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In situ observation of a fluid amorphous phase formed in isolated nanometer-sized particles in the Sn-Bi system

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It is revealed by *in situ* transmission electron microscopy that a unique, fluid amorphous phase is produced in Sn-Bi alloy particles at room temperature when the size of particles is below 10 nm. Bright and dark spots in the granular contrast in the high-resolution electron microscopy images of the fluid amorphous phase exhibited continuous changes in position and intensity with time, suggesting a high atomic mobility in the amorphous phase. Upon heating the fluid amorphous phase went to melt without crystallization and upon cooling it solidified again into the fluid amorphous phase with no traces of crystallization. These results indicate that due to the finite-size effect, the eutectic point T_{eu} in this system is lowered to a temperature below room temperature where observations were carried out, and that the glass transition temperature T_g, where a liquid goes to an amorphous solid, locates near room temperature.

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Understanding the structure (or phase) stability of nanometer-sized condensed matter is one of the key issues in current general physics, and dramatic progress in the understanding has been achieved by virtue of the rapidly advancing technique of transmission electron microscopy.[1,2] In fact, with the technique, the structure (or phase) stability of isolated nanometer-sized alloy particles can be studied as a function of temperature, composition, and size of the particles, and this technique has made a remarkable contribution to experimental physics on nanometer-sized condensed matters in various aspects.[3]

One hot topic revealed by the technique is the finding that the finite-size effect on the eutectic point T_{eu} in binary alloy systems is so strong that in nanometer-sized alloy particles T_{eu} can be lowered down to a temperature even below the glass transition temperature T_g.[4,5] This is a situation ascribed to the large suppression of T_{eu} across T_g, induced by the size reduction, and to our best knowledge, this situation never takes place in bulk materials.[4,5] As a result of such a situation, in a particular system of the Au-Sn system at room temperature (RT) at which observations were carried out, lies in such an order as $T_g > \mathrm{RT} > T_{eu}$, a crystalline-to-amorphous (C-A), solid-to-solid transition has been observed by simply adding solute atoms (i.e., Sn atoms) onto nanometer-sized crystalline particles of a pure substance of Au, whereas in the Sn-In system where RT lies in such an order as $\mathrm{RT} > T_g > T_{eu}$, a crystalline-to-liquid (C-L) transition has been observed by simply adding solute atoms (i.e., In atoms) onto nanometer-sized crystalline particles of a pure substance of Sn. It should be emphasized here that neither the amorphous phase in the former system nor the liquid phase in the latter system is the equilibrium phase at RT in bulk materials. These phases can be present at RT as the equilibrium phase only when the size of the system is in the nanometer range.

One quite interesting relative position among the three temperatures, RT, T_g, and T_{eu}, is the case where they lie in such an order as $\mathrm{RT} \sim T_g > T_{eu}$, and in this case it is predicted that a crystalline phase would change into an amorphous phase with fluidity by simply adding (appropriate) solute atoms onto nanometer-sized crystalline particles of a pure substance. The present paper presents the formation of such a unique, fluid amorphous phase, found in nanometer-sized particles in the Sn-Bi system.

Preparation of nanometer-sized tin particles and subsequent vapor deposition of bismuth onto tin particles was carried out using a double-source evaporator installed in the specimen chamber of a Hitachi H-800-type 200-kV transmission electron microscope (TEM). The evaporator consisted of two spiral-shaped tungsten filaments. Source substances (i.e., Sn and Bi) were put on the filaments. The distance between the filaments and a supporting film (substrate) for particles was approximately 100 mm. An amorphous carbon film was used as the supporting film, and was mounted on a molybdenum grid. Using this evaporator, tin was first evaporated from one filament onto the supporting film kept at ambient temperature in a base pressure of around 5×10^{-5} Pa, and nanometer-sized tin particles were produced on the film. Next, bismuth was evaporated from the other filament onto the same film kept at ambient temperature. Alloy phase formation in the nanometer-sized particles associated with bismuth deposition was studied by both bright-field image (BFI) and selected area electron diffraction pattern (SAED). In the present experiments, the electron flux used was approximately $1.5\times10^{20}\ \mathrm{e\,m^{-2}\,s^{-1}}$.

