Preparation of Ultrafine Particles of Copper by Reduction in a W/O Emulsion System

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(Received August 20, 1990)

Synopsis. Ultrafine particles (UFP) of Cu were prepared by reduction in a w/o emulsion system, in which Cu(II) ions dissolved in aqueous droplets were reduced by a reducing agent. This method gave a very narrow particle size distribution. Moreover, the average size of UFP could be controlled by choosing the concentration of Cu ions.

Many studies to prepare metallic UFP have been carried out. Although a liquid-phase reduction method[1-3] in which metal ions dissolved in a solution are reduced by a reducing agent is one of these techniques, the conventional liquid-phase reduction method often produces nonreproducible results. The primary objective of this study was to develop a method to prepare UFP having a narrow distribution of particle size. A w/o (water-in-oil) type emulsion system is applied to the conventional liquid-phase reduction method, in which metal ions are dissolved in aqueous droplets in the emulsion.

Experimental

Cu UFP were prepared by reducing Cu(II) ions in an emulsion system. A mixture of a predetermined amount of a $CuCl_2$ aqueous solution, toluene and glycerol monooleate as an emulsifier was vigorously shaken by hand to make an emulsion. The Cu(II) ions were dissolved in water in a w/o-type emulsion as droplets. An excess amount of a $NaBH_4$ aqueous solution was added to the emulsion. A dark-brown "solution" was obtained and then stirred for 1 h. After dilution of the precipitate in the solution with methanol for convenience of subsequent handling, the precipitate was filtered and washed with methanol. The resulting particles were dried in vacuo.

The UFP of Cu were also prepared differently by a conventional liquid-phase reduction method for a comparison. An aqueous solution of $NaBH_4$ was added to the aqueous solution of $CuCl_2$. After being well stirred, the resulting precipitate was first washed with water and then with methanol. The precipitate was dried in vacuo.

All of the procedures were carried out in a nitrogen atmosphere in order to prevent the product from being oxidized.

The average size of aqueous droplets in the emulsion was measured using an optical microscope. The obtained UFP were analyzed by inductively coupled plasma emission spectrometry regarding the chemical composition and by X-ray diffraction method regarding the crystal structure and crystallite size. The particle size distribution was determined by the use of a transmission electron microscope. The size of the UFP was obtained according to a method of Feret,[4] which is one of the methods used to measure the size of irregularly shaped particles. The particle size was defined as being the perpendicular distance between parallel tangents touching opposite sides of the profile.

Results and Discussion

Emulsions. The emulsion prepared by the above-mentioned procedure remained stable upon standing for several hours. An optical micrograph of a typical emulsion is shown in Fig. 1. The sizes of droplets in the emulsion were distributed widely. It is obvious from Fig. 1 that the droplets of the aqueous phase stuck together. The droplet size distributions for emulsions containing the $CuCl_2$ aqueous solution in various concentrations are shown in Fig. 2. It was found that the size of the droplets in the emulsion was independent of the $CuCl_2$ concentration. The mean volumetric diameters of the droplets were determined to be about 15 μm for all of the emulsions used in this study.

Particles. The results of the chemical analysis and the X-ray diffraction analysis are given in Table 1 and Fig. 3, respectively. These results show that the powders obtained in this work were composed of metallic copper and a small amount of Cu_2O. It is not apparent whether the oxide was formed in the course of preparation or during subsequent handling.

Transmission electron micrographs of the UFP prepared in the emulsion system showed sphere-shaped particles, as can be seen in Fig. 4. Similar shaped particles were also observed on the UFP obtained by the conventional method. Figure 5(B) gives the particle size distribution, the mean volumetric diameter (D_v) and the standard deviation of the particle size (SD) of Cu powder prepared in the emulsion system. The particles had a size range from 5 to 40 nm, with a maximum at around 20 nm. The

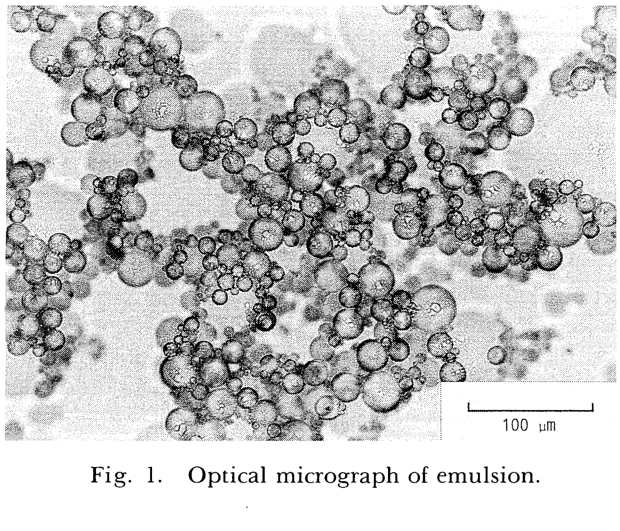

Fig. 1. Optical micrograph of emulsion.

