# Alumina-Zirconia Composite Coating Fabricated from Nano-size Powders

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Alumina-zirconia composite coatings were fabricated by plasma spraying using both of mixture from usual powders and agglomerated feedstock from fine powders of about 100 nm. The coating from mixture had an ordinary lamella structure which consisted of alumina splats and zirconia splats, whereas that from fine powders showed dense microstructure composed inhomogeneous splat. X-ray diffraction profiles revealed that the latter contained $\gamma$-alumina, m-zirconia and t'-zirconia crystals, which sizes were under 10 nm. The nano-composite coating had a higher Vickers hardness than the coating from mixture. Despite its lower porosity, the nano-composite coating shows very lower thermal conductivity, which was a half of that of deposit from mixed powders.
Key words: nano-composite coating, plasma spraying, alumina, zirconia, low thermal conductivity

## 1. INTRODUCTION

Applying nano-technological methodology to R&D is widely noticed in various fields, recently. In the field of coating, many investigations are also conducted and revolutionary progress is expected to improve the properties of the coating. Most of the works are based on either the two concepts; building up from the atomic level or fabricating the coating by keeping nano-structure of raw materials. The former tends to take long time for production, and the latter tends to restrict the process and it becomes hard to realize the sufficient performance. On the contrary, plasma spray process is essentially rapid production process and sprayed deposit is originally composed of very fine crystals owing to the prompt quenching. So it is thought that the proper controlled plasma spray process could easily make the nano-structured coating quickly. From this point of view, we tried to make a Al₂O₃/YAG nano-composite coating and already reported its microstructure[1].

In this work, we tried to fabricate Al₂O₃/ZrO₂ nano-composite coatings by plasma spraying. From the equilibrium phase diagram[2], Al₂O₃ and ZrO₂ hardly form a solid solution, so the formation of thermally stable composite is expected. Its microstructure and its mechanical and thermal properties were investigated.

## 2. EXPERIMENTAL PROCEDUERS

### 2.1 Material

*Composite powder*: Fine Al₂O₃ powder (TM-DAR from TAIMEI Chemicals Co., Ltd., average diameter: 160 nm) and fine zirconia powder stabilized 3 mol.% yttria (TZ-3Y from TOSOH Corporation, average diameter: 34 nm), which were both commercially available powders prepared for sintering, were used for starting materials. These powders were mixed in equal volumes. Granulated powder was then prepared by spray drying with polyvinyl alcohol as binder and was classified between 25 and 63 μm for spraying.
*Reference mixed powder*: Mixed feedstock was prepared by ball-milling in dry condition for comparison. It was
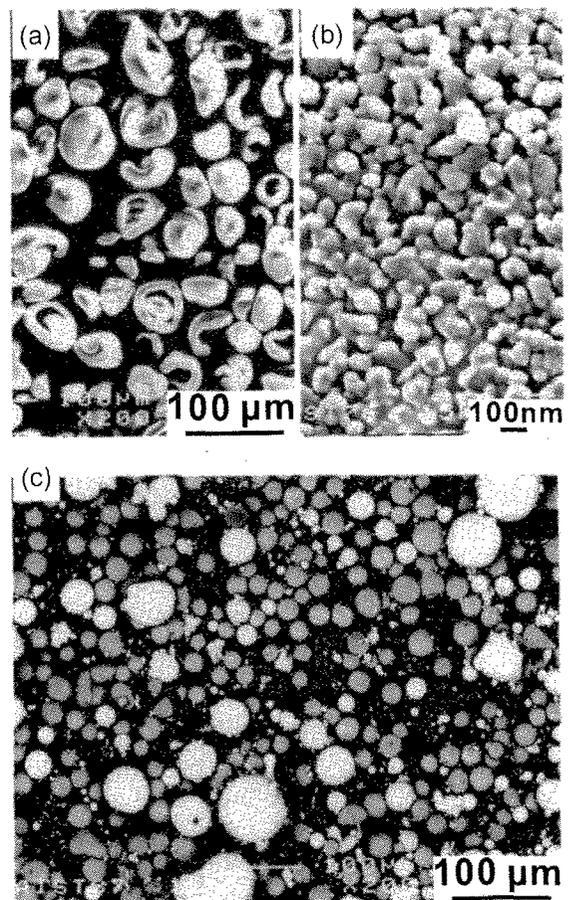


Fig.1 SEM photograph of two kind of feedstock.
(a) morphology of spray dried Al₂O₃/ZrO₂ composite feedstock, (b) the primary powders on the surface of spray dried grain, small white powder: ZrO₂, gray powder: Al₂O₃, (c) reference mixed powder, white powder: ZrO₂, small gray powder: Al₂O₃.

