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ATOM PROBE MICROANALYSIS OF THE METALLIC GLASSES

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Abstract—The chemical inhomogeneities over the order of nanometers in two transition metal-metalloid amorphous alloys have been investigated by means of atom probe field ion microscopy (APFIM). In as quenched $\text{Fe}_{82.3}\text{Ni}_{1.7}\text{B}_{16}$ glass the existence of two amorphous phases with different boron concentrations was revealed. The mean size of the precipitated $(\text{FeNi})_3\text{B}$ -phase was determined to be about 3 nanometers. The interface between the two phases seems to be rather distinct. However, in as quenched or at 350°C for an hour annealed $\text{Fe}_{80.7}\text{B}_{12.8}\text{Si}_{3.9}\text{C}_{2.6}$ -glass, no regions depleted or enriched in one component detectable can be found. In annealing the glass kept homogeneous on the scale of nanometer, although the specimen underwent a ductile-brittle transition. It was concluded that in this metallic glass phase separation is not involved in the annealing embrittlement.

I. Introduction:

It has become clear in recent years that some sort of inhomogeneities must be influencing many of the properties of the metallic glasses such as the magnetic properties, superconductivity and ductility. Up to now extensive informations on nearest neighbours have been accumulated by Moessbauer spectra (1), NMR (2), EXSAFS (3) et al. However, less information concerning the chemical inhomogeneities in the range of several angstroms to 10 nm has been reported. Atom probe field ion microscopy (APFIM) has been proved to be very useful in studying the concentration fluctuation and phase separation in glassy metals, because this method has the advantage that it allows the local composition of the area as small as several angstroms in diameter to be determined in a quantitative manner. This method has been successfully applied to the investigation of amorphous alloys $\text{Fe}_{40}\text{Ni}_{40}\text{B}_{20}$ (4), $\text{Ti}_{50}\text{Be}_{40}\text{Zr}_{10}$ (5) and $\text{Pd}_{40}\text{Si}_{16}$ (6).

In the present work APFIM investigations were performed to examine the chemical inhomogeneity and phase separation in the transition metal-metalloid glasses $\text{Fe}_{82.3}\text{Ni}_{1.7}\text{B}_{16}$ and $\text{Fe}_{80.7}\text{B}_{12.8}\text{Si}_{3.9}\text{C}_{2.6}$ respectively.

II. Experimental procedure:

The amorphous alloys $\text{Fe}_{82.3}\text{Ni}_{1.7}\text{B}_{16}$ and $\text{Fe}_{80.7}\text{B}_{12.8}\text{Si}_{3.9}\text{C}_{2.6}$ were prepared from high purity materials by a single side drum technique. Long ribbons about 10 μm thick 1 mm wide and about 25 μm thick 8 mm wide were obtained respectively. No indication of crystallization in the specimens can be detected by large angle X-ray diffraction measurement, in which the first and second halo peaks were observed which is usually recognized to be an indication of the amorphous state. The ribbons were first ground from the side until an approximately square cross section was obtained. Some of the ground ribbons of $\text{Fe}_{80.7}\text{B}_{12.8}\text{Si}_{3.9}\text{C}_{2.6}$ were then encapsulated in a glass tube which has been evacuated to a pressure 10^{-4} Pa and backfilled with high purity argon and isothermally annealed at 350°C for an hour. The annealed specimen was tested by X-ray diffraction measurement. Again, no crystalline state can be detected. The FIM tips of all materials were prepared by electrochemical polishing in a mixture of 30 ml perchloric acid, 10 ml acetic acid and 60 ml ethylene glycol monobutyl ether at 8-20 VDC.

The APFIM investigations were performed in the instrument of Nanjing University, which has been described in detail elsewhere (7). The tips were imaged at a temperature of 85K, using neon as imaging gas at a pressure of 7×10^{-3} Pa. In order to prevent preferential evaporation effect from interfering, a high pulses fraction (20%-22%) was used. In addition, the averaged number of pulses per collected ion was kept greater than 50 so as to minimize ion pile-up artifacts. On these conditions, the determined chemical compositions of the glasses are in agreement with their nominal compositions.

