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Preparation of pore gradient silicon nitride ceramics by a high-velocity oxy-fuel spraying technique

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The preparation of pore gradient silicon nitride (Si_3N_4) ceramics was investigated by thermally spraying dense Si_3N_4 coatings onto the porous Si_3N_4 ceramic substrates via a high-velocity oxyfuel (HVOF) spraying method. Spray powders with excellent processability were developed and produced by spray drying and sintering in a nitrogen atmosphere. After sieving, the powders with average particle size of 45–75 μm were selected. Optimization of spray parameters such as spray distance and hydrogen flow rate was carried out in order to find the most decisive factor necessary for the production of dense and well-adhering coatings and pore gradient stuctures. Zirconium phosphate bonded Si_3N_4 porous ceramics were used as the substrate and coatings were obtained only when spray distance was 200 mm. A pore gradient structure was obtained at lower H_2 flow rate, while poor-adhering coatings were obtained at higher H_2 flow rate due to the etching. The hardness is significantly improved after Si_3N_4 coatings were successfully applied.

Key-words : Silicon nitride, Pore gradient, High-velocity oxyfuel (HVOF), Spraying

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1. Introduction

Pore gradient structure ceramics, as one of the special functionally graded materials (FGM), has been investigated for years because of their superior mechanical and thermal properties, and potential aerospace applications.[1] In particular, several fabrication processes such as ceramic/carbon mixtures,[1] packing ceramic powders to varying densities followed by partial sintering[2] and tape casting[3] techniques have been explored to prepare pore gradient ceramics. As a high temperature ceramic, silicon nitride (Si_3N_4) ceramic is used in numerous applications because of its high-temperature strength, good oxidation resistance and low thermal expansion coefficient.[4),5] Nowadays, various processing techniques have been developed to prepare both porous and dense Si_3N_4 ceramics for structural and functional applications.[6),7] However, little effort has focused on pore gradient structure Si_3N_4 ceramics which may be used in heat insulation applications. Our previous work reported on the preparation of pore gradient Si_3N_4 ceramics by using the spark plasma sintering (SPS) method, involving the packing of the porous and dense Si_3N_4 ceramics separately and the SPS sintering thereafter.[8]

Thermal spray processes like plasma spray have demonstrated the potential in producing graded deposits, where researchers have used twin powder feed systems to mix different proportions of powders.[9] FGMs vary in composition and/or microstructure from one boundary (substrate) to another (top service surface). HVOF (High Velocity Oxy-Fuel)[10),11] is a thermal spray with extremely high spray temperature and velocity that makes it possible for preparing dense ceramic coatings and for the spray powders to penetrate into the porous substrate. **Figure 1**(a) shows a schematic illustration of the HVOF system we used in this study. The HVOF system can be operated with hydrogen, propane, propylene and ethene as fuel gases. During spraying, fuel and oxygen are fed into the chamber. The powder is injected axially into the combustion area and accelerated through a convex-concave nozzle because of a hot high pressure flame. Spray distance, fuel-to-oxygen flow rate and fuel gas category are considered to be the three most important factors that influence the coating quality. For example, when spray distance is decreased and fuel-to-oxygen flow rate is increased, the particle velocity, temperature and impact energy will be increased. As a result, coatings with reduced porosity and enhanced mechanical properties will be obtained. Compared with the other processes shown in Fig. 1(b) HVOF has the particle temperature ranging from 1400–2000°C, and particle velocity of ~500 m/s.[12] Because Si_3N_4 does not melt, but decomposes at temperatures exceeding 1900°C, the HVOF process is ideal for the spray of Si_3N_4, which is considered to be a nonsprayable material.

The most successful attempt to prepare Si_3N_4-based coatings thus far was made by Sodeoka et al.[13] using powders obtained from β'-SiAlON ($Si_{6-z}Al_zO_zN_{8-z}$) with different degrees of substitution, z. The initial powders, including Si_3N_4, Al_2O_3 and AlN with different ratios to achieve β'-SiAlON with different z values, were fired at 1600°C for 2 h before spray. The powder was then used to deposit coatings by atmospheric plasma spraying (APS) with Ar/H_2 or $Ar/H_2/N_2$ as plasma gases, with the maximum $z = 4$ in all classes and with $z = 3$ at higher plasma power. The reference also mentioned that no coatings could be obtained from powders with low degrees of substitution ($z = 1$–2). However, when the degree of substitution is too high, e.g., $z > 2$, the Si_3N_4 content is less than 70 mass%. The presence of the other elements in the material may severely influence the properties of the material. So, it is significant to explore a proper way to spray Si_3N_4 ceramic with high Si_3N_4 content.