A series of alloy formation experiments were additionally carried out in a 200-kV high-resolution electron microscope (HREM) of Hitachi HF-2000 type, in order to study the atomistic structure of alloy phases formed. The base pressure in the specimen chamber of this microscope was below 5×10^{-7} Pa. A flake of graphite was used as a supporting substrate. Prior to experiments, the flake was baked at 1073 K for 60 s to get a cleaned surface of graphite. After being baked, the graphite substrate was cooled down to room temperature. The preparation of nanometer-sized alloy particles

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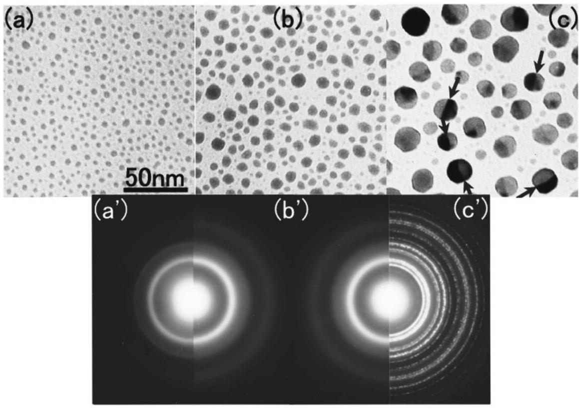

FIG. 1. Alloy phase formation in nanometer-sized particles in the Sn-Bi system at room temperature. (a) BFI of as-produced tin particles on an amorphous carbon film, and (a′) the corresponding SAED. (b) BFI of particles after depositing bismuth atoms, and (b′) the corresponding SAED. Particles shown in (b) contained, on average, about 60 at. % Bi. (c) BFI of particles after additional deposition of bismuth and tin, and (c′) the corresponding SAED. In this additional deposition, the amount of bismuth and tin deposited were so controlled that the composition of particles remained unchanged as compared to that of particles shown in (b).

was carried out by a similar method as that mentioned above. For *in situ* HREM observation of the alloying process, a television camera and video tape recorder (VTR) system was employed. The chemical composition of individual particles on the substrate was analyzed by energy-dispersive x-ray spectroscopy (EDS).

A typical example of alloying process of bismuth atoms into tin particles examined by a conventional transmission electron microscope (Hitachi H-800-type TEM) is shown in Fig. 1. Figures 1(a) and (a′) show a BFI of as-produced tin particles on an amorphous carbon film and the corresponding SAED, respectively. The mean diameter of tin particles is approximately 6 nm. The Debye-Scherrer rings can consistently be indexed as those of pure β-Sn with a tetragonal structure with lattice constants of $a=0.583$ nm and $b=0.318$ nm. The structure is the same as that of bulk β-Sn. Figures 1(b) and (b′) show a BFI of particles after bismuth deposition and the corresponding SAED, respectively. The particle size increased from 6 to 10 nm by bismuth deposition. The size increment partially came from the coalescence among particles. It was revealed by electron probe microanalysis (EPMA) that particles shown in Fig. 1(b) contained, on average, about 60 at. % Bi. It should be noted here that no interfaces were recognized in the interior of individual particles in Fig. 1(b) and only halos appeared in the SAED [Fig. 1(b′)]. This fact indicates that when bismuth atoms are vapor deposited and come in contact with tin particles they dissolved quickly into tin particles to form either amorphous or liquid Bi-Sn alloy particles. To examine the atomic structure of the noncrystalline alloy particles as shown in Fig. 1(b), a series of *in situ* alloying experiments was carried out in the HREM. The results will be shown later in Fig. 2. Figures 1(c) and (c′) shows a BFI of particles after additional deposition of bismuth and tin and the corresponding SAED, respectively. The mean particle size increased to approximately 20 nm. In this additional deposition, the amounts of bismuth and tin deposited were controlled so that the composition of particles was kept constant at about 60 at. % Bi, i.e., at the same composition as that in Fig. 1(b). It is evident in Fig. 1(c) that there appeared definite interfaces (arrowed) within individual particles. The Debye-Scherrer rings in the SAED can be consistently indexed as those of pure tin superimposed with those of pure bismuth.[6] All these observations in Figs. 1(c) and (c′) indicate that in approximately 20-nm-sized particles of a Sn-60-at. % Bi alloy, each isolated particles was composed of two phases (i.e., pure tin and bismuth), which is the same phase equilibrium at RT in the bulk alloy of the same composition. Thus it seems safe to conclude the following from Fig. 1: When the size of particles of a Sn-60-at. % Bi alloy is approximately 20 nm or above, a mixture of pure tin and bismuth is the most stable equilibrium microstructure at RT as in the case of bulk materials, but when the size of particles is approximately 10 nm or below, such a noncrystalline phase as shown in Fig. 1(b) and (b′) appears as the stable phase. This fact clearly indicates the strong finite-size effect on the phase equilibrium in the binary alloy system.