To test the homogeneity of the metallic glasses, the concentration profiles of each component along a cylinder with a diameter of about 2 nm were determined layer by layer. Exactly speaking, "atomic layer" is meaningful only for crystalline specimen. One "atomic layer" is defined here by collecting 40 ions (hydrogen ions are excluded) and corresponds to a thickness of about 0.2 nm. Due to the small number of atoms collected from each layer the statistical fluctuation is so large that it is difficult to determine the true size and composition of the areas enriched in some elements. For this reason the concentration profiles were analysed by the statistical method of autocorrelation (8,9), which is calculated according to the formula:

$$R(K) = \frac{n}{(n-K)} \frac{\sum_{i=1}^{n-K} (C_i - C_0)(C_{i+K} - C_0)}{\sum_{i=1}^n (C_i - C_0)^2} \quad (1)$$

C_i being the concentration of an element in i -th evaporated layer; C_0 the mean concentration of the element in the specimen; n the total number of evaporated layers; K the correlation length in unit of interlayer distance.

III. Results and discussion:

1. The phase separation in $\text{Fe}_{82.3}\text{Ni}_{1.7}\text{B}_{16}$ glass:

The neon field ion image of an as quenched specimen is shown in figure 1. The image spots are irregularly distributed. This implies that there is no long range ordering in the structure. It can be seen in figure 1 that there seems to be two kinds of spots i.e. the bigger spots and the smaller ones. Since the atom probe analysis revealed that the metal ions evaporate preferentially, we guess the bigger spots corresponding to boron atoms. Some efforts have been made to check the correspondence between the appearance of the spots and the atoms of different elements. Unfortunately, one to one correspondence has not been achieved. However, it follows that most of the bigger spots are due to boron atoms. This is in agreement with the observation of Piller and Haasen (4).

To investigate the composition fluctuation in the material, atom probe random area analysis was performed. Figure 2 a) shows the concentration profile of boron and iron, in which small excursion from statistical scatter about the mean composition can be observed. The concentration profiles were then analysed by autocorrelation as shown in equation 1. In figure 2 b) the autocorrelation $R(k)$ for the boron concentration profile shown in figure 2 a) is plotted versus the layer spacing K , from which the mean size of the boron rich area was determined to be about 3 nm. The size of the boron-rich regions was believed to be large enough to ensure these regions as well-defined independent second amorphous phase. The compositions of the precipitated boron-rich phase and the boron-depleted matrix were estimated to be $(\text{Fe,Ni})_3\text{B}$ and $(\text{FeNi})_{96}\text{B}_{14}$ respectively.

Some hydrogen dissolved in the material was detected by atom probe, although the specimen was outgassed for more than 12 hours before the investigation started. The integral concentration profile of hydrogen was shown in figure 3 together with that of boron. It is very interesting to note that the distribution of hydrogen is not homogeneous. The hydrogen concentration in boron-rich phase was found to be much lower than that in boron-depleted phase. This is another evidence confirming that the phase separation has really occurred in the specimen. Furthermore, it can be seen that the boundary between the two amorphous phases are probably fairly distinct.

2. The chemical homogeneity of $\text{Fe}_{80.7}\text{B}_{12.8}\text{Si}_{3.9}\text{C}_{2.6}$ glass

The metallic glass $\text{Fe}_{80.7}\text{B}_{12.8}\text{Si}_{3.9}\text{C}_{2.6}$ and some glasses quite close in composition to the present one undergo a transition from the ductile state to brittle state when annealed at temperature well below the crystallization temperature. However,

the processes which are involved in the annealing embrittlement are not yet understood and quite different explanations have been proposed up to now (10): phase separation in the glasses, local enrichment of one component, reduction of free volume or onset of crystallization at the surface. To test whether these explanations to be true, more experimental verifications of the defects and inhomogeneities, especially the chemical inhomogeneities in the glassy specimens before and after ductile-brittle transition are needed. For this purpose two typical specimen of $\text{Fe}_{0.7}\text{B}_{12.8}\text{Si}_{1.9}\text{C}_{2.6}$ glass were investigated by APFIM. One is in the as-quenched melt spun state and was tested to be ductile by the bend test, in which the strip was bent into a U-shape and slowly brought together until the fracture occurred. Another specimen was annealed isothermally at 350°C for 1 hour and was found to be very brittle.

