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THE COMPOSITION FLUCTUATION IN AN Fe₄₆Ni₃₁V₈Si₈B₁₄ GLASS

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Abstract--The as quenched metallic glass Fe₄₆Ni₃₁V₈Si₈B₁₄ has been investigated by atom probe field ion microscopy. The results have shown that the material had separated into a fine-scaled mixture of a boron and silicon-rich phase and an iron-enriched phase. Their chemical compositions have been determined. The composition profile of the specimen revealed that the characteristic length of the two-phase structure was in the order of 10 nm. It is proposed that the observed structure originated from the nucleation and growth of molecular cluster-like zones in the material.

I. INTRODUCTION

Among the large variety of transition-metal based amorphous alloys, those having the same composition as single-phase crystalline compounds represent the exception rather than the rule (1). From the chemical structural point of view, there may be some kind of chemical short range ordering and long range compositional fluctuation. While much attention has been given to the chemical short range ordering, mainly on nearest neighbours, there has been less investigation of the structure concerning larger separation in space. These works are mainly based on transmission electron microscopy and small angle scattering techniques. However, it seems that these techniques can not give the details of the chemical structure, especially for multi-component metallic glasses. Atom probe field ion microscope (APFIM) is a powerful tool for microstructural and microchemical analysis of a wide range of metallurgical problems at the atomic level and has been used in the investigation of the phase separation in metallic glasses (2-3). This technique has the advantage that it allows the local composition of the area as small as 1 nm in diameter and a depth of 0.2-0.3 nm to be determined in a quantitative manner without relying on tedious calibration or complex background correction, which often obscure the result obtained from various other microanalytical techniques.

With their high thermal stability and excellent physical properties, some multi-component metallic glasses have increasingly found wide application in magnetic and other electronic devices. The knowledge about their chemical inhomogeneity is essential for the understanding of their properties as well as to develop new materials. In this APFIM study, the long range composition fluctuation was investigated for a metallic glass Fe₄₆Ni₃₁V₈Si₈B₁₄.

II. EXPERIMENTAL

The as quenched amorphous alloy supplied to us by Shanghai Institute of Iron and Steel Research was prepared by the melt-spinning method. Its amorphous structure was verified by X-ray measurement. The ribbons about 50 µm thick and 20 mm wide were cut into strips and ground from the sides until an approximately square cross section was obtained. The FIM tips were then prepared by electrochemical polishing in a mixture of 30 ml perchloric acid, 10 ml acetic acid and 60 ml ethylene glycol monobutyl at 8-20 VDC. FIM imaging and atom probe analyses were obtained on the APFIM system at Nanjing (4). FIM imaging was carried out in 7X10⁻³ Pa of neon with a specimen temperature of 90K. Atom probe analyses were obtained in UHV (3X10⁻¹⁰ Pa) with a pulse ratio of 20%. The average number of pulses per collected ion was kept greater than 60 so as to minimize ion pile-up artifacts.
III. RESULTS

A neon field ion micrograph of the glassy material is shown in Fig.1, in which the atoms can be resolved but no regular arrangement of image spots typically observed for crystalline metals can be revealed. Considering there are five elements in the material and the limited resolution of the microscope, no attempt was made to investigate the short range ordering or composition fluctuation direct from the micrograph. Field evaporation of the material does not occur smoothly. The rate of the evaporation changes from area to area. This phenomenon was thought to be an indication of certain heterogeneity in the structure. The mass spectrum from the material studied is presented in Fig.2. Boron was found to appear both in $B^+$ and $B^{2+}$ charged states, whereas all other elements appear predominantly in the doubly charged state. Since the peaks of the elements do not overlap each other, the atomic species can be identified.

To examine the long range composition fluctuation in the specimen, the technique of atom probe random area analysis (5) was performed. In this approach the atoms in a cylinder of material with the diameter of that of the effective probe hole are collected from the tip without regard to any feature in the image. In this way the composition variations are measured as a function of probing distance, yielding a composition profile. The local composition was determined by dividing the ion-by-ion data into blocks each containing 40 atoms and calculating the composition in each block. The scaling of the probing depth in metallic glasses is not as straightforward and as accurately performed as in most crystalline materials, but can be carried out by assigning the number of atoms in a block to a certain probing depth by reference to field evaporation of most densely packed planes in crystalline tips with the same composition at fixed experimental conditions. In this study, it has been determined that a block containing 40 atoms corresponds to a probing depth $0.2 \pm 0.02$ nm.

The ladder diagrams for various elements analyzed in the metallic glass are shown in Fig.3 a) and b), respectively. They are the plots of the cumulative number of the atoms of each element versus the cumulative number of atoms detected during atom probe analysis. The local slope of the curve presents the local atomic concentration of the corresponding element. This integral composition profile revealed that the material had separated into a fine scaled mixture of a boron-rich phase and an iron-enriched phase. Silicon was found to go with boron, whereas nickel concentrations in the two phases are nearly equal. The chemical compositions of the two phases are listed in Table 1.

In order to estimate the characteristic length of the composition fluctuation in the material, a composition profile with a depth of 230 atomic blocks (46 nm) was cumulated by atom probe. The results are shown in Fig. 4. Keeping in mind that the multi-component transition metal-metalloid amorphous alloys were often simplified as quasi-binary systems and considering nickel and iron are ferromagnetic metals, the total concentration of metalloid elements $B$ and $Si$ was summarized in one curve, the total concentration of Fe and Ni was summarized in another curve. The composition profile of Fig.4 shows that the size of the boron+silicon rich regions is approximately 50 atomic blocks, i.e. 10 nm.

