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Control of Size and Composition of Sn based nanoparticles prepared by Ar-H_2 arc

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The purpose of this study was to control size and composition of Sn-Ag-Cu nanoparticles prepared by Ar or Ar-H_2 arc. The vaporization and condensation rate should be controlled to prepare alloy nanoparticles. These rates could be controlled by the composition of raw material and H_2 concentration. An increase in H_2 concentration in the arc led to an increase of Cu fraction in prepared nanoparticle. An increase of Sn fraction in nanoparticle made particle size larger. The obtained results indicated that the nanoparticles were spherical shape. Another purpose of this study was to investigate the vaporization mechanism from molten Sn-based alloy with Ar-H_2 arc. The vaporization enhancement of Cu from Sn-Ag-Cu mixture by hydrogen in arc plasma was confirmed. The vaporization enhancement would be attributed to the activity modification by hydrogen in molten metals.
Key words: DC arc, hydrogen arc, nanoparticle, Sn-based alloy

1. INTRODUCTION

Attractive material processes with thermal plasma have been proposed for the production of nanoparticles, because thermal plasmas offer unique advantages; these advantages include high enthalpy to enhance reaction kinetics, high chemical reactivity, oxidation and reduction atmosphere in accordance with required chemical reactions and rapid quenching (10^5-10^6 K/s) to produce chemical non-equilibrium materials.

DC arc method has attracted great interest because it is the method providing high quality nanoparticles with high productivity at low cost. For example, metal [1], oxide [2], alloys and intermetallics and surface-coated nanoparticles [3] prepared successfully by DC arc have been reported. However, researches about control size and composition by DC arc method have rarely been reported in previous works due to the difficulty of control for vapor concentration in region of nanoparticle growth.

The objective of the present study was to control size and composition of nanoparticles prepared by DC arc method. Previous works have revealed the relationship between the particle size of Sn-Ag nanoparticle and H_2 concentration in the arc [4]. In this work, we investigated the relationship between the composition of Sn-Ag-Cu raw material and prepared particle size.

2. EXPERIMENTAL

2.1 Experimental setup

Fig.1 shows a schematic illustration of experimental setup for the production of nanoparticles. The setup consists of the DC power supply, an arc chamber, a particle collector and gas circulator. An ingot of 30 g, a mixture of Sn-Ag-Cu used as a raw material, was placed on the water cooled copper anode. An Ar or Ar-H_2 arcs were used for the vaporization of the raw material. Typical operating conditions are as follows: arc current: 200 A, arc voltage: 20-45 V, total pressure: 101 kPa, shield gas flow rate: 25 Nl/min, circulation gas flow rate: 160 Nl/min, H_2 concentration: 0, 50vol%, discharge time: 1-30 min.

The metal fume was generated from the raw material

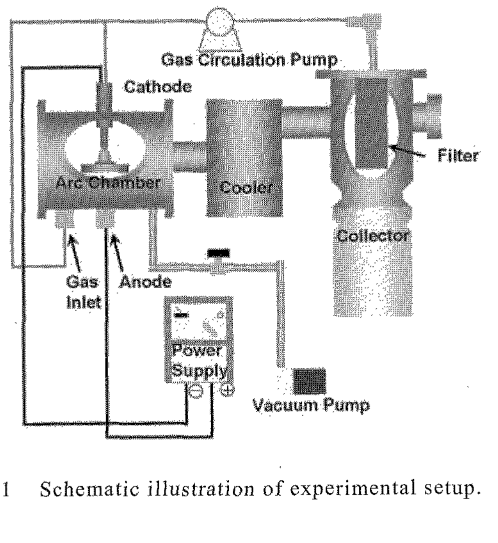

Fig. 1 Schematic illustration of experimental setup.

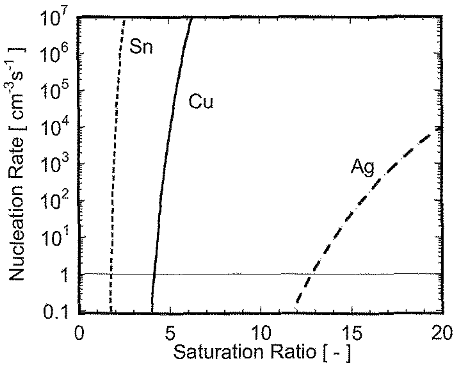

Fig. 2 Relationship between homogeneous nucleation

surface on the anode soon after the raw material arc-melted. The gas generated fume was transported by a circulation gas flow to the collection filter. Ar and H_2 gases without the entrained particles were reintroduced into the arc chamber by a gas circulation pump.

