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In situ high resolution electron microscopy observation of amorphous phase formation in isolated nanometer-sized alloy particles

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ABSTRACT

The size dependence of the glass transition temperature in alloys has been studied using particles in the Au-Sn and Sn-Bi systems by transmission electron microscopy. A solid amorphous phase was produced in approximately 5.5- and 4- nanometer-sized alloy particles in the Au-Sn system at room temperature. Upon heating, the amorphous phase directly changed into a liquid phase, and upon cooling, the liquid phase directly solidified into the amorphous phase. The temperature range in which the granular contrast in the particles starts to fluctuate and eventually disappear were almost the same for the two different-sized particles. In the Sn-Bi system, a fluid and solid amorphous structure is obtained at room temperature in 9-nm-sized and 6-nm-sized alloy particles, respectively. These two sets of observations indicate that the dependence of the glass transition temperature on the size of a system (i.e., of a particle) is rather weak, if any.

1. Introduction

The suppression of melting point, T_m, in nanometer-sized *pure* particles is one of typical phenomena related to the finite size effect. There are a lot of theoretical [1–5] and experimental [6,7] work reporting that the melting point of pure substances reduces linearly with the inverse of the particle radius R. This is mainly because the surface-to-volume ratio becomes large with decreasing the size of the system, and usually the surface energy of solid substance is higher than that of liquid substance. With regard to nanometer-sized *alloy* particles, it is recently revealed that the eutectic point, T_{eu}, could be suppressed much faster than the melting point of pure components with decreasing the size of particles, which was explained by the fact that in addition to the surface energy in pure substance, the interfacial energy for an interface between two different crystalline phases significantly contributes to the total Gibbs free energy in nanometer-sized alloy particles [8–10].

On the other hand, quite recently, it was revealed that a thermodynamically stable amorphous phase, which has never been observed in bulk materials, does appear in isolated nanometer-sized alloy particles in the Au-Sn and the Bi-Sn systems over a compositional range near the eutectic composition when the size of particles is smaller than about 10 nm in diameter [8,10]. Here, the wording of "thermodynamically stable amorphous phase" comes from the observation that upon heating, it went to melt without crystallization, and upon cooling, it solidified into an amorphous solid with no traces of crystallization. In the previous paper, we discussed the appearance of the thermodynamically stable amorphous phase is ascribed to the large suppression of the eutectic point induced by the size reduction. With this large depression of T_{eu}, it becomes possible that the relative position between the glass transition temperature, T_g and T_{eu}, which are dependent on the size of particles, becomes in the reverse order. As a result, it is considered that the thermodynamically stable amorphous phase would appear in such a case where temperature at which observations are carried out lies in a temperature range higher than T_{eu} but lower than T_g by decreasing the size of particles [8,10].

In fact, it was recently reported that T_m decreases much faster than T_g with deceasing size of organic particles, and when the size of particles is smaller than a critical size, T_m lies below T_g [11]. However, no studies on the size dependence of the glass transition temperature have been reported so far for inorganic materials, although it is essential to examine the size dependence of not only melting point but also glass transition temperature for a deep understanding of the formation of thermodynamically stable amorphous phases in nanometer-sized alloy particles.

Based on this premise, in the present work, the size dependence of glass transition temperature in the Au-Sn and the Bi-Sn systems was studied by in situ transmission electron microscopy.

2. Experimental procedure

Preparation and subsequent heating experiment of nanometer-sized alloy particles were carried out in a 200-kV high resolution electron microscope (HREM) of Hitachi HF-2000 type using a unique side-entry holder equipped with a double-source evaporator at the tip. A photograph of the holder used in the present experiment is shown in previous paper [12,13]. It is essentially consists of three spiral-shaped tungsten filaments, the middle of which was attached

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with a flake of graphite used as a supporting substrate, and two other filaments were attached with source materials such as gold, bismuth, and tin. Prior to experiments, the flake of graphite was baked at 1073 K for 60 s to obtain a cleaned surface of graphite. After being baked, the graphite substrate was cooled down to room temperature (RT). Gold (or tin) was first evaporated from one filament heated by the Joule effect onto the edge of graphite attached to the middle of filaments kept at ambient temperature, and nanometer-sized gold (or tin) particles were produced. Nanometer-sized alloy particles were formed by subsequent tin (or bismuth) evaporation onto the gold (or tin) particles at ambient temperature. The composition of particles in the both systems was controlled to be near the eutectic composition. As for the Au-Sn system, after preparation of nanometer-sized alloy particles, these particles were subjected to annealing experiments to monitor the temperature range where phase transition from an amorphous (or liquid) to a liquid (or amorphous) phase takes place during heating (or cooling down to RT). A supersensitive television camera (GATAN 622SC) with a time resolution of 30 frames s^{-1} and video tape recorder system were used for the in situ experiments. All micrographs presented in this paper were reproduced from the videotapes. The base pressure in the specimen chamber of this microscope was below 5×10^{-7} Pa. The chemical composition of individual particles on the substrate was analyzed by energy-dispersive X-ray spectroscopy, if necessary.

