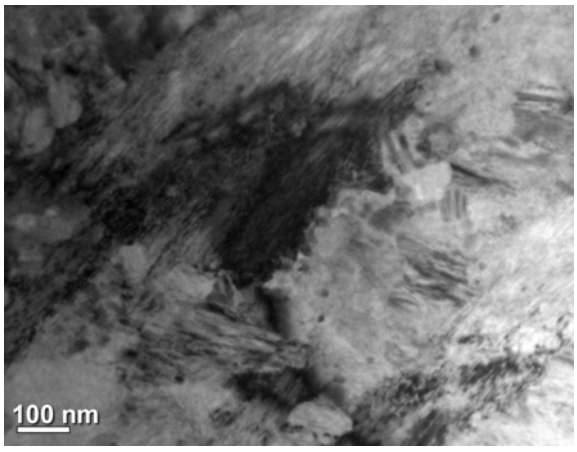

Fig. 4: *TEM micrograph of the center of $Co_{47}Fe_{20.9}B_{21.2}Si_{4.6}Nb_{6.3}$ as-cast rod with 5 mm diameter*

5. Conclusion

In this paper we have studied the structure of as-cast $Co_{47}Fe_{20.9}B_{21.2}Si_{4.6}Nb_{6.3}$ ribbon, bilayer and bulk samples in form of rods up to 5 mm diameter. Amorphous structure of the ribbons and bilayer prepared by PFC was confirmed by XRD characterization. XRD analysis of the bulk sample with 5 mm diameter indicated the presence of crystalline phases. However, XRD analysis of the bulk sample with 4 mm diameter indicated no significant crystalline peaks. From TEM analysis it was found that in-situ BMG composite was obtained in bulk sample. The edge of bulk sample with 4 mm diameter was fully amorphous, however, the center of this sample contains crystalline particles of micron sizes dispersed in the amorphous matrix. Our results suggest that the system $Co_{47}Fe_{20.9}B_{21.2}Si_{4.6}Nb_{6.3}$ has high GFA because we have prepared various amorphous materials with different shape and thickness using the techniques of suction casting, modified PFC and PFC. The critical diameter of bulk samples with chemical composition $Co_{47}Fe_{20.9}B_{21.2}Si_{4.6}Nb_{6.3}$ for emergence amorphous phase is 4 mm.

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