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Synthesis of spherical copper powders and control of the particle diameter in RF induction thermal plasma

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Spherical submicron-size copper powder was synthesized through condensation from a vapor phase with a significantly high degree of supersaturation in Ar-H_2 plasma. The degree of supersaturation was increased by the relatively high rate feeding of raw copper powder of 40 μm in size. The copper vapor concentration depended on the powder feed rate, reactor pressure and hydrogen flow rate. Relatively large particles of up to 0.1μm were prepared. Quench gas gave the formation of nanoparticles of 50nm in diameter even from a high concentration copper vapor. The quenching gas in the counter direction of the plasma flow restrain the particle growth due to increase of cooling rate. Also, Cu-W composite powders were synthesized through the Ar-H_2 plasma treatment of mixture of Cu-WO_3 powders. The starting temperature of shrinkage of Cu-20wt%W composite was significantly higher than pure Cu powders.
Key words: Thermal plasma, nanoparticle, copper, submicron-size powder

1. Introduction

RF thermal plasma has a high temperature (over 10^4 K) and presents an attractive route for synthesis of powders in the nanometer size range. The plasma is rapidly cooled in the tail flame region. The supersaturation of vapor species, which provides the driving force for particle condensation, can be very high in the plasma tail, leading to the production of ultrafine particles through homogeneous nucleation. When metal powders such as iron are injected into the plasma, they evaporate instantly and nanoparticles are produced through homogeneous nucleation and subsequent heterogeneous condensation [1]. The size of such nanoparticles was reported to be 10～70 nm at relatively low powder feed rates [2, 3].

In this work, copper powder with a relatively low melting point was supplied to thermal plasma. The powder evaporated, and a fine powder formed from the vapor phase. Particle size and its distribution in the synthesized powders were controlled by changing the interaction factors between plasma and solid particles, such as heat transfer, cooling rate, and vapor concentration. The interaction depended on the plasma generation conditions and powder feed rate. Fine spherical powders of submicron size were synthesized through condensation from a vapor phase with a significantly high degree of supersaturation. Nanoparticles were synthesized by quenching gas injection at relatively high powder feed rate. Tungsten addition to copper gave the increase of the starting temperature of thermal shrinkage. The spherical copper powders can be applied to the inner electrodes of multilayer ceramic capacitors (MLCC), the conductive fillers, etc. The purpose of this work is to control the particle size distribution and shape of the resulting copper particles.

It is expected that the mixing of high melting point metal tungsten should improve the thermal shrinkage property. During the production process of MLCC, a rapid shrinkage of the green electrode sheets results in the cracking and warpage. The increase of starting temperature of shrinkage is necessity during calcination.

2. Experimental

The experimental apparatus consisted of a water-cooled induction plasma torch (MODEL PL-50, TEKNA Plasma System Inc., Quebec, Canada), a 2-MHz radio frequency power supply system (Nihon Koshuha Co. Ltd., Japan), a water-cooled stainless steel reactor, and a porous stainless steel filter connecting the reactor and a vacuum pump. The Ar-H_2 plasma was generated in the induction plasma torch in connection with the radio-frequency power-supply system [4]. High-purity argon was injected along the central axial of the induction coils as the central plasma gas, and a mixture of Ar and H_2 was input as the sheath gas surrounding the central gas. Raw copper powder (average size: 40 μm, Mitsui mining & smelting Co., Ltd.) that had been synthesized by electrolysis was injected through the top of the torch through a water-cooled probe with a carrier gas. Table I lists the plasma generation and powder feed conditions.

Table I: Experimental conditions.

	(a) Cu	(b) Cu - W
Plate power (kW)	40	40
Reactor pressure (kPa)	39, 53, 67	39
Central gas (l/min)	Ar 30	Ar 30
Sheath gas (l/min)	Ar+H_2 90 (H_2 5,10,15)	Ar 85, H_2 5
Carrier gas (l/min)	Ar 5	Ar 5
Powder feed rate (g/min)	0.33, 1.7, 3.5	1
WO_3 additive ratio (wt%)	0	3, 5, 10, 20
Quenching gas (l/min)	Ar 0, 50,100	0

Most of the powders were collected on the reactor wall. To avoid rapid oxidation of the synthesized particles, the plasma reactor was filled with a 1% O_2-Ar mixture for 2 hours to ensure slight oxidation of the powder surface.

