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1 Introduction

Ultrafine particles (UFPs) have recently come to attract attention as new materials. A considerable number of experiments have been carried out to find the size effects due to the electron energy level quantization predicted by Kubo[1]. UFPs exhibit a variety of characteristics quite different from those of bulk metals and are expected to be applied to magnetic materials, catalyses and others.

In the field of physics, UFPs are usually defined as particles smaller than 100 nm. From the standpoint of powder technology, however, a critical particle size of

about 1 μm seems more reasonable, because the flow-ability of powders decreases rapidly due to agglomeration caused by the strong inter-granular adhesion of particles below this size.

There are two types of processes for manufacturing UFPs; breaking-down processes such as milling or grinding, and building-up processes in which particles are formed through nucleation and subsequent growth. Processes of the latter type are more efficient for producing particles below 1 μm. The building-up processes include gas-phase methods such as inert-gas evaporation process[2], hydrogen arc plasma process[3], gas-phase reaction process[4] and thermal decomposition process[5], as well as liquid-phase methods such as solution precipitation[6] and hydrolysis methods[7].

A gas-phase reaction process was used in this study. The process is considered suitable for industrially producing UFPs. Particles precipitate from gas phases as a result of the chemical reaction of volatile metal compounds. The production of ceramic particles was studied by Kato et al.[5] and was industrialized for TiO_2 and SiO_2.

In the case of metallic UFPs, Lamprey et al.[8] produced UFPs of W and Mo by hydrogen reduction of
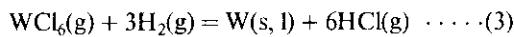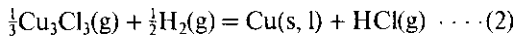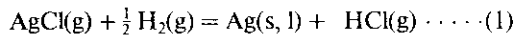
chlorides of those metals in the vapor phase. Recently Dugleux et al.[9] and Yoshizawa et al.[10] prepared UFPs of Fe, Co, Ni and their alloys under the same method and applied the UFPs to magnetic recording tapes. Morooka et al.[11] investigated the effect of reaction temperatures and partial pressures of metal chloride vapors on average particle sizes for Mo and Ni particles prepared under the same method.

The variety of metals which have been reported as being producible under the gas-phase reaction process is narrower, which is attributable to less active studies using gas-phase reaction process than those using inert-gas evaporation process. It is, however, expected from thermodynamic considerations that more metallic UFPs in type are producible by this process. The dependence of particle sizes on the species of metals also requires systematic investigation.

In this study the hydrogen reduction of chloride vapors process was applied for the first time to the preparation of ultrafine Cu and Ag particles. The conditions for the formation of the particles by hydrogen reduction of chloride vapors were examined according to thermodynamic considerations and experimentation. The factors determining the particle size, including the characteristics of Cu, Ag and W particles, is discussed below based on the experimental results.

2 Thermodynamic Examination of the Conditions for the Formation of Metallic Particles

The possibility of forming Cu, Ag and W particles by hydrogen reduction of chloride vapors was examined thermodynamically by considering the equilibrium of the following reactions:

$$AgCl(g) + \tfrac{1}{2} H_2(g) = Ag(s, l) + HCl(g) \cdots\cdots(1)$$

$$\tfrac{1}{3}Cu_3Cl_3(g) + \tfrac{1}{2}H_2(g) = Cu(s, l) + HCl(g) \cdots(2)$$

$$WCl_6(g) + 3H_2(g) = W(s, l) + 6HCl(g) \cdots\cdots(3)$$

The equilibrium constants of the reaction (K_P) calculated from thermodynamic data[12] are given in **Fig. 1** together with the equilibrium vapor pressures of chlorides (P). The vapor pressure of AgCl at 1000—1500 K was not available according to the current literature, and was extrapolated from the values at temperatures above the boiling point (1837 K). The formation of particles requires homogeneous nucleation, which is facilitated by increasing the supersaturation ratio (SS) defined below[5]:

$$SS = K_P P_A{}^a P_B{}^b / P_D{}^d \cdots\cdots\cdots\cdots\cdots\cdots\cdots(4)$$

for the reaction,

$$aA(g) + bB(g) = cC(s) + dD(g) \cdots\cdots\cdots\cdots(5)$$
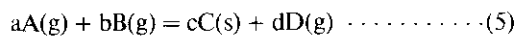
where K_P is the equilibrium constant of the reaction, and P_A, P_B and P_D are the partial pressures of gas phases A, B and D, respectively.

