The microstructure of melt-spun alloys with liquid miscibility gap

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Abstract. Effect of the melt ejection temperature on the microstructures of \((\text{Fe}_{x}\text{Cu}_{1-x})_{62}\text{Si}_{13}\text{B}_{9}\text{Al}_{8}\text{Ni}_{6}\text{Y}_{2}\) \((x=0.48, 0.60 \text{ and } 0.71)\) alloys was investigated. Rapid cooling of the examined alloys from the temperature range conventional to single-phase amorphous alloys brought about a non-uniform microstructure due to a liquid/liquid phase separation prior to cooling. The systems with a miscibility gap need to be heated over a critical temperature where homogeneous liquid exists. Microstructures of the ribbons melt spun from the homogeneous melt region are characterized by presence of the spherical precipitates distributed in homogeneous matrix. Both, precipitates and matrix, can constitute either the Fe-rich or the Cu-rich phases depending on the alloy composition. The studies confirmed amorphous nature of the Fe-rich phases, both matrix and precipitates whereas the Cu-rich liquid crystallized due to lower glass forming ability.

1. Introduction

Low ductility of metallic glasses could be improved by formation of composite materials consisting crystalline phases dispersed in the amorphous matrix. A presence of ductile phase may disrupt shear band propagation and thus improve alloy ductility. In 2004 Kündig et al. [1] for the first time showed two-phase amorphous structure in metallic system including one pair of elements with high positive heat of mixing (La-Zr) while negative heat of mixing of the other elements to both of them (La-Zr-Al-Cu-Ni alloy). This work initiated research of systems consisting liquid miscibility gap. Several two-phase metallic glasses were reported up to date: Y-Ti-Al-Co [2], Ni-Nb-Y [3], Ag-Cu-Zr [4], and Cu-Zr-Al-Y [5].

The Fe-Cu phase diagram does not contain a liquid miscibility gap but a heat of mixing for the Fe-Cu liquid binary system was estimated as high as +13 kJ/mol [6]. Moreover Turchanin et al. [7] and Dong et al. [8] proved that undercooling of the liquid below the metastable binodal line leads to liquid phase separation into the Fe-rich and the Cu-rich melts. This make the Fe-Cu-based systems as good candidate for investigation of the phase separation in metallic glasses. In order to improve glass forming ability (GFA) of both melts Si, B, Cu, Al, Ni and Y were selected. Since Fe-Si-B alloys

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are known as relatively good glass formers, silicon and boron are expected to improve glass forming ability of the Fe-rich melt. Aluminium and yttrium were selected to enhance glass forming ability of the Cu-rich melt due to the strong negative heat of mixing with this liquid [6]. Since nickel reveals similar heat of mixing to both Fe and Cu [6], it is expected to enhance GFA in both melts as it must be redistributed between forming phases.

This work aimed to investigate effect of the melt ejection temperature on microstructure of the Fe-Cu-based alloys with the liquid miscibility gap. In order to study effect of the Fe and Cu content on microstructure of the melt-spun ribbons, three compositions were investigated: \((\text{Fe}_{x}\text{Cu}_{1-x})_{62}\text{Si}_{13}\text{B}_{9}\text{Al}_{8}\text{Ni}_{6}\text{Y}_{2}\) \((x = 0.48, 0.60 \text{ and } 0.71)\).

2. Experimental procedure

\((\text{Fe}_{x}\text{Cu}_{1-x})_{62}\text{Si}_{13}\text{B}_{9}\text{Al}_{8}\text{Ni}_{6}\text{Y}_{2}\) \((x = 0.48, 0.60 \text{ and } 0.71)\) alloys ingots were prepared by arc melting a mixture of high purity elements (99.9 % or higher) under titanium gettered argon atmosphere. Rapidly solidified ribbons were prepared by single roller melt spinning facility equipped with infrared radiation pyrometer under an argon atmosphere at constant surface velocity of 40 m/s and a gas pressure of 50 kPa.

Two melt ejection temperatures were chosen in order to study its effect on the microstructure of resultant ribbons. First, the ribbons were melt-spun in a conventional manner. Typical melt ejection temperature is about 50 K above liquidus. Those temperatures were read as high as 1230°C, 1300°C and 1330°C for \((\text{Fe}_{x}\text{Cu}_{1-x})_{62}\text{Si}_{13}\text{B}_{9}\text{Al}_{8}\text{Ni}_{6}\text{Y}_{2}\) \((x = 0.48, 0.60 \text{ and } 0.71)\) alloys, respectively. Then, each alloy (ingot) was melt-spun from temperature 100°C above the first one.

X-ray diffraction (XRD) studies were carried out using TuR M62 device equipped with goniometer HZG4 (Co-K\(\alpha\) radiation). The microstructures of ribbons were studied by means of light microscopy (LM), scanning electron microscopy (SEM) equipped with energy dispersive X-ray (EDX) spectrometer and transmission electron microscopy (TEM, JEM 200CX). Differential scanning calorimetry (Perkin-Elmer DSC7) allowed observations of thermal effects during heating the samples. The samples were heated up to 727°C applying a heating rate of 40 K/min.

3. Results and discussion

XRD patterns of the ribbons melt-spun both from conventional temperature and 100°C overheated are presented in figure 1. No typical halo for single amorphous phase is observed.