The products were a mixture of a vapor-condensed fine deposit and coarse melt-solidified particles. The fine deposit was separated from the coarse powders through sedimentation. The powders were dispersed in ethanol (assisted by ultrasonic vibration), and the sediment of the bigger particles was removed. The separated vapor-condensed products were characterized by scanning electron microscopy (SEM). The shapes of the particles were examined with SEM (Model S-5000, Hitachi, Japan), and its particle size distribution was determined by image analysis. The primary sizes of 1000 synthesized particles were measured, and the cumulative volume curve was drawn by assuming that all particles were spherical, and the diameter, d_{50}, at the 50% accumulation was determined to be the mean diameter.

3. Numerical analysis

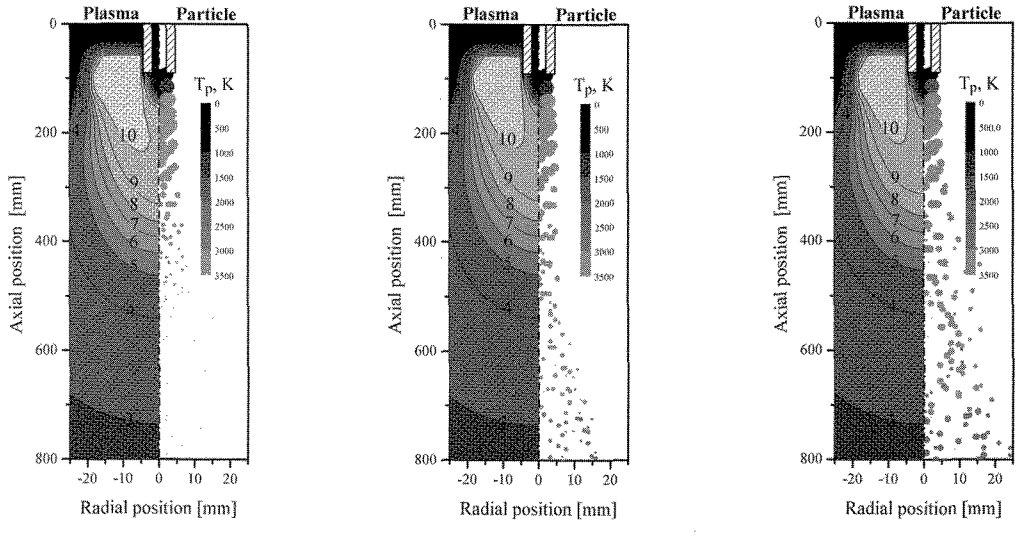
The conditions of plasma with copper powder injection and powder evaporation were numerically analyzed. The mathematical model includes a conservation equation for the RF plasma and k-ε turbulence model. The plasma model is based on the assumptions that the plasma is a steady-state turbulent flow in an axisymmetric cylindrical geometry, it is in local thermodynamic equilibrium (LTE) and optically thin, and there is negligible viscous dissipation. The particle model assumes that a particle is spherical and has infinite internal thermal conductivity [5]. The coil consists of three turns and the applied induction frequency is 2 MHz. As the plate power is 40 kW, the actual power deposited in the plasma is assumed to be 28 kW.

4. Results and discussion

The powder feed rate was changed to examine its influence on the particles formed through evaporation and subsequent coagulation. More heat is absorbed by a particle, when powder feed rate decreases. As a result, an increase in the evaporation ratio in the powder was expected.

Figure 1 (a)-(c) shows the numerical results of the temperature in the plume, the particle trajectory, and the change in particle size for various powder feed rates. The numerical model indicates more powder evaporation than in the experimental results because it ignores the transport properties of the particle vapor. Vapor clouds surrounding evaporating particles move along with the particle, reducing the convective plasma-particle heat transfer rate. The vapor mass flows in the direction opposite to that of energy, bringing some energy back to the plasma. When the rate was 0.33 g/min, almost all of the supplied powder evaporated in the plasma. In contrast, some parts remained un-evaporated at 1.7 and 3.5 g/min. The evaporation ratio decreased as the powder feed rate increased because less heat was absorbed by the particles. The temperature of the plasma fell, as much heat was transferred from it to the particles.

