Process Visualization of Thermal Nanoparticle Spraying Using Micro Composite Fragments*

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Thermal nanoparticle spraying has been developed to create fine ceramic layers with a high deposition rate. Micro composite fragments containing ceramic nanoparticles could be successfully introduced into a plasma flame using a conventional powder feeding equipment. Yttria-stabilized zirconia (YSZ) nanoparticles with an average diameter of 200 nm were dispersed in a thermosetting acrylic liquid resin at a volume fraction of 40-60 %. The paste material was placed into a sealed container having an inner capacity of 150 cm³. Dispersing and degassing were performed using a planetary mixer. The mixed paste was solidified by heating at 150 °C for 30 min. The composite bulk was crushed using a high-speed vibrating milling machine. The obtained micro composite fragments having particle sizes in the range of 45–106 μm were separated by sieving. The moving behaviors of the micro composite fragments in the plasma flame were visualized using a high-speed camera. In the plasma flame, the resin matrix was burned down, and the heated nanoparticles were deposited on a metal substrate. The microstructure of the coated layers was examined using scanning electron microscopy (SEM). The hardness distributions of the coated layers were measured using a micro Vickers hardness tester.

Key Words: Plasma Thermal Spraying, Micro Composite Fragments, Powder Feeding, Fine Ceramic Coating, Zirconia Nanoparticle

1. Introduction

Thermal spraying methods using ceramic nanoparticles have been developed in order to reduce and control porous amounts in coated layers. However, nanoparticles with large specific surface areas could be coagulated in the powder feeder and the transfer tube, and the risks of nanomaterials for human health should be strictly prevented [1-3]. Moreover, it is difficult to introduce sufficient amounts of these extremely lightweight particles with lower inertial forces into the plasma flame [4-7].

Novel plasma spraying processes using nanoparticle suspensions or pastes have been developed to solve the above-mentioned technical difficulties in fine particle transfers and introductions [8,9]. In the suspension plasma spraying process, nanoparticles are dispersed in aqueous or organic solvents to be injected into plasma or gas flames. The continuous injection of nanoparticle suspensions with a high volume fraction of above 10 vol.% is difficult. Particle dispersant materials have been added to suspensions in order to increase the deposition rates in a coating process for volume fractions of ~15 vol.%. In the paste plasma spraying process, dense coated layers could be formed at high deposition rates by using slurries with high particles contents of above 40 vol.%. These suspension and paste thermal spraying processes should be carried out with specialized feeding machines in the production area.

In this study, we attempt to develop micro composite fragments with nanoparticle dispersions of above 40 vol.% to be introduced into the plasma flame, as shown in Fig. 1. The fragments are then transported using conventional powder feeders, and fine coated layers are prepared by employing high deposition rates. The resin matrix is burned out in the plasma flame, and the nanoparticles are deposited on the substrate. The microstructure of the coated layers is examined using scanning electron microscopy (SEM).

Fig. 1 Schematic of the thermal nanoparticle spraying process using micro composite fragments.

2. Experimental procedure

Yttria-stabilized zirconia (YSZ) nanoparticles (KZ-8YF, KCM, Japan) of 200 nm in average diameter were dispersed in a thermosetting acrylic liquid resin (JSR, Japan) with volume fractions of 40 to 60 %. The paste material was placed in a sealed container with an inner capacity of 150 cm³. Dispersing and degassing were carried out using a planetary mixer (SK-350T, Shasin Kagaku, Japan) for 840 s at the rotation and revolution

*Received: 2016.10.17

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speed of 1340 rotations per minute (rpm). The mixed paste was solidified by heating the sample at 150 °C for 30 min. The composite bulk material was crushed using a high-speed vibrating milling machine (TI-200, CMT, Japan). The obtained micro composite fragments with particle sizes of 45 to 106 μm were separated by sieving.

The micro composite fragments were introduced into a conventional plasma spraying equipment (F4, Sulzer Metco, Switzerland) using a powder-feeding machine (TWIN-120-A / H 1.0, Switzerland). Argon and hydrogen gases were introduced into the plasma gun at flow rates of 40 and 10 standard liter per minute (slpm), respectively. The input power in the plasma formation process was set as 33.6 kW. The YSZ coated layer was formed on a SUS-316 stainless steel substrate having dimensions of 50 $\times$ 50 $\times$ 6 mm. The traverse speed of the spraying gun was set as 165 mm/s.

The moving behaviors of the micro fragments in the plasma flame were visualized at a frame rate of 10 kfps using a high-speed camera (MEMRECAM GX-8, Nac Image Technology, Japan). A high temperature filtering lens (VSZ-1745, VS Technology, Japan) with a central wavelength of 528 nm and a half bandwidth of 12.4 nm was used.