2.2 Sample preparation

Pellets were made from powders of Sn-Ag alloy, which contain 3.5 wt.% Ag (3-6 μm), with Cu powders (6 μm) of various compositions. All powders have a purity of 99.9%. The initial fractions of Cu were 0, 0.5, 5, 10, 30, 50, 70 wt.% for the Sn-Ag-Cu system. The prepared pellets were 20-mm diameter and 18-mm height.

2.3 Analysis

The size distribution of the particles was measured from the photographs of transmission electron microscopy (TEM, Phillips, CM200, 200 kV) for approximately 300 particles. TEM specimens were prepared by ultrasonic dispersing of several drops of the nanoparticles solution, and then deposited on copper grids. The sample was dried in a vacuum oven at ambient temperature before analysis. Besides, the specific surface area and the average particle diameter were determined by BET method applying to nitrogen adsorption. The compositions of the prepared nanoparticles collected at the metal filter were determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES, SHIMADZU, ICPS-8100). The structures of the particles were determined by X-ray diffractometry (XRD, Rigaku, MiniFlex). The weight decrease of the raw material was measured after treatment to estimate the vaporization rate of the constituent metal elements from the raw material.

3. RESULTS AND DISCUSSION

Nucleation temperature of the metals could be estimated by Eqs. (1-3)

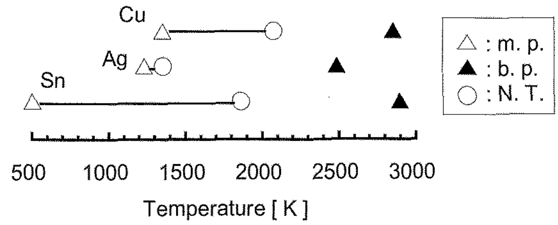

Fig. 3 Nucleation temperature (N.T.) of constituent metals.

$$J = \frac{\beta_{ij} n_s^2 S}{12}\sqrt{\frac{\Theta}{2\pi}}\exp\left(\Theta - \frac{4\Theta^3}{27(\ln S)^2}\right) \quad (1)$$

$$\Theta = \frac{\sigma s_1}{kT} \quad (2)$$

$$\beta_{ij} = \left(\frac{3v_1}{4\pi}\right)^{1/6}\sqrt{\frac{6kT}{\rho_P}\left(\frac{1}{i}+\frac{1}{j}\right)}\times\left(i^{1/3}+j^{1/3}\right)^2 \quad (3)$$

where n_s is the equilibrium saturation monomer concentration at temperature T, S the saturation ratio, β_{ij} the collision frequency function between i-mers and j-mers, and Θ the dimensionless surface tension given by Eq. (2), s_1 is the monomer surface area and σ the surface tension. The collision frequency function β_{ij} can be estimated by Eq. (3), v_1 is the monomer volume and ρ_p particle mass density. In this model, the particle nucleation is due to the metal vapor collision, therefore i=j=1.

Relationship between the nucleation rate and saturation ratio was shown in Fig.2. The nucleation rate is strongly dependent on surface tension and the saturation ratio. When the nucleation rate is over 1.0 $cm^{-3}s^{-1}$, particle formation can be observed experimentally. Therefore, the corresponding value of saturation ratio is defined as the critical saturation ratio [5]. The critical ratio of Ag was estimated to be 10, while the other metals have the critical saturation ratio from 2 to 4. The nucleation temperature at the critical saturation ratio was shown in Fig.3 for the constituent metals. All constituent metals have liquid range between the nucleation and melting temperature. Sn has wider range between the temperatures, while Ag has narrower range than other metals.

The XRD patterns of the prepared nanoparticles are shown in Fig.4. The diffraction peaks are identified to be the intermetallic compounds, Cu_6Sn_5, as well as Sn and Ag in the case of 30 wt.% Cu. In the case of 50 wt.% Cu, Cu_6Sn_5 and Cu_3Sn were found, while the peaks of Cu and Sn were not found. In the case of 70 wt.% Cu, the peaks of $Cu_{5.6}Sn$ and $Cu_{41}Sn$ were identified. These results indicated all the copper vapor coagulates to form the intermetallic compounds when Cu fraction increases more than 30 wt.%. In the Sn-Ag-Cu system, copper vapor becomes supersaturated earlier than tin and silver vapor as temperature decreases according to Fig.3.