Figure 2 shows the change in particle size, amount of evaporation and evaporation ratio of the raw material, as a function of powder feed rate. As the powder feed rate increased, the evaporation amount increased and the evaporation ratio decreased. The particle size increased from 0.05 μm to 0.28 μm as the evaporation amount increased. Homogeneous nucleation was followed by particle growth through subsequent heterogeneous condensation. Vaporized metal was transported into the reactor with the plasma gas, thereby decreasing its temperature. The temperature decrease gave rise to a decrease in the equilibrium saturation pressure of the vapors. Thus, the supersaturation led to homogeneous



(a) 0.33 g/min (b) 1.7g/min (c) 3.5 g/min

Fig. 1 Numerical analysis of the temperature distribution in the plume (Left, x10^3 K), the particle trajectory, the change of in particle size and particle temperature (Right) for three different powder feed rates: (a) 0.33 g/min, (b) 1.7 g/min, and (c) 3.5 g/min.

nucleation and heterogeneous condensation. Because the degree of supersaturation was high, particles grew to submicron size at the powder feed rate higher than 1.7 g/min.

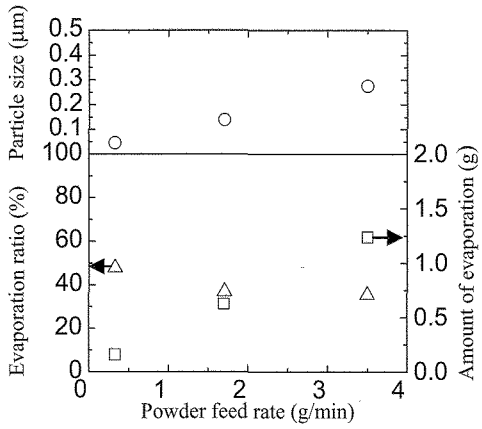


Fig. 2 Particle size, amount of evaporation, and evaporation ratio of the raw material for three different powder feed rates.

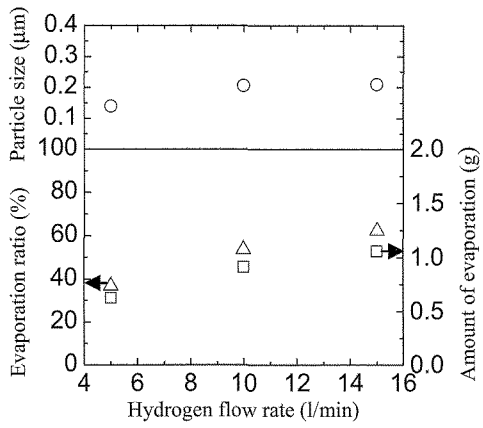


Fig. 3 Particle size, amount of evaporation, and evaporation ratio of the raw material for three different gas flow rates of hydrogen.

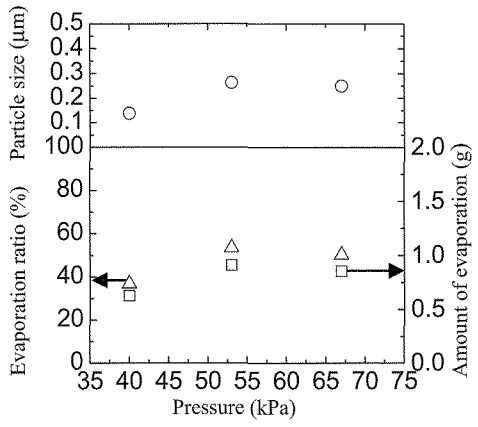


Fig. 4 Particle size, amount of evaporation, and evaporation ratio of the raw material for three different reactor pressures.

Next, the reactor pressure was changed to examine the effect of the volume of the high-temperature region and the residence time of floating particles in plasma on the particles formed through evaporation and coagulation. The particle residence time in the high-temperature region increases as reactor pressure increases. As a result, an increase in powder evaporation can be expected. The copper powder was introduced at the feed rate of 1.7 g/min, while the reactor pressure was varied (39, 53 and 67 kPa).

Figure 3 shows the variation in particle size, amount of evaporation, and evaporation ratio of raw material for various reactor pressures. The amount of powder evaporation decreased at 67 kPa because the length of the high-temperature region shortened as a result of the higher pressure. The evaporation amount of raw powder was smaller at 39 kPa because the residence time in the high-temperature region was shorter at that pressure. The figure shows that the particle size depended on the evaporation amount. The particle growth was attributed to the heterogeneous condensation under a high degree of supersaturation when the amount of copper vapor increased. Thus, the average particle size increased with reactor pressure, from 0.139, to 0.263 and 0.250 μm at 39, 53 and 67 kPa, respectively.