Table I. Spray parameters

| Torch | Sulzer-Metco F4-VB |
|---|---|
| atmosphere | open air |
| spray distance | 100 mm |
| plasma gases | Ar + H$_2$ (42, 10 l/min) |
| Torch current | 620 A |
| Torch input power | approx. 42 kW |
| powder feed rate | 22 g/min |
| powder injector | internal, 1.5mm dia. |
| substrate | SS400,   3mm $^t$ |

made of Al$_2$O$_3$ powder (CB-A20S from SHOWA DENKO K. K., average diameter: 21.9 μm) and 8wt.% yttria stabilized zirconia powder (AMDRY 6610 from Sulzer Metco, diameter: 11 - 60 μm), which were both commercially available granulated and sintered powders.

## 2.2 Spraying

Plasma spraying was carried out with a Sulzer Metco F4VB gun in air. The same plasma spraying parameters (Table.I) were applied for both feedstock. Argon gas was used as the primary plasma gas and hydrogen was added as secondary gas.

The substrate was mild steel (JIS-SS400) 3mm thick that was blasted with alumina grit (24 mesh) just prior to spraying. The coating was formed directly on the substrate without any bond coating. Temperature was not controlled actively, so the substrate was heated up to 180 °C during spraying.

## 2.3 Properties measurements

Bulk density and open porosity of the coating were measured by water immersion method, where the free-form deposit was separated from the substrate by using hydrochloric acid. True density was measured by the gas pycnometer method with Helium after the deposit was pulverized into fine powder. The crystallographic phases and the crystallite size were determined by the X-ray powder diffraction technique. Microstructures were observed by SEM. Vickers micro-hardness was measured with load of 2.94N according to JIS R1610 (HV 0.3) on the polished cross section. The thermal diffusivity and the specific heat of free-stand deposit were measured by laser flush method, and the thermal conductivity was calculated.

## 3. RESULT AND DISCUSSION

### 3.1 Phases and microstructures

X-ray diffraction profiles of the feedstock and the sprayed deposit were shown in Fig.2. The deposit from the mixed powder and one from the spray-dried powder are hereinafter abbreviated M-film and C-film, respectively. M-film was composed of three phases, γ-Al$_2$O$_3$, t'-ZrO$_2$ and a small amount of m-ZrO$_2$. These phases are quite the same as the ones of coatings when raw material powders are plasma sprayed individually. In C-film, the same phases as M-film appeared, but each peek was very broad. To determine the crystallite size, the contributions of the lattice strain and crystallite size were extracted from the full width of half max (fwhm) values of peaks through the eq. 1[3]. The relationship
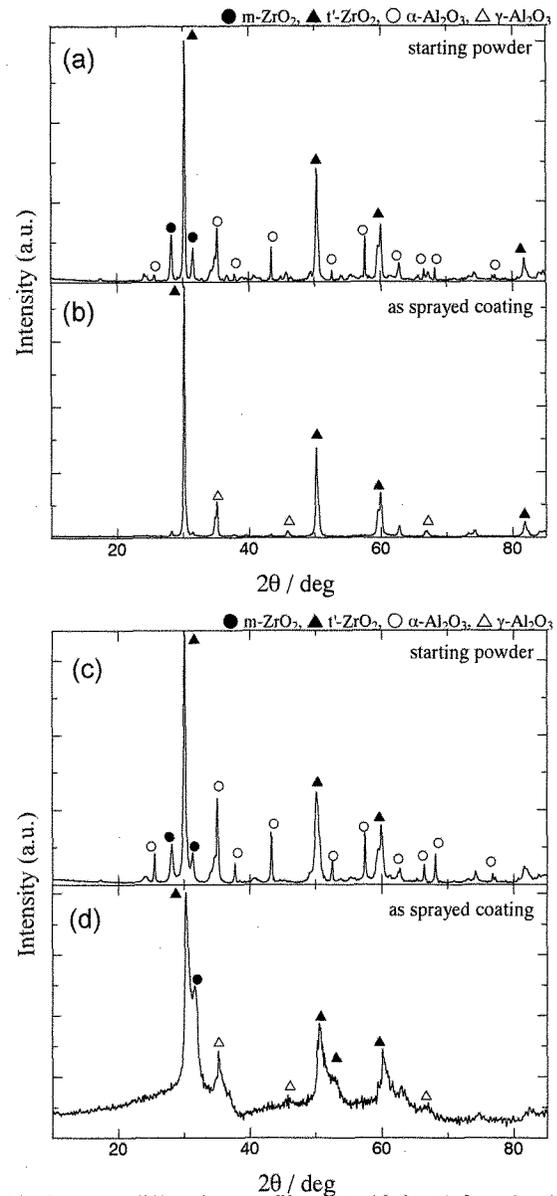


