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Microstructural characterization of spray formed $Fe_{66}B_{30}Nb_4$ alloy

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ABSTRACT

In this paper we report the use of the spray forming process for the glass former $Fe_{66}B_{30}Nb_4$ (at.%) alloy aiming at evaluating the production of bulk amorphous deposit. The ratio between the gas volumetric flow rate and the metal mass flow rate used was 0.7, and nitrogen was used as the atomization gas. The substrate consisted of 5 disks of 80 mm diameter positioned to collect samples in the peripheral area of the atomization cone where the deposition occurs with high volume fraction of fully solidified particles. The deposits that have maximum thickness of 5 mm were characterized by X-ray diffraction, differential scanning calorimetry and scanning, and transmission electron microscopy. The thinner part of the deposit, with 0.5 mm thickness formed under the peripherical position of atomization cone and that presents a high volume fraction of the porosity (15%), is consistent with a high solid fraction of fully solidified particles during the deposition expected in this part. Nevertheless, only 8.5% of the volume fraction of this part presents amorphous structure. Considering that the $Fe_{66}B_{30}Nb_4$ (at.%) alloy with 1.5 mm was reported completely amorphous [11] and the cooling rate was maximized by the characteristic deposition discussed above, it can be concluded that the process was strongly influenced by a heterogeneous nucleation that increased the critical cooling rate to allow an amorphous phase formation.

1. Introduction

Spray forming via gas atomization involves the conversion of a liquid metal stream into various sized droplets, which are propelled away from the region of atomization [1] by the fast flowing, atomizing gas. The droplet trajectories are interrupted by a substrate which collects and solidifies the droplets into a coherent, near fully dense deposit [2]. In the spray forming process, the powder that is not incorporated in the deposit and is collected at the bottom of the atomization chamber is called overspray. Since the cooling rate experienced by the atomized particles depend on their size, both amorphous and well-developed microstructures can be found in an atomization batch if an amorphizable alloy is processed. The two different examples reported illustrate clearly this situation. The first shows that the $Al_{85}Y_8Ni_5Co_2$ billet processed using high ratio between the gas volume flow rate and the metal mass flow rate (G/M = 10.0 m^3/kg) contained about 76% volume fraction of the amorphous phase [3]. Another processing using low G/M ratio (0.25 m^3/kg) of the $Fe_{83}Nb_4Zr_1Ti_1B_9Cu_2$ (at.%) alloy resulted in a fully crystalline deposit with irregular porosity due to the high fraction of solid particles that hit the substrate when the deposition stage was obtained [4]. The production of fully or partially amorphous deposits through spray forming requires very high gas-to-metal ratio that guarantee a deposition with high volume fraction of fully rapidly solidified particles, and it also requires a high glass forming ability (GFA) of the alloy composition. Bulk glassy alloys have been produced by copper mold casting in the maximum amorphous thickness up to 4 mm for the Fe–Co–Ni–B–Si–Nb system [5], 5 mm for the Fe–Co–B–Si–Nb [6], 12 mm for $(Fe–Co–Mo–Mn–C–B)_{98.5}Y_{1.5}$ [7] and 1.5 mm for the $Fe_{66}B_{30}Nb_4$ (wt.%) [8]. The $Fe_{66}B_{30}Nb_4$ alloy, with relatively low critical cooling rate, is one of the few ternary Fe-based glass former alloys with relative high glass-forming ability combined with good mechanical properties, which is a very interesting composition for bulk glassy material. The objective of this work is to investigate the amorphous phase formation in the deposit obtained through spray forming of the glass former $Fe_{66}B_{30}Nb_4$ alloy.

2. Experimental procedure

The $Fe_{66}B_{30}Nb_4$ (wt.%) alloy was processed by the spray forming process using nitrogen as the atomization gas. Elements of high purity (Fe–99.97%, B–99.5% and Nb–99.8%) were used. A superheat of 150 K over the melting temperature (1565 K) was used to homogenize the alloy before pouring. The molten alloy was poured into a nozzle bore of 6 mm diameter in the bottom of a tundish and then atomized by nitrogen (N_2) gas with the pressure of 1.0 MPa. The flight distance was of 700 mm, and the material was deposited onto a 5 steel substrate formed by a central and

