# Thermal Plasma Processing for Functional Nanoparticle Synthesis

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**ABSTRACT:** The purpose of this study is to describe the synthesis of metal alloy and intermetallic nanoparticles by a DC arc method. Sn-based nanoparticles have been successfully prepared by DC arc with hydrogen addition. The prepared nanoparticles were characterized by transmission electron microscopy and inductively coupled plasma-atomic emission spectrometry. The prepared nanoparticles have high-purity and spherical shape. Obtained results indicated that the mean diameter and the composition of the nanoparticles could be controlled by the hydrogen concentration in the arc. Another purpose of this study is to investigate the vaporization mechanism from molten metal mixture with Ar and Ar-$H_2$ arc. The spectroscopic measurements of the vaporized species were carried out. The vaporization enhancement by hydrogen addition would be attributed to the formation of metal hydride from the molten metal.

**Keywords**: DC arc method, hydrogen arc, nanoparticles; spectroscopy

## INTRODUCTION

Reactive thermal plasmasoperated at atmospheric pressure have been anticipated as a potent tool for nanoparticleproduction, because thermal plasmasprovide distinctive advantages, such as high enthalpy and high chemical reactivity.These advantages increase the advances and demands in plasma chemistry and plasma processing (Shigeta and Watanabe, 2005, 2007, 2008).

Figure 1 shows the conceptual diagram of the DC arc method for nanoparticle synthesis. A large amount of raw material, even that with a high melting/boiling point, can be vaporized by high-temperature of the arc. Subsequently, the vapor is transported to the tail of the arcwith a high cooling rate ($10^4$–$10^5$ K $s^{-1}$) and the vapor falls into a highly supersaturated state, which achieves effective formation of nanoparticles by nucleation and condensation. Consequently,DC arc can be regarded as an innovative tool that automatically creates nanoparticles with a notable production rate at low cost.For example, metal, oxide, alloys, intermetallics, and surface-coated nanoparticles prepared successfully by DC arc have been reported (Watanabe et al., 2001).However, the practical fabrication of the functional nanoparticles by DC arc is a complicated phenomenon which involves interaction among the thermofluid field, the induced electromagnetic field and the processed particle phases with numerous variables.

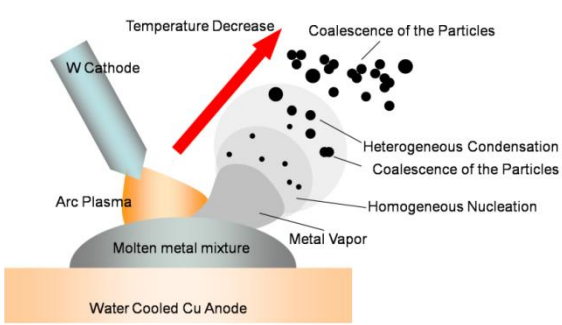



**Figure 1. Conceptual diagram of the DC arc method**

The purpose of this study is to investigate the growth mechanism of the Sn-Ag nanoparticles, which would be applicable for the lead-free soldering, by the DC arc method. Another purpose is to investigate the mechanism of Vaporization enhancement of particular metals from molten metal mixture by the DC arc method with hydrogen addition.These investigations are important for the control of size, phase, and composition of intermetallic compound nanoparticles in thermal plasma processing.

## MATERIALS AND METHODS

### Modeling of nanoparticle growth mechanism

The homogeneous nucleation rate was proposed by Girshick et al. (1990). They derived the expression as an extension of kinetic nucleation theory. The proposed expression can be used over a wide range of physical conditions. Furthermore, the expression for homogeneous nucleation rate $J$ was used for the estimation of critical saturation ratio.

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

where $n_s$ is the equilibrium saturation monomer concentration at temperature $T$, $S$ the saturation ratio, $\beta_{ij}$the collision frequency function between $i$-mers and $j$-mers, and$\Theta$the dimensionless surface tension. The dimensionless surface tension is given by

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

where $s_1$ is the monomer surface area and the surface tension.

The particle growth by heterogeneous condensation is calculated by

$$\frac{dv_p}{dt} = \frac{\pi d_p^2 v_1 (p_{vapor} - p_S)}{\sqrt{2\pi m k_B T}} \quad (3)$$

where $v_p$is the particle volume, $P_{vapor}$ and $P_s$ are the vapor pressure of the metal and saturation vapor pressure, respectively.