In this paper, SiAlON powder, including Si_3N_4, Al_2O_3 and AlN powders, together with Y_2O_3 powder, which is the most effective additive for Si_3N_4 sintering, was used as the initial powders. β'-

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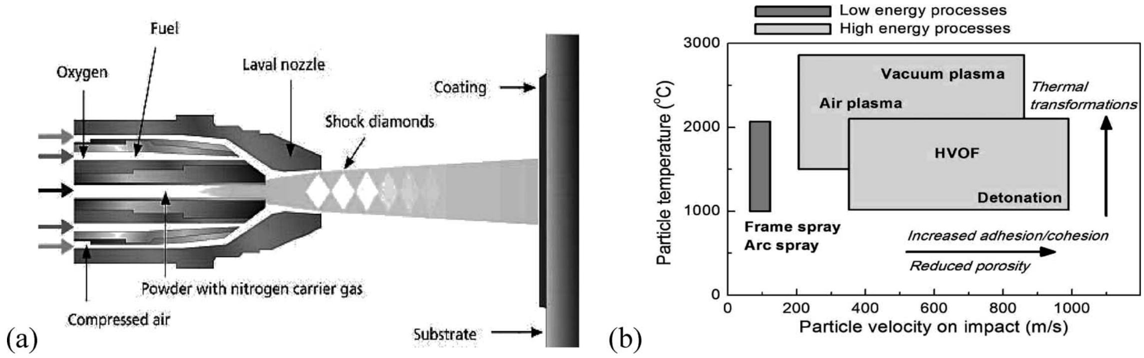

Fig. 1. (a) Schematic illustration of the HVOF system from http://www.fst.nl; (b) particle velocity and temperature among different spray processes.

Table 1. Chemical Composition of β-SiAlON Raw Material

Powder	Compositions, mass%	z in $Si_{6-z}Al_zO_zN_{8-z}$
β-SiAlON	90 Si_3N_4, 3 Al_2O_3, 6 Y_2O_3, 1 AlN	1

SiAlON powder with very low z value was synthesized then as the spray powder. Si_3N_4 matrix coatings were sprayed via HVOF and the effect of spray parameters such as spray distance and fuel-to-oxygen ratio on the structure and properties of the coatings was investigated.

2. Experimental procedure

2.1 Raw materials

β-SiAlON raw powder was prepared by mixing of the individual commercially available Si_3N_4, Al_2O_3, and AlN powders, while Y_2O_3 powder was used as a sintering aid, was added by agglomeration (spray dring). This powder was produced by International Syalons Newcastle Limited, England. The raw powder characteristics are shown in **Table 1**.

2.2 Spray powder preparation

The raw β-Sialon powder was put into an Al_2O_3 crucible, and then sintered in a tube furnace at 1600°C for 2 h in pure N_2 at a flow rate of 50 sccm as a reaction and carrier gas, subsequently mechanically treated by a mild milling process, and finally fractionized by sieving. In accordance with the other successful experimental results,[14] the spray powder with the particle size of 45–75 μm was used.

2.3 HVOF spray process

HVOF spray experiments were performed with a Top Gun (gas) system, using facilities at Plasma Technology Inc. (PTI), Torrance, CA, USA. The HVOF deposition conditions are listed in **Table 2**. Only hydrogen gas was used as the fuel gas. The spray distance and H_2 flow rate were changed in order to optimize the spray parameters as shown in Table 2. The 30 mm ZrP_2O_7 bonded Si_3N_4 porous ceramics reported in Ref.[6] with porosity of ~40% were used as the substrate material. The HVOF spray process is clearly shown in **Fig. 2**.

2.4 Characterization

The phase compositions were analyzed by X-ray diffraction (XRD) using a Rigaku-D/Max-IIIA diffractometer operated at 45 kV and 40 mA. Copper (Cu) radiation was used. The microstructures of both the spray powders and coatings were observed by scanning electron microscopy (SEM; JSM–5610LV, Japan). The amount of porosity was determined by image analysis. Microhardness testing was performed using a Vickers microhardness tester, with an indentation load of 50 g and 10 measurements for each sample.

Table 2. HVOF Spray Conditions

Sample	1	2	3	4
Spray distance (mm)	200	200	300	300
H_2 flow rate (l/min)	600	700	600	700
O_2 flow rate (l/min)	350			
Substrate cooling	Air jet			
Carrier gas	N_2			
Combustion gas	$O_2 + H_2$			
Powder feed rate (g/min)	60			
Substrate Temp.	100–300°C			
Spray passes	40			

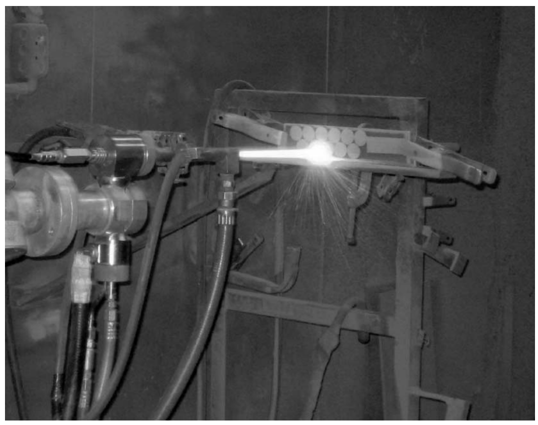

Fig. 2. HVOF spray experimental process at PTI.