The equation shows that a large K_P, increased P_A and

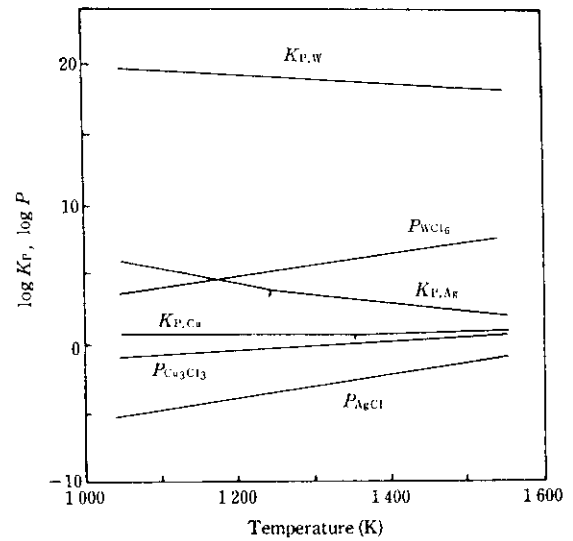Fig. 1 Equilibrium constants of reactions and vapor pressures of chlorides

P_B, and a decreased P_D are favorable for increasing SS. The formation of ceramic particles has been reported as requiring K_P to be larger than 10^2—10^{3}[5] or 10^{3}[13], while for metals a reaction with K_P around 10^0 has been proved to form Fe particles.[10]

In the case of silver, K_P is as large as 10^4 at 1300 K, which suggests that reaction (1) should proceed readily at 1300 K. However, the vapor pressure of AgCl is relatively low and therefore high evaporation temperatures above 1300 K are considered necessary in order to obtain a sufficient amount of chloride vapor.

Copper chloride vapor is supposed to exist mainly as Cu_3Cl_3. The vapor pressure is high and reaches almost 1 atm at 1300 K. However, K_P of the reaction (2) is as low as 10 at 1300 K, and therefore it is difficult to predict whether copper particles form.

The boiling point of WCl_6 is low (614 K) and K_P of reaction (3) is extremely large. Tungsten particles are therefore considered to be easily obtained. In fact, a previous study has reported this formation.[8]

Kinetic approach as well as thermodynamic examinations are considered necessary to explain the possibility of forming particles. Particles may be formed even with low K_P if the reaction proceeds rapidly enough. Unfortunately, reaction rates are usually unknown, and it is difficult to predict the formation of particles from this approach. Experiments are needed to finally determine the possibility of particle formation for individual metals.

3 Experimental Procedure

3.1 Experimental Apparatus

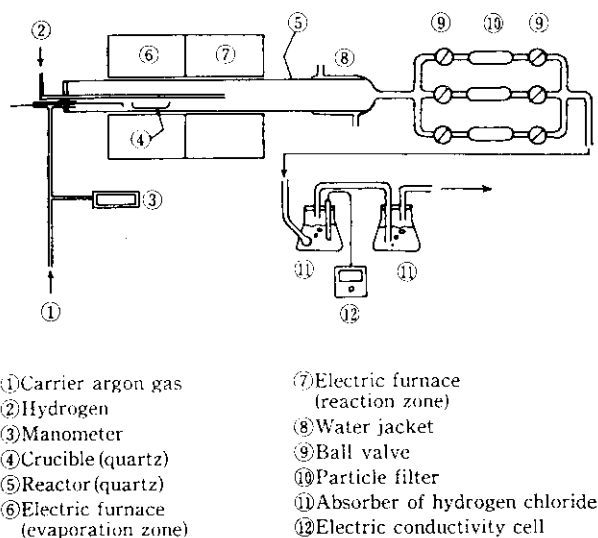An experimental apparatus illustrated in **Fig. 2** was

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Fig. 2   Experimental apparatus

used for carrying out the reactions. A quartz tube 33 mm i.d. and 1000 mm long was placed in an electric furnace with two independently controlled zones. The reactor comprised an evaporation zone (300 mm), a reaction zone (300 mm), and a cooling zone (150 mm). Metallic chlorides were vaporized from a quartz crucible in the evaporation zone and the vapors were carried to the reaction zone by argon gas and reacted with hydrogen to form UFPs. The UFPs were discharged from the reactor together with the gas through the cooling zone and were collected by a filter. Hydrogen chloride was absorbed in water and the reactions were monitored by an electric conductivity cell in the absorbing water.