The cross sectional microstructures of the YSZ coated layer were examined using SEM, and the hardness distributions of the samples were examined using a micro Vickers hardness tester (MVK-E, AKASHI, Japan). The test force and the dwell time were set as 0.98 N and 15 s, respectively. The coatings were peeled off from the substrate in order to examine the residual carbon contamination deriving from the resin using thermogravimetry (EXSTAR TG/DTA7200, Hitachi High-Technologies, Japan).

3. Results and discussion

The cross sectional microstructure of the composite bulk sample in which the YSZ nanoparticles were dispersed with 42 vol.% was examined using SEM (Fig. 2). The nanoparticles of 200 nm in average diameter are evenly dispersed in the sample. The micro composite fragments were obtained by crashing the composite bulk material and screening the composite fragments.

The micro composite fragments could be supplied into the plasma spray gun using the conventional powder feeder without leading to coagulations in the transfer tube. As visualized using a high-speed camera (Fig. 3), these fragments containing nanoparticles were continuously introduced for the nozzle top of the plasma gun from the upper feeder tube, and could be dispersed in the plasma flame. The resin matrix is burned out in the high temperature plasma, and the busted nanoparticles are

smoothly transferred through the flame jet.

As shown in Fig. 4, the length of the spray formed with the micro composite fragments introduced to the plasma flame (distance of the particles flying at a high temperature state) is less than half of that achieved with conventional micro particles of 26.4 μm in average diameter.

Fig. 2 An SEM image revealing the cross sectional microstructure of the composite bulk containing 42 vol.% YSZ nanoparticles.

Fig. 3 The visualization of the process of micro fragment introduction into the plasma flame. The composite fragments containing 42 vol.% YSZ nanoparticles.

Fig. 4 The length of the spray formed (a) with micro composite fragments containing 42 vol.% YSZ nanoparticles and (b) with conventional micro particles of 26.4 μm in average diameter.

Fig. 6 TG curves for the YSZ coated layer formed with micro composite fragments containing 42 vol.% YSZ nanoparticles. Heating rate used was 10 $^{\circ}\text{C}/\text{min}$ in Ar.

Vickers hardness: 437-1097 HV

Vickers hardness: 882-1267 HV

Fig. 5 An SEM image revealing the cross sectional microstructure of the YSZ coated layer formed by micro composite fragments containing YSZ nanoparticles at (a) 42 vol.% and (b) 57 vol.%.

The cross sectional microstructure of the YSZ coated layer formed on the SUS-316 substrate using the composite fragments containing nanoparticles is shown in Fig. 5. At 42 vol.%, dense parts and non-sintered parts can be observed. For the sample with 57 vol.% nanoparticles, a dense coated layer is obtained. A small number of micro cracks and pores having average sizes of 1 μm can be observed. In this case, the nanoparticles are assumed to be heated to a higher temperature in plasma flame after the resin matrix was burned out, in comparison to the case in which 42 vol.% nanoparticles was used, owing to the low resin ratio. The deposition rate was reached at 13 μm for one path traversing of spraying gun on the substrate.

The Vickers hardness of each coatings with micro composite fragments and conventional micro particles was compared. In the case of the micro composite fragments containing nanoparticles with 57 vol.%, a maximum Vickers hardness of 1267 HV is achieved. A lower value of Vickers hardness of 882 HV was partly obtained. The nanoparticle sintering is assumed to be incomplete. For comparison, the hardness distribution in the ceramic-coated layer formed by plasma spray using conventional micro particles of 26.4 μm in average diameter was measured. An average Vickers hardness of 967 HV is obtained, and the hardness values are distributed homogeneously.

The residual carbon contamination deriving from the resin was evaluated using thermogravimetry. Since the pyrolysis temperature of the thermosetting resin is $\sim 480^{\circ}\text{C}$, the sample was heated up to 500 $^{\circ}\text{C}$. Fig.6 shows the thermogravimetry measurement results obtained in the case of the coated layer formed with the micro composite fragments containing 42 vol.% nanoparticles. The weight loss values are found to be less than 1 wt%. Since the micro composite fragments contain 21.9 wt.% thermosetting resin, the resin matrix of the fragments were successfully burned out in the plasma flame.

4. Conclusions

Micro composite fragments with YSZ nanoparticles were developed for producing fine ceramic coatings using a conventional plasma spraying system. On visualizing the process using a high-speed camera, these fragments were found to be well dispersed in the flame. After burning out the resin matrix, the busted nanoparticles were smoothly transferred by the flame jets. A spraying deposition rate could be reached at 13 μm for one path traversing of spraying gun on a stainless steel substrate. A maximum Vickers hardness value of 1267 HV was achieved.

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