Instability of nanoscale metallic particles under electron irradiation in TEM

X Y Chen\textsuperscript{a}, S G Zhang\textsuperscript{b}, M X Xia\textsuperscript{c} and J G Li\textsuperscript{d}
School of Materials Science and Engineering, Shanghai Jiao Tong University, Shanghai, 200240, China

Email: \textsuperscript{a}jennychenxy@sjtu.edu.cn, \textsuperscript{b}sgzhang@sjtu.edu.cn, \textsuperscript{c}mingxu.xia@sjtu.edu.cn and \textsuperscript{d}lijg@sjtu.edu.cn

Abstract. The stability of nano metallic glass under electron beam in transmission electron microscope (TEM) was investigated. The most common voltage of TEM used in metallic materials characterization was either 200 kV or 300 kV. Both situations were investigated in this work. An amorphous metallic particle with a dimension of a few hundred nanometers was tested under 300 keV electron irradiation. New phase decomposed from the parent phase was observed. Moreover, a crystal particle with the same composition and dimension was tested under 200 keV irradiation. Decomposition process also occurred in this situation. Besides, crystal orientation modification was observed during irradiation. These results proved that the electron beam in TEM have an effect on the stability of nanoscale samples during long time irradiation. Atomic displacement was induced and diffusion was enhanced by electron irradiation. Thus, artifacts would be induced when a nanoscale metallic sample was characterized in TEM.

1. Introduction

Amorphous alloys (metallic glasses) are non-equilibrium materials, which will process phase transformations when heated or mechanically forced. Crystallization is the most important phase transition of amorphous alloys. Crystallization is not only a question related to the service life of glass materials, but also a scientific question including glass transition process and nucleation and growth in glass state. There is another phase transition which is frequently found and gets more attention in metallic glasses, that is phase separation [1]. Phase separation is originated from the positive mixing enthalpy between atoms [1, 2]. It is found that metallic glasses show obvious different mechanical properties after phase separation occurs [3, 4].

In-situ observation is favored in phase transformation investigation. As to now, in-situ observations of metallic glasses are mainly based on small angle scattering (SAS) [5] and transmission electron microscope (TEM) [6-8]. To induce phase transition, samples are reheated during SAS examination, while in TEM observation the interaction between the electron beam and the sample could stimulate or accelerate phase transitions. Moreover, TEM can provide direct morphology observation. Thus, TEM is more convenient and useful than SAS. However, the energy of the electron beam should be more than mega-electron-volt (MeV) to induce crystallization in metallic glass [6-8]. On the contrary, it seems that 200–300 keV electron beam is safe for metallic samples to be characterized without extra artifacts.

However, considering the size effect, small samples with large surface to volume (S/V) value may
be unstable even under 200–300 keV electron irradiation. The unstable phenomenon is confirmed in this work. Not only the metallic glass particle, but also the crystal particle process transformations during electron irradiation.

2. Experiments

(Fe_{62.6}Mn_{12.5}Cr_{9.3}Ni_{4.6}Si_{11})_{90}C_{10} alloy with low glass forming ability (GFA) and phase separation potential was chosen. Low GFA was aimed to limit the dimension of the glass phase in the composited samples as prepared. The phase separation potential was expected on Fe-Mn, Fe-Cr, Fe-Ni and Mn-Cr atomic pairs, whose mixing enthalpy are either positive or close to zero [9].

The master alloy was prepared by induction-melting in an argon atmosphere and injected into copper mold. To obtain nano particles, chemical collection process was used. Slices cut from the cast sample were firstly polished to 50 μm thick. Then they were soaked in a mixed solution of H2O:H2O2:HF (10:50:3) to etch for 6 hours. After that the solution was diluted with alcohol to ease corrosion. In this way, the non-corrosive solution containing metallic particles was obtained. At last, the solution was dropped onto the copper grid to make the particles attach to the carbon film on the copper grid for TEM (JEOL JEM-2100, 200kV and JEM-2100F, 300 kV) observation. During the continuous irradiation and graphing, each bright field (BF) image was taken under the same condition. Each selected area diffraction (SAD) pattern was taken 1.5 min after the corresponding BF image taken. The exposure time for each SAD pattern was kept the same.

3. Results and discussion

3.1 Amorphous particle under electron irradiation

Figure 1 shows the evolution of an amorphous particle under electron irradiation in-situ in TEM (JEM-2100F, 300 kV). Figure 1 (a, b, c) present the BF images of the particle during irradiation, while (d, e, f) show the SAD patterns corresponding to (a, b, c), respectively. The particle is made up of several small pieces, and the thickness is not homogeneous. Around the particle, new phases with round shape and dark contrast come up during irradiation. The new phase concentration areas are marked by arrows. Even in the middle of the particle (the arrow place), the contrast changed. However, the figurations of the new phases in the middle area are not as clear as the outside ones. It may be caused by the overlapping of the small piece samples with new phases. Each SAD pattern in (d, e, f) consists of 4 halo rings, indicating the particle keeps amorphous structure during irradiation. However, 4 halo rings are not regularly seen in SADs of amorphous alloys. The 4 halo rings here imply the amorphous structure is partly ordered. R_{1} is the brightest one, while the others show lower brightness. The radiuses of R_{1}~R_{4} are almost the same from (d) to (f), but the brightness is increasing. Halo rings in SAD represent an amorphous microstructure, while brightness increasing indicates the local clusters taking part in diffraction are coming up during irradiation. That is to say, electron irradiation promotes the formation of short-range-ordered clusters. Thus, it is concluded that the microstructure of the particle is kept in an amorphous state under irradiation, but the local atomic structure is ordering.