3.2 Experimental Method

High purity commercial AgCl, CuCl and WCl_6 were used as starting materials. The chlorides were placed in the quartz crucible outside the furnace and were inserted into the evaporation zone, which was maintained at

a given temperature, to start the reaction. The formation of smoke-like UFPs was observed in the glass tubes in which particle filters were set. By using the time from the first observation to the end of reaction and the total weight of the metallic chloride evaporated, the evaporation rate of the chloride was calculated. The reaction degree was calculated from the quantity of hydrogen chloride in the absorbing water and the total weight of the chloride evaporated.

Evaporation conditions were varied for the evaporation temperatures from 600 to 1100°C, the crucible area from 8 to 40 cm^2, and the flow rate of carrier argon gas from 1 to 8 l/min. Reaction conditions were varied for the reaction temperatures from 700 to 1100°C, and the flow rate of hydrogen gas from 1 to 4 l/min.

The particles obtained under these various conditions were subjected to examinations including X-ray diffraction, electron microscopy, chemical analysis and the measurement of specific surface area.

4 Results and Discussion

4.1 Particle Shapes

UFPs of W, Ag and Cu were successfully prepared in the above mentioned experiments. Ag and Cu particles were obtained for the first time by the gas-phase reaction process. TEM photographs in **Photo 1** and SEM photographs in **Photo 2** show spherical particles for Ag and Cu and polyhedral particles with crystal habits for W.

The fact that particles can be formed by gas-phase reactions with a small K_P, such as 10^1 for Cu and 10^0 for Fe[10], suggests that the process can be applied to the production of UFPs of a wide range of metals. The difference in the values of K_P required for the formation of metallic and ceramic UFPs is attributed to the difference in reaction rates. The reactions of hydrogen and chloride vapors to form metallic UFPs are considered to proceed more rapidly than the reactions of oxygen,
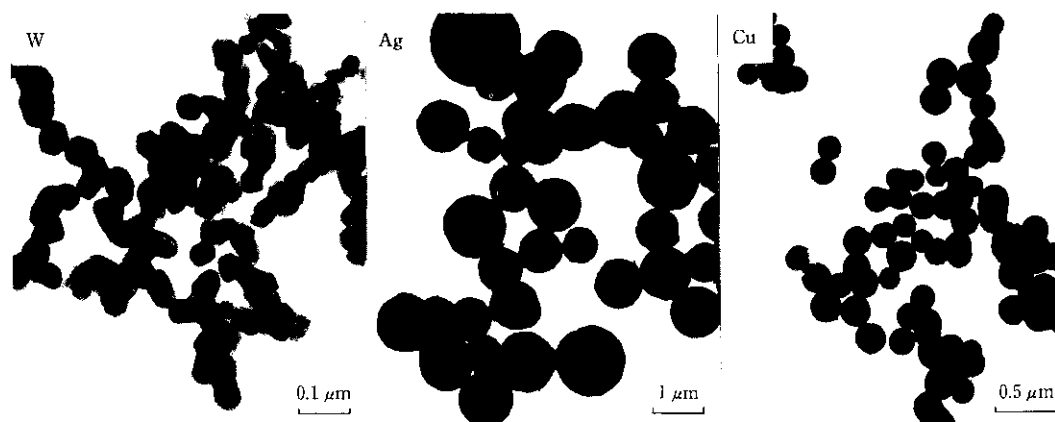