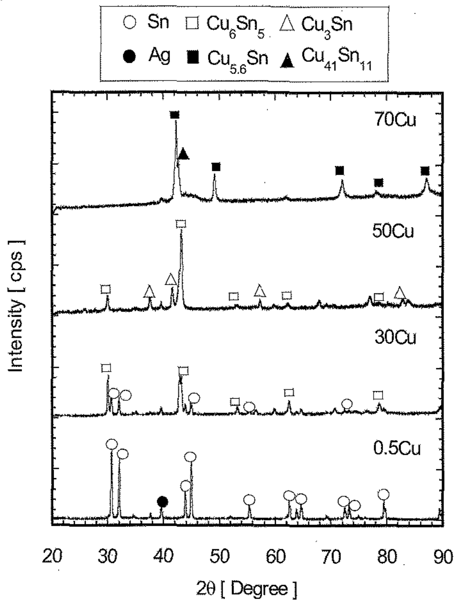

Fig. 4 XRD patterns of the nanoparticles prepared with 50%-H_2 arc.

During the liquid stage of copper, other metal vapor heterogeneously co-condense on the liquid copper, resulting in preparation of intermetallic compounds and alloys preferentially.

Nanoparticles produced from molten metal were enhanced by hydrogen addition with DC arc. The vaporization rate from the raw material of 70wt.% Cu, was 0.04 g/min with 100%-Ar arc, while that was 4.3 g/min with 50%-H_2 arc. Furthermore, Cu fraction in nanoparticles by 50%-H_2 arc was richer than that by 100%-Ar arc, as shown in Fig.5. These results could not be explained by only the thermal effect of H_2 addition in the arc. Our previous work [4], it was suggested that the vapor-liquid equilibrium state would be modified by hydrogen in arc. In this study, similar discussions about Sn-Cu system were carried out. The relationship between the Cu fraction in the prepared nanoparticles neglecting Ag fraction and that in the raw materials is shown in Fig. 6. The gas phase composition was calculated by Eqs. (4) and (5) under the assumption that molten Sn-Cu metals is regular solution.

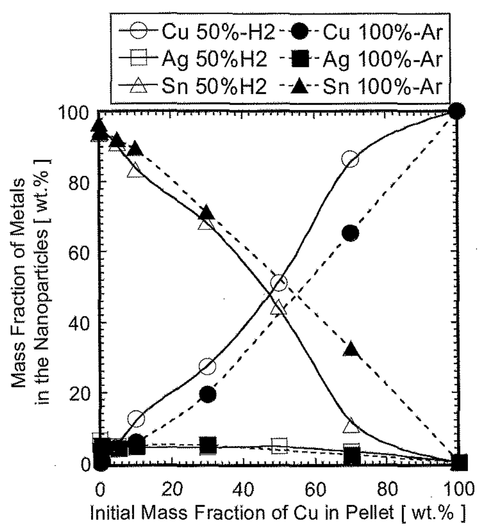

Fig. 5 The relationship between the composition of the nanoparticles prepared by 50%-H_2 arc and 100%-Ar arc.

$$a_M = N_M \left(\frac{a_M^0}{N_M} \right)^{\frac{T_0}{T}} \tag{4}$$

$$P_M = a_M P_M^0 \tag{5}$$

where a_M is the activity of the metal (Sn or Cu), N_M is the mole fraction of the metal, $a^0{}_M$ is the known activity at temperature T_0. P and P_0 are the vapor pressure. The composition of the prepared nanoparticles with Ar arc agreed to the gas phase composition calculated by Eqs. (4) and (5). On the other hand, the composition with 50%-H_2 arc is richer Cu fraction than that of calculated value at equilibrium state. These results revealed that the vaporization mechanism for pure metal proposed by Ohno and Uda [6] may not be applied for molten alloy. These indicated that the vaporization enhancement of Cu from the molten Sn-Ag-Cu alloy occurred by hydrogen addition. Therefore, the vaporization enhancement of particular metals by H_2 arc would be mainly attributed to the activity modification of the molten metal mixture by H_2 addition in the arc.

Fig.7 shows the representative TEM images and particle diameter distributions of Sn-Ag-Cu nanoparticles, prepared from the pellet of Sn-Ag-Cu mixture, (a) initial mass fraction of Cu was 10 wt.% with 100%-Ar arc and (b) that with 50%-H_2 arc, respectively. From the TEM images, the particle diameter distributions and the average particle diameter of nanoparticles were determined. About the raw materials that initial mass fraction of Cu was 10 wt.%, the average diameter of the nanoparticles prepared with 100%-Ar arc was 18.8 nm, while that with 50%-H_2 arc was 68.0 nm. The main reason for having different average

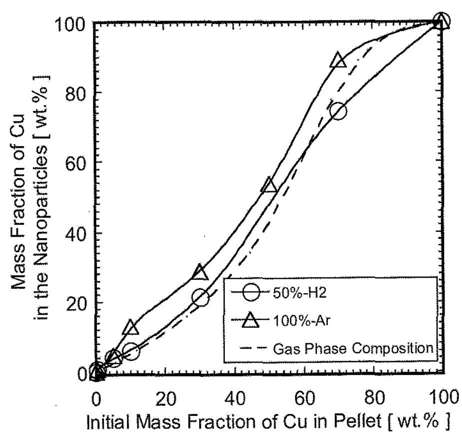

Fig. 6 The relationship of Cu fractions between prepared nanoparticles and raw materials.