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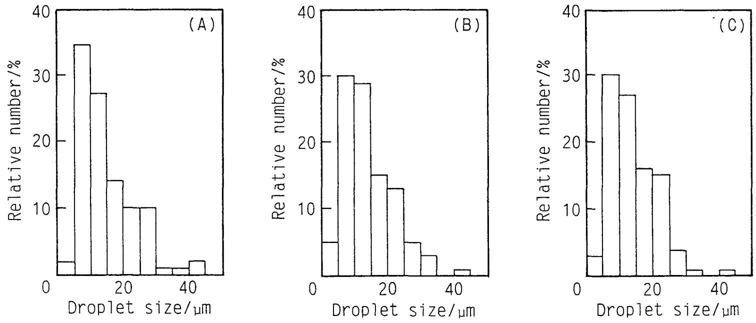

Fig. 2. Effect of $CuCl_2$ concentration in aqueous droplets on distribution of droplet size in emulsions. $CuCl_2$ concentration: A, 0.1; B, 0.5; C, 1 mol dm^{-3}.

Table 1. Composition of Cu UFP Prepared in Emulsion System[a)]

Sample	Composition/wt%			
	Cu	B	Na	Others
A	91.5	Trace	Trace	8.5
B	88.6	Trace	0.2	11.2
C	96.3	Trace	Trace	3.7
D	94.0	Trace	Trace	6.0

a) $CuCl_2$ concentration: A, 1; B, 0.5; C, 0.25; D, 0.1 mol dm^{-3}.

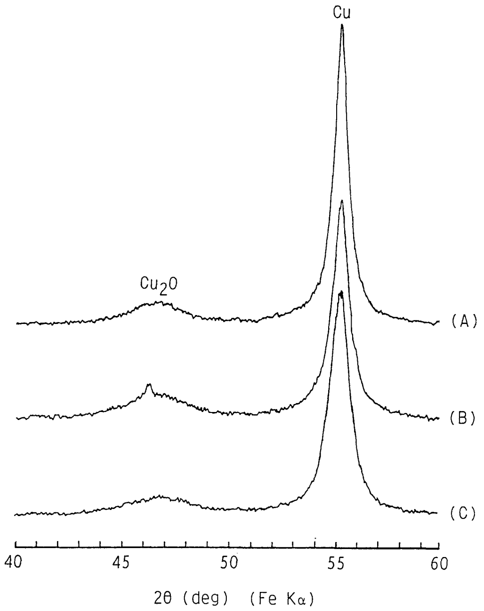

Fig. 3. X-Ray diffraction patterns for Cu UFP prepared in the emulsion system. $CuCl_2$ concentration: A, 1; B, 0.5; C, 0.1 mol dm^{-3}.

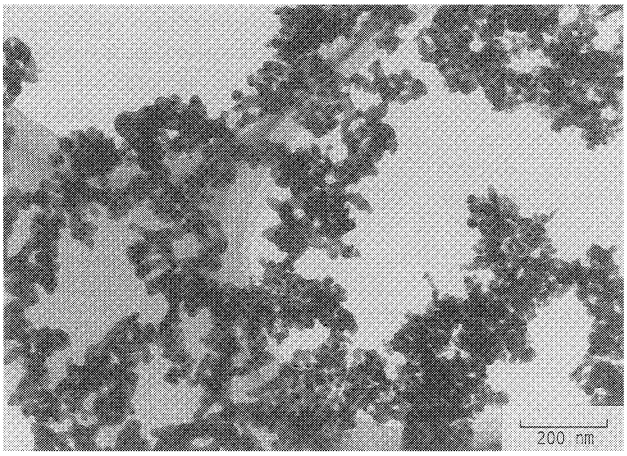

Fig. 4. Transmission electron micrograph of Cu UFP prepared in the emulsion system.

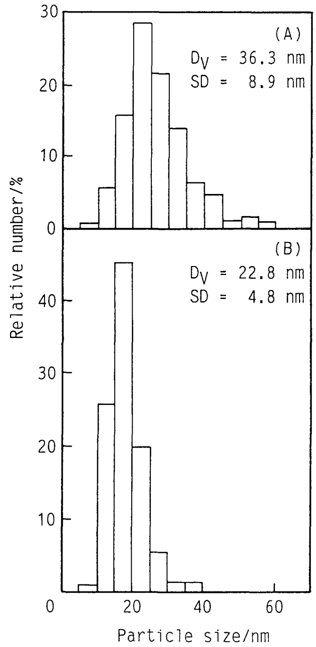

Fig. 5. Particle size distributions, mean volumetric diameters and standard deviations of particle size of Cu UFP obtained by a conventional method (A) and using emulsion system (B).

size distribution of the particles obtained according to this method was very narrow, when compared with that obtained by the conventional method (Fig. 5(A)).