Using Eqs. (1) and (3), the vapor consumption rate is calculated by

$$\frac{dn_m}{dt} = -I\frac{v_p^*}{v_1} - \frac{N_p}{v_1}\frac{dv_p}{dt} \qquad (4)$$

where $n_m$ is the monomer concentration, $v_p^*$ is the particle volume at nucleation, $N_p$ is the concentration of the generated nanoparticles. The nucleation rate and condensation rate of the metal vapor was calculated by solving above equations to investigate the growth mechanism of Sn-Ag nanoparticles using DC arc method. More details of this modeling are mentioned in our previous work (Tanaka and Watanabe, 2008a).

## EXPERIMENTAL

Figure 2 shows a schematic illustration of experimental setup for the nanoparticle production. The setup consists of a power supply, an arc chamber, a particle collector, and a gas circulation pump. An ingot of 50 g, a mixture of Sn-Ag alloy used as a raw material, was placed on the water-cooled copper anode. The initial fractions of Ag in the raw materials were 1, 3.5, 5, 30, 50, and 70wt%.An Ar or Ar-$H_2$ arc was used for the vaporization of the raw material. Typical operating conditions are as follows: current: 100 A, voltage: 20-40 V, total pressure: 101 kPa, gas flow rate: 25 Nl/min, $H_2$ concentration: 0, 5, 20, 50vol%, discharge time: 1-30 min.

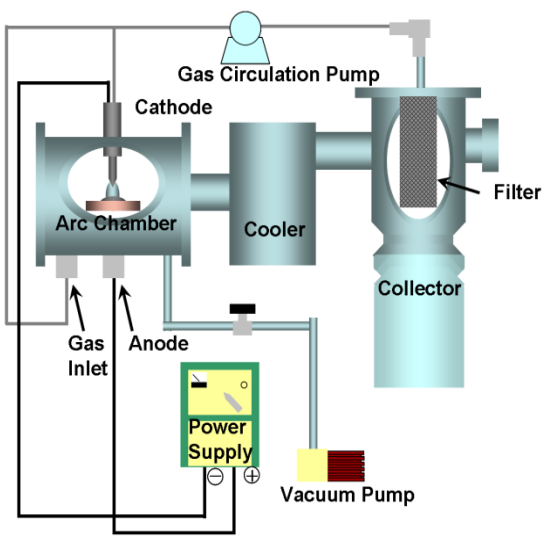



**Figure 2. Schematic of the experimental setup**

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

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 size distribution of the particles was measured from the photographs of transmission electron microscopy (TEM, Hitachi, H-8100, 200kV) for approximately 500 particles. TEM sample were prepared by ultrasonic dispersing of several drops of the Sn-Ag nanoparticles solution, and then deposited on copper grids. The sample was dried in a vacuum oven at ambient temperature before the analysis.The vaporized species from the molten metal mixture during the treatment were identified by spectroscopic diagnostics with a spectrometer (Horiba Jobin Yvon, iHR-550) and a CCD detector (Horiba Jobin Yvon, Synergy).

## RESULTS AND DISCUSSION

Metal vapor generated from the molten metal is transported by the plasma gas flow with a high cooling rate. Then, the metal vapor becomes supersaturated state and form the nanoparticles by nucleation and condensation; i.e. the metal vapors are consumed by nucleation and condensation processes. Figure 3 represents the relationship between the metal vapor consumption rate and the temperature of the metal vapor with (a) 100%-Ar arc and (b) 50%-$H_2$ arc. The metal vapor and the particles are transported from the high temperature region to the low temperature region, which means that the vapors are transported from the right side of this figure to the left side. Sn vapor nucleates at the temperature of 1836 K and starts to condense soon after nucleation starts. Then, Ag vapor condenses to the Sn particles at the temperature of 1376 K. In this system, both of the nucleation temperature and the condensation temperature are higher than the melting points of constituent metals (Sn: 505 K, Ag: 1234 K), so that the nuclei and the nanoparticles grow in the liquid state.

