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Preparation of Ag/Al_2O_3 Nanocomposite Using Suspension Plasma Spraying: A Feasibility Study

H.Sekiguchi, M.E.Bonneau*, F.Gitzhofer*, M.I.Boulos*, and R.Munz**
Tokyo Institute of Technology, Department of Chemical Engineering, O-okayama Meguro-ku, Tokyo 152-8552, Japan
Fax: 81-3-5734-2110, e-mail: hsekiguc@chemeng.titech.ac.jp
*University of Sherbrooke, Department of Chemical Engineering, Sherbrooke, Quebec, J1K2R1, Canada
**McGill University, Department of Chemical Engineering, Montreal, Quebec, H3A2B2, Canada

Feasibility to prepare nanometer-sized Ag particulates in Al_2O_3 was investigated using suspension plasma spraying (SPS) by radio frequency plasma. The precursor for SPS was sub-micron Al_2O_3 particles suspended in silver nitrate aqueous solution. The precursor was atomized by Ar carrier gas into the plasma and then the evaporation and decomposition of the precursor were followed. Nanocomposite film was deposited on SUS substrate. The plasma power was kept in 52 kW and the pressure in the chamber was about 35kPa. The mixture of N_2 and Ar was used for the plasma gas. The film was analyzed by FE-SEM with EDX and XRD. The following two films were prepared to compare the results; heat treatment of Al_2O_3 suspension and SPS with TiO_2 suspension. The observation of SEM showed that Ag nanoparticles having a diameter of 10 to 100 nm were well dispersed on porous Al_2O_3. The peaks of XRD identified that the film was composed of Ag and Al_2O_3. The results suggested that the present technique was feasible to make nanocomposite materials.
Key words: suspension plasma spraying, silver, alumina, nanocomposite, radio frequency plasma

1. INTRODUCTION

Nanocomposite has attracted much attention and been widely studied to improve its mechanical properties and to functionalize its optical or magnetic properties using various methods such as sol-gel processing and slurry drying for bulk materials, sputtering and chemical vapor deposition for thin films, etc. [1-6]. Supported catalysts are also considered as nanocomposite. The supported catalysts have metal or oxide particles dispersed on porous ceramics having high surface area such as Al_2O_3. The nanostructure of the catalyst, especially the size of dispersed particles, affects its catalytic activity strongly.

Recently, a novel technology called suspension plasma spraying (SPS) was developed for the production of ceramic powders and films [6]. In SPS process, a suspension of fine powders and precursor components is fed into radio frequency (RF) plasma using an atomization probe. The whole in-fight process including atomization, drying, and melting with or without chemical reactions proceeds in the plasma within about 10 ms. The products are collected as powders or deposited on a substrate. This technology can reduce time and energy requirements compared with conventional production routes such as precipitation, calcinations and sintering in sintering techniques. The SPS processes have been applied for the preparation of hydroxyapatite, perovskite etc. [7,8].

The purpose of the study is to investigate feasibility for the preparation of Ag-dispersed alumina nanocomposite using suspension of alumina (Al_2O_3) ultrafine particles with silver nitrate ($AgNO_3$) solution. We use this system for a model combination of metal-ceramic nanocomposite because oxidation of Ag does not proceed in high temperatures. Moreover Ag-Al_2O_3 composite shows higher fracture toughness than the monolithic alumina [9] and exhibits high ability to reduce NOx [10-12]. We have characterized the nanocomposite prepared by SPS using scanning electron microscopy (SEM) with electron dispersive analysis (EDX) and X-ray diffraction (XRD).

2. EXPERIMENT

The experimental apparatus is shown in Fig.1 which is almost the same as in Ref.[8]. The plasma was generated by RF plasma torch (PL-35, Tekna Plasma System) at a frequency of 3 MHz. The plasma power was kept in 52 kW and the pressure in the chamber was about 35kPa. The suspension was prepared using Al_2O_3 ultrafine particles (Alcoa Alumina) with $AgNO_3$ aqueous solution. The concentrations of Al_2O_3 and $AgNO_3$ in the suspension were respectively 204g/l (2mol/l) and 0.5mol/l. A peristaltic pump was used to feed the suspension through an atomization probe with a flow rate of about 4 ml/min. The central gas and atomizing gas were Ar. A mixture of Ar and N_2 was used for the sheath gas because more power could be inputted, resulting in higher ehtalpy flow compared with pure Ar. The flow rates were respectively 25 l/min for central gas, 7 l/min for atomizing gas, and 45 l/min (Ar) + 50 l/min (N_2) for sheath gas. The composite was deposited on SUS substrate of 7cm long and 2.5cm wide. The substrate holder was moved horizontally into plasma flow for 1.5s. The explosion was repeated ten times to make a thick film.