IV. DISCUSSIONS

For simple transition metal-metalloid glasses, Gaskell proposed a structural model (6), according to which the structural units of the glasses consist of trigonal prisms of transition metal atoms with metalloid atoms in the middle. These units are essentially identical to the structural units observed in crystalline transition metal borides or carbides. The trigonal prisms are connected along edges and corners to construct a random glass structure. If the glassy structure is composed only of the described units, a local metalloid concentration of 25% is expected. A tendency towards this ideal glassy structure will lead in off-stoichiometric glasses to composition fluctuation, and eventually to phase separation, during which in some areas the T$_3$M-phase could be formed. This model is well supported by the work of
Dubois and Le Caer (7). These authors investigated the structure of $\text{Fe}_{1-x}\text{B}_x$ glasses with Mössbauer spectroscopy and concluded that for $x > 0.2$, the glasses are well described in terms of the Gaskell model, whereas when $x < 0.2$, the glasses undergo phase separation into boron-rich and boron-poor regions. Another type of structural unit has been reported by Mehra et al. in the study of $(\text{Ru}_3\text{Zr}_2)_x\text{B}_y$ glasses with $0.40 < x < 0.53$ (8). They showed that a form of irregular prismatic packing based on the Ru$_2$B crystal structure gives good, though not perfect, agreement of the radial distribution functions.

Recently, the crystallization behavior of the metallic glass $\text{Fe}_{46}\text{Ni}_{31}\text{V}_1\text{Si}_{18}\text{B}_{14}$ has been examined using X-ray diffraction and electron microscope in situ observation by Mao et al. (9). They found that the crystallization of the multi-component glass is very complicated. Finally three stable crystalline phases, $(\text{Ni,Fe})$ solid solution, $\text{Ni}_{31}\text{Si}_{12}$ and $(\text{Fe, Ni, V})_2(\text{Si, B})$, are formed. Based on this conclusion, it can be reasonably supposed that the molecular-like unit $(\text{Fe, Ni, V})_2(\text{Si, B})$ may constitute the structural unit of the ideal glass, because it corresponds to a relatively stable structure. From a dynamical point of view, the formation of these structural units is also favourable, as the chemical composition of the units is not quite different from the mean composition of the material.

The composition of the boron and silicon-rich phase in $\text{Fe}_{46}\text{Ni}_{31}\text{V}_1\text{Si}_{18}\text{B}_{14}$ glass as determined in this work is about $(\text{Fe, Ni, V})_70(\text{Si, B})_{30}$. This composition approximates to that of $(\text{Fe, Ni, V})_2(\text{Si, B})$. We suppose the boron and silicon-rich phase is constructed by irregularly interconnected $(\text{Fe, Ni, V})_2(\text{Si, B})$ structural units, although with the present experimental method the detailed structure of the units can not be given unequivocally. The composition fluctuation originates from the nucleation and growth of the $(\text{Fe, Ni, V})_2(\text{Si, B})$ molecular cluster-like zones in the metallic glass.

V. CONCLUSION

1. The microstructure of an as quenched metallic glass $\text{Fe}_{46}\text{Ni}_{31}\text{V}_1\text{Si}_{18}\text{B}_{14}$ has been investigated by atom probe field ion microscopy.
2. There are at least two amorphous phases in the material. Their composition is $\text{Fe}_{52.3}\text{Ni}_{31.5}\text{V}_{2.5}\text{Si}_{4.5}\text{B}_{1.5}$ and $\text{Fe}_{46}\text{Ni}_{32.5}\text{V}_{13.2}\text{Si}_{12.4}\text{B}_{16.4}$ respectively.
3. The characteristic length of the fine scaled two phase-structure was estimated to be in the order of 10 nm.
4. The origin of the observed structure was thought to be the nucleation and growth of the $(\text{Fe, Ni, V})_2(\text{Si, B})$ molecular cluster-like zones in the metallic glass.

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REFERENCES

Figure 1. Neon field ion micrograph of an as quenched metallic glass Fe$_{46}$Ni$_{31}$V$_1$Si$_8$B$_{14}$ at 7 kV and 90K.

Figure 2. Atom probe mass spectrum of a metallic glass specimen Fe$_{46}$Ni$_{31}$V$_1$Si$_8$B$_{14}$. 
Figure 3. Integral concentration profile of five elements in the specimen. A boron and silicon-rich region between two iron-rich regions is evident.
Figure 4. The composition profiles covering a depth of about 46 nm. Long range composition fluctuation is evident.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Fe</th>
<th>Ni</th>
<th>V</th>
<th>Si</th>
<th>R</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si, B-rich</td>
<td>36.4±3</td>
<td>32.5±3</td>
<td>1.5±0.6</td>
<td>13.2±1</td>
<td>16.4±1</td>
</tr>
<tr>
<td>Fe-rich</td>
<td>52.3±3</td>
<td>31.9±3</td>
<td>2.2±0.6</td>
<td>4.5±1</td>
<td>9.1±1</td>
</tr>
</tbody>
</table>

Table 1. Composition of a silicon and boron-rich phase and an iron-rich phase in an as quenched Fe$_{46}$Ni$_{31}$V$_{1}$Si$_{8}$B$_{14}$ glass. The results were obtained by atom probe (in atomic %).