Figure 4 shows the representative TEM images and particle diameter distributions of Sn-Ag nanoparticles, with (a) 100%-Ar arc and (b) 50%-$H_2$ arc, respectively.Both images indicate that these nanoparticles have spherical morphology. From the TEM

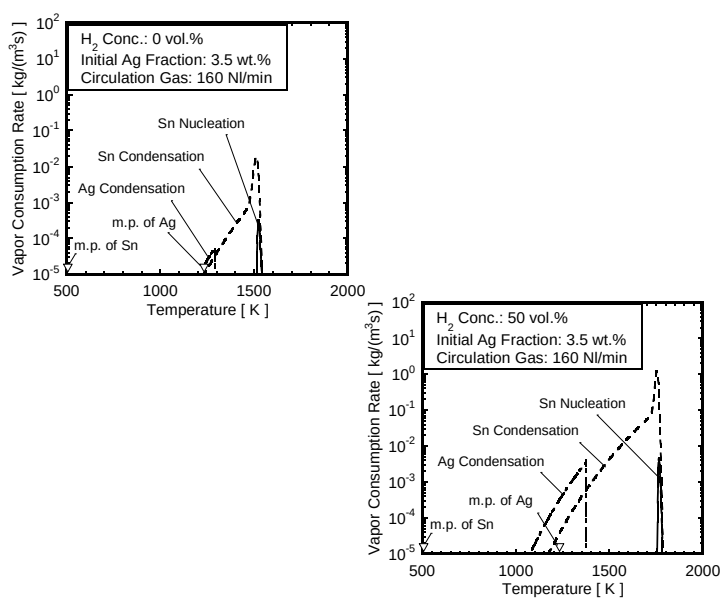
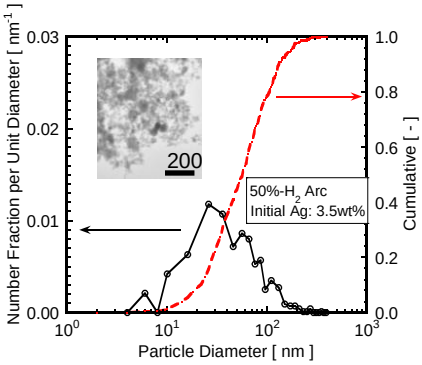



**Figure 3. Temperature dependence of vapor consumption rate with (a) 100%-Ar arc and (b) 50%-$H_2$ arc**

images, the particle size distributions were estimated and the average diameter of the particles was determined. The average diameter of the nanoparticles with Ar arc observed from the TEM image was about 20 nm, while that with 50%-$H_2$ arc was about 70 nm.

Figure5 shows the effect of hydrogen concentration in the arc on the mean diameter of the prepared nanoparticles. The mean diameter becomes larger with an increase of the hydrogen concentration in the arc. The reason of this result is the difference of the vaporization rate. Higher vaporization rate due to the hydrogen addition in the arc leads to higher vapor

concentration, resulting in larger diameter of the nanoparticles. This result agreesthe analytical result mentioned above. Consequently, the mean diameter of the prepared nanoparticles could be controlled by changing the hydrogen concentration in the arc.



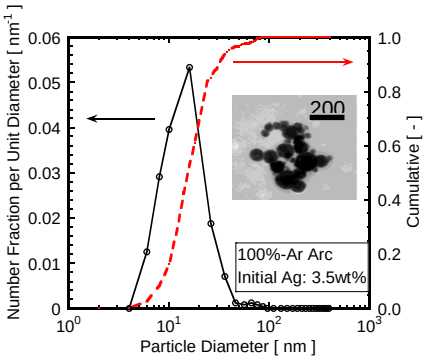




**Figure 4. Particle diameter distributions and morphology of nanoparticles from the raw material contain 3.5wt% of Ag with (a) 100%-Ar arc and (b) 50%-$H_2$ arc.**

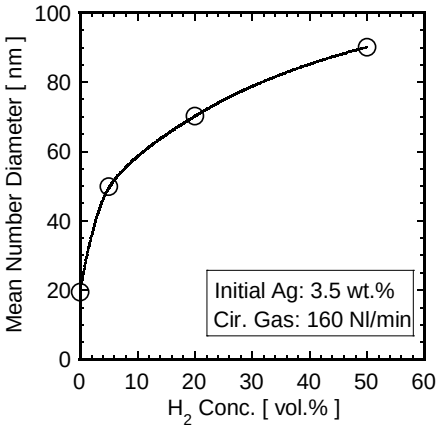



**Figure 5. The effect of $H_2$ concentration in the arc on the mean particle diameter.**

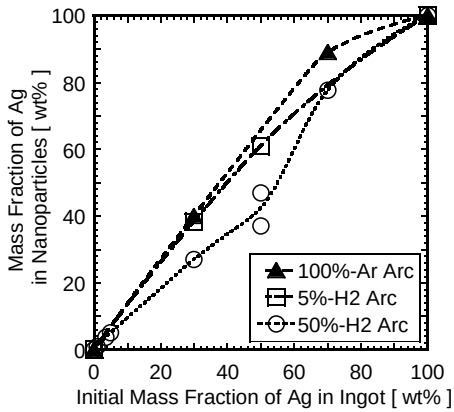



**Figure 6. The effect of $H_2$ concentration in the arc on the composition of prepared nanoparticles as a function of the composition of the raw material.**