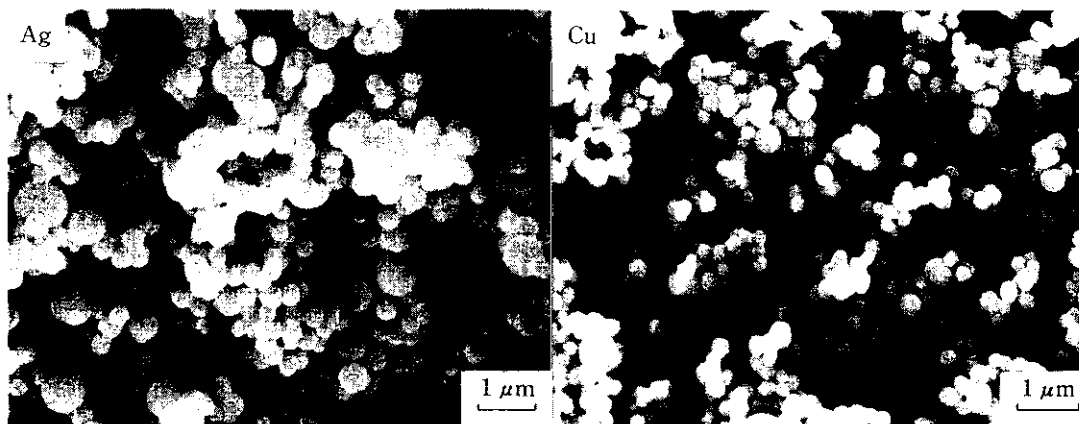Photo 1   TEM photographs of W-, Ag- and Cu- particles

Photo 2 SEM photographs of Ag- and Cu-particles

nitrogen, ammonia or methane with chloride vapprs to form ceramic UFPs.

4.2 X-Ray Diffraction Patterns

X-ray diffraction patterns shown in **Fig. 3** identified W, Ag, and Cu. Sharp peaks show that particles are crystalline and not amorphous. Unreacted chlorides were also identified. In some cases, W particles included WCl_2 as well as WCl_6.
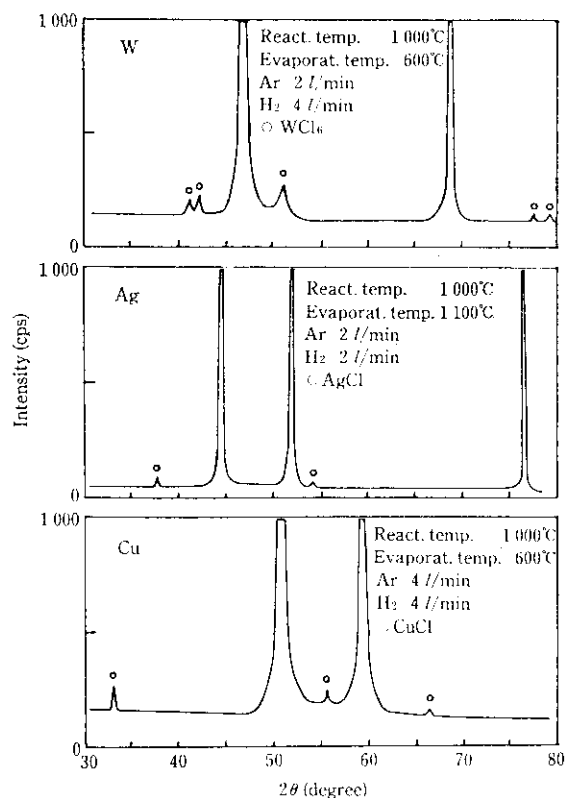
The morphology of CuCl in Cu particles was investi-

