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Silver Fine Particle aggregate on an $Al_2O_3 \cdot 3SiO_2$ Surface using a Sonochemical Reaction

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The cavitation phenomenon is caused, when ultrasound which is comparatively strong is irradiated for aqueous solution, and the water decompose into H atom and OH radical, $H_2O \rightarrow H+OH$. The Ag^+ ion is reduced to the Ag by forming H atom, when cavitation is induced in $AgNO_3$ · propanol aqueous solution, $Ag^+ + H \rightarrow Ag + H^+$. Optical characteristic of silver aggregate formed on the $Al_2O_3 \cdot 3SiO_2$ surface by irradiating ultrasound under $Al_2O_3 \cdot 3SiO_2$ coexistence were examined by XRD,EDX,UV － VIS reflectivity measurements and SEM observation.

Key words: ultrasound, redox reaction , plasmon absorption, scattered light, fractal structure of Ag aggregate on an $Al_2O_3 \cdot 3SiO_2$

1. INTRODUCTION

Even if the metal is a very thin film, the light is well reflected. The visible light is reflected on the metal surface, because the wavelength in corresponding to plasma frequency is shorter than that of visible light. For example, the plasma frequency of silver in bulk condition is about 310nm (4eV)[1] . Anomalous optical absorption of a metallic thin film deposited on insulator is studied in the relation with the property of surface plasmon resonance induced on the surface of the metal fine particle in a thin film. Generally, the deposition film is formed from the aggregate of fine crystal that it does not compose the single crystal of the one linkage and that the clearance existed by three － dimensional insular crystal growth mechanism by the Volmer － Weber type . The optical constant receives various effects by form, size and cluster situation of the crystallite which constitutes a metallic thin film. In addition, the optical constant of crystallite in which the crystal size falls below an electronic mean free path is different from the value for the bulk crystal.

It was shown that Nagata et al. could stably dispersed the silver particle which consists of the narrow distribution with the peak of 15nm grain size in water medium, when it irradiates the ultrasound for $AgNO_3$ or $AgClO_4$ aqueous solution[2]. The Ag fine particles are formed by the following reaction under the ultrasound irradiation.

$$H_2O \rightarrow H+OH \quad (1)$$

$$Ag^+ + H \rightarrow Ag + H^+ \quad (2)$$

$$Ag + nAg \rightarrow Ag_{n+1} \text{ (Ag atom aggregate)} \quad (3)$$

It is reported that the cavitation

phenomenon is caused, when water medium is irradiated with a relatively strong ultrasound, and that the radical decomposition of water molecule is caused, and that it forms H atom and OH radical (reaction(1))[3]. It is reduced to Ag atom by one electronic reception by oxidation − reduction reaction between the formed H atom and Ag^+ ion in aqueous solution (reaction(2)). Ag atom which is created by the continual ultrasound irradiation repeatedly collides under the ultrasound irradiation field, and the more large size Ag cluster is formed, and it finally grows to the nano-meter size Ag fine particle in the aggregate (reaction (3)).

In this paper, the adsorption of the silver fine particle to the aluminium silicate ($Al_2O_3 \cdot 3SiO_2$) which was produced by irradiating ultrasound for $AgNO_3$ · propanol aqueous solution under the $Al_2O_3 \cdot 3SiO_2$ coexistence was examined from measurement of the powder X − ray diffraction (XRD),the energy dispersible X − ray (EDX) analysis, the reflection spectrum in ultraviolet − visible wavelength region and the scanning electron microscope (SEM) observation.

