Journal of Alloys and Compounds xxx (2016) 1–6

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

On the ternary eutectic reaction in the $Fe_{60}Cr_8Nb_8B_{24}$ quaternary alloy

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ARTICLE INFO

Article history:
Received 30 July 2016
Received in revised form
1 November 2016
Accepted 21 November 2016
Available online xxx

Keywords:
Phase evolution
Crystallography
Thermodynamic calculation
Ternary eutectic
Convergent beam electron diffraction

ABSTRACT

Recently a $Fe_{60}Cr_8Nb_8B_{24}$ quaternary amorphous/nanocrystalline composite coating has been successfully synthesized by high velocity oxygen fuel in our group. The composite coating shows excellent wear and corrosion resistance. In order to understand the phase evolution of the quaternary alloy during cooling and interpret its good glass forming ability, the stable phases in the as-melted ingot of the same composition were studied by X-Ray diffraction, scanning electron microscopy, transmission electron microscopy and differential scanning calorimetry. Thermodynamic calculation was performed based on a database compiled from literature. The calculated results show good agreement with the microstructural observation. It was found that $Fe_{60}Cr_8Nb_8B_{24}$ alloy lies very close to the eutectic point of the system, which is related to its high glass forming ability. The thermodynamic calculation could provide insightful understanding and guidance for the future amorphous composition designing in Fe-Cr-Nb-B quaternary system.

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1. Introduction

Due to its relatively small critical size, metallic glass might be difficult to be used as bulk structural material [1]. However, the size limitation is not a problem for protective coating. The Fe-based amorphous coating has received increasing attention due to its low cost and good glass forming ability [2–8]. Moreover, because of its excellent corrosion and wear resistance [9–14], the Fe-based amorphous coating could find its application in oil and petroleum industry. The Fe-Nb-B ternary phase diagram shows that the ternary system contains many high melting temperature borides [15,16]. High melting temperature indicates strong bonding between component elements, which could be related to high hardness of the material. Particularly, in Nb-B binary system, the high melting temperature borides possess very high hardness, e.g. NbB_2 HV 2600, Nb_3B_4 HV 2290, NbB HV 2200 and Nb_3B_2 HV 1720 [17]. These hard borides are very interesting for the enhancement of wear resistance. In addition, it has been shown by our previous research that addition of Cr in the aforementioned Fe-Nb-B ternary system can improve its corrosion resistance in NaCl, acid and alkaline solutions [9,10].

A $Fe_{60}Cr_8Nb_8B_{24}$ quaternary alloy was recently designed and successfully vitrified by melt spinning. The ribbon shows excellent glass forming ability and possesses a supercooled liquid region as large as 60 K [3]. Its onset glass transition temperature and crystallization temperature is as high as 615 °C and 675 °C, respectively. The coating of the same composition was fabricated by various techniques, including spray deposition [3], low velocity oxygen fuel (LVOF) [3] and high velocity oxygen fuel (HVOF) [18] in our group. It was found that the HVOF coating exhibits largest volume fraction of amorphous phase (up to 66%) and shows excellent wear and corrosion resistance due to the amorphous/nanocrystalline composite structure [18].

In contrary to the above fruitful results, the reason why $Fe_{60}Cr_8Nb_8B_{24}$ quaternary alloy is a good glass former remains unknown. It has been shown that it is easier to obtain metallic glass if the composition locates close to the eutectic point of the alloy system, where the liquid could be kept as low temperature as possible and facilitates the formation of glass [1,19].

In order to find out the possible eutectic transformation, the phase diagram of the current system is required. However, there is not quaternary phase diagram reported for Fe-Cr-Nb-B in the literature. In the present study, we assume that small portion of Cr addition could be considered the same as Fe, and the quaternary system could be reduced to ternary Fe-Nb-B, for which a few phase diagrams have been reported. The assumption is based on the fact that Fe and Cr form solid solution at elevated temperature as shown in the Fe-Cr binary phase diagram [20], exhibit similar atomic size and similar chemical properties [21]. In fact, the small addition of Cr in the alloy is expected to enhance its corrosion resistance [10],

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http://dx.doi.org/10.1016/j.jallcom.2016.11.293
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Please cite this article in press as: Y. Guo, et al., On the ternary eutectic reaction in the $Fe_{60}Cr_8Nb_8B_{24}$ quaternary alloy, Journal of Alloys and Compounds (2016), http://dx.doi.org/10.1016/j.jallcom.2016.11.293

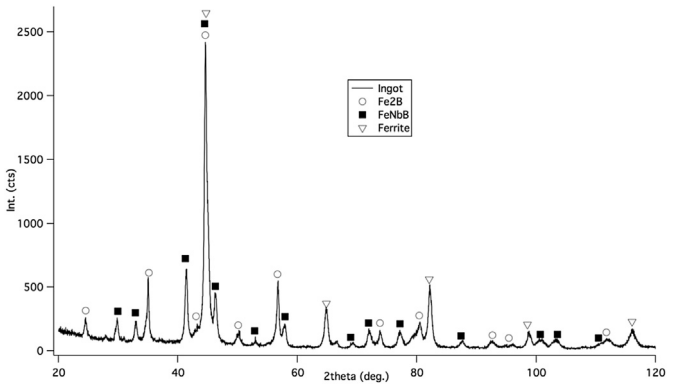

Fig. 1. The XRD pattern of as-melted $Fe_{60}Cr_8Nb_8B_{24}$ alloy.

both for its effect in the matrix and for its likely presence in the borides.