(a) SEM photograph

(b) EDX of the above particle
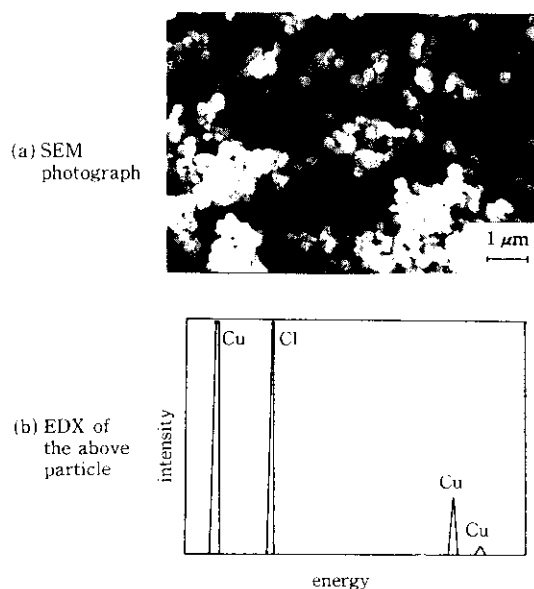
intensity

Cu   Cl

Cu

Cu

energy

Fig. 4 Analysis of CuCl contained in Cu particles

gated by EPMA and EDX. As shown in **Fig. 4**, the large particles of about $1 \mu m$ observed in the SEM photograph (a) are CuCl particles identifiable from the intensity of the peak of chlorine indicated in the EDX (b). It is considered that these chloride particles were formed during the cooling process by the condensation and subsequent growth of the chloride vapor which remained unreacted after the reaction to produce UFPs. Other probable appearances of the morphology of CuCl, such as precipitation on the surface of metallic particles or inclusion in the metallic particles were not determinable.

4.3 Particle Size Distributions

Figure 5 shows the particle size distributions with geometric standard deviations (σ) obtained from TEM photographs by image processing. Each distribution is

W

React. temp.   1 000°C
Evaporat. temp.   600°C
Ar 2 l/min
H₂ 4 l/min
○ WCl₆

Ag

React. temp.   1 000°C
Evaporat. temp. 1 100°C
Ar 2 l/min
H₂ 2 l/min
○ AgCl

Cu

React. temp.   1 000°C
Evaporat. temp.   600°C
Ar 4 l/min
H₂ 4 l/min
○ CuCl

Intensity (cps)

2θ (degree)

Fig. 3 X-ray diffraction patterns of W-, Ag- and Cu-particles
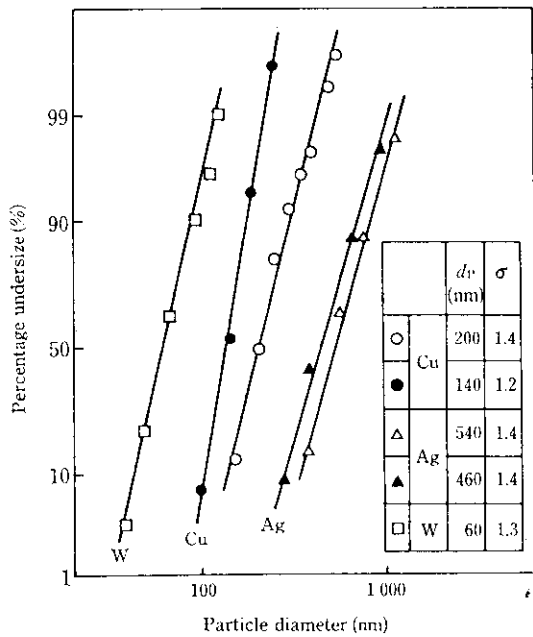
Fig. 5 Log-probability plots for W-, Cu- and Ag-particles

long-normal and very narrow with σ ranging from 1.2 to 1.4, equivalent to the case of UFPs prepared by the inert-gas evaporation process[14]. From Fig. 5 it can be seen that σ does not vary with reaction conditions and metal species, although the average particle size (d_P) varies considerably. The constancy of σ can be understood according to the particle formation mechanism, already discussed by Otsuka et al[15].

4.4 Average Particle Size

Average particle size (nm) was calculated from BET surface area (m²/g) and the bulk density (g/cm³) by assuming the sphericity of particles through,

$$d_P = \frac{6}{S_V \rho} \times 1000 \cdots\cdots\cdots\cdots\cdots\cdots\cdots(6)$$

where d_P is average particle size, S_V the specific surface area, and ρ the bulk density. It is known that for UFPs the values calculated from surface area agree well with the values measured on micrographs[15].