3. Results and discussion

3.1. The Au-Sn system

Fig. 1(a–d) depicts sequential micrographs showing the melting and the subsequent solidification of a 5.5-nm-sized Au-Sn alloy particle on graphite substrate, whereas Fig. 1(a′–d′) depicts those of a 4-nm-sized one. Fig. 1(a and a′) shows as-produced alloy particles at RT sitting on the edge of graphite (upper part in figure). Only granular contrast, which is characteristic of an amorphous phase, could be observed in the Fig. 1(a and a′). It should be noted here that Fig. 1(a and a′) was taken at RT and that each pair of Fig. 1(b and b′, c and c′, and d and d′) was taken at almost same temperature. Over a temperature range from RT to 400 K, both particles exhibited essentially the same features as those observed at RT (Fig. 1(b and b′), taken at 400 K). With continued heating, the time frequency of fluctuation in the granular contrast in both particles became high, suggesting an enhanced atomic mobility within particles. With further heating, particles eventually melted, and in the molten state, there appeared only a quite uniform contrast typical of a liquid state (Fig. 1(c and c′), taken at 500 K). It is noted here that prior to the melting, no traces of crystallization were observed, and upon cooling down to room temperature, the liquid particle solidified again into the amorphous state, as shown in Fig. 1(d and d′). No traces of crystallization were recognized prior to and during the solidification. An important observation pertinent to Fig. 1 is that the temperature range in which the granular contrast in the amorphous particles starts to fluctuate and eventually disappears, being replaced with a uniform contrast, was almost the same for the two different-sized particles. If the T_g has similar size dependence as the melting point, it can be easily expected that the temperature range where amorphous to liquid transition takes place is significantly different. This observation indicates that T_g for the two different-sized particles are not so much different, and the size dependence of T_g is rather weak compared with the melting point. Based on the experimental results, size dependence of T_g and T_{eu} is schematically shown in Fig. 2. T_g and T_m intersect at approximately 8 nm, which is the critical size of the formation of thermodynamically stable amorphous (TSA) phase in the Au-Sn system. As the particle size decreases, the region at TSA can be formed increases, as shown in Fig. 2.

Fig. 3 shows sequential micrographs showing the melting and the subsequent solidification of an approximately 10-nm-sized Au-Sn alloy particle on graphite substrate. Fig. 3(a) shows an as-produced amorphous particle. It should be noted here that amorphous-to-crystalline (A → C) transition first took place, and then it became liquid phase during heating (Fig. 3(b), taken 450 K). Upon Cooling down to RT, the liquid particle solidified directly into crystalline state (Fig. 3(c), taken 600 K, and Fig. 3(d)). The sequence of phase transition (amorphous-to-crystalline-to-liquid-crystalline) is significantly different from that observed in Fig. 1 (amorphous-to-liquid-to-amorphous). This result indicates that the amorphous phase formed in 10-nm-sized Au-Sn particle is in thermodynamically unstable state, which is the case in the corresponding bulk glass. These results indicate that Fig. 2 could be a useful guide for TSA.

3.2. The Sn-Bi system

Fig. 4(a–c) depicts a sequence of micrographs showing a typical alloying process of bismuth atoms into a 5-nm-sized tin particle, while Fig. 4(a′–c′) depicts that showing the same process into a 3-nm-sized tin particle. Fig. 4(a–a′) shows as-produced pure tin

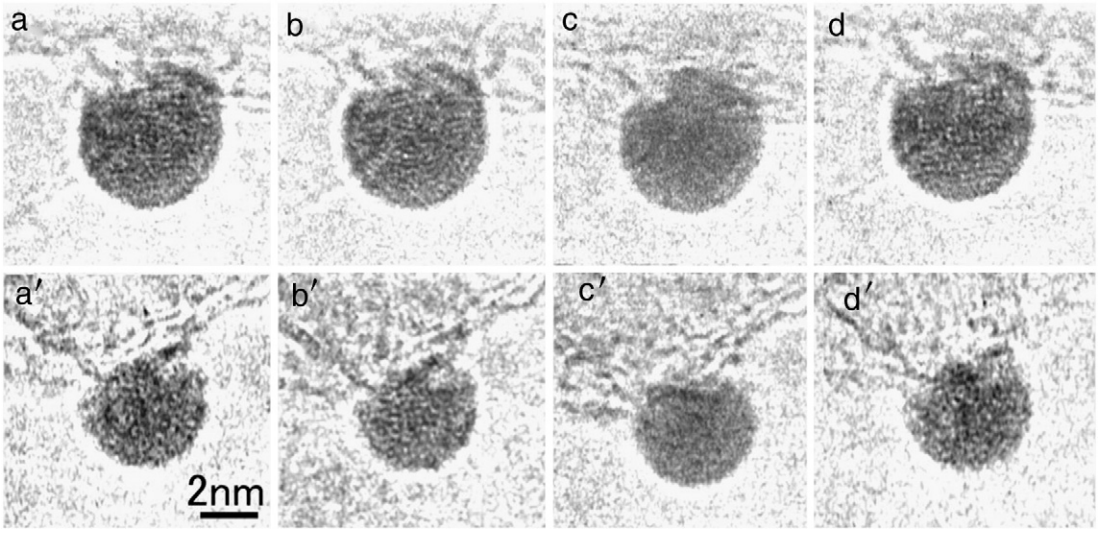

Fig. 1. Typical sequences of electron micrographs, taken from a video recording, showing the annealing and cooling process in an approximately 5.5-nm-sized (a–d) and 4-nm-sized (a′–d′) Au-Sn alloy particles. See text for details.