Thirdly, the gas flow rate of hydrogen was changed to examine the effect of the specific thermal conductivity between the plasma and the raw particle. The evaporation ratio increases as the hydrogen flow rate increases because much heat is transferred to the raw copper particles. As a result, an increase in powder evaporation can be expected.

Figure 4 shows the variation in particle size, amount of evaporation, and evaporation ratio of raw material for various gas flow rates of hydrogen. The evaporation ratio increased as hydrogen flow rate increased, as hydrogen have high specific thermal conductivity. The particle size increased depending on the evaporation amount. The particle growth was attributed to the heterogeneous condensation under a high degree supersaturation when the amount of copper vapor increased.

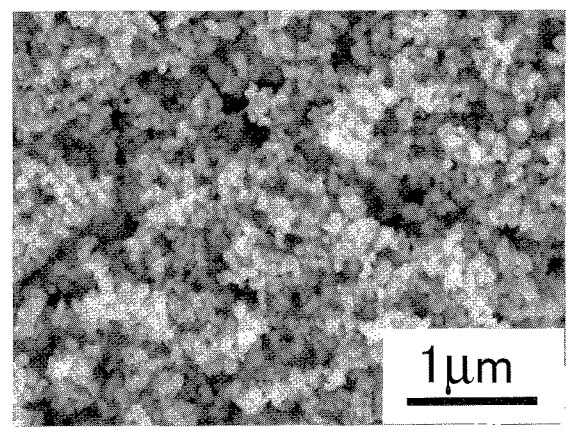


Fig. 5 FE-SEM image of the copper nanoparticles synthesized with quenching gas of Ar 50l/min in the counter direction of plasma flow.

By the counterflow Ar quench gas injection, smaller the size of the particles were prepared even though the

concentration of copper vapor was high. Figure 5 shows morphologies of the copper particles synthesized with quenching gas injection of Ar at 50l/min. The particles assumed rounded shapes with several tens nanometer in diameter.

Higher feed rate of counter flow uniformed the thermal trajectory of the particle. Figure 6 shows the size distribution of the copper nanoparticles synthesized with quenching gas of Ar 50, 100l/min in the counter direction of plasma flow. The size of spherical particles decreased when the quenching gas flow rates was increased. Size distribution of the particles was narrowed by the increase counter flow injection of Ar.

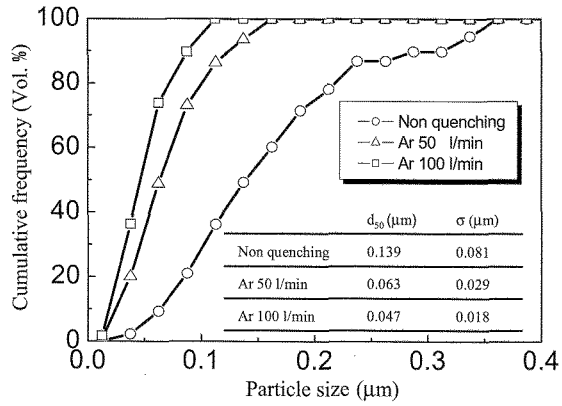


Fig. 6 Size distribution of the copper nanoparticles synthesized with quenching gas of Ar 50, 100l/min in the counter direction of plasma flow.

Figure 7 shows the thermal shrinkage of Cu–W composite powders. The starting temperature of shrinkage increased with the increase of W ratio. The sintering was inhibited when the tungsten existed on the surface of the copper particle, because the melting point of the tungsten is higher than that of the copper, and the sintering temperature is also high.

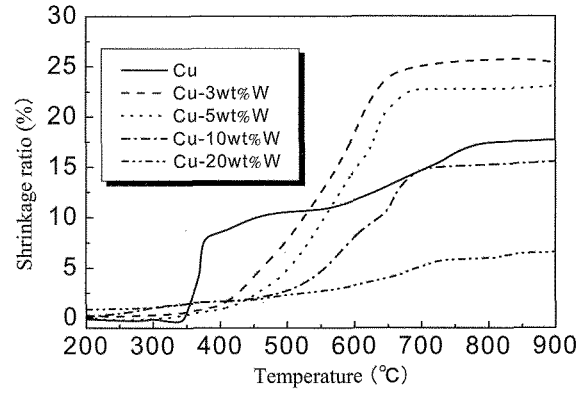


Fig. 7 Thermal shrinkage of Cu–W composite powders.

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