Figure 2 shows a typical sequence of alloying process of bismuth into a nanometer-sized tin particle as observed by HREM. This observation was carried out to see whether such a noncrystalline phase as shown in Figs. 1(b) and (b′) was in an amorphous state or in a liquid state. The images were reproduced from the videotape. Figure 2(a) shows an as-produced pure tin particle on a graphite substrate. The 0.291 nm-spaced fringes seen in this particle is the (020) lattice fringes of β-Sn. Figure 2(b) shows the same particle after bismuth deposition. The particle increased from 5 to 6 nm in diameter by bismuth deposition, but remained a single crystal, indicating that a solid solution is formed in the particle. With continued deposition of bismuth, the structure of the particle changed from crystalline to amorphous, as shown in Fig. 2(c). Namely, granular contrast, which is often called as the ‘‘salt-pepper contrast’’ and is characteristic of an amorphous structure, appeared in the particle after bismuth depo-

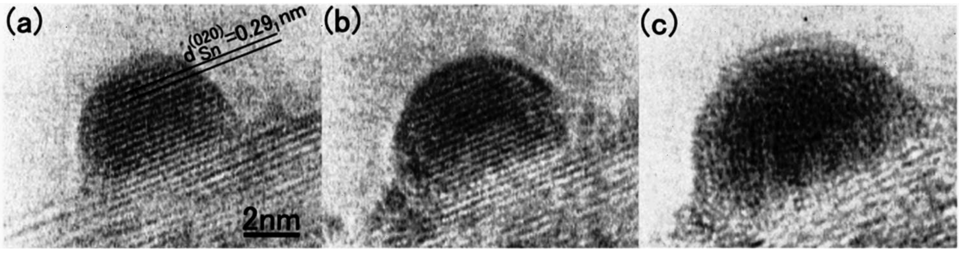

FIG. 2. A sequence from a video recording of the alloying process of bismuth into a nanometer-sized tin particle. A crystalline-to-amorphous transition took place during deposition of bismuth onto the tin particle kept at room temperature [compare (b) with (c)].

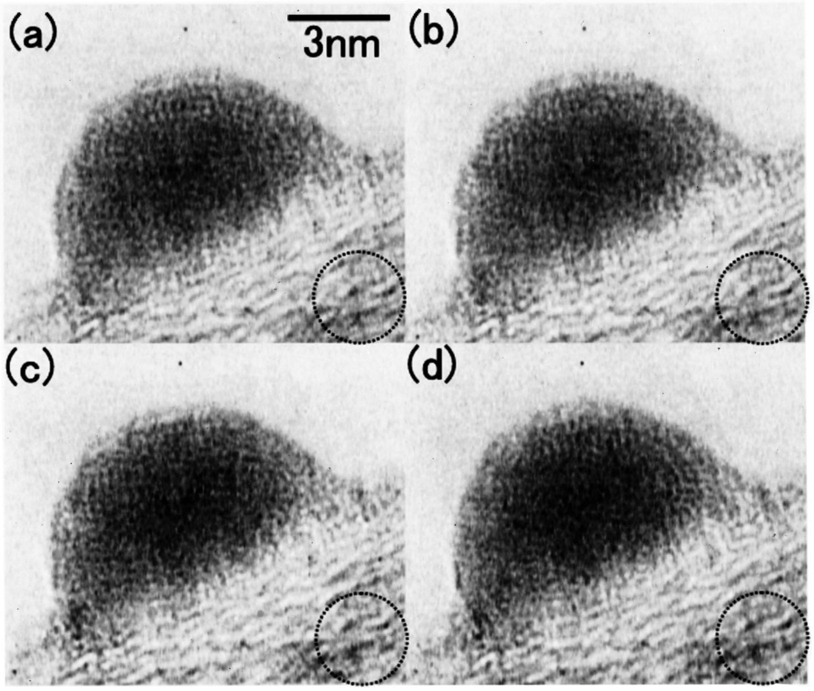

FIG. 3. *In situ* observation of fluid amorphous formed in a 9-nm-sized Sn-Bi alloy particle. Sequential micrographs (a)–(d) were taken at a time interval of 100 ms. It is shown that bright and dark spots in the granular contrast in the particle changed in position and intensity with time whereas such lattice fringes in the graphite substrate as those encircled remained fixed. This fluctuation in the granular contrast reflects a high atomic mobility in the particle.

