

## Formation of Amorphous and Liquid Phases in Isolated Nanometer-Sized Alloy Particles

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Alloy formation in nm-sized alloy particles has been studied as a function of the particle size by in-situ transmission electron microscopy using particles in the Au-Sn and In-Sn systems. Rapid dissolution of solute atoms into nm-sized particles of a pure substance, took place in both systems. As a result, amorphous alloy particles were formed over a compositional range near the eutectic composition when the size of particles is smaller than about 6nm in diameter in the former system, whereas liquid alloy particles were formed when the size of particles is smaller than about 10nm in diameter in the latter system. When the size of particles is larger than these critical values an essentially similar phase equilibrium was observed in nanoparticles and bulk materials in the both systems. The formation of the amorphous and liquid phase in nm-sized alloy particles can be ascribed to the large suppression of the eutectic temperature associated with the size reduction.

*Key words* : Nanoparticles; Glass transition; HREM; Au-Sn alloy; In-Sn alloy

### 1. INTRODUCTION

In recent years, small particles in the size range from a few to several nanometers have been the subject of extensive experimental work. This is because these nm-sized particles often exhibit significantly different physical properties from those of corresponding bulk materials [1,2]. For example, it is well known that the phase transition temperatures such as the melting point change significantly with decreasing size of particles [3,4,5]. But, most of these studies have been focused on pure substances, being carried out by employing the temperature as the experimental parameter. To the authors' knowledge, on the other hand, studies on the phase transition associated with changes in the solute concentration in nm-sized alloy particles are quite limited.

Quite recently it is discovered that a thermally stable amorphous phase, which has never been observed in bulk materials, does appear in isolated Au-Sn alloy particles over a compositional range near the eutectic composition when the size of particles is smaller than about 6nm in diameter [6,7]. In the previous papers, we discussed the appearance of the thermally stable amorphous phase is ascribed to the large suppression of the eutectic temperature ( $T_{eu}$ ) 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 both dependent on the size of particles becomes in the reverse order. It is reasonable to consider that  $T_{eu}$  has much stronger dependence on the size of particles than  $T_g$ . In fact, it was reported that  $T_m$  decreases much faster than  $T_g$  with decreasing size of organic nm-sized particles, and when the size of particle is smaller than a critical size,  $T_m$  lies below  $T_g$  [8]. Based on this premise, it is considered that the thermally stable amorphous phase would appear in such a case where observation temperature lies in a temperature

range higher than  $T_{eu}$  but lower than  $T_g$  by decreasing the size of particles. Because the binary system having a high  $T_{eu}$  is considered to have a relatively high  $T_g$ , such an order as  $T_g > RT > T_{eu}$  is possible below a critical size of particles, and in this case it is predicted that a crystalline-to-amorphous ( $C \rightarrow A$ ) transition will be observed at RT by simply adding solute atoms onto nm-sized crystalline particles of a pure substance. On the other hand, such an order as  $RT > T_g > T_{eu}$  is possible in the binary system having a relatively low  $T_{eu}$ , and in this case, a crystalline solid solution phase can be directly converted into a liquid phase by simply adding solute atoms onto nm-sized crystalline particles of a pure substance. The former case will be realized in the Au-Sn binary system whereas the latter case in the In-Sn system. We examined the latter case in detail in this work, in an attempt to verify the view mentioned above. The present paper reports on the first direct observation of such a crystalline-to-liquid ( $C \rightarrow L$ ) transition found in particles in the In-Sn system.

### 2. EXPERIMENTAL PROCEDURES

Preparation of nm-sized indium particles and subsequent vapor-deposition of tin onto indium particles were carried out using a double-source evaporator installed in the specimen chamber of a Hitachi H-800 type 200kV transmission electron microscope (TEM). The evaporator consisted of two spiral-shaped tungsten filaments and source substances were put on the filaments. The distance between the filaments and a supporting film (substrate) for particles was approximately 100mm. An amorphous carbon film was used as the supporting film, and was mounted on a molybdenum grid. Using this evaporator, indium was first evaporated from one filament onto the supporting film kept at ambient temperature in a base pressure of around  $5 \times 10^{-5}$  Pa, and nm-sized indium particles were produced on the film.

Next, tin was evaporated from the other filament onto the same film kept at ambient temperature. Alloy phase formation in nm-sized particles associated with tin 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  $1.5 \times 10^{20} \text{ e} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$ .

