Journal of Alloys and Compounds 509S (2011) S148–S154

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

Amorphous phase formation by spray forming of alloys $[(Fe_{0.6}Co_{0.4})_{0.75}B_{0.2}Si_{0.05}]_{96}Nb_4$ and $Fe_{66}B_{30}Nb_4$ modified with Ti

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ARTICLE INFO

Article history:
Received 23 July 2010
Received in revised form 28 January 2011
Accepted 5 February 2011
Available online 2 March 2011

Keywords:
Metallic glasses
Iron based alloys
Spray forming
Amorphous phase

ABSTRACT

This paper describes results obtained by spray forming three iron-based alloys, namely $[(Fe_{0.6}Co_{0.4})_{0.75}B_{0.2}Si_{0.05}]_{96}Nb_4$, $Fe_{65}B_{30}Nb_4Ti_1$ and $Fe_{63}B_{29}Nb_4Ti_4$, whose compositions derive from rapid solidification studies, in an attempt to obtain metallic glasses. The $[(Fe_{0.6}Co_{0.4})_{0.75}B_{0.2}Si_{0.05}]_{96}Nb_4$ alloy presented higher glass-forming ability and showed a high fraction of amorphous phase formation up to a depth of 4 mm in the deposit. On the other hand, the spray formed deposits of the $Fe_{65}B_{30}Nb_4Ti_1$ and $Fe_{63}B_{29}Nb_4Ti_4$ alloys showed fully crystalline microstructure, despite the fact that the melt spun ribbons were fully amorphous.

1. Introduction

Spray forming (SF) can be classified as a two-stage manufacturing process, where the solidification begins during the flight of the particles, which can be considered a rapid solidification step (10^3–10^5 K/s), and finishes during the building of the preform or deposit, where the remaining liquid droplets solidify under considerable slower cooling rates (10^1–10^2 K/s) [1]. SF has been successfully applied in processing both commercial and advanced alloys aiming at: the extension of the solid solubility, fine dispersion of second phase particles, low porosity, low segregation level, and finally metastable or even amorphous phases. Nowadays, amorphizable material studies are focused on compositions and processes leading to thicker pieces of bulk metallic glasses (BMGs). For BMG alloys developed in the last decade spray forming may provide the suitable cooling rates associated to a mass production and a near net shape process route.

The $[(Fe_{0.6}Co_{0.4})_{0.75}B_{0.2}Si_{0.05}]_{96}Nb_4$ alloy was proposed in 2004 by Inoue et al. [2] and the authors reported super-high yield strength above 4000 MPa. Rods of fully glassy material were produced with 4 mm diameter by the ejection casting method in a copper mould and the alloy presented $T_g = 552\,^{\circ}C$, $T_x = 602\,^{\circ}C$ ($(T_x = 50\,^{\circ}C$), denoting a very high glass-forming ability with critical cooling rates in the range of 10^1–10^2 K/s.

Bulk glassy $Fe_{66}B_{30}Nb_4$ has been produced by copper mould casting with maximum amorphous thickness up to 1.5–2.0 mm as reported by Stoica et al. [3]. In order to get this result the authors purified the master alloy by fluxing it with B_2O_3 during a long period of time. Despite its relatively low glass forming ability to be considered a BMG, this is one of the few ternary Fe-based glass former alloys with good mechanical properties, being a very interesting composition for bulk glassy material due to the low cost of the constituent elements. In addition, this alloy presents a high hardness even in the crystalline state, reaching up to 804 $HV_{0.2}$, and can be considered as a candidate for applications where the wear resistance is of importance. Attempts to produce this ternary composition in an amorphous state by spray forming using commercial raw materials led to a maximum amorphous thickness of 0.5 mm, as reported by Bonavina et al. [4]. The affinity between B and Ti suggests a high possibility of titanium boride formation by adding Ti to $Fe_{66}B_{30}Nb_4$ alloy, a process that can result in the precipitation of hard borides, still improving the hardness of these compositions.

