Effect of Annealing on Plasma Sprayed Zirconia/ Alimina Composite Coating†

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Abstract

In thermal barrier coatings (TBC), failure occurs near or at the interface between the metallic bondcoat and topcoat. During high temperature service an oxide scale consisting mainly of α-alumina forms and is named thermally grown oxide (TGO) along the bond/topcoat interface. For diminishing the creation of thermally grown oxide (TGO), a dense coating with low residual stress and thermal stress buffer layer was preferable. In this study, to deposit such a kind of coating, a gas tunnel type plasma spraying system was utilized to produce an alumina/zirconia functionally graded thermal barrier coating and discussed its physical and mechanical properties, thermal behavior and high temperature oxidation resistance of the coating are discussed. Consequently, the proposed system exhibited superior mechanical properties and oxidation resistance at the expenses of a slightly lower thermal insulating effect. This interlayer is preferred in order to minimize the detrimental effect of the phase transformation of γ- Al_2O_3 to α-Al_2O_3.

KEY WORDS: (Plasma Spraying), (Thermal Barrier Coating), (Oxidation), (X-Ray Diffraction), (Scanning Electron Microscope), (Hardness).

1. Introduction

Yittria stabilized Zirconia (YSZ) has been widely used as the topcoat of the thermal barrier coating (TBC) in gas turbine components such as burners, transition ducts, vane, rotors and stators.

Commercial TBC systems typically consist of a metallic bondcoat and a ceramic topcoat. While there are many failure mechanisms by which the TBC can fail, oxidation of bondcoat has been repeatedly identified as one of the important factors affecting durability of ZrO_2 topcoat during service [1]. The thermally grown oxide (TGO), which is mainly α Al_2O_3, forms along the irregular bondcoat/topcoat interface. It is due to oxygen penetration to the interface though the intrinsic pores of the coating and cracks generated by heat cycles. In addition, residual stress in the coating develops the TGO. Hence, in order to diminish the TGO generation, dense coatings with thermal stress buffer layer are required.
Previously, high hardness ceramic coatings could be obtained by means of gas tunnel type plasma spraying [2-4] and it was proved that the deposited coating had superior property in comparison with those deposited by conventional type plasma spray method. The Vickers hardness of this sprayed coating became 20-30% higher than the conventional one. Zirconia composite coating formed by gas tunnel type plasma spraying has a high hardness layer at the surface side of the coating, which shows the graded functionality of hardness [5-10].

In this study, in order to develop the dense coating with thermal stress buffer layer for evaluation the oxidation behavior of plasma sprayed coating, deposition of duplex and functionally graded alumina and zirconia/alumina composite coating by gas-tunnel type plasma spraying was carried out. In addition, in order to confirm the effect of annealing, post heat treatment of the zirconia/alumina composite coating at 650℃ for 5hrs and the treatment of alumina coating at 1050℃ for 5hrs were conducted. Phase transformations during heat treatment were studied by X-ray diffraction, microstructures were analyzed by FE-SEM and mechanical properties characterization were also discussed within the context of the effectiveness of Al_20_3 coating as the oxygen barrier layer.

2. Experimental

Figure 1 shows the schematic diagram of the gas tunnel type plasma spraying equipment used in this study. This equipment consists of gas tunnel type plasma torch, DC power source, feedstock powder feeder and working gas supplying system. The operating conditions are given

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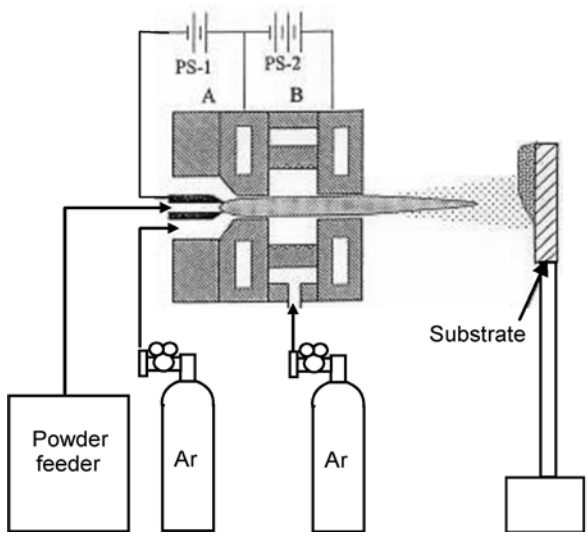


Fig.1 Schematic diagram of the gas tunnel type plasma spraying torch system.

in **Table 1**.

Commercial feedstock powders (7.9% yttria-stabilized zirconia-K90 and alumina-K16T) were premixed and formed a composite coating in the form of 50%ZrO_2-50%Al_2O_3, 100%ZrO_2 and 100% Al_2O_3 have been described in the previous papers. The particle size and chemical composition of powders are given in **Table 2**.

The square plates of stainless steel SUS304 were sandblasted and cleaned in acetone. The substrate dimensions were 50X50X3mm. In this case, the gas divertor nozzle diameter was *d*=20mm. The plasma torch was operated at power levels up to 21kW which was chosen to carry out all the experiments. The plasma jet was generated with the aid of argon gas which was fixed at 180 l/min. The torch was maintained at a spray distance of 40 mm far from the substrate plane. The powder injection was external to the torch and directed parallel to the plasma flow and parallel to the torch trajectory. The maximum feed rate was 45 g/min.

The mixing ratio of alumina to zirconia powders was given as 20-80 weight %. To study the oxidation behaviors of TBC systems, the specimens were pre treated at 650ºC for 1 and 5 hrs respectively in furnace.

