Microstructural Control of Thermal Nanoparticle Spraying Using Micro Composite Fragments

Makoto KATSUKI*, Soshu KIRIHARA** and Hanako ITOH***

(Received November 2. 2016)

In the newly developed thermal nanoparticle spraying process, micro-composite fragments that contain ceramic nanoparticles can be introduced into a plasma flame to form fine-coating layers at high deposition speeds, by transporting the fragments using conventional powder feeders. In this work, we investigated the effect of the spraying distance, and the nanoparticle concentration in the micro-composite fragments, on the microstructure and mechanical property of the coating. Specifically, micro-composite fragments containing yttria-stabilized zirconia (YSZ) nanoparticles were utilized at concentrations varying between 42-57% v/v, and spraying distances in the 50-85 mm range. The microstructure of the coated layers was examined using scanning electron microscopy (SEM), and the hardness distributions were measured using a micro Vickers hardness tester.

Key Words: Microstructure, Vickers Hardness, Spraying Distance, Yttria-Stabilized Zirconia Nanoparticle, Micro Composite Fragments

1. Introduction

Thermal spraying is widely used in the industrial field as a surface modification technique for improving the heat, corrosion, and abrasion resistance of materials. In conventional thermal spraying methods, coarse particles of about 10-100 μm are introduced into a plasma flame or gas flame, and the molten particles are rapidly deposited on the substrate, forming a coating layer. However, the coating layers obtained with this method have pores and micro cracks, and therefore they do not have good mechanical properties. If fine particles could be used, it is expected that a finer coating layer could be obtained. Thermal spraying methods that use ceramic nanoparticles have been developed in order to reduce and control the porosity of the coating layers. However, nanoparticles with large specific surface areas can coagulate in the powder feeder and the transfer tube, and the risks of nanomaterials on human health should be prevented. Moreover, it is difficult to introduce sufficient amounts of these extremely lightweight particles, with low inertial forces, into the plasma flame.

Novel plasma spraying processes have implemented the use of nanoparticle suspensions, or pastes, to solve the above-mentioned technical difficulties. In nanoparticle suspension plasma spraying processes, the nanoparticles are first dispersed in aqueous or organic solvents before being injected into the plasma or gas flame. However, the continuous injection of high volume percentage nanoparticle suspensions, i.e. above 10 % v/v, is difficult. As a result, particle dispersant materials have been added to suspensions with nanoparticle concentrations of ~15 % v/v, in order to increase the deposition speed during the coating process. In the paste-based plasma spraying process, dense coating layers can be achieved at high deposition speeds by using slurries with high particle concentrations above 40 % v/v. In the production area, these suspension and paste thermal spraying processes should be carried out with specialized feeding machines.

In our research group, it was possible to introduce micro-composite fragments with nanoparticle concentrations above 40 % v/v into the plasma flame, as shown in Fig.1. The fragments were transported using conventional powder feeders, and fine coating layers were obtained by employing high deposition speeds. The resin matrix was burned out in the plasma flame, and the nanoparticles were deposited on a stainless steel substrate. In this study, the influence on the microstructure of the coating by the nanoparticle concentration in the micro-composite fragments, and the spraying distance, were investigated. The microstructure of the coated layers was examined using scanning electron microscopy.
microscopy (SEM).

2. Experimental procedure

First, yttria-stabilized zirconia (YSZ) nanoparticles (KZ-8YF, KCM, Japan), of an average diameter of 200 nm, were dispersed in a thermosetting acrylic liquid resin (JSR, Japan) at different volume percentages varying from 42 to 57 %. Then, the paste material was placed in a sealed container with an inner capacity of 150 cc. Thereafter, the paste underwent dispersion and degassing using a planetary mixer (SK-350T, Shasin Kagaku, Japan) for 840 s, at a rotation and revolution speed of 1340 rotations per minute (rpm). The mixed paste was solidified by heating it to 150ºC for 30 min. The composite bulk material was crushed using a high-speed vibrating milling machine (TI-200, CMT, Japan). Lastly, the obtained micro-composite fragments, with particle sizes between 45 to 106 μm, were separated by sieving.