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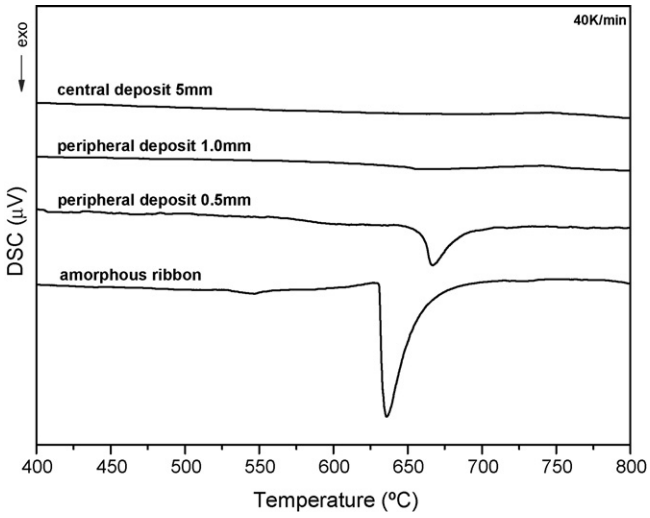

Fig. 1. DSC curves for the different thick parts of the deposit (5 mm, 1 mm and 0.5 mm).

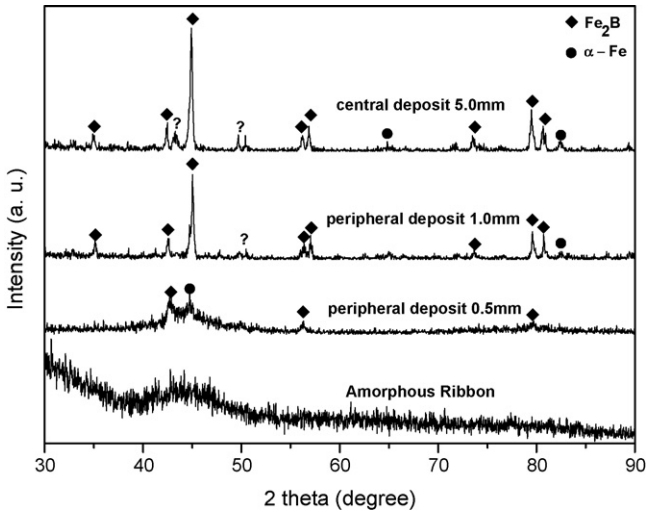

Fig. 2. X-ray diffraction patterns of the amorphous ribbon and from different thick parts of the deposit (5 mm, 1 mm and 0.5 mm).

4 peripheral substrates with 80 mm diameter each. The collection of samples from the peripheral area of the atomization cone is due to occurrence of the deposition in this area with high volume fraction of fully solidified particles. The gas-to-metal ratio, ratio between the gas mass flow rate (0.063 kg/s) and the metal mass flow rate (0.09 kg/s) used was G/M = 0.7. The thickness of the deposit formed was 5 mm on the central substrate and 1 mm and 0.5 mm peripheral deposits were obtained. The deposits were characterized using an X-ray diffractometer (XRD) Siemens D5000 with Kα-Cu radiation, differential scanning calorimetry (DSC) DSC 404 Netzsch, and scanning electron microscopy (SEM) Philips FEG 30 kV equipped with energy dispersive spectroscopy (EDS) microanalysis capabilities. The porosity in the deposit was evaluated through quantitative analysis of SEM micrographs using the Software Quantimet/Leizt.

3. Results and discussion

Thermograms for the different thickness deposit are shown in Fig. 1. The exothermic crystallization reaction observed only in the deposits with 0.5 mm thickness indicates an amorphous phase presence by crystallization reaction through a single exothermic event at the crystallization temperature T_x of 659 °C and the glass transition temperature of T_g = 635 °C. Considering the crystallization energy of a fully amorphous ribbon with the same composition, the volume fraction amount of the amorphous phase in this deposit was estimated as 8.5%.

The diffractogram from the thinner part of deposit (Fig. 1) consists of the intermetallic phase Fe_2B and the diffusing peak, which is around $2\theta = 45^\circ$, indicating that the deposit is partially amorphous in agreement with the thermograms. The 1 mm and 5 mm thick part indicate a fully crystalline microstructure, in agreement with the thermograms, with α-Fe and Fe_2B intermetallic phases (Fig. 2).