The formation of particles in the emulsion system was followed by an optical microscope observation, which suggested that the formation of particles or the reduction of Cu ions proceeded according to the following steps, as shown in Fig. 6: (1) initiation of reduction in aqueous droplets, (2) evolution of

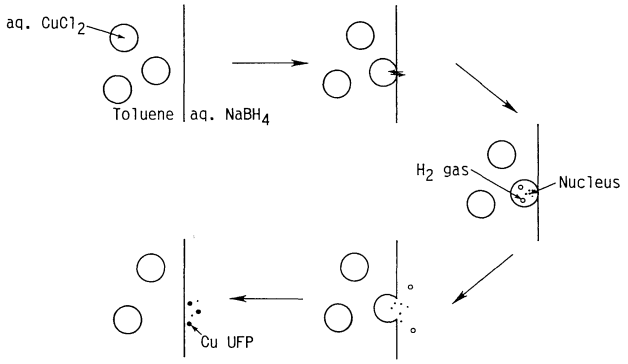

Fig. 6. Model for particle formation in emulsion system.

hydrogen and rupture of the droplets, (3) mixing of the content in droplets with the bulk of the solution of the reducing agent resulting in a further reduction to completion.

From these presumptions, the difference between the powder prepared in the emulsion system and that prepared by the conventional method regarding their particle size distribution is interpreted as being due to a homogeneous reduction of Cu ions: In the case of the conventional method, Cu ions were immediately reduced when the reducing agent was added. Consequently, a local inhomogeneity was unavoidable. On the other hand, in the case of preparation using the emulsion system, the reduction of Cu ions was retarded by toluene, which prevented the Cu ions dissolved in the aqueous droplets from the action of reducing agent. As the aqueous droplets ruptured, reduction took place independently at every droplet. Therefore, homogeneous reduction leading to a narrow particle size distribution was achieved by the use of the emulsion system.

Figure 7 summarizes the effect of the concentration of Cu ions dissolved in aqueous droplets in the emulsion. It is obvious from Fig. 7 that the average particle size was reduced, and that the particle size distribution became narrow with decreasing concentration of Cu ions.

The results presented in this study show that the preparation method using the emulsion system produces UFP having a narrow size distribution. Moreover, the average size of UFP could be controlled by the concentration of Cu ions. It is expected that this method can be used for preparing UFP composed of other materials.

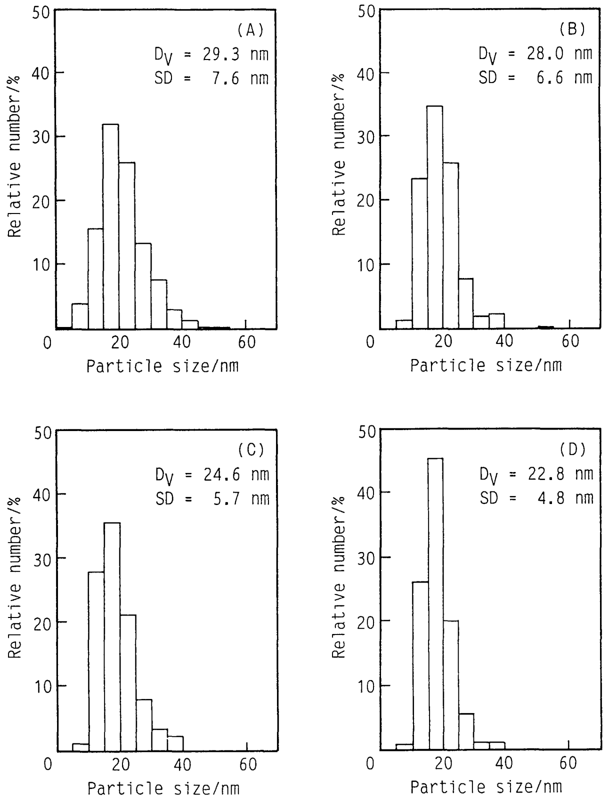

Fig. 7. Effect of $CuCl_2$ concentration in aqueous droplets on particle size distribution, mean volumetric diameter and standard deviation of particle size of Cu UFP. $CuCl_2$ concentration: A, 1; B, 0.5; C, 0.25; D, 0.1 mol dm^{-3}.

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