To deposit the coatings, 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 liters per minute (slpm), respectively. The input power of the plasma formation process was set to 33.6 kW. The rotational speed of the powder feeder metering disk was set to 3 rpm. The YSZ coating layer was deposited on a SUS-316 stainless steel substrate with dimensions of 50 × 50 × 6 mm. The traverse speed of the spraying gun was set to 165 mm/s, and the spraying distance was set to 50 mm.

Micro-composite fragments containing different YSZ nanoparticle concentrations (42, 50, and 57 % v/v) were prepared to investigate the influence of the nanoparticle concentration on the microstructure of the YSZ coating layer. First, micro-composite fragments containing YSZ nanoparticles at 57 % v/v were prepared to investigate the influence of the spraying distance (50, 70, and 85 mm) on the microstructure of the YSZ coated layer. The cross sectional microstructures of the YSZ coated layer were observed 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 to 100 gf and 15 s, respectively.

3. Results and discussion

The cross sectional microstructure of the YSZ coating layer, which was deposited on the SUS-316 substrate using the micro-composite fragments that contained the nanoparticles, is shown in Fig.2. In these coating layers, dense parts and non-sintered parts can be observed. The coating layer became dense as the nanoparticle concentration increased. The least number of non-sintered parts was observed at the nanoparticle concentration of 57 % v/v. In addition, for this same concentration, the resin concentration was at its lowest, therefore the nanoparticles were assumed have been heated to a higher temperature in plasma flame after the resin matrix was burned out, in comparison to coatings obtained with lower nanoparticle concentrations.

The Vickers hardness of the YSZ coating layers is shown in Fig.3. The minimum value of the Vickers hardness increased as the nanoparticle concentration increased due to the coating layer becoming denser. At a nanoparticle concentration of 57 % v/v, the highest hardness value of 1267 HV was obtained. The deposition speed for the traversing path of the spraying gun on the substrate is shown in Table 1. The deposition speed increased for higher nanoparticle concentrations. For example, the 50 and 57 % v/v nanoparticle concentrations had higher deposition speeds than the 42 % v/v nanoparticle concentration. The deposition speed of the 57 % v/v nanoparticle concentration reached 13 μm for one of the traversing paths of the spraying gun. One of the reasons that this value was slightly lower than that of the 50 % v/v nanoparticle concentration is inferred that the nanoparticles were deposited more densely.

The cross sectional microstructure of YSZ coating layers obtained with various spraying distances is shown in Fig.4. The coating layer became porous as the spraying distance increased. This is assumed to be caused by a cooling of the heated nanoparticles when longer spraying distances were used, leading to the nanoparticles being not sintered easily on the substrates. The Vickers hardness of the YSZ coating layer formed using micro-composite fragments with a 57 % v/v YSZ nanoparticle concentration is shown in Fig.5. The Vickers hardness value decreased as the spraying distance increased because the coating layer became porous. The deposition speed for one traversing
Fig. 2 SEM images of the cross sectional microstructure YSZ coating layers, which were formed using micro-composite fragments with different YSZ nanoparticles concentration of (a) 42%, (b) 50%, and (c) 57% v/v at a spraying distance of 50 mm. The gray and dark-gray contrasts show sintered and non-shintered area, respectively.

Fig. 3 Nanoparticle-concentration dependence of Vickers hardness with YSZ coating layers formed using micro-composite fragments at a spraying distance of 50 mm.