Fig.2 X-ray diffraction profiles. (a) Al$_2$O$_3$+ZrO$_2$ mixed powder, (b) deposit from mixed powder, (c) Al$_2$O$_3$/ZrO$_2$ spray dried composite powder, (d) deposit from composite powder.
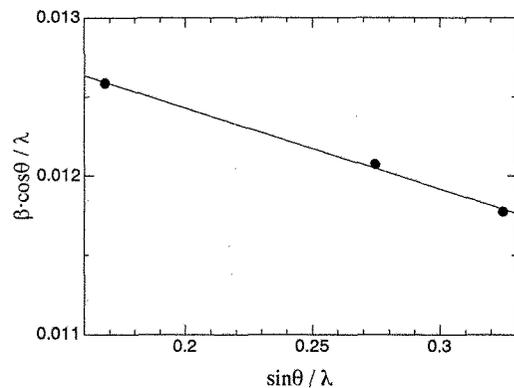


Fig.3 βcosθ/λ vs sinθ/λ plot for the deposit from composite powder to determine the effective crystallite size and effective strain.

between $\beta \cdot \cos\theta/\lambda$ and $\sin\theta/\lambda$ from the t'-ZrO$_2$ [111], [202], [131] peaks is plotted in Fig.3.

$$\frac{\beta \cos\theta}{\lambda} = \frac{1}{\varepsilon} + \frac{\eta \sin\theta}{\lambda} \quad\cdots\cdots\cdots(1)$$

Where $\beta$ is the measured fwhm in radians, $\theta$ is the Bragg angle of the diffraction peak, $\lambda$ is the X-ray wavelength, $\eta$ is the effective strain and $\varepsilon$ is the effective particle size. The calculated crystallite size of t'-ZrO$_2$ is 7.4 nm. The slope of fitted line in Fig.3 is negative, indicating the presence of compressive strain. Though the intensity of the Al$_2$O$_3$ diffraction peaks was too low for the similar calculation, the crystallite size seemed to be same order because of the simultaneous quenching.

Cross-sectional micrographs of M-film and C-film are shown in Fig.4. In the M-film (a), white splats of YSZ and gray splats of Al$_2$O$_3$ were piled up alternately, and formed a lamella structure peculiar to the sprayed deposit. This means that the each powder was melted individually to a droplet and impinged. On the other hand, C-film (b) also had a lamella structure, but the striped contrast owing to the difference of chemical composition was observed within the splat. Considering the crystallite size determined above, this contrast is probably led by the distribution of the fine crystals. The melting point of Al$_2$O$_3$ is much lower than that of ZrO$_2$. When the aggregation of fine powders was thrown into

the plasma, Al$_2$O$_3$ powder was melted first. So the unmolten ZrO$_2$ powder was moved by the surface tension of the molten liquid and/or the discrepancies in the specific gravity. Due to the very short dwell time before the impingement onto the substrate and solidification, the inhomogeneous state remained even if ZrO$_2$ powder was melted. C-film was very dense and the vertical micro-cracks were observed. The densification was probably owing to lowering the liquid curve by the eutectic reaction[2].

3.2 Properties

The results of the density and porosity measurement are shown in Fig.5 (a), (b). The measured true density was about 4400 kg/m$^3$ for both deposits, which was slightly higher than the estimated value from γ-Al$_2$O$_3$: 2400 kg/m$^3$ and t-ZrO$_2$: 6100 kg/m$^3$ [4]. It probably indicated that Al$_2$O$_3$ was vaporized during spraying and ZrO$_2$ content increased. The C-film was much denser than the M-film because the primary particle in the spray-dried powder was further small and melted easier. The open porosity of the C-film was half of the open porosity of the M-film and very low value as a sprayed deposit.

Vickers hardness was measured on the polished cross section by the load of 2.94 N for 15 s. The hardness of C-film was about 100 higher than the M-film (Fig.5 (c)). This effect was probably owing to the higher density and refined crystallite size.
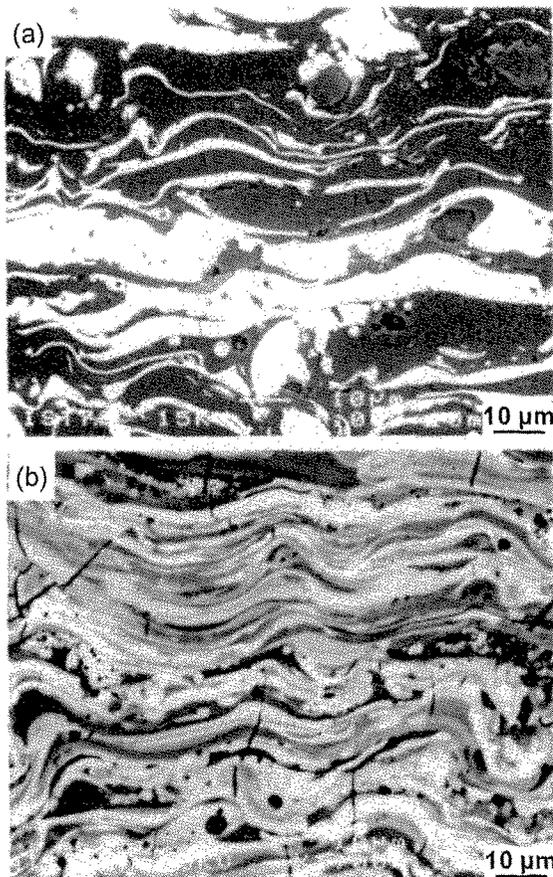


