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The Time-Dependence Growth of Metallic Crystal Ultrafine Particles

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By using x-ray diffraction technique and transmission electron microscopy the in situ growth property of metal crystal ultrafine particles (CUFP) which are deposited on the silica-substrates have been studied experimentially. It is found that the diffraction intensity and the nucleus diameter of Ag CUFP are grown with time by power-law. Thus, the changes of crystal nucleus and the structure of Ag CUFP with time shows a crystallization trend, at the same time, the in situ growth of Ag CUFP displays a self-similarity character.

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Ultrafine particle (UFP) is a transitive form of materials between the macrocosmos and the microcosmos. It has the property in analogy with cluster, that is the unstability and mobility of interface or surface of cluster.[1-3] The changes of metal CUFP with time display two trends: one trend towards perfect crystallization, the other trend towards the amorphous state or 'atom gas' form, see Fig. 1. The crystallization trend of metal CUFP is discussed in more detail in this paper.

On the amorphous silica substrate, by means of the vacuo-sputtering-deposition method, the Ag CUFP were prepared. Before sputtering the pressure in vacuum chamber was 0.1 Pa, and then Ar gas was introduced into the chamber, the pressure was 10 Pa during sputtering. By means of the x-ray diffraction technique, the structure of Ag CUFP sample was measured. At six different times t=0.14, 0.40, 1.2, 6, 19 and 23 d, we have measured six diffractive spectrums, see Fig. 2. The changes of three diffraction peaks versus time corresponding to the (111), (200) and (220) planes as shown in Fig. 2 have revealed that the Ag CUFP has a trend to perfect crystallization.

The sample of particle systems has been measured by direct observation for several weeks during the *in situ* growth of Ag CUFP, utilizing transmission electron microscopy (TEM). Two TEM micrographs of Ag CUFP sample for two different times at t=0.4 d and at t=6 d are shown in Fig. 3, where full scale is 300 nm.

By measuring and computing diffraction spectra of Ag CUFP, the diffraction intensity of the (111) reflection at times 0.14, 0.4, 1.2, 6, 19 and 23 d were obtained, see Fig. 4.

Changes of the diffraction intensity would be an evident demonstration of the crystallization of Ag CUFP. A least-squares fit to the data gave a power-law dependence

$$I = I_0(t/t_0)^{\alpha} \tag{1}$$

with α=0.3, as indicated by the oblique line in the figure. This functional form found

shows that crystallinity of Ag CUFP increased with time and tends to perfect crystallization. At the same time, it is shown that the growth-process possesses self-similarity.

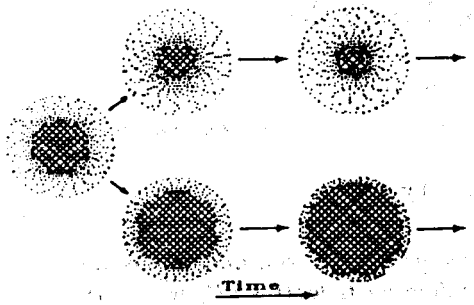


Fig. 1: Schematic representation of two evolutions of UFP.

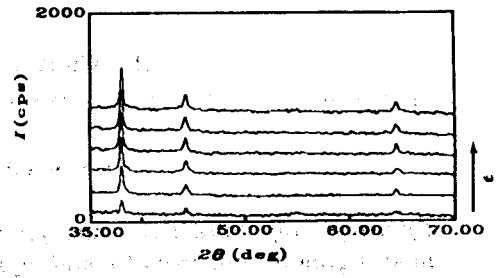
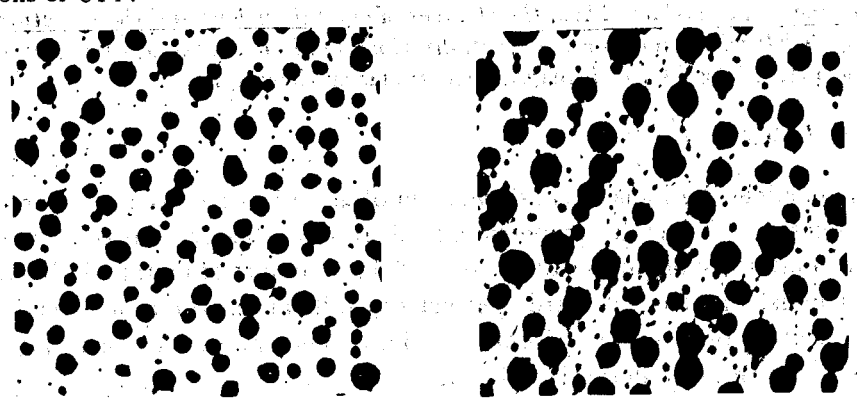


Fig. 2: Diffraction spectrums of Ag CUFP for six different times.