sition [Fig. 2(c)], instead of the lattice fringes characteristic of a crystalline solid solution [Fig. 2(b)]. This fact indicates that a crystalline-to-amorphous (C→A) transition was induced in the tin particle by alloying of bismuth. The particle increased to 9 nm in diameter, and EDS analysis of the particle revealed that it contained 70 at. % Bi. One point to be noted here is the observation that the bright and dark spots in the granular image changed in position and intensity with time during observation. This is in sharp contrast to the feature of images obtained from the conventional amorphous material, in which these spots remain unchanged with time. An example of such fluctuation in granular contrast is shown in Fig. 3 as photographs which were reproduced from the videotape. Figures 3(a)–(d) show sequential micrographs of one particle taken at a time interval of 100 ms, keeping the objective lens excitation constant. The particle depicted in Fig. 3 is the same as in Fig. 2(c). It is evident from Fig. 3 that the bright and dark spots in the granular contrast exhibited continuous changes in position and intensity with time whereas lattice fringes in the graphite substrate remained fixed with time (for example, refer to such fringes as enclosed with a circle). This fluctuation in the granular contrast reflects fluctuation of the electron-optical phase shift, which comes from the fluctuation of local mass thickness. Therefore the observed fluctuation in granular contrast provides evidence for the high atomic mobility enough to induce the mass-thickness variation in the nanometer-sized particle in a time interval less than 100 ms. In other words, such high atomic mobility is responsible for the fluid amorphous structure observed in the particle in Fig. 3.

In an attempt to study the phase stability of the fluid amorphous structure, annealing experiments of Sn-Bi alloy particles were carried out. Figure 4 shows a sequence from a video recording of the melting and the subsequent solidification of a Sn-40-at. % Bi alloy particle heated and subsequently cooled *in situ* in the HREM. Figure 4(a) shows an as-produced alloy particle at RT with a fluid amorphous structure, sitting on a flake of graphite (top). With increasing temperature, the time frequency of fluctuation in the granular contrast became high, suggesting an enhanced atomic mobility. With continued heating, the particle eventually melted, and in the molten state there appeared only a quite uniform contrast typical of a liquid state [Fig. 4(b)]. It should be noted here that prior to the melting no traces of crystallization were observed. Upon cooling to room temperature, the liquid particle solidified again into the fluid amorphous phase, as illustrated in Fig. 4(c). No traces of crystallization were again recognized prior to the solidification. It is evident from Fig. 4 that the fluid amorphous phase possesses a high phase stability so that upon heating it melts without prior crystallization and upon cooling the melt solidifies directly into the amorphous phase. This fact indicates that at least at temperatures near and above room temperature the Gibbs free energy of the fluid amorphous phase is lower than that of a crystalline counterpart(s) and in this context the amorphous phase is more stable than a crystalline phase(s), which is not the case for the conventional amorphous alloys in bulk. Namely, in the case of the conventional bulk materials, the Gibbs free energy of an amorphous phase is higher than that of a crystalline counterpart(s) and therefore crystallization always takes place once the atomic mobility in the amorphous phase becomes high.

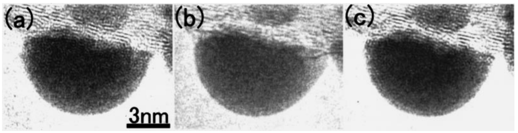

FIG. 4. A sequence from a video recording of the melting and subsequent solidification of a Sn-40-at. % Bi alloy particle heated and subsequently cooled *in situ* in a HREM.

It is shown in Figs. 1–4 that an amorphous phase is produced in nanometer-sized Sn-Bi alloy particles at RT when the size of particles is below 10 nm, and that the amorphous phase is more stable than a crystalline phase(s). These results present direct evidence for the fact that due to the finite-size effect, T_{eu} in the Sn-Bi system is suppressed to a temperature below RT where observations were conducted, and that T_g in this system locates near RT.

The present work, being in conjunction with our previous work,[4,5] can be summarized as follows. Although different types of transitions are observed in nanometer-sized alloy particles in particular systems (i.e., C→A transition in the Au-Sn system,[4] C→L transition in the Sn-In system,[5] and C→fluid *A* in the Sn-Bi system mentioned above), all these behaviors are consistently explained in terms of the relative position among T_g, RT, and T_{eu} in the systems. These observations provide concrete evidence for the formation of the thermally stable amorphous phase in nanometer-sized alloy particles over a temperature range from T_g to T_{eu}. Here, the wording of ‘‘thermally stable amorphous phase’’ comes from the sense that upon heating it goes to melt without crystallization and upon cooling it solidifies into an amorphous solid with no traces of crystallization, and it should be noted that such a thermally stable amorphous phase never appears in bulk materials and is, in this sense, an alloy phase characteristic to materials in the nanometer range.

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