The field ion images of the two specimens are very similar. The micrograph taken from the annealed specimen was shown in figure 4. Again, the image spots distributed randomly, neither long range ordering nor image contrast indicating different phases can be observed. Like in the images of $\text{Fe}_{0.7}\text{Ni}_{1.7}\text{B}_{1.6}$ and other amorphous materials, the abundance of the image spots is markedly lower than for crystalline materials. The reason of which was believed to be the random distribution and the irregular field evaporation behaviour of the surface atoms in the amorphous materials resulting a thinner effective Moore shell (11).

Figure 5 shows the mass spectrum of the as quenched specimen taken by atom probe. The carbon was found to be remarkably lower than 2.6%. This discrepancy was thought to be due to the complex charged state and the occurrence of carbon cluster ions which made it very difficult to resolve all carbon atoms in the atom probe data.

The concentration profiles obtained by atom probe from the annealed glass were shown in figure 6, in which no any indication of two phase microstructures can be found. A more detailed and reliable examination of the concentration fluctuation was obtained by analyzing the concentration profiles by autocorrelation analysis method. Figure 7. shows the correlogram of the Fe-,B-,Si-concentration profile of figure 6. The correlation coefficients for the three elements drop to zero already for $K=1$. This indicates that the alloy does not have any fine precipitates detectable by atom probe random area analysis. The atom probe analysis was also performed to investigate the as quenched specimen. The same results were obtained. The specimen was found to be homogeneous on the scale of nanometer.

Based on their APFIM investigation of $\text{Fe}_{40}\text{Ni}_{40}\text{B}_{20}$, Piller and Haasen concluded that the ductile-brittle transition takes place when the mean size of $(\text{FeNi})_3\text{B}$ -precipitates becomes larger than 30 nm during annealing. However, from the results of the present work, it can be concluded that in $\text{Fe}_{0.7}\text{B}_{12.8}\text{Si}_{1.9}\text{C}_{2.6}$ glass phase separation and local enrichment of one component are not involved in the annealing embrittlement. Some different hypotheses in which chemical inhomogeneity is not involved have been proposed. Argon (12), on the basis of his comprehensive soap-bubble simulations, attributes thermal embrittlement to an alteration in the distribution of free volume. Gerling et al. (13) conclude that thermal embrittlement is due to a critical degree of cluster formation or a critical reduction in free volume. Obviously, to understand the embrittlement mechanism of metallic glasses unequivocally, further experimental works are needed.

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Figure 1. Neon field ion image of an as quenched amorphous $\text{Fe}_{2.3}\text{Ni}_{1.7}\text{B}_{16}$ specimen at 7kV and 85K.

a)

b)

Figure 2. a) Fe- and B-concentration profile of the as quenched $\text{Fe}_{2.3}\text{Ni}_{1.7}\text{B}_{16}$ glass. b) Autocorrelation $R(k)$ of the boron concentration profile shown in a).

Figure 3. Integral concentration depth profile of B and H in as quenched $Fe_{2.3}Ni_{1.7}B_{16}$ glass. The H-concentration in B-enriched phase is lower.

Figure 4. Neon field ion image of a $Fe_{90.7}B_{12.8}Si_{3.9}C_{2.6}$ specimen annealed at $350^\circ C$ for 1 hour.

Figure 5. Mass histogram of the as quenched $Fe_{90.7}B_{12.8}Si_{3.9}C_{2.6}$ glass taken by atom probe.

Figure 6. The concentration profiles of $\text{Fe}_{80.7}\text{B}_{12.8}\text{Si}_{3.7}\text{C}_{2.6}$ glass. The specimen was annealed at 350°C for an hour. No phase separation can be detected.

Figure 7. Autocorrelogram of Fe-, B-, Si- concentration profiles shown in figure 6.