For analyses of the deposited films, the measurements of XRD (Philips, PW1700) and SEM-EDX

(Hitachi, FE-SEM, S-800) were carried out.

The suspension was also treated using electric furnace at 900K for 2hr under atmospheric pressure to compare the results with SPS's. Moreover the experiment using TiO_2 particles instead of Al_2O_3 was carried out for further comparison.

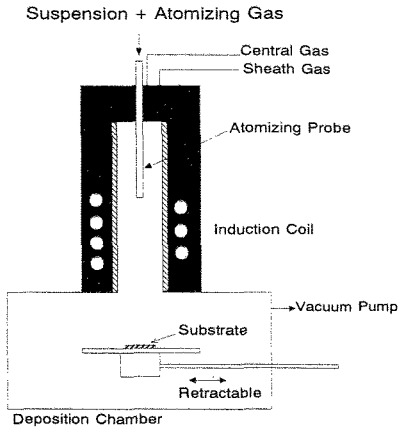

Fig.1 Experimental apparatus

Figure 2 shows the observations of SEM and XRD for initial Al_2O_3 particles. The diameter of the particles is around 100-400 nm. The phase of Al_2O_3 could not be specified. This might be attributed to special treatment given to the particles to stabilize them.

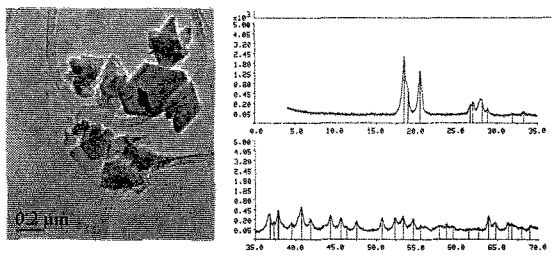

Fig.2 SEM photograph and XRD pattern of initial Al_2O_3 ultrafine particles

3. RESULTS AND DISCUSSION

Figure 3 shows the thick film deposited on the substrate. The film was tightly adhered to the substrate and looked dark gray in spite of white color for the initial suspension.

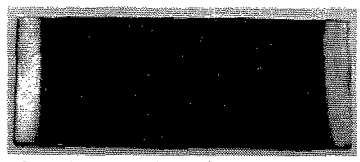

Fig.3 Photograph of Ag/Al_2O_3 thick film prepared by SPS

The results of the deposition are show in Fig.4 and 5 respectively for SEM and XRD observations. The deposition film has porous structure. Small particles having below 100 nm in diameter are well dispersed and attached on the bulk structure. From EDX analysis, the particles were composed of Ag element and the bulk was Al element. Some big particles appearing in Fig.4 are the only Al_2O_3 particles which are not well mixed in the suspension and the plasma. The quantitative evaluation by EDX showed that the ratio of Ag to Al was higher than that of the suspension, suggesting that Ag relatively existed on the surface of the bulk structure.

The pattern of XRD indicates that the film contains Ag and Al_2O_3 where γ-phase of Al_2O_3 is observed. McPherson concluded that metastable γ-Al_2O_3 was formed in thermal plasma because rapid quenching caused γ-Al_2O_3 nucleation due to its lower critical free energy for nucleation compared with α-Al_2O_3 [13]. The deposition process here gave high cooling rate, so that the bulk phase consisted predominantly of γ-Al_2O_3.