Regarding the phase diagram for Fe-Nb-B system, there is only one experimentally assessed in the literature, that is, the ternary isotherm reported by Kuz'ma in solid region at 800 °C [15,16]. However, it is not suitable for amorphous alloy development, because it does not provide information for liquid state. Recently, Ohtani et al. reported thermodynamic assessment for Fe-Nb-B ternary system at all temperature range [22], which could be used for the thermodynamic calculation of Fe-Cr-Nb-B alloys with small Cr content under our previous assumption.

In the present work, the phase evolution of $Fe_{60}Cr_8Nb_8B_{24}$ quaternary alloy was studied by combination of microstructural observation and thermodynamic calculation. The calculated results were compared to experimental results and show very good agreement. The knowledge of phase formation of $Fe_{60}Cr_8Nb_8B_{24}$ alloy reported here could provide guidance for the future alloy development and coating synthesis in Fe-Cr-Nb-B quaternary system.

2. Experimental

The ingot of the composition $Fe_{60}Cr_8Nb_8B_{24}$ was prepared by arc-melting in a protective Ar atmosphere. The raw Fe/Cr/Nb/B element is of the purity of 99.98%, >99%, 99.8% and 99.5%, respectively. The ingot button was melted for six times to achieve chemical homogeneity. The button was flipped over after each melting, and no weight loss was monitored during melting. The as-melted ingot was cut by slow speed diamond saw, followed by SiC paper. grinding. The slice was polished by Al_2O_3 suspension before chemical etching. The solution for chemical etching is composed of 5 ml HCl, 1.5 ml HNO_3, 43.5 ml ethanol and 5 g $FeCl_3$. The chemical etching was performed to remove ferrite and better reveal the morphology of different phases. The etched sample was observed by scanning electron microscopy (SEM) in back scattered electron (BSE) mode via a FEI Inspect S50 operated at 25 kV. The SEM is coupled with an energy dispersive X-ray spectroscopy (EDX) detector. The transmission electron microscopy (TEM) foil was prepared by ion milling with Gatan PIPS 691. The thinning begins with an energy of 5 keV at ±5°, followed by 2 keV at ±2°. The TEM observation was conducted with a FEI Tecnai LaB6 operated at 200 kV. The X-ray diffraction (XRD) was performed by Rigaku Geigerflex with graphite monochromator under Cu kα radiation. Because of intensive fluorescence of Fe under Cu kα radiation, long

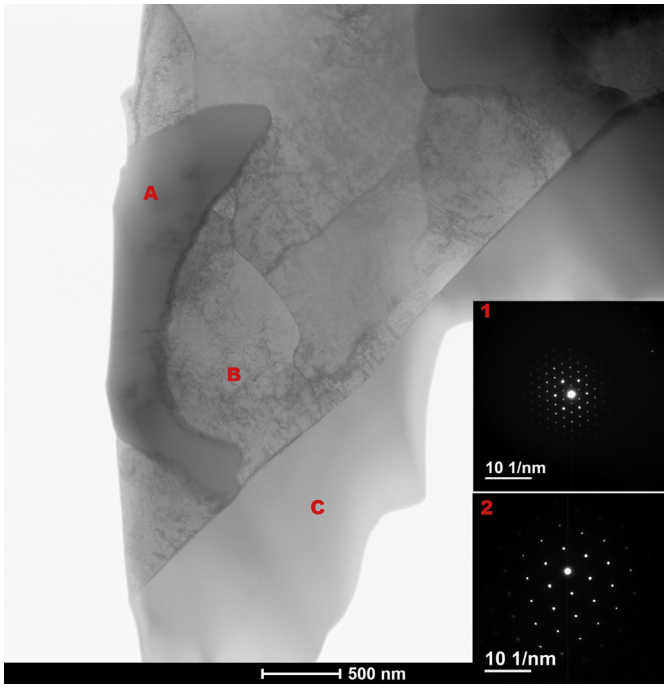

Fig. 3. The BF image of as-melted alloy. Three different regions (A/B/C) are marked, which corresponds to FeNbB, ferrite and Fe_2B, respectively. Inset 1 shows the SAED patterns of FeNbB, zone axis [001], and inset 2 shows that of ferrite, zone axis [111].

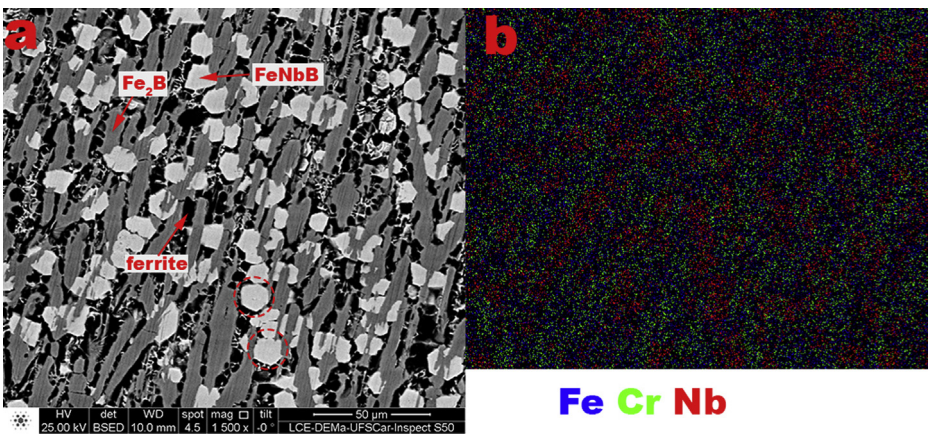

Fig. 2. (a): The BSE image of as-melted $Fe_{60}Cr_8Nb_8B_{24}$ alloy after chemical etching. (b): The elemental mapping of Fe/Cr/Nb in the same region.

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