The new dark phases decomposed from the parent phase are supposedly related to phase separation. These dark phases nucleate and grow up as (b, c) shown. While phase separation occurs, SAD is suspected to present different rings since the new phase has different local atomic distances from the parent phase. However, SAD rings in (d, e, f) present the same radiuses. This can be explained that the diffraction intensity of the new phase is not strong enough. To clarify this question, energy dispersive spectrometer (EDS) exam is needed. If it is phase separation, the composition of the dark phase will be rich of one or more elements and the light phase will be rich of the other elements. However, the electron beam spot is larger than the decomposed phase. Also, the magnetism of the sample lead drifting of electron imaging, which will disturb the beam spot position. These facts make it unreliable for EDS in TEM to reflect the real composition difference of the decomposed phase and the matrix phase.
3.2 Crystal particle under electron irradiation

Figure 2 shows the evolution of a crystal particle of the same composition with the amorphous particle under electron irradiation in-situ in TEM (JEM-2010, 200 kV). Figure 2 (a, b, c) present the BF images of the particle during irradiation, while figure 2 (d, e, f) shows the SAD patterns corresponding to figure 2 (a, b, c) respectively. The particle is gathered of 3 small particles, and the microstructure is non-homogeneous. Around the particle, new phases appear as same as figure 1 shows. Moreover, the round dark new phases occupy the whole particle in figure 2 (c). The 3 small particles grow up into one particle. The SAD in figure 2 (d) shows some diffraction spots located in several rings, indicating the particle consists of nanocrystals. R₁ and R₂ are the main rings marked by arrows and their radiuses are 3.39, 4.86 nm⁻¹, respectively. The interplanar spacing of R₁ is 0.295 nm, of R₂ is 0.206 nm. SAD in figure 2 (e) is almost the same with that in figure 2 (d), except the brightness decreased a little. In figure 2 (f), there is one diffraction ring R₂ left and less few spots at further radius. R₁ disappeared and only R₂ remained with an increased brightness, indicating crystal lattice orientation modification is performed in the crystal particle under electron irradiation.

Phase separation not only occurs in the amorphous particle, but also in the crystal particle under electron irradiation. Nevertheless the SADs in figure 2 can’t reflect the decomposition process either. The mechanism of crystals modifying orientation under electron irradiation can be crystal rotation or re-crystallization. Re-crystallization is preferred to take charge of the orientation adjusting process because the brightness of SAD pattern decreased in (e) and increased in (f). If rotation is the main mechanism, the brightness of R₂ will increase all the way.
Figure 2. In-situ evolution of crystal particle under electron irradiation (200 keV). (a, b, c) are bright field (BF) images. (d, e, f) are the SAD patterns corresponding to (a, b, c), respectively. Shot time of each picture is marked in the bottom-left corner. (d) and (e) show similar diffraction patterns, while (f) shows less diffraction rings and spots than (d, e). The radius of the main SAD rings are $R_1 = 3.39$ nm$^{-1}$ and $R_2 = 4.86$ nm$^{-1}$.

3.3 Effect of electron irradiation on the samples

The interaction between the incident electron and the metallic sample includes electron excitation and knock-on displacement. The former effect is between electron and electron, while the latter is between electron and nucleus. Electron excitation can release very fast in metallic materials thus it doesn’t cause significant influence. Knock-on displacement means the incident electron hit a nucleus to move. To achieve knock-on displacement, the electron beam requires high energy to satisfy the threshold energy of atoms [6-8]. The threshold voltage of electron beam to stimulate knock-on displacement of the elements composed in the particles are Fe (370 kV), Mn (360 kV), Cr (440 kV), Ni (440 kV), C (200 kV) and Si (140 kV) [7]. Thus, only carbon atoms and silicon atoms are displaced directly by electron irradiation of 200~300 keV.

It is noticeable that the shape of particles in figure 1 and figure 2 are changing with irradiation as figure 3 shows. The shape change route of the particle is 1a-1b-1c or 1a-2b-2c. The areas of the particles are decreasing. It implies that the atoms have moved a long distance during transitions under electron irradiation. Atomic diffusion is the key of the transitions under electron irradiation. The atomic radius of carbon (0.077 nm) is smaller than the other atoms, whereas the atomic radius of silicon (0.117 nm) is similar to the metallic elements (0.112~0.125 nm) [9]. That is to say, the vacancies induced by the displacement of Si can be taken up by the other metallic elements. Thus, the diffusion of all the atoms in the sample is enhanced by low energy electron beam.
Figure 3. The shape change of the particles during electron irradiation is painted by dashed lines. The left one is the particle in figure 1, while the right one is the particle in figure 2. The shapes of particles corresponding to each image are marked. For example, ‘1a’ means corresponding to figure 1 (a).

Another factor improving atomic diffusion is the large S/V value of the nanoscale particles. As know to all, atoms at surface are inherent of higher energy than the inside atoms. A large S/V value indicates a large amount of atoms in the particle are carrying high energy. These atoms are active and are easy to diffuse. It is concluded that, transitions are induced by electron irradiation through atoms diffusion.

Radiation-induced diffusion provides a means for the atoms to rearrange to a more stable form of nanoscale metallic particles. The voltage of the electron beam and the size of the particle both have an effect on the stability of metallic particle inside a TEM.

4. Conclusions
Decomposition occurred in the amorphous alloy particle under 300 keV electron irradiation and in the crystal particle under 200 keV irradiation. Moreover, orientation modification occurred in the crystal particle. It proved that 200 or 300 kV TEM would introduce artifacts during long time observation.

The atomic displacement was induced by electron irradiation even with low energy as 200 keV. It is suggested that the electron irradiation should be reduced when nanoscale amorphous alloys was characterized.

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