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APPLICATION OF THE LIQUID MISCIBILITY GAP IN METALLIC GLASSES

ABSTRACT

A possibility of the liquid miscibility gap application in metallic glasses with respect to improve their ductility is presented. The microstructure of arc-melted and slow-cooled multicomponent Fe-Cu-based alloy revealed separation of the liquid into two stable liquids, Fe-rich and Cu-rich, and two phase-separated regions were observed after solidification, consequently. Rapid cooling from the temperature within the liquid miscibility gap enabled amorphization of the Fe-rich liquid. The microstructure of resultant ribbons was characterized by scanning and transmission electron microscopy.

KEYWORDS: *liquid miscibility gap, metallic glasses, amorphization.*

1. INTRODUCTION

Metallic glasses represent a new class of materials with superior properties that cannot be achieved in the crystalline state, e.g. very high strength, high elastic limit or corrosion resistance. These properties designate amorphous materials to structural application, if the ductility level would be acceptable. However single-phase amorphous alloys completely lack ductility in tensile mode. Many recent studies are intended to improve ductility of metallic glasses by formation of ductile crystalline particles in the amorphous matrix, which surely enhances its plasticity. The particles could be either introduced to the alloy prior to solidification [1, 2] or in-situ precipitated during cooling [3, 6].

This paper pays attention to another possibility of amorphous-crystalline composite formation in alloys with monotectic transformation (Fig. 1) by a proper selection of chemical elements and cooling condition. Monotectic transformation appears if a heat of mixing between forming elements is strongly positive and the liquid miscibility gap, where two liquids coexists, is an accompanying phenomenon. Above the critical temperature, T_C, both elements are fully miscible in liquid state. Cooling of the alloy in the range between x_m and x_{L2} brings about the existence of two equilibrium liquids of different compositions, A-rich and B-rich. At the monotectic temperature, T_{Mon}, liquid with higher melting point decomposes into solid solution and liquid with lower melting point, $L_1 \rightarrow S_A + L_2$ [7].

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The addition of proper components to the A-B base alloy, followed by a rapid cooling, enable formation of amorphous-crystalline composite or even two amorphous phases. Elements with negative heat of mixing that increase glass forming ability of melts are required for this purpose. The presence of two amorphous phases was revealed in three systems based on elements that satisfy above considerations: multi-component La-Zr-based [8], quaternary Y-Ti-Al-Co [9] and ternary Ni-Nb-Y [10], so far.

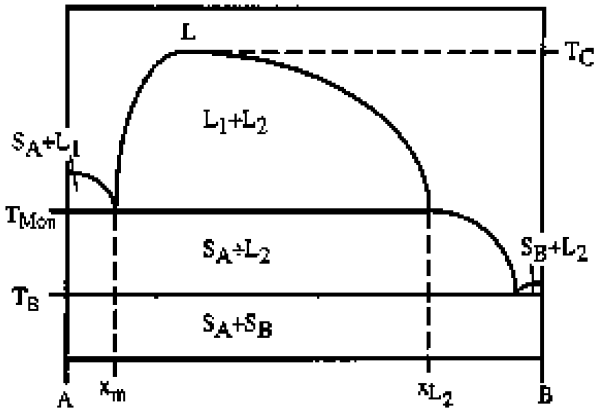

Fig. 1. Typical binary phase diagram with a liquid miscibility gap [7].

Fe-Cu-based alloy with positive heat of mixing was selected in this study. A heat of mixing is as high as +13 kJ/mol [11], however no liquid miscibility gap can be observed in the equilibrium Fe-Cu binary diagram (Fig 2). The Si addition to this system increases the liquid-liquid separation susceptibility [13] and leads to the coexistence of two liquids, Fe-rich and Cu-rich, in wide composition range, consequently (Fig. 3). According to empirical rule given by Inoue [14], Ni, Sn, B and Y, i.e. elements with negative heat of mixing to Fe and/or Cu, were selected in order to increase glass forming ability of both melts.