3. Results and discussion

3.1 Structure and properties of spray powders

The morphology of the spray powder particles is shown in **Fig. 3**(a). It is seen that the spray powders are made up of agglomerate particles with the size of 45–75 μm. The agglomerates have porous structure composed of small crystals < 200 nm in size. The X-ray diffraction patterns of the raw material mixture, the

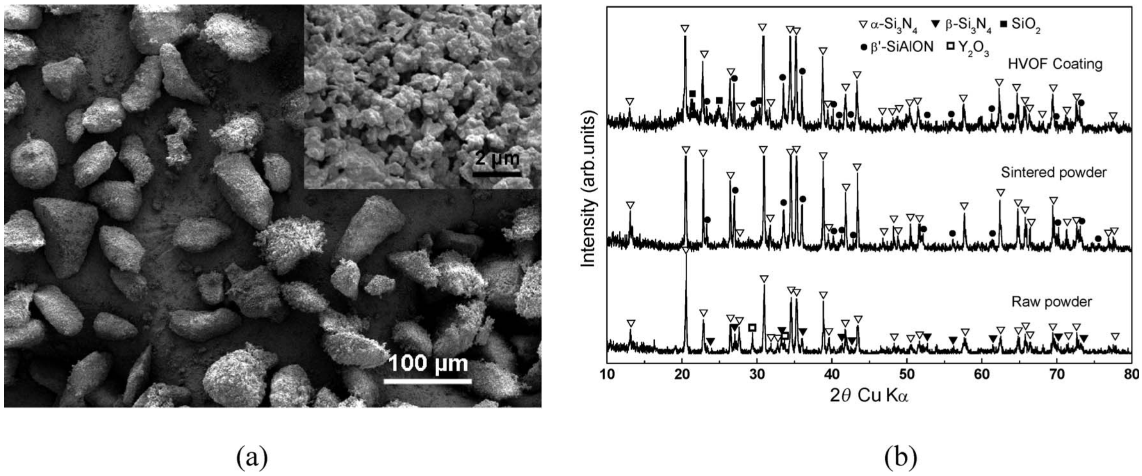

Fig. 3. (a) Morphology of the spray powder, the inset highlights the surface of the particle; (b) X-ray diffraction patterns of raw material, synthesized spray powder and the HVOF sprayed coating.

synthesized spray powder, and the sprayed coating are shown in Fig. 3(b). Comparing with the raw powder composite, which consists of α-Si_3N_4, β-Si_3N_4 and Y_2O_3 phases, the spray powder synthesized after sintering at 1600°C consists of α-Si_3N_4 and β'-SiAlON phases. During sintering of the spray powder, partial phase transformation of α-Si_3N_4 to β-Si_3N_4 takes place by solution and reprecipitation processes. The porous powder structure shown in Fig. 3(a) is believed to be the reason for the incomplete transformation from Si_3N_4 to β'-SiAlON. The sprayed HVOF coating also consists of α-Si_3N_4, β'-SiAlON and a small amount of SiO_2 phases, which illustrates that oxidation during the HVOF process is quite limited.

3.2 Effect of spray parameters on the structure and hardness of the coatings

For all spray samples listed in Table 2, only samples 1 and 2 were found to be coated with Si_3N_4 coatings. No coatings were observed on samples 3 and 4. So, the spray distance played a more significant role in the formation of Si_3N_4 ceramic coatings than the fuel flow rate. In the HVOF process, the spray distance is a practical method of controlling the amount of energy the powder has at impact. The shorter the spray distance, the higher the particle velocity and particle impact force on the surface. The other effect of spray distance is the temperature of the deposit. The longer the particle takes to reach the substrate, the more heat it loses to the atmosphere, and the less thermal energy it has to transfer to the substrate. Consequently, the spray distance of 300 mm may cause a severe heat loss and the spray distance of 200 mm was the prerequisite for formation of Si_3N_4 ceramic coatings.