In order to study the atomistic structure of alloy phases formed, a series of alloy formation experiments were additionally carried out in a 200kV high resolution electron microscope (HREM) of Hitachi HF-2000 type. The base pressure in the specimen chamber of this microscope was below  $5 \times 10^{-7}$  Pa. A flake of graphite was used as a supporting substrate. Prior to experiments, the flake was baked at 1073K 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 nm-sized alloy particles 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 positives were reproduced from the images recorded with the VTR system.

### 3. RESULTS

A typical example of alloying behavior of tin atoms into indium particles is shown in Fig.1. Figure 1(a) and (a') show a bright-field image (BFI) of as-produced indium particles on a supporting film and the corresponding selected area electron diffraction pattern (SAED), respectively. The mean diameter of indium particles is approximately 7nm. The Debye-Scherrer rings in the SAED can consistently be indexed as those of a crystal with the face-centered cubic (fcc) structure with a lattice constant of  $a=0.47_1$  nm. This is essentially consistent with the results in a previous report [9]. Figure 1(b) and (b') show a BFI of particles after tin deposition and the corresponding SAED, respectively. The particle size increased from approximately 7nm to 16nm in the mean diameter, as seen from a comparison of Fig.1(a) with (b). Electron probe microanalysis (EPMA) of the same sample shown in Fig.1(b) revealed that the material on the supporting film contained, on the whole, about 70at%Sn. One point to be noted here is the fact that a distinct heterointerface is present in individual particles (as indicated with arrows in Fig.1(b)). This fact suggests that individual particles are composed of two phases, and the Debye-Scherrer rings depicted in Fig.1(b') can consistently be indexed as those of  $\text{In}_3\text{Sn}$  (which has a tetragonal structure belonging to the space-group  $I4/mmm$  with lattice constants of  $a=0.34_6$  nm and  $c=0.43_9$  nm) superimposed on those of  $\text{InSn}_4$  (which has a hexagonal structure belonging to the space-group  $P6/mmm$  with lattice constants of  $a=0.32_0$  nm and  $c=0.29_9$  nm). These two phases are nothing but the conjugate phases predicted from the bulk equilibrium phase diagram [10]. All these observations indicate that when tin atoms are vapor-deposited onto 7nm-sized indium particles, rapid spontaneous alloying of tin atoms into indium particles takes place and as a result a mixture of two phases, one is  $\text{In}_3\text{Sn}$  and the other is  $\text{InSn}_4$ , is developed within each particle. The formation of the two-phase mixture in individual particles is consistent with alloy phase formation predicted from the phase diagram for the bulk.

The above observation is consistent with a recent result that when the size of particles is larger than about 10nm

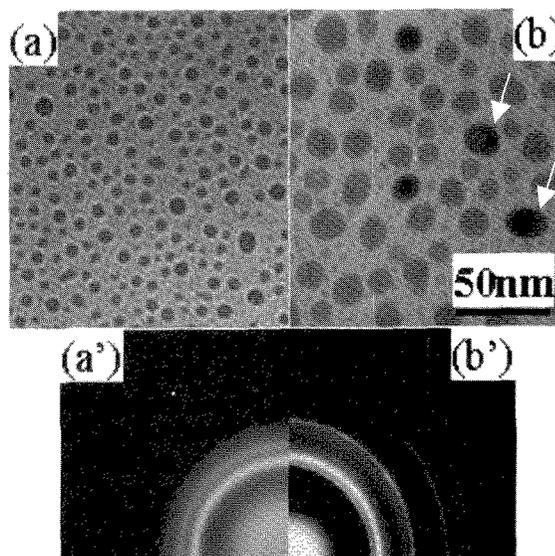


Fig.1 Alloying behavior of tin atoms into indium particles at ambient temperature. (a) BFI of as-produced indium particles on an amorphous carbon film, and (a') the corresponding SAED. (b) BFI of particles after depositing tin atoms, and (b') the corresponding SAED. The mean size of particles in (b) was 16nm in diameter. The chemical composition of the particles was evaluated to be approximately Sn-30at%In.

an essentially similar phase equilibrium was observed both in particles and bulk materials in the Au-Sn binary system [7]. Therefore, it seems safe to consider that the finite size effect on the phase stability in alloy particles is rather small when the size of particles is larger than approximately 10nm.