Table 1 Deposition speeds for the YSZ coating layers formed using micro-composite fragments containing YSZ nanoparticles at a spraying distance of 50 mm, and at nanoparticle concentrations of 42, 50, and 57 vol. %.

| Nanoparticle concentration (vol.%) | 42 | 50 | 57 |
|-----------------------------------|----|----|----|
| Deposition speed (μm/traverse)    | 8.0| 14.5| 13.0|
path of the spraying gun on the substrate, using micro composite fragments containing a 57 % v/v YSZ nanoparticle concentration, is shown in Table 2. The deposition speed decreased as the spraying distance increased. As the spraying distance increased, the deposition efficiency decreased due to colder nanoparticles being deposited.

4. Conclusions

The nanoparticle concentration in the micro-composite fragments, and the spraying distance during the plasma spraying process, were investigated in order to obtain dense and high-strength coatings. The YSZ coating layer became denser as the nanoparticle concentration increased. The nanoparticle concentration of 57 % v/v yielded the most dense and high-strength coatings. The maximum Vickers hardness value recorded was 1267 HV. The spraying deposition speed reached 13 μm for one traversing path of the spraying gun on a stainless steel substrate. The YSZ coating layer became porous as the spraying distance increased. At a spraying distance of 50 mm, fine coating layer was obtained. The closer distance and more particle would be expected to produce more dense and high-strength coating.

Table 2 Deposition speed of the YSZ coating layer formed with micro-composite fragments containing YSZ nanoparticles at a 57 % v/v concentration, and at spraying distances of 50, 70, and 85 mm.

| Spraying distance (mm) | 50  | 70  | 85  |
|-----------------------|-----|-----|-----|
| Deposition speed (μm/traverse) | 13.0 | 12.6 | 9.3 |

Fig.5 Spraying-distance dependence of Vickers hardness with YSZ coating layer formed using micro-composite fragments at nanoparticle concentrations of 57 % v/v.

References

1) A.Killinger, M.Kuhn and R.Gadow: High-Velocity Suspension Flame Spraying (HVSFS), a new approach for spraying nanoparticles with hypersonic speed, Surface & Coatings Technology 201 (2006) 1922-1929.
2) R.S.Lima and B.R.Marple: Thermal Spray Coatings Engineered from Nanostructured Ceramic Agglomerated Powders for Structural, Thermal Barrier and Biomedical Applications: A Review, Journal of Thermal Spray Technology 16-1 (2007) 40-63.
3) L.Pawlowski: Suspension and solution thermal spray coatings, Surface & Coatings Technology 203 (2009) 2807-2829.
4) R.S.Lima, A.Kucuk and C.C.Berndt: Evaluation of microhardness and elastic modulus of thermally sprayed nanostructured zirconia coatings, Surface and Coatings Technology, 135 (2001) 166-172.
5) Y.Wang, S.Jiang, M.Wang, S.Wang, T.D.Xiao and P.R.Strutt: Abrasive wear characteristics of plasma sprayed nanostructured alumina/titania coatings, Wear, 237 (2000) 176-185.
6) R.S.Lima, A.Kucuk and C.C.Berndt: Integrity of nanostructured partially stabilized zirconia after plasma spray processing, Materials Science and Engineering, A313 (2001) 75-82.
7) M.Suzuki: Suspension Plasma Spraying, Journal of the Japan welding society, 83-2 (2014) 26-29 (in Japanese).
8) D.Waldbillig and O.Kesler: The effect of solids and dispersant loadings on the suspension viscosities and deposition rates of suspension plasma sprayed YSZ coatings, Surface & Coatings Technology 203 (2009) 2098-2101.
9) S.Kirihara and Y.Itakura: Effective Injection of Ceramics Nanoparticle Pastes into Plasma Spray for Speedy Layer Formation, Quarterly journal of the Japan welding society, 33-2 (2015) 148-151.
10) M.Katsuki and S.Kirihara: Introduction of Micro Resin Fragments with Ceramic Nanoparticles into Plasma Flame to Create Fine Coated Layers, International Thermal Spray Conference & Exposition (ITSC 2016), Shanghai, China, May 2016, p.1079-1082.