Fig.4 SEM cross sectional micrographs of plasma sprayed deposits. (a) deposit from mixed powder (M-film), (b) deposit from composite powder (C-film).
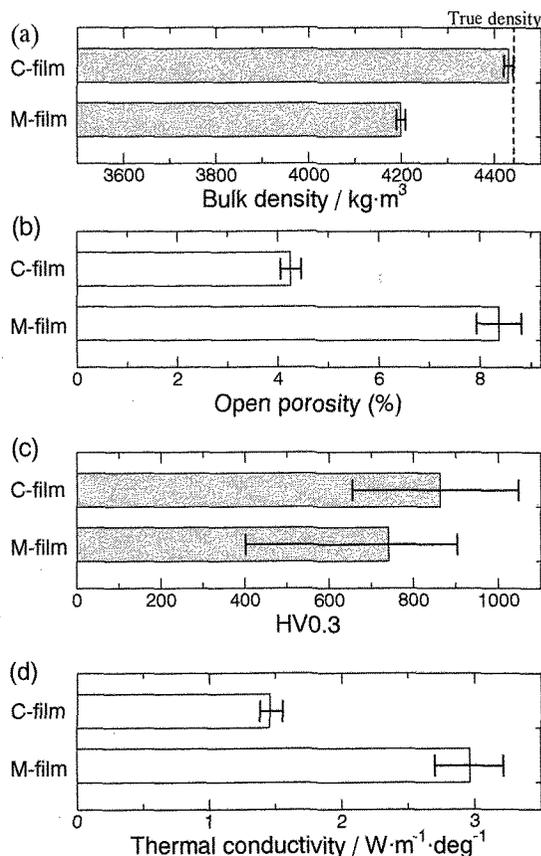


Fig.5 Comparison in the mechanical and thermal properties between M-film and C-film. (a) bulk density, (b) open porosity, (c) Vickers hardness, (d) thermal conductivity.

Thermal conductivity at room temperature was shown in Fig.5 (d). The estimated thermal conductivity values from the reported values[4] are 18.4 W/m·K for the linear law of mixture and 3.4 W/m·K for the parallel plates model, respectively. The value of M-film is slightly lower than the latter value, due to the peculiar structure of plasma sprayed deposit such as splats interface and pores. On the contrary, the C-film showed very low thermal conductivity, which was about a half of M-film.

We considered that $Al_2O_3/ZrO_2$ interface, which existed more in C-film than M-film, created some thermal resistance, and conducted following experiment. $Al_2O_3/ZrO_2$ double layered specimen was fabricated by plasma spraying. And its apparent thermal conductivity was measured by laser flush method. But its value was well agreed with the calculated value from the thermal conductivity of each monolithic deposit, that is, no thermal resistance detected between $Al_2O_3$ layer and $ZrO_2$ layer. It is suggested that some kinds of mechanism due to the microstructure of the C-film lower the thermal conductivity, as follows: the crystallite size of C-film is close to the mean free path of the phonon, so the grain boundaries possibly scatter the phonon effectively. Quenching during plasma spraying possibly formed some amorphous phase in C-film. The large mismatch of thermal expansion coefficient between $Al_2O_3$ and $ZrO_2$ possibly created nano size spacing around the grains. But it is difficult to explain the reason of low thermal conductivity of C-film now.

The sintered $Al_2O_3/ZrO_2$ nano-composite system was reported to have excellent strength and toughness[5]. So we expect to apply this coating to severe stress part in a coating system, such as the under coating close to metal substrate or metal bond coating. We will proceed to examine the mechanical properties in detail in the coating system like TBC.

## 4. CONCLUSIONS

- $Al_2O_3/ZrO_2$ nano size particle dispersed composite coating was successfully fabricated by plasma spraying using the spray-dried composite feedstock with fine primary powders about 100 nm.
- The deposit from composite feedstock shows the higher density and higher hardness than the deposit from mixed feedstock.
- Nano size composite coating had very low thermal conductivity, which was a half of that of deposit from mixed powders.

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