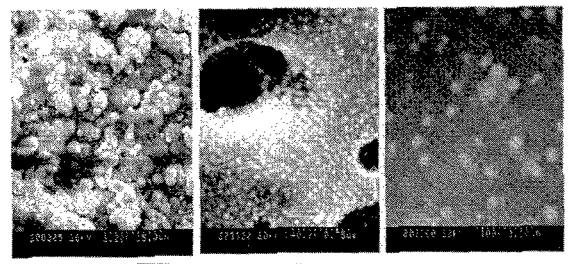

Fig.4 SEM photographs of Ag/Al_2O_3 thick film prepared by SPS

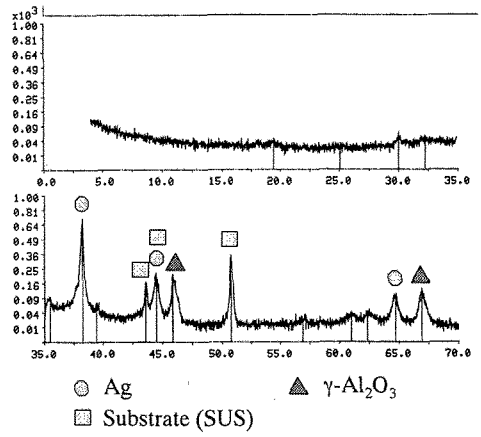

Fig.5 XRD pattern of Ag/Al_2O_3 thick film prepared by SPS

As mentioned above, the heat treatment of the suspension was done and SEM photograph and XRD pattern are shown in Fig.6. The film looks relatively sintered compared with the plasma deposition films. The pattern of XRD for this film is different from that deposited by the plasma and γ-phase of Al_2O_3 is not identified from the pattern.

The particles of TiO_2 having bigger diameter than Al_2O_3 was also examined to make a nanocomposite film using their suspension with $AgNO_3$. The film was not deposited well in this case. The results are shown in Fig.7 where nanosize Ag particles are also dispersed on the bulk phase. The initial TiO_2 reveals a mixture of rutile and anatase phases from XRD pattern of the particles, however the film almost consists rutile, suggesting anatase phase is transferred to rutile phase by the plasma. Heat treatment of the suspension containing TiO_2 was also carried out and the results showed that the particles of TiO_2 remained their shape and Ag particles

were deposited on them. Both rutile and anatase phases clearly existed in this case.

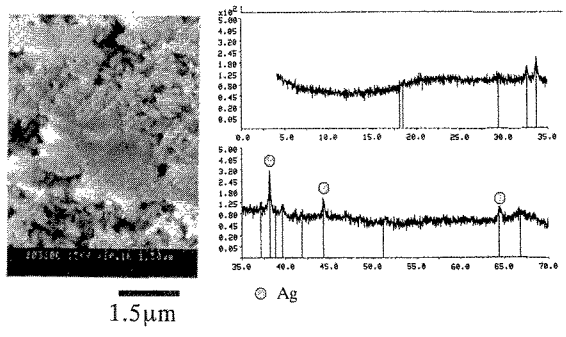

Fig.6 SEM photograph and XRD pattern of Ag/Al_2O_3 film prepared by heat treatment

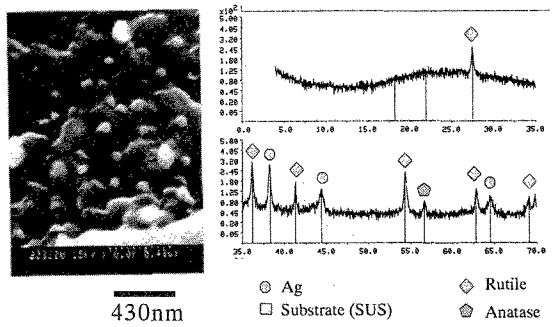

Fig.7 SEM photograph and XRD pattern of Ag/TiO_2 film prepared by SPS

The diffracted grain size, D, of Ag regarded as particle diameter is estimated using Scherrer equation with half maximum line bread, B, expressed as

$$B = \frac{k\lambda}{D\cos\theta}$$

where k is constant, λ is the wavelength of the incident diffraction x-ray, and θ is the measured diffraction angle. Table I shows the estimated values for all the nanocomposites prepared in this study. It is clear that the SPS provides smaller particles than those by heat treatment. This is because the sintering of Ag particles is proceeded in the heat treatment due to longer treatment time compared with SPS process where only few ms is required.

Table I Estimated particles size

	SPS	Heat treatment
Ag / Al_2O_3	47 nm	66 nm
Ag / TiO_2	39 nm	101 nm

As shown before, both the composites of Ag/Al_2O_3 and Ag/TiO_2 prepared by SPS are similar except for the morphology of the deposited films. This suggests that SPS has possibility to prepare metal-ceramic nanocomposite. However the study here is preliminary investigation and further experiments under various experimental conditions such as power, suspension feed rate and composition should be required to develop SPS process for nanocomposite including the evaluation of the film properties such as catalysis activity.

4. CONCLUSION

The suspension plasma spraying was examined to make the nanocomposite of Ag/Al_2O_3. The results suggested that SPS has the potential to prepare nanocomposite materials.

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