An example of alloying behavior of tin atoms into relatively small indium particles is presented in Fig.2. Figure 2(a) and (a') show a BFI of as-produced indium particles and the corresponding SAED, respectively. The mean diameter of indium particles is approximately 5nm. The Debye-Scherrer rings in the SAED can again be indexed as those of fcc pure indium. Figure 2(b) and (b') show a BFI of particles after tin deposition and the

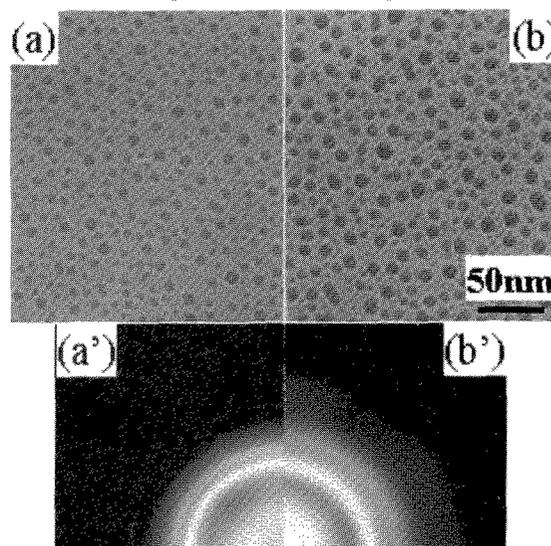


Fig.2 Alloying behavior of tin atoms into indium particles at ambient temperature. (a) BFI of as-produced indium particles on an amorphous carbon film, and (a') the corresponding SAED. (b) BFI of particles after depositing tin atoms, and (b') the corresponding SAED. The mean size of particles in (b) was 10nm in diameter. The chemical composition of the particles was evaluated to be approximately Sn-30at%In.

corresponding SAED, respectively. The particle size has increased from approximately 5nm to 10nm in the mean diameter, as seen from a comparison of Fig.2(a) with (b). It should be noted here that no interfaces are recognized in the interior of individual particles in Fig.2(b), in contrast to the particles depicted in Fig.1(b). In the SAED (Fig.2(b')), halos are recognized. This fact indicates that vapor-deposited tin atoms came in contact with indium particles and dissolved quickly into the particles to form either amorphous or liquid In-Sn alloy particles. EPMA of the same sample shown in Fig.2(b) revealed that the material on the supporting film contained, on the whole, about 70at%Sn. The stable phases in the Sn-30at%In bulk alloy at room temperature are  $\text{In}_3\text{Sn}$  and  $\text{InSn}_4$ , as mentioned before. Accordingly, it can be said that in Sn-30at%In alloy particles of approximately 10nm in the mean diameter, stable phases in the corresponding bulk material are not realized. It is of significance to investigate whether the structure of alloy particles shown in Fig.2(b) is amorphous or liquid. However, it is difficult to solve this problem from halo rings only shown in the SAED (Fig.2(b')). Based upon this premise, a series of in situ alloying experiments were carried out in a HREM to monitor the structural change of the noncrystalline alloy particles from an atomistic point of view.

Figure 3 is a typical sequence of alloying process in an approximately 4nm-sized particle. Figure 3(a) shows an as-produced, pure tin particle on a graphite substrate. The 0.29 nm-spaced fringes seen in this particles is the (020) lattice fringes of  $\beta$ -Sn. The same particle after indium deposition is shown in Fig.3(b). The particle remains being a single crystal, indicating a solid solution is formed in the particle. The diameter of the particle has increased from approximately 4.0nm (Fig.3(a)) to 4.4nm (Fig.3(b)) by indium deposition. With continued deposition of indium, the particle underwent a crystalline-to-liquid ( $\text{C} \rightarrow \text{L}$ ) transition, as shown in Figs.3(b) and (c). Namely, all the lattice fringes in the particle disappeared abruptly and there appeared only a uniform contrast typical of the liquid state (Fig.3(c)). The time interval between Fig.3(b) and (c) is shorter than 1/15s, indicating that the  $\text{C} \rightarrow \text{L}$  transition took place very quickly. The indium concentration in the liquid estimated from the size difference between the particle shown in Fig.3(a) and that in Fig.3(c) is approximately 30at%In. Therefore, it can be said that the stable phase of approximately 4nm-sized Sn-30at%In alloy particle at room temperature is liquid, and this is in sharp contrast with the equilibrium phase(s) in bulk materials (i.e., a two phase mixture of  $\text{In}_3\text{Sn}$  and  $\text{InSn}_4$ ). Through the HREM observations shown in Fig.3, it is confirmed that the

structure of such alloy particles as depicted in Fig.2(b) is not amorphous but liquid.