The relationship between the Ag fraction in the prepared nanoparticles and the initial Ag fraction in the raw materials is shown in Fig. 6 for Ar arc, with 5%-$H_2$ and 50%-$H_2$ addition. An increase ofhydrogenconcentration in the arc leads to a decrease in the Ag fraction in the prepared particles. These results depict that the addition of the $H_2$ in the arc leads to strong interaction with the molten metal.

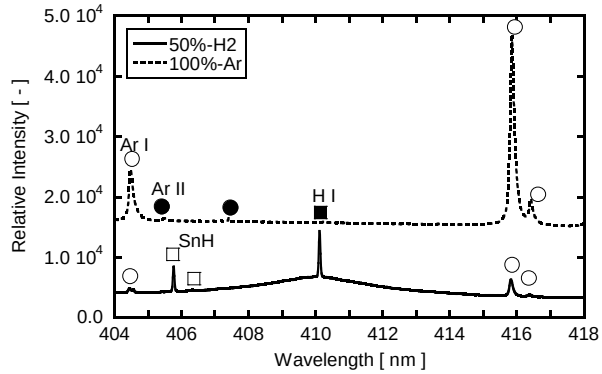



**Figure 7. Emission spectrum of the vaporized species from the arc-anode boundary region with 100%-Ar arc and 50%-$H_2$ arc**

The spectroscopic measurements of the vaporized species were carried out to investigate the vaporization behavior. Figure 7 shows the comparison of the emission spectrum between 100%-Ar arc and 50%-$H_2$ arc. With the hydrogen arc, the emissions from hydrogen atom at 410.174 nm and tin hydride at 405.4 nm were observed. The vaporization enhancement of tin from molten Sn-Ag mixture has been reported in our previous work(Tanaka and Watanabe, 2008b). This enhancement would be attributed to the formation of metal hydride.

## CONCLUSION

Sn-Ag nanoparticles were successfully prepared by the DC arc method. The obtained results suggest that the mean diameter and the composition of the prepard nanoparticles could be controlled by the $H_2$ concentration in the arc.The mechanism of the vaporization enhancement of particular metal from molten metal mixture using hydrogen arc was investigated experimentally. This enhancement would be attributed to the formation of the metal hydride.

It is necessary to investigate the growth mechanism of nanoparticles analytically in order to apply the DC arc method with hydrogen addition effectively. To introduce the procedure mentioned in this paper enables us to find the optimum conditions for synthesis of the alloy/intermetallics nanoparticles using thermal plasmas in short time.

## REFERENCES

Girshick, S.L., Chiu, C.P., &McMurry, P.H., (1990). Time-Dependent Aerosol Models and Homogeneous Nucreation Rates, Aerosol Sci. Thechnol, 13, 465-477.

Shigeta, M.&Watanabe, T., (2005). Numerical Analysis for Co-condensation Processes in Silicide Nanoparticle Synthesis Using an Induction Thermal Plasma under Atmospheric Pressure, J. Mater. Res., 20,2801-2811.

Shigeta, M.&Watanabe, T., (2007). Growth Mechanism of Silicon-Based Functional Nanoparticles Fabricated by Inductively Coupled Thermal Plasmas, J. Phys., D: Appl. Phys., 40, 2407-2419.

Shigeta, M.&Watanabe, T., (2008). Numerical Investigation of Cooling Effect on Platinum Nanoparticle Formation in Inductively Coupled Thermal Plasmas, J. Appl. Phys., 103, 074913.

Tanaka, M.& Watanabe, T., (2008a). Control of Size and Composition of Sn Based Nanoparticles Prepared by Ar-$H_2$ Arc, Trans. Mater. Res. Soc. Japan, 33, 687-690.

Tanaka, M.& Watanabe, T., (2008b). Vaporization Mechanism from Sn-Ag Mixture by Ar-$H_2$ Arc for Nanoparticle Preparation, Thin Solid Films, 516, 6645-6549.

Watanabe, T., Itoh, H., &Ishii, Y. (2001). Preparation of Ultrafine Particles of Si Base Intermetallic Compound by Arc Plasma Method, Thin Solid Films, 390,44-50.