2. EXPERIMENTAL

The preparation of sample solution was carried out by the following procedures. First, the silver nitrate ($AgNO_3$) was added for 1 − propanol ($CH_3CH_2CH_2OH$) aqueous solution of 20.0×10^{-3}mol·dm^{-3}, and it was prepared at the concentration of 10.0×10^{-3}mol·dm^{-3}, and finally, it was prepared by the adding of $Al_2O_3 \cdot 3SiO_2$ in $AgNO_3$ · propanol aqueous solution at 10.0×10^{-3}mol·dm^{-3}. The grade of the reagent for the silver nitrate (WAKO: < 99.8 %) and 1 − propanol (WAKO: < 99.5 %) was a special grade. The $Al_2O_3 \cdot 3SiO_2$ samples used the made of WAKO Co.,Ltd as it is, and the average size was about 100nm. In this time, the further determination of the particle size was not carried out. It was used without the further purification of the commercial special grade reagents at as it is purity. The water as a solvent used the commercial pure water (WAKO). Ultrasound irradiation was performed using commercial bathtub type 60W ultrasonic cleaning machine at 47kHz frequency (Branson:Bransonic model 1210J). Ultrasound was irradiated for 200cc sample solution introduced into the Erlenmyer flask made of pyrex glass. The bottom of the flask was accurately placed from the ultrasonic wave ossillation boad in 5mm place. The temperature of the sample solution in the flask was kept to 20.0±0.1℃ by mading to circulate the cooling water in the ultrasonic cleaning bathtub. It was separated after the ultrasound irradiation, by the centrifugal separation for 1min in low rotational speed (1000rpm), because the silver fine particle and the silver · $Al_2O_3 \cdot 3SiO_2$ adsorption complex coexistence in the irradiated sample solution. By adding pure water after it removed the supernatant liquid by centrifugal separation, the similar separation was repeated at 10 times. Drying under reduced pressure was carried out under the room temperature for the Ag − $Al_2O_3 \cdot 3SiO_2$ adsorption complex after the centrifugal separation. The confirmation of the silver fine particle to the $Al_2O_3 \cdot 3SiO_2$ was performed by XRD (Rigaku:RAD − II VC Cu − K α line). The ratio of the adsorbed silver on $Al_2O_3 \cdot 3SiO_2$ was evaluated by the elemental analysis from EDX analysis (JEOL:JXA − 840A). The aggregated structure of silver particle on the $Al_2O_3 \cdot 3SiO_2$ was observed using SEM (JEOL:JXA-8600). In order to clarify the optical property by plasmon oscillation of silver fine particle aggregate which adsorbed on $Al_2O_3 \cdot 3SiO_2$ surface, the reflection spectrum in the ultraviolet −

visible wavelength region was measured by using the reflection spectroscopy photometer (JEOL:JMN – LA300). The weight of the samples for the reflection spectrum measurements were about 1g. The cell holder for the measurements used the result of equipping quartz window plate in standard way.

3.RESULTS AND DISCUSSION

The coloration of the sample solution was able to be confirmed even in the macroscope from the start of the ultrasound irradiation in about 1 hour, and the color of the sample solution finally showed the purple by the irradiation for 12 hours. The time profile of initial pH value of 5.5 which the dissolved 10.0×10^{-3}mol·dm^{-3} $AgNO_3$ in 20.0×10^{-3}mol·dm^{-3} propanol aqueous solution under the 10.0×10^{-3}mol·dm^{-3} $Al_2O_3\cdot3SiO_2$ coexistence shifted to 4.3 by the 300min ultrasound irradiation.

Fig.1 shows the results of the measurements of the XRD pattern of $Al_2O_3\cdot3SiO_2$ sample before ultrasound irradiation (A) and the sample which precipated by the centrifugal separation of sample solution obtained by the ultrasound irradiation for 12 h (B).

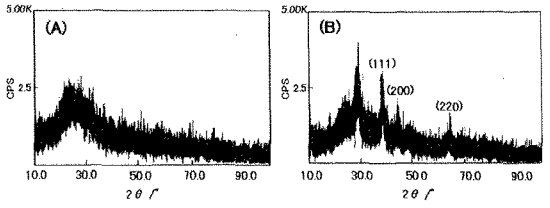

Fig.1 X-ray diffraction pattern of $Al_2O_3\cdot3SiO_2$ before (A) and after (B) the ultrasound irradiation.

It became clear that commercial $Al_2O_3\cdot3SiO_2$ was the amorphous crystal from XRD pattern with no clear reflection peak, as it is shown in Fig.1 (A). On the other hand, it was possible to confirm the existence of the reflection peak. Pattern in Fig.1 (B) was confirmed the silver from the comparison with the literature, and it was able to be attributed in miller indexes in corresponding to the crystal plane shown in figure.

Table.1 show the abundance ratio of silver (Ag), aluminum (Al) and silicon (Si) element for all element which exists on the sample surface, respectively. The change of the elemental composition of the sample surface after ultrasound irradiation was confirmed. Ratio of atom number between aluminum and silicon on the surface for $Al_2O_3\cdot3SiO_2$ before the ultrasound irradiation were about 1:3, and it become equal the stoichiometric mole ratio in $Al_2O_3\cdot3SiO_2$ molecular formula between Al_2O_3 and SiO_2. On the other hand, it become clear that relative elemental composition ratio on the surface of the $Al_2O_3\cdot3SiO_2$ sample after the ultrasound irradiation for Ag, Al and Si was about 2:1:7. The abundance ratio of the aluminum relatively decreased.