#### 4. DISCUSSION

In this work, it is verified that a liquid phase was formed in approximately 10 nm-sized particles of a Sn-30at%In alloy (Fig.2(b)) and in 4nm-sized particles of a Sn-30at%In alloy (Fig.3(c)) kept at room temperature, although particles of pure tin (Fig.3(a)) and of pure indium (Fig.2(a)) in the comparable size range remain crystalline at room temperature. The formation of the liquid phase is thought to come from a situation that due to the suppression of  $T_{\text{eu}}$  induced by the size reduction, the three temperatures, RT,  $T_{\text{g}}$ , and  $T_{\text{eu}}$ , lie in such an order,  $\text{RT} > T_{\text{g}} > T_{\text{eu}}$ . It is interesting to note here that in case room temperature where observations were conducted lies between  $T_{\text{g}}$  and  $T_{\text{eu}}$ , then a crystalline-to-amorphous ( $\text{C} \rightarrow \text{A}$ ) transition, in stead of the  $\text{C} \rightarrow \text{L}$  transition observed in the present work, is predicted to take place when solute atoms are deposited. In fact such a  $\text{C} \rightarrow \text{A}$  transition has been observed in 6 nm-sized particles in the Au-Sn system [7]. In this context, the present observations shown in Figs.2 and 3 provide further evidence for the finite size effect on  $T_{\text{eu}}$  and for the fact that the relative position among RT (the temperature where observations are carried out),  $T_{\text{g}}$ , and  $T_{\text{eu}}$  plays an important role in understanding the phase stability.

Another point to be noted here is the fact that the formation of the liquid phase is in disagreement with a previous result that an amorphous phase was formed in alloy particles in the In-Sn system when the size of particles were less than approximately 20nm [5]. The reasons for the disagreement are not clear at this moment, but it is worth noting that in the previous report [5] the formation of the amorphous phase was concluded only from the SAED showing diffuse rings and no complementary HREM study was done to draw the conclusion. So, there may be a possibility that the diffuse rings observed in the previous study came from not an amorphous but a liquid phase.

#### 5. SUMMARY

Alloy formation in nm-sized alloy particles has been studied as a function of the particle size using particles in the Au-Sn and In-Sn systems. Amorphous alloy particles were formed over a compositional range near the eutectic composition when the size of particles is smaller than about 6nm in diameter in the former system, whereas liquid alloy particles were formed when the size of particles is smaller than about 10nm in diameter in the

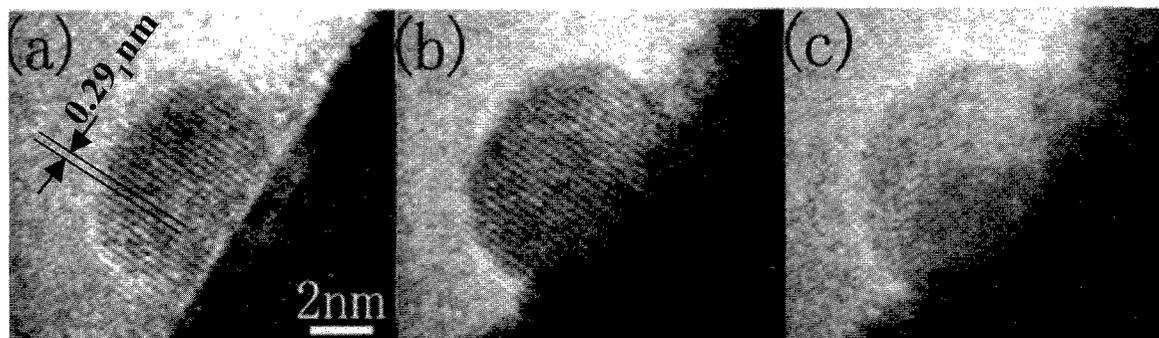


Fig.3 In situ observation of alloying process of indium atoms into an approximately 4nm-sized tin particle. A crystalline-to-liquid ( $\text{C} \rightarrow \text{L}$ ) transition took place during deposition of indium onto the nm-sized tin particle kept at room temperature (compare Fig.(b) with (c)).

latter system. When the size of particles is larger than these critical values an essentially similar phase equilibrium was observed in nanoparticles and bulk materials in the both systems. The formation of the amorphous and liquid phase in nm-sized alloy particles can be ascribed to the large suppression of the eutectic temperature associated with the size reduction.

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