Figure 6 shows the effect of the partial pressure of metallic chlorides on particle size. Partial pressure can be controlled by the evaporation temperature and the flow rate of argon gas. The average particle sizes for each metals become larger with increasing partial pressure. Reaction conditions being equal, the particle size of Ag is the largest, and that of W is the smallest among the three. The particle size of Ag, Cu and W increases in proportion to the 0.25, 0.42 and 0.33 power of the partial pressure of chloride vapor, respectively. It has been predicted[16] that the final particle size is proportional to the 0.4 power of the vapor concentration of
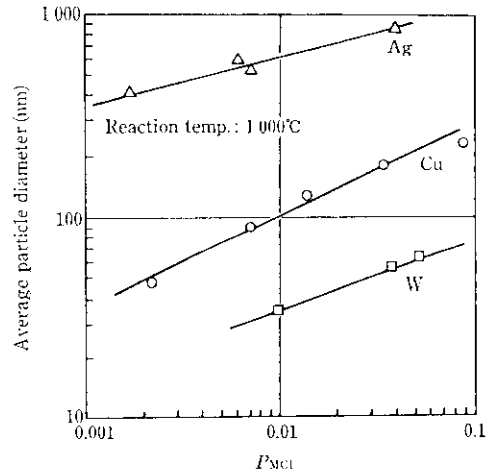
Fig. 6 Effect of partial pressure of metal chlorides on average diameter
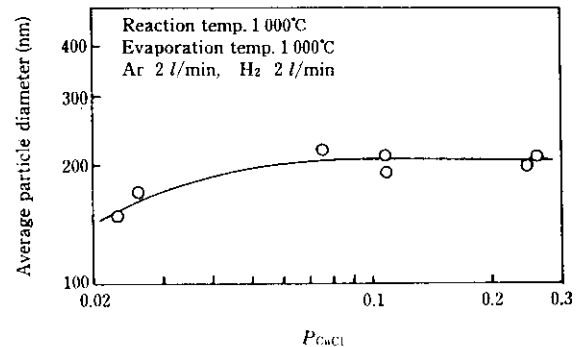

Fig. 7 Effect of partial pressure of copper chlorides on average diameter

metal chlorides, provided that the particles grow by coagulation after collision through the Brownian movement.

The effect of the partial pressure of copper chloride vapor on the size of Cu particles was further investigated in a higher pressure range. In this case the partial pressure was controlled by the crucible area through which the rate of evaporation was determined, while the flow rate of argon and the evaporation temperature were kept constant. As the partial pressure of chloride vapor increases, the particle size increases asymptotically toward about 200 nm as shown in Fig. 7. This behavior may be explained by a decrease in the probability of collision and in the readiness of fusion or coalescence of particles as the particle size increases.

Figure 8 shows the effect of the reaction temperature on the average particle size of Cu and W particles. Within the range of 800 to 1100°C a higher reaction temperature favors the production of a larger particle for copper and, in contrast, a smaller particle for W.
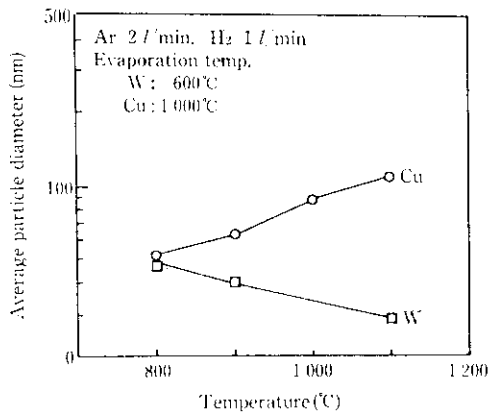
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Fig. 8 Effect of reaction temperature on average diameter

Fig. 10 Relation between average particle size and reaction temperature/melting point

4.5 Reaction Degree

Figure 9 shows the effect of the reaction temperature on the reaction degree in producing Cu particles. A greater than 90% conversion rate of chlorides to metals was accomplished within the temperature range of 900 to 1100°C, and the maximum reaction degree was obtained at about 1000°C. The reaction degree is considered to maximize at some specific temperature, because it depends on two important factors; the equilibrium constant of reaction, which decreases with increasing temperature, and the rate of reaction, which increases with the temperature.
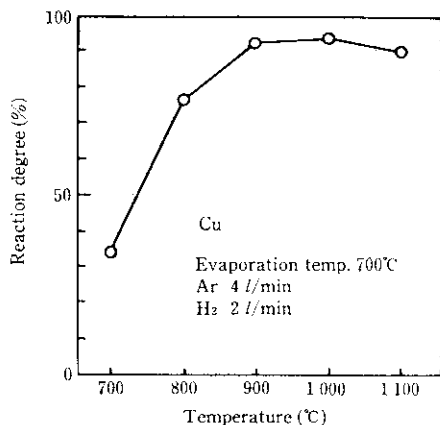