Element	Atom% before ultrasound /%	Atom% after ultrasound /%
Ag	0	18.69
Al	24.01	11.50
Si	72.69	65.01
Inpurity	3.30	4.80

Table.1 Percentage for number of the Ag, Al and Si elements on $Al_2O_3\cdot3SiO_2$ surface where the silver fine particle adsorbed by ultrasound iradiation.

Fig.2 show the SEM photographs *of the $Al_2O_3\cdot3SiO_2$ without $AgNO_3$ (A) and the $Al_2O_3\cdot3SiO_2$ with $AgNO_3$ (B) after 12h ultrasound irradiation. From the comparison of the both SEM photographs, it became clear that the

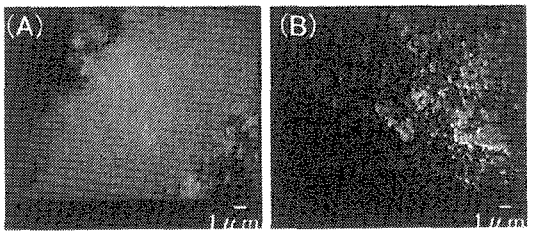

Fig.2 SEM photograph of the samples without $AgNO_3$ (A) and with $AgNO_3$ (B) obtained the ultrasound irradiation (×10000).

sample which adsorbs the silver fine particle (B) had formed the lump aggregate of gravel state of the μ m size. This fact strongly indicate that the adsorption in the silver fine particle which is produced in the ultrasound irradiation process does the adhesion between $Al_2O_3 \cdot 3SiO_2$ particles.

Fig.3 show the results of reflection spectrum in ultraviolet and visible wavelength region. (A) and (B) shown by the distinguishing in Fig.3 deal with the

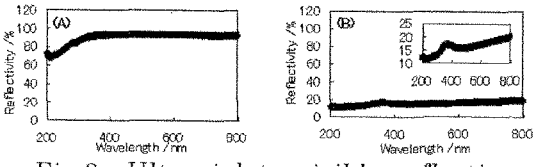

Fig.3 Ultraviolet－visible reflection spectrum before (A) and after (B) ultrasound irradiation.The insertion figure shows the spectrum which expanded the spectrum.

results of the reflection spectrum measured for each sample. It was shown that the reflectivity on the surface before the ultrasound irradiation of $Al_2O_3 \cdot 3SiO_2$ sample was about 90% from 340nm to 800nm for all visible wavelength irradiation light, and that it does not show the peculiar reflected wavelength characteristics. On the other hand, the reflectivity monotonously decreased by the irradiation of the ultraviolet light from 340nm to 200nm , and the reflectivity of about 70% was shown by the irradiation of 200nm wavelength light. Fig.3(B) show the spectrum on the surface of $Al_2O_3 \cdot 3SiO_2$ sample which adsorbed the silver formed after ultrasound irradiation. In comparison with the result of Fig.3(A), the reflectivity of sample in which the silver adsorbed showed the remarkable decrease from 200nm to 800nm in all wavelength ranges. The reflectivity was about 10% without accepting large irradiation light wavelength dependence of reflectance characteristics for the optical illumination. Insertion figure in Fig.3 (B) is enlarged view of the reflectivity of vertical axis for the reflection spectrum measured for the sample in which the silver adsorbed, as it is above－mentioned. The reflection spectrum of the sample which adsorbed the silver produced under the ultrasound irradiation process seemed to cause the lowering of reflectivity by the generation of the absorption which originates from the silver plasmon oscillation which makes near 470nm to be minimal value of the reflectivity. The reflectivity showed the gentle increase further than the minimal value of the reflectivity in the 470nm vicinity with optical illumination of long－wavelength side. On the other hand, there was the increase of the similar reflectivity by the optical illumination in short－wavelength side than minimal value, and the sharp maximal value was shown near 360nm, and in addition, the reflectivity rapidly decreased by the optical illumination in short－wavelength side than 360nm. The decrease of the reflectivity in the short wavelength side from 360nm is gentler than the decrease in the reflectivity of $Al_2O_3 \cdot 3SiO_2$ sample which Fig.3 (A) show, and this seems to be a result of the competition between the reflection characteristic which originates from the plasmon absorption. The interaction between silver aggregate formed on the surface of $Al_2O_3 \cdot 3SiO_2$ under the ultrasound irradiation process and illumination light seems to become that a scattering is more dominant than the plasmon absorption, and the reflectivity remarkably lowers as the result.

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