The SEM images for samples 1 and 2 are shown in **Fig. 4**. It is shown clearly that a pore gradient structure is obtained in sample 1, with the lower H_2 flow rate. From the pore distribution analysis shown in Fig. 4 (a), the relatively dense (with porosity < 5%) Si_3N_4 coating is ~50 μm in thickness, followed by a pore gradient area (~100 μm thick). The area with porosity of ~30% is the porous Si_3N_4 substrate. It is also observed that the coating and the substrate are well bonded by the pore gradient area and no cracks are generated during spraying. From the SEM image of the coating surface shown in the right of Fig. 4 (a), the elongated β'-SiAlON grains are clearly seen with an average grain size of ~2 μm. For sample 2, with higher H_2 flow rate, no obvious pore gradient area is observed both the SEM image and the image

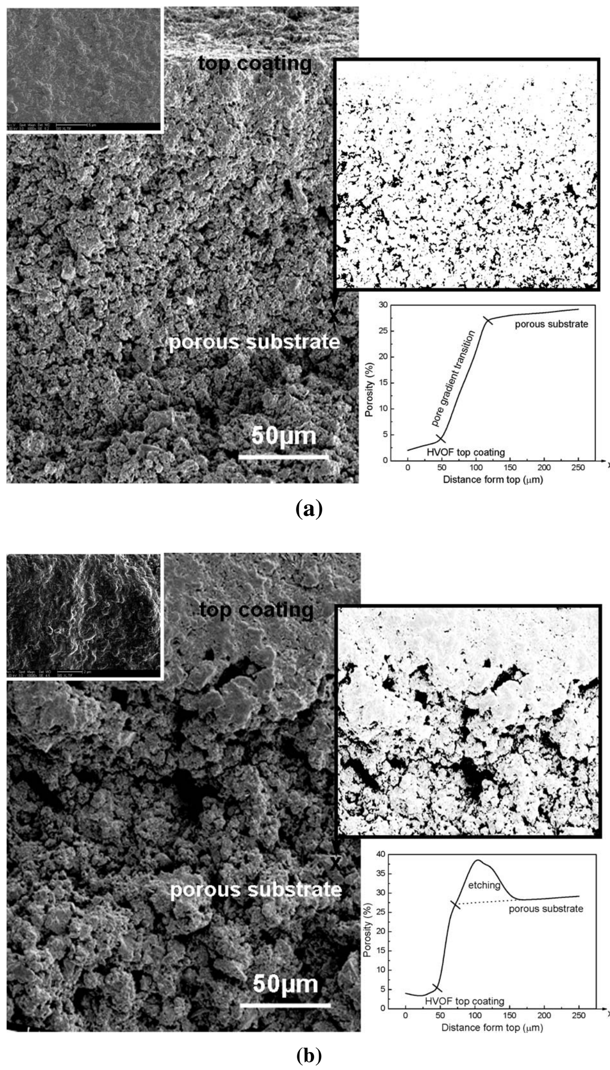

Fig. 4. (a) SEM image for cross section of sample 1 (left), the pore distribution image and curve are obtained by image analysis, and the coating surface morphology image (inset); (b) SEM image for cross section of sample 2 (left), the pore distribution image and curve, and the coating surface morphology image (inset).

Table 3. Porosity and Microhardness of Sprayed Coatings

Sample	Porosity, %	Microhardness, GPa	Spray conditions	
			H_2-to-O_2 Ratio	Spray distance
1	3	3.8	1.67	200
2	5	3.5	2	200
3	28	2.5	1.67	300
4	25	2.3	2	300

analysis results. The coating is also ~50 μm in thickness and the relative density is higher than 95%. There is an area with relatively high porosity between the coating and the substrate, which is believed to result from an etching phenonmenon during the HVOF process due to the high powder velocity and temperature caused by the higher H_2 flow rate. It is known that the amount of thermal energy (enthalpy heat content) transferred from the flame to the powder varies depending on the fuel flow rate and oxygen flows.[15] As the H_2-to-O_2 ratio is increased, by increasing the H_2 flow rate, more thermal energy is transferred to the powder. Thus the particle temperature and velocity are increased with the H_2-to-O_2 ratio. From the surface image of the coating, the apparent powder melting phenomenon is also observed.

The Vickers microhardness values for the HVOF spray samples are shown in **Table 3**. The hardness increases as apparent porosity decreases. It is also shown that samples 3 and 4 have almost the same porosity with the porous substrate material, indicating the failure to form dense Si_3N_4 coatings. For samples 1 and 2, the hardness is significantly improved after Si_3N_4 coatings were successfully sprayed. The maximum hardness, is about 3.8 GPa, is still significantly lower than that for sintered Si_3N_4 ceramics.[16]

4. Conclusions

Thermal spraying of Si_3N_4 with β'-SiAlON (z = 1) phase by using HVOF was attempted. Coatings were obtained only when spray distance was 200 mm. A pore gradient structure was obtained at lower H_2 flow rate, while poor-adhering coatings were obtained at higher H_2 flow rate due to the etching caused by the high particle velocity and temperature. The hardness is significantly improved after Si_3N_4 coatings were successfully applied.

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