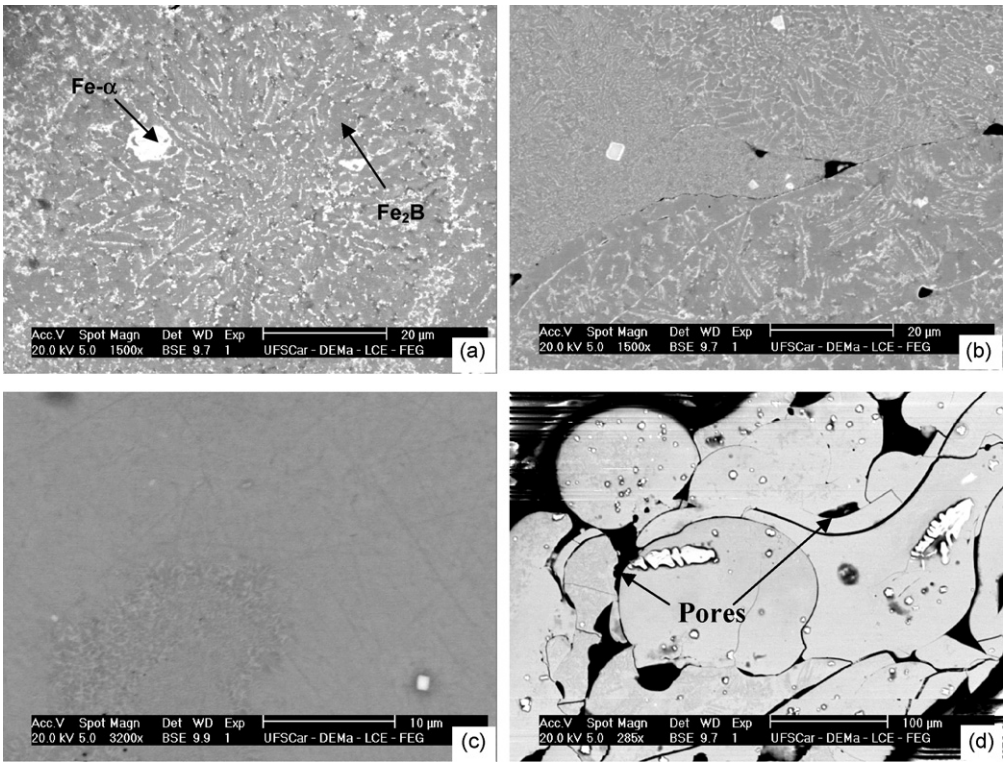

Fig. 3. SEM micrographs, backscattered electron contrast from different thick part of the deposit (a) 4 mm, (b) 1 mm, (c) 0,5 mm and (d) porosity in 0.5 mm thick part.

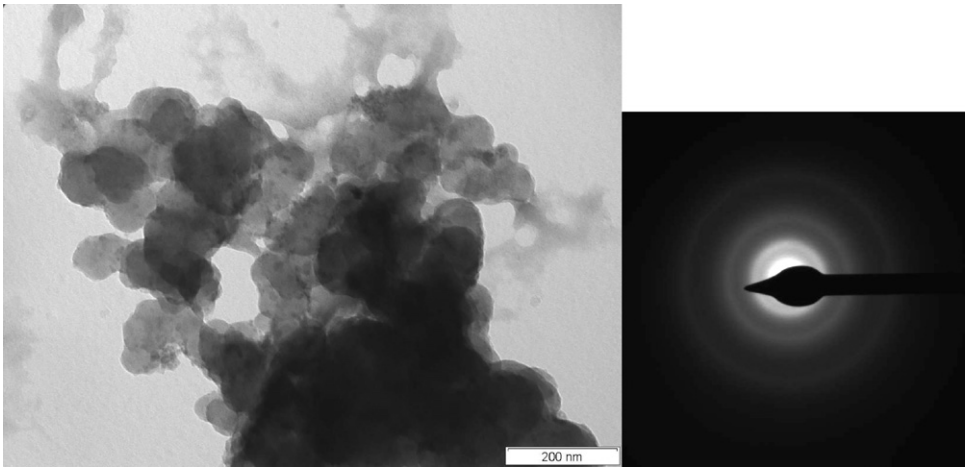

Fig. 4. TEM analysis, bright field image and selected area diffraction pattern of the thinner part of the deposit (0.5 mm thick) with typical homogeneous microstructure (the gray tones are related with the thickness of the sample) and broad ring pattern of amorphous structures.

The SEM micrographs of the deposits (Fig. 3) showed a microstructure that confirms a crystalline structure indicating no amorphous phase formation. The irregular morphology of the porosity (15%) (Fig. 3d) indicates, as expected, that the deposition in the peripheral area of substrates occurred with high volume fraction of fully solidified particles. The formation of an amorphous phase in the thinner part of the deposit, although in small amount, is confirmed by TEM analysis and by the corresponding selected area diffraction pattern (SADP) showing a typical amorphous ring pattern in the microstructure of Fig. 4.

4. Conclusions

The thinner part of the deposit, with 0.5 mm thickness, formed under the peripherical position of the atomization cone that presents a high volume fraction of the porosity (15%), is consistent with a high solid fraction of fully solidified particles during the deposition expected in this part. Nevertheless, only 8.5% of the volume fraction of this part presents an amorphous structure. Considering that the $Fe_{66}B_{30}Nb_4$ (at.%) alloy with 1.5 mm was reported as being completely amorphous [8] and that the cooling rate was maximized by the characteristic deposition discussed above, it can be concluded that the process was strongly influenced by heterogeneous nucleation that increased the critical cooling rate for an amorphous phase formation.

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