(a) (b)

Fig. 3: TEM micrographs of Ag CUFP for times t=0.4 d (a) and t=6 d (b), full scale of both is 300 nm.

The self-similarity character of the growth-process of Ag CUFP are more clearly shown in Fig. 5. The relationship for nucleus diameter L in the [111] direction of Ag CUFP with to respect time t were represented by the straight line with both logarithmic-coordinates as in Fig. 5. Thus, the time dependence of the growth of the size of Ag CUFP is fit with the following power-law:

$$L = L_0(t/t_0)^{\gamma} , \tag{2}$$

where γ=0.095. Because the changes of the nucleus diameter L versus time t would be a direct measure of the growth of metal CUFP, then Eq. (2) represents time dependence of the growth of Ag CUFP.

The diffraction intensity and the nucleus diameter of Ag CUFP for (200) and (220) planes have been researched by using the same above-mentioned method, the result is the same as Eqs. (1) and (2).

The information of all TEM micrographs that was observed for six different times has been studied, the trend of change of Ag CUFP average size and size distribution with time has been revealed. By use of digital simulation analysis, the relation between

average size L and time t is fit with power-law, in accord with Eq. (2). Multiple peak shape of size distribution trends towards the single peak shape with time, spatial ordering of metal UFP can thus be thought proper to as a function of time.

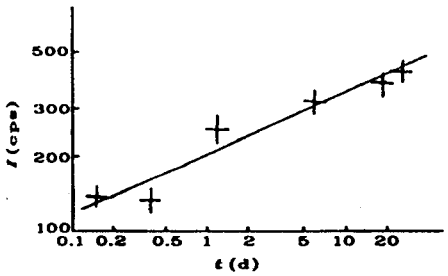


Fig. 4: Plot of diffraction intensity I vs time t.

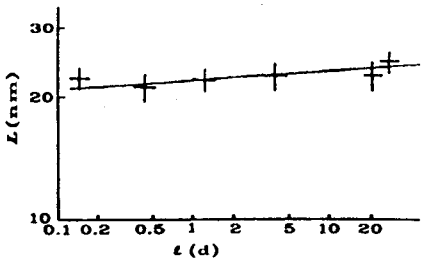


Fig. 5: Plot of crystal nucleus diameter L vs time t.

According to fractal theory, γ in Eq. (2) is represented by anomalous diffusion exponent $dw(a)$, it may be written as

$$\gamma = 1/dw(a) . \tag{3}$$

Owing to the fractal theory,[4] the diffraction intensity I is related to wave number k and particle diameter L as $I \sim k^{-d_f} \sim L^{d_f}$, where d_f is the fractal dimension. By virtue of Eq. (2), we have

$$\alpha = dw/dw(a) . \tag{4}$$

Assume that the dominant growth process of Ag CUFP on the crystal-face (111) is a diffusion-aggregate process which is formed by the attraction of central potential on the fractal surfaces. In such a case the anomalous-diffusion exponent is represented as follows,[5]

$$dw(a) = dw + a\, d_f/(1 - a) . \tag{5}$$

where dw is the potential-free anomalous-diffusion exponent, a is a parameter that depends on the potential well deepness.

For the d=3, dw=3.7, d_f=2.5, a is among the interval 0 – 1. If a=0.66, we find α=0.3, γ=0.117 which are in accord with the measured values of α and γ. It is shown that crystal-face (111) possess the strong effect of attraction potential, and leads the Ag atoms to stay on surface of crystalline nucleus of UFP for a long time. Because aggregate-attraction process of Ag atoms is stronger than desorption or resputtering process of them, the growing trend of Ag CUFP were reinforced

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