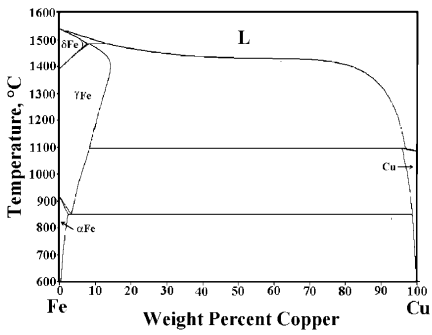

Fig. 2. Fe-Cu binary phase diagram [12]

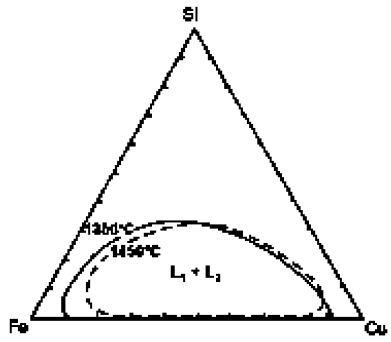

Fig. 3. Liquid miscibility gap in Fe-Cu-Si ternary system at 1350° and 1450°C [13]

2. EXPERIMENTAL PROCEDURE

The $Fe_{30}Cu_{32}Ni_{10}Si_{13}Sn_4B_9Y_2$ alloy was prepared by arc melting of high purity elements under Ti gettered argon atmosphere. Such slow-cooled ingot was remelted several times and microscopically examined to see if the liquid-liquid separation occurred. A rapid cooling was achieved by the melt spinning process at linear wheel speed of 23 m/s under an argon atmosphere. Resultant ribbon was 3 mm in width and 20 μm in thickness. Surface of the melt-spun ribbon was examined by means of scanning electron microscopy (SEM), a Stereoscan 120. Detailed study of the ribbon included transmission electron microscope (TEM), a JEM 200 CX, operated at 200 kV.

3. RESULTS

The microstructure of slow-cooled $Fe_{30}Cu_{32}Ni_{10}Si_{13}Sn_4B_9Y_2$ alloy, Fig 4, clearly confirms presumptions of liquid-liquid separation. A mutual solubility of two major elements in both melts decreases as the temperature falls below critical temperature. Cooling through the miscibility gap induced continuous precipitation of spherical liquid particles: Fe-rich in Cu-rich melt and Cu-rich in Fe-rich melt, respectively. The precipitation of spherical particles in both melts, as well as in the as-precipitated spheres, proceeded until the monotectic temperature was reached. The microstructure can be referred to as fractal-like microstructure.

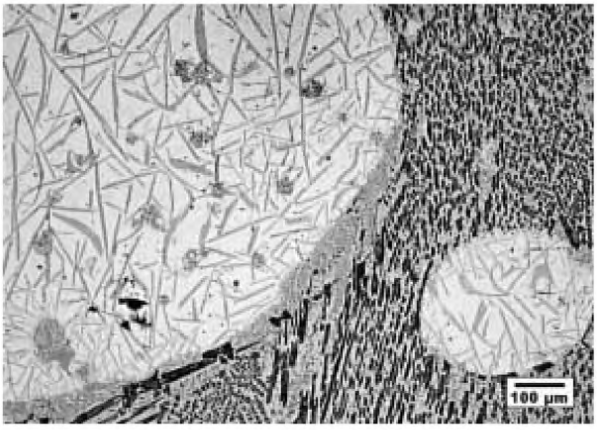

Fig. 4. Optical micrograph of the examined arc-melted and slow-cooled alloy (ingot).

Fig. 5 presents SEM images of the melt-spun ribbon with energy dispersive spectroscopy (EDS) analysis of bright and dark areas. This microstructure indicates that the starting temperature prior to rapid cooling was within the liquid miscibility gap. The elongation of each region is a result of contact with rotating wheel. EDS analysis of dark areas (A) indicates these constituted of Fe-rich liquid before solidification. Moreover Ni, Si and low Cu content were identified. Boron is most probably presented in these regions as well, but light elements could not be detected during analysis. Bright areas in SEM (B), on the other hand, were Cu-rich liquid enriched with Sn, Ni, Y and relatively low Fe content.