However for some ribbons broad intensity maximum, below the peaks from the crystalline phases, is observed indicating possibility of partial amorphization.

LM microstructures of the alloys melt-spun from different temperatures, figure 2, demonstrate the importance of the melt ejection temperature. Lower melt ejection temperatures (figure 2 a-c) result in the presence of non-uniform microstructure and presence of two distinct regions, bright and dark, with some spherical precipitates. This indicates, that the temperature prior to cooling was within the miscibility gap, where two melts, the Fe-rich and the Cu-rich, coexisted.

Effect of the melt ejection temperature on microstructure of the examined \((\text{Fe}_{x}\text{Cu}_{1-x})_{62}\text{Si}_{13}\text{B}_{9}\text{Al}_{8}\text{Ni}_{6}\text{Y}_{2}\) \((x = 0.60 \text{ and } 0.71)\) alloys is presented in figure 2. No influence was observed for system with lowest iron content \((x=0.48)\) (figure 2a). For the system with higher iron content (figure 2b), on the other hand, significant microstructure refinement is found but still some
elongated dark areas are observed. The precipitates are much finer at the wheel side that has been in direct contact with the rotating wheel. Increase of the melt ejection temperature for system with highest iron content (x = 0.71) leads to the presence of very fine dark precipitates dispersed in a bright matrix (figure 2c). EDX analysis (figure 2d) proves that the matrix consists of the Fe-rich melt before solidification enriched with silicon and most probably boron (could not be detected by our instrument). Low copper and aluminum contents are detected in these areas. EDX spectrum from the precipitates, on the other hand, reveals higher concentration of copper, aluminum and yttrium. Relatively high iron content is observed due to a small size of the particles as well as presence of the secondary Fe-rich spheres formed upon further cooling. LM studies prove, that the melt ejection temperature should be over the miscibility gap if relatively uniform microstructure is expected.

Figure 2. LM images of the (Fe_{1-x}Cu_{x})_{62}Si_{13}B_{9}Al_{8}Ni_{6}Y_{2} alloys: a) x = 0.48, b) x = 0.60, c) x = 0.71 (cross sections) and d) SEM image of the ribbon melt-spun from 1430°C (x=0.71) with EDX analysis

The DSC investigations of the (Fe_{1-x}Cu_{x})_{62}Si_{13}B_{9}Al_{8}Ni_{6}Y_{2} (x = 0.48, 0.60 and 0.71) alloys (figure 3) reveal presence of exothermic peaks corresponding to crystallization of amorphous phase for x = 0.71 (both melt ejection temperatures) and for x = 0.60 (melt-spun from 1400°C). No peaks are observed for system with lowest iron content.

Figure 3. DSC diagrams of the (Fe_{1-x}Cu_{x})_{62}Si_{13}B_{9}Al_{8}Ni_{6}Y_{2} (x = 0.48, 0.60 and 0.71) alloys

Bright field image of the (Fe_{1-x}Cu_{x})_{62}Si_{13}B_{9}Al_{8}Ni_{6}Y_{2} (x = 0.48, 0.60 and 0.71) (figure 4), reveal amorphous nature of the matrix which was fully confirmed by presence of the halo ring on the electron diffraction pattern. Presence of spherical crystalline particles with some small secondary amorphous phase inside is also observed. It confirms that the alloy was rapidly cooled from the homogeneous melt region through the miscibility gap inducing precipitation process due to decrease of mutual solubility of the two major elements. The temperature drop induced precipitation of the Cu-rich spheres from the Fe-rich supersaturated liquid. The secondary Fe-rich spheres within the Cu-rich
primarily formed particles appear if the solubility limit has been reached. The precipitation occurs in the liquid state which is fully confirmed by the spherical shape of particles.

Figure 3. DSC curves recorded for $(\text{Fe}_{x}\text{Cu}_{1-x})_6\text{Si}_{13}\text{B}_9\text{Al}_8\text{Ni}_6\text{Y}_2$ $(x = 0.60$ and $0.71)$ melt-spun alloys at a heating rate of $40$ K/min

4. Conclusions
Significant effect of the melt-ejection temperature on the microstructure of $(\text{Fe}_{x}\text{Cu}_{1-x})_6\text{Si}_{13}\text{B}_9\text{Al}_8\text{Ni}_6\text{Y}_2$ $(x = 0.48$, $0.60$ and $0.71)$ systems with liquid miscibility gap was proved. Increase of this temperature allows to obtain more uniform microstructure if critical temperature for attaining homogeneous melt is exceeded. Increase of the temperature by $100^\circ\text{C}$ was not sufficient for systems with lower iron content $(x=0.48$, $0.60)$. Non uniform, banded microstructures were observed indicating cooling from the miscibility gap. Microstructure of the ribbon melt-spun from homogeneous melt region, on the other hand, was characterized by presence of the spherical particles distributed within matrix. An existence of amorphous phase for $x=0.71$ (both melt ejection temperatures) and $x=0.61$ (melt-spun from $1400^\circ\text{C}$) was confirmed by DSC analysis. TEM studies proved amorphous nature of the Fe-rich matrix formed from previously existing the Fe-rich melt.

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