Fig. 9 Effect of reaction temperature on reaction degree

5 Mechanism Determining the Particle Size

The mechanism determining the particle size is discussed in the following from the experimental results. The finding by Morooka, et al. about Ni particles[11] show that when a given temperature is higher than 70% of the melting point of Ni, an increase in that tempera-
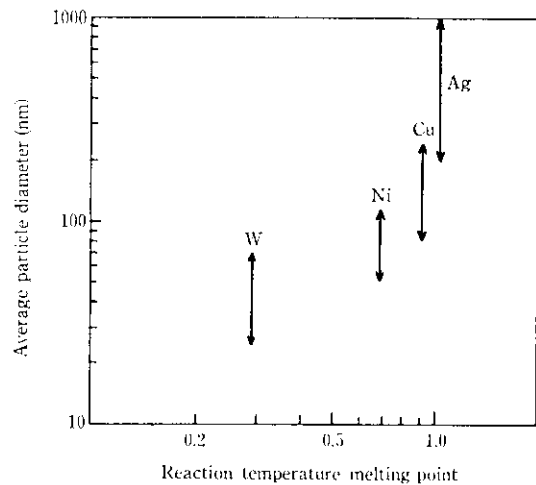
ture level results in increased particle size; while, the particle size is decreased at temperatures below the above mentioned level. it was explained that at lower temperatures the chloride vapor existing with metal clusters promotes the growth of particles because of a slow reaction of the chloride vapor with hydrogen. At higher temperatures, particles can easily fuse or coalesce after collision by the Brownian movement. in the present report, Cu particles were prepared at temperatures rated 0.74 to 1.01 to the melting point of Cu, while W particles were prepared at temperatures rated 0.24 to 0.33 to the melting point of W. This suggests that the same mechanism stands between the results of Morooka et al. about Ni and the present results of Cu and W.

Figure 10 summarizes the relationship between average particle size and the ratio of reaction temperature to the melting point of metals (T/T_m). The results for Ni were quoted from the previous paper by the present authors[10]. Arrows indicate the range of average particle size, when the experimental conditions varies except for reaction temperature (mainly partial pressure of chloride vapor). From Fig. 10 it can be seen that at a constant reaction temperature (1000°C), the higher the ratio T/T_m, the larger the average particle size. This phenomenon indicates that particle growth, which is controlled predominantly by the coalescence of particles at high temperatures[10], is accelerated at higher T/T_m.

It has been reported that the relaxation time (τ_{CC}) to complete coalescence of two particles with radius R_0 (cm) is given by[17]

$$\tau_{CC} = 0.890 \frac{R_0^4}{B} \quad (sec) \quad \cdots\cdots\cdots\cdots\cdots(7)$$

where

$$B = \frac{D_s \gamma_0 N_0 \Omega^2}{\kappa T} \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots(8)$$

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and D_S is the surface diffusion coefficient (cm^2/s), γ_0 the surface energy (erg/cm^2), N_0 the number of surface sites per unit area $(atom/cm^2)$, Ω the atomic volume $(cm^3/atom)$, κ Boltzmann's constant and T the absolute temperature (K). Considering that D_S is expressed by the empirical relationship[17],

$$D_S = 0.014 \exp\left(-\frac{13T_m}{\kappa T}\right) \quad (cm^2/s) \cdots\cdots\cdots(9)$$

and that γ_0 remains largely unchanged with varied temperatures, a larger value of T_m/T results in larger B, and hence a shorter relaxation time τ_{CC}, thus, as a result, the coalescence occurs more easily.

6 Conclusions

Ultrafine particles of Ag, Cu and W were prepared by hydrogen reduction of chloride vapors. The results are summarized as follows.

(1) Cu and Ag ultrafine particles were successfully obtained by gas-phase reaction for the first time in this experiment. Metallic particles can be formed even with smaller equilibrium constants K_p such as 10^0 or 10^1 when compared with ceramic particles.

(2) Spherical particles were obtained for Ag and Cu and polyhedral particles for W. Particles obtained under various reaction conditions showed narrow log-normal distributions of particle size with geometric standard deviations from 1.2 to 1.4. Average particle size was controlled by the vapor concentration of metal chlorides and reaction temperature.

(3) Under constant reaction conditions, the particle size of Ag is the largest, and that of W is the smallest

among the three. A large ratio of reaction temperature to the melting point is favorable for promoting particle growth by fusion or coalescence.

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