The main objective of this paper is to evaluate the potential of spray forming to produce metastable or amorphous phases with these iron based alloys that display very distinct abilities for forming metallic glasses, namely $[(Fe_{0.6}Co_{0.4})_{0.75}B_{0.2}Si_{0.05}]_{96}Nb_4$ and $Fe_{66}B_{30}Nb_4$. In addition, even considering the possibility to decrease the glass forming ability, the later alloy was modified

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doi:10.1016/j.jallcom.2011.02.026

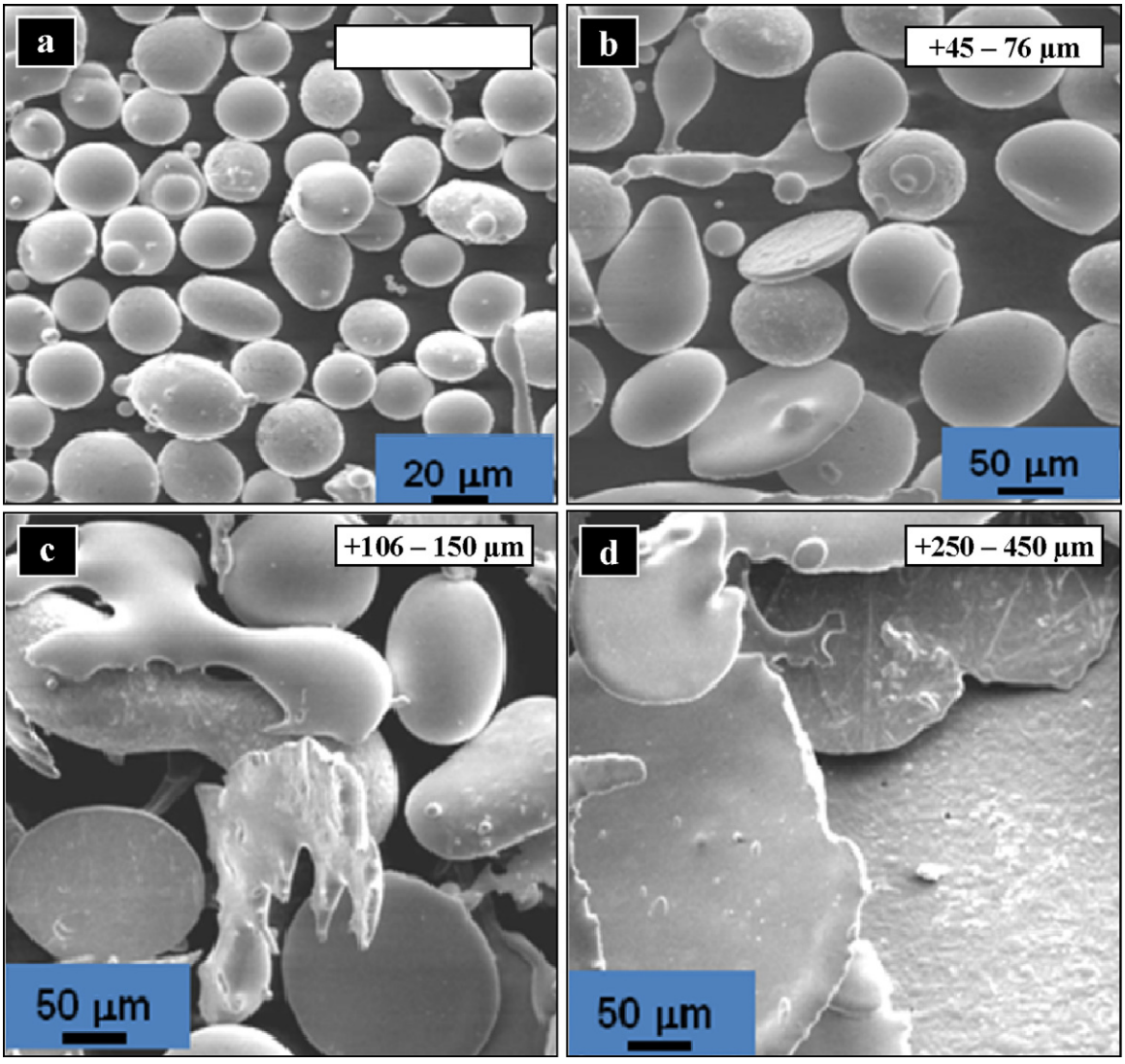

Fig. 1. SEM of the overspray powder obtained in experiment SF0. All particles size range (a) +25 to −45 μm to (d) +250 to −450 μm showed a featureless aspect, indicating amorphous phase formation even for the coarser size ranges and confirming the high glass-forming ability of SF0 composition. Note the deformation of the particles of coarser size ranges and rounded shape of the finer ones.

with the addition of titanium resulting in two distinct alloys: $Fe_{65}B_{30}Nb_4Ti_1$ and $Fe_{63}B_{29}Nb_4Ti_4$, as an attempt to obtain deposits with elevated hardness values, aiming at wear resistance applications.