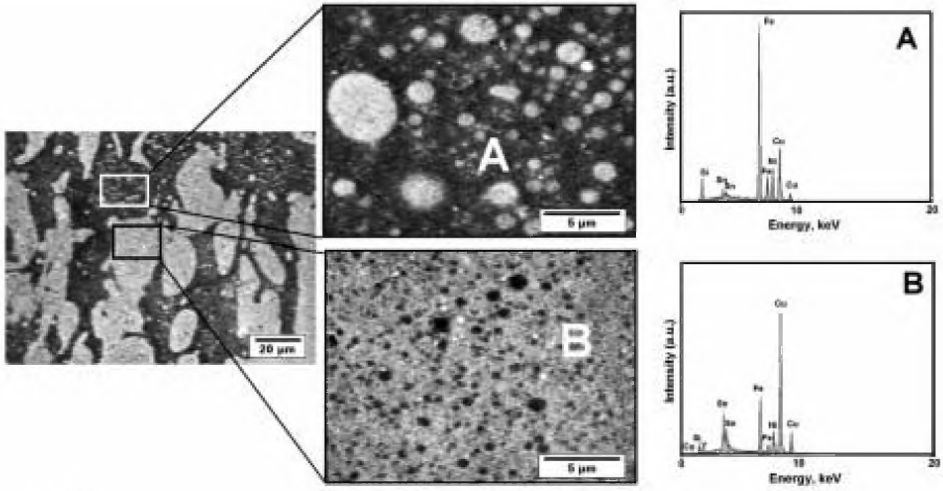

Fig 5. SEM images of the examined melt-spun ribbon with EDS analysis of bright and dark areas.

TEM study of the melt-spun ribbon, Fig. 6, pointed out, vitrification of one liquid, whereas the second crystallized due to its lower glass forming ability. This was fully confirmed by presence of the halo ring on selected area electron diffraction (SAED) pattern, corresponding to an average atomic distance of about 0.203 nm in amorphous phase, indicating amorphization of the Fe-rich liquid. Moreover, the Fe-rich spheres as-precipitated from Cu-rich liquid, also became amorphous. The precipitation process was continued until the glass transition temperature of the Fe-rich liquid was achieved. The unique structure of melt-spun ribbon can be described as an amorphous-crystalline composite.

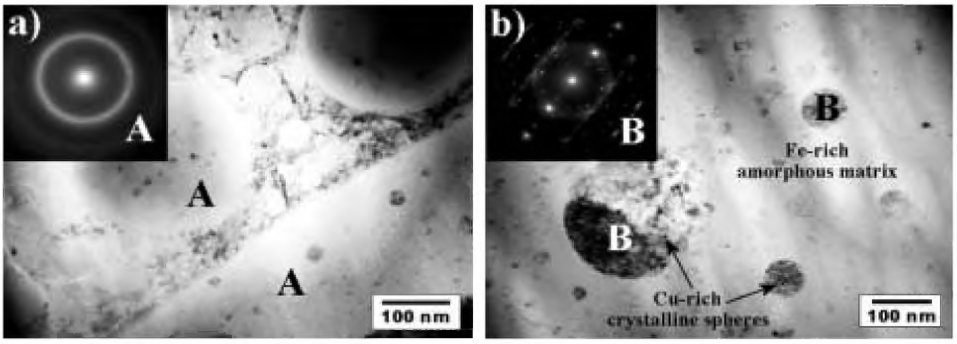

Fig 5. TEM images and SAED patterns of a) amorphous phase; b) crystalline area.

4. DISCUSSION

An application of the liquid miscibility gap in the Fe-Cu-based alloy enabled in-situ formation of the amorphous-crystalline composite. A presence of the crystalline phases distributed in amorphous matrix should enhance plasticity, compared to conventional single-phase metallic glasses. The volume fractions of both phases can be varied with the concentration of two major elements, Fe and Cu. It is expected that proper selection of elements should enhance a glass forming ability of the Cu-rich melt enough to obtain two amorphous phases, Fe-rich and Cu-rich.

Moreover, different composition of both glassy structures affects its different thermal stability and crystallization temperatures, consequently. Controlled heating of the amorphous-amorphous precursor should allow formation of the amorphous-crystalline composite with nanocrystalline structure.

5. CONCLUSIONS

A possibility of the liquid miscibility gap application in the metallic glasses was pointed out by in-situ formation of the amorphous-crystalline composite in the $Fe_{30}Cu_{32}Ni_{10}Si_{13}Sn_4B_9Y_2$ alloy during a melt spinning process. The Fe-rich amorphous phase constitutes either matrix or spherical precipitates.
An application of described phenomenon opens opportunity for fabrication of the amorphous-(nano)crystalline composite by formation of two amorphous phases followed by devitrification of the phase with lower thermal stability.

Acknowledgments

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