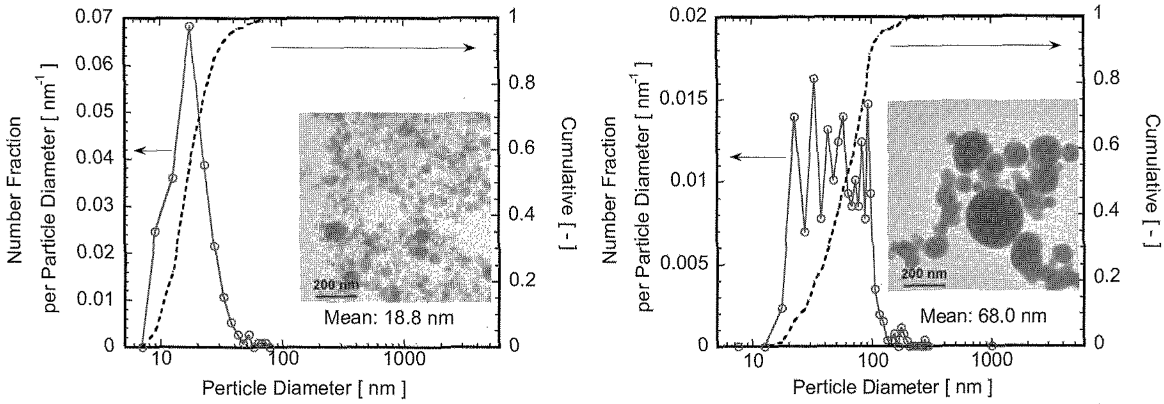

Fig. 7 Particle diameter distributions and morphology of nanoparticles prepared from raw material contain 10 wt.% of Cu (a) with 100%-Ar and (b) with 50%-H_2 arc.

diameter between the 100%-Ar arc and the 50%-H_2 arc is the difference of vaporization rates. Higher vaporization rate leads to higher vapor concentration, resulting larger diameter of nanoparticles.

Fig.8 shows that the relationship between the average particle diameters and initial mass fraction of Cu in pellets. In Fig.8, the open plots represent the diameters measured by TEM images, and the closed plots indicated the diameters calculated from the specific surface area by BET method. The diameters from BET mesurement represented the larger values than these from TEM observation due to the aggregation of the nanoparticles in gas phase. Particle diameters of Sn-Ag-Cu nanoparticles become smaller, when Cu fraction in raw materials increases. Main reason for this result is the Sn has wider liquid range between the nucleation temperature and melting temperature. Wider liquid range enhances particle coalesce, resulting in larger diameter of the nanoparticles.

Control size of nanoparticles by DC arc is attributed to the following factors: liquid range between the nucleation temperature and melting temperature; vapor concentration that is related with the vaporization rate of the metals; production of alloy and/or intermetallic compound. Besides, the control of composition of nanoparticles is attributed to the vaporization behavior of the metals. H_2 addition in the arc occur vaporization enhancement of Cu from molten Sn-Ag-Cu mixture. Hence, to control the size and composition with more controllability, it is necessary that the control vapor concentration near the arc and to investigate vaporization enhancement by H_2 arc in more detail, which will be our future study.

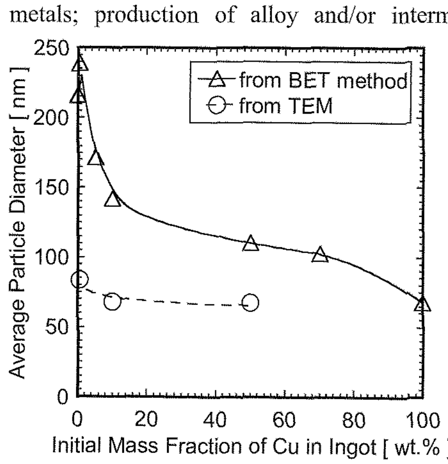

Fig. 8 The relationship between the particle diameter of prepared nanoparticles.

4. CONCLUSION

1) Sn-Ag-Cu nanoparticles were successfully prepared by DC arc method. The average diameters of the nanoparticles were controlled by the initial composition of the raw materials and H_2 concentration in the arc.

2) The vaporization enhancement of particular metals from metal mixture by hydrogen in arc plasma was confirmed. The prepared nanoparticles with 50%-H_2 arc contained richer Cu fraction than these with Ar arc.

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