

In Situ TEM Study of the Characteristics in Nanometer-sized Alloy Particles

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ABSTRACT

Alloy phase formation in nanometer-sized particles has been studied by in-situ transmission electron microscopy. From the experimental results, it was revealed that the eutectic temperature of nanometer-sized alloy particles is significantly suppressed from that of the corresponding bulk materials. The suppression of the eutectic temperature could be explained from a theoretical study based on thermodynamics which is modified in such a manner that Gibbs free energies for bulk materials available in the CALPHAD database system were modified by taking factors affecting the phase equilibrium of nanometer-sized alloy particles into consideration.

KEY WORDS: in-situ TEM, alloy, nanoparticles, interfacial energy, eutectic temperature.

INTRODUCTION

The structure and property of small particles in the size range from a few to several nanometers have been of interest to many researchers from both scientific and technological viewpoints. This is because these nanometer-sized particles often exhibit physical and chemical properties that are significantly different from those of the corresponding bulk materials and therefore afford promise of use as advanced materials with new electronic, magnetic, optic, and thermal properties (Halperin, 1986; Andres et al., 1989).

The nanometer-sized particles consist of 10^2 to 10^4 atoms and the surface-to-volume ratio of them becomes remarkably large. The surface atoms have some broken bonds and are in a high-energy state compared with the inner atoms. So the surface atoms make great contributions to many peculiar properties seen in nanometer-sized particles. This can be mentioned as the *surface effect*. To get a fundamental understanding of this effect, intensive research has been carried out so far.

For example, Takagi (1954) studied the structural changes of thin films of Pb, Sn and Bi at various temperatures by the electron diffraction method and found that the melting temperatures (T_m) of thin films, the mean thickness of which ranged from 1 nm to 100 nm, are definitely lower than those of the corresponding bulk materials. This was a frontier work that clearly showed the size effect on the thermodynamical properties. It is now well established that such phase

transition temperatures as T_m are significantly reduced with decreasing size of particles (Sambles, 1971; Buffat and Borel, 1976; Allen et al., 1986). With regard to structures, a structure type called A15 was found in nanometer-sized chromium particles, which have a structural type of body center cubic (bcc) in bulk (Kimoto, 1967). Multiply twinned particles (MTPs) were found in nanometer-sized gold and silver particles, which have a structural type of face center cubic (fcc) in bulk by Ogawa et al. (1966). Most of these works mentioned above are, however, concerned with phase transitions in nanometer-sized *pure* substances, and in these experiments the temperature (T) and size (D) of particles were employed as experimental parameters. On the other hand, studies on nanometer-sized *alloy* particles examined as a function of T, D, and composition (X), are quite limited (Allen and Jesser, 1984; Jesser et al., 1999), although in recent years much attention has been paid to nanometer-sized *alloy* particles as candidates for new functional materials.

This limitation of studies on nanometer-sized alloy particles is mainly due to the fact that it was rather difficult to control and measure the three parameters, T, D, and X, at the same time in a particle. However, recent remarkable progress in transmission electron microscopy (TEM) enables us to study not only the structure, but also the chemical composition of an isolated nanometer-sized target material at a fixed temperature. With the use of this technique it now becomes possible to examine such alloy properties as the alloy phase formation in isolated nanometer-sized particles as a function of T, D, and X of the system. This situation opens a wide, unexplored research field on the structural stability of nanometer-sized condensed matter in two- (or multi-) component systems.

On the other hand, the thermodynamic calculation based on the CALPHAD (CALculation of PHase Diagram) method can be extended from bulk to nanometer-sized systems if one takes the finite size effect into consideration in the calculation, which provides a useful approach to construct the phase diagram of nanometer-sized alloy particles.

In the present study, the effects of an interface between two solid phases on the phase equilibrium in isolated nanometer-sized alloy particles in the Bi-Sn system have been studied by *in situ* TEM. The experimental results are then compared with results of thermodynamic calculations in which factors affecting the phase equilibrium of nanometer-sized alloy particles were taken into consideration.