2. Methods

Three alloys were processed by melt spinning and spray forming: $[(Fe_{0.6}Co_{0.4})_{0.75}B_{0.2}Si_{0.05}]_{96}Nb_4$, $Fe_{65}B_{30}Nb_4Ti_1$ and $Fe_{63}B_{29}Nb_4Ti_4$ alloys (at%). The molten alloys were poured into a tundish which had a quartz nozzle with a bore of 6 mm diameter in the bottom and then atomized by nitrogen (N_2) with the pressure of 1.0 MPa and flow rate of 3.84 kg/min. A plain carbon steel disk with a diameter of 305 mm was used as a substrate for the atomized droplets in order to form the deposit. The following elements of high purity were used for the alloys preparation: Fe – 99.98%, B – 99.7%, Nb – 99.98% and Ti – 99.99%.

The $[(Fe_{0.6}Co_{0.4})_{0.75}B_{0.2}Si_{0.05}]_{96}Nb_4$ alloy was spray formed at 1421 °C at a G/M (gas to metal ratio) of 0.94 m^3/kg and a flight distance of 425 mm; this experiment is denominated hereinafter as SF0. The overspray powders (materials that were not incorporated in the deposit) were sieved and separated in the size ranges of 20–30, 45–76, 106–150 and 250–450 μm.

The high boron alloys $Fe_{63}B_{29}Nb_4Ti_4$ (used in experiment denominated hereinafter as SF1) and $Fe_{65}B_{30}Nb_4Ti_1$ (used in experiment denominated hereinafter as SF2) are modifications of a known glass-former alloy, $Fe_{66}B_{30}Nb_4$. The processing parameters of SF1 were selected to improve the cooling rate in order to investigate the formation of metastable phases due to its higher Ti content. On the other hand, SF2 was intended to produce a thicker and slowly cooled deposit with higher yield (efficiency from feedstock to final product conversion) and the presence of stable phases. Flight distances (distance between nozzle to substrate) and pouring temperatures were: 700 mm; 1600 °C for SF1 (cold spray condition, higher cooling rates) and 500 mm; 1700 °C for SF2 (hot spray condition, lower cooling rates), respectively. Melt spun ribbons were produced in order to determine the thermal properties of the alloys studied. For the melt spinning a similar procedure was described in a previous work [1], except for the ejection temperature which was 1650 °C.

The microstructures obtained were characterized by optical microscopy, X-ray diffraction (XRD) in a Siemens D5000 using Cu-Kα radiation (with a filter to avoid fluorescence due to iron), Scanning Electron Microscopy (SEM), Philips XL-30, FEG coupled with Energy Dispersive Spectroscopy (EDS), Differential Scanning Calorimetry (DSC), DSC 404 Netzsch, and bulk chemical analysis by Inductively Coupled Plasma Atomic Energy Spectroscopy – ICP-AES and N by thermal conductivity. Porosity was measured using Archimedes method. Vickers hardness measurements were made at low loads ranging from 0.2 and 5 kgf. A number of thirty high load hardness measurements were made onto machined and polished surfaces of SF2 samples using a load of 30 kgf. Test loads were maintained for 20 s.

3. Results and discussion

The chemical analysis of the deposits by ICP-AES and EDS/SEM showed that the compositions for SF0 ($[(Fe_{0.6}Co_{0.4})_{0.75}B_{0.2}Si_{0.05}]_{96}Nb_4$), SF1($Fe_{63}B_{29}Nb_4Ti_4$) and SF2 ($Fe_{65}B_{30}Nb_4Ti_1$) experiments are close to the desired nominal compositions, although it was not possible to confirm through