Microstructure characterization was performed on the as-sprayed and oxidized specimens to evaluate the oxidation layer and the effectiveness of Al_2O_3, as an oxygen barrier layer. A scanning electron microscope (NIKON-FESEM 2700) equipped with energy dispersive X-Ray spectrometry (EDS) was used to examine microstructures and chemical composition of coatings. X-ray diffraction analysis with a JEOL JDX-3530M was carried out to determine phases of coatings prior to and after heat treatment.

The surface morphology and cross-section of the coatings was analyzed by the SEM.

Table 1 Experimental conditions.

Powder:	ZrO_2+ Al_2O_3 Mixture
Traverse number, *N*:	4,10 & 20
Power input,*P*(kW):	17-21
Working gas flow rate, *Q*(l/min):	180
Powder feed gas, Q_{feed}(l/min):	10
Spraying distance,*L* (mm):	40
Traverse speed, *v* (cm/min):	50 & 100
Powder feed rate, *w* (g/min):	25-45
Gas divertor nozzle dia., *d* (mm):	20

Table 2 Chemical compositions and sizes of zirconia and alumina powders.

	Composition (wt%)					Size(μm)
ZrO_2	ZrO_2	Y_2O_3	Al_2O_3	SiO_2	Fe_2O_3	
	91.65	7.72	0.02	0.01	0.14	10-45
Al_2O_3	Al_2O_3	Na_2O	SiO_2	Fe_2O_3		
	99.8	0.14	0.01	0.01		10-45

3. Results and Discussion

3.1 Effect of the annealing on the Al_2O_3/ZrO_2 composite coating at 650℃

Figure 2 shows the XRD patterns of the plasma sprayed coatings, showing the evidence of the absence of chemical reaction in the 'composite' blend. As for the rapid cooling from plasma spraying, α-Al_2O_3 transformed into γ phase, while zirconia structure was essentially in monoclinic and tetragonal phases. The effect of residual stress on high hardness observed in this layer was ruled out based on the hardness tester, showing that there are no significant differences in residual stress among Al_2O_3, ZrO_2 and Al_2O_3/ZrO_2 composite layers [11)]. Since the indented regions cover several sprayed particles, a higher hardness value, or a graded layer, would indicate a good interlamellar contact of Al_2O_3 and ZrO_2 [12)]. Moreover, the Al_2O_3+ZrO_2 layer was shown to exhibit a lower porosity compared to Al_2O_3 and ZrO_2 coatings (Fig.3). Since a pore is simply filled with air (and by the resin for specimen mounting), it tends to lower the measured hardness. Thus generally, a lower porosity can also contribute to the higher hardness values.

To evaluate phase transformation of Al_2O_3 due to plasma spray process, a free standing Al_2O_3 layer was oxidized at 650ºC for 5 hr. X-ray diffraction was conducted to examine phases of the sprayed layers. A comparison of diffraction patterns of the as-sprayed and heat-treated Al_2O_3/ZrO_2 is summarized in Fig.2. The α-Al_2O_3 that was formed during plasma spray undergoes a phase transformation to a more stable α-Al_2O_3 during heat treatment, although some fraction of γ phase was retained in the coating. Other phases, namely δ-, θ-Al_2O_3 were also identified. Levin and Brandon, 1998 [13)] explained that the transformation of γ to α had never been direct such that δ and θ phases can be regarded as the intermediate phases, suggesting that the transformation of γ to (δ,θ) to α occurred in the annealed coating. This finding is consistent with the results by Tolpygo et al., 2000 [14]. The phase transformation of α to γ involves a volume change, resulting in additional residual stresses. Density values of coated samples indicated that an additional volume change could be attributed to the porosity closing during heating.

Figure 3 shows the cross sectional microstructure of alumina/zirconia composite coatings after oxidation at 650ºC for 5hr. It shows that there is no indication of thermally grown oxide scale formation along topcoat and substrate interface because this temperature is not sufficient to form TGO scale in TBC coatings. The fracture surface of 50%Al_20_3-50%ZrO_2 coatings showed sufficient bonding between Al_2O_3 and ZrO_2 with the subsequent layer. It was observed that separation occurred at the splat boundaries leading to low measured-bond strengths. This finding indicates the mechanical interlocking at Al_2O_3 and ZrO_2 interface. The observation shows that higher surface roughness of alumina resulted in higher bond strengths in comparison with bond strengths of Al_2O_3/ZrO_2 composite coatings. Further improvement by applying a graded region between bond coat and topcoat will be developed in future. Such increases of bond strength in the system containing metal-ceramic graded regions could be expected since interfacial thermal stresses generated during the deposition process were lower compared to those generated in a TBC.

Figure 4 shows surface morphology of the substrates before and after annealing. In the case of the substrate before annealing, the surface morphology is rough and ZrO_2 regions are separated from Al_2O_3 regions.

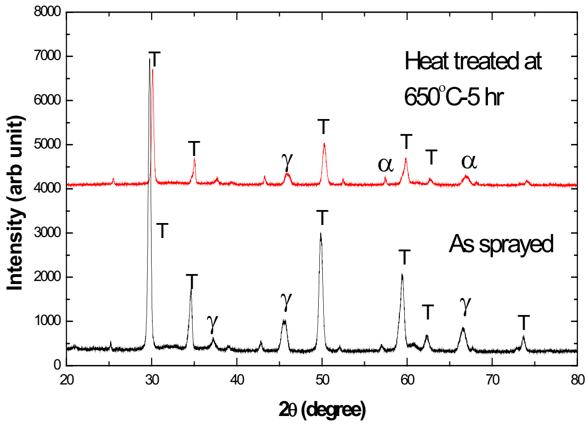


Fig.2 XRD patterns of free standing 50%Al_2O_3+50%ZrO_2 coatings in the as-sprayed state and after heat treatment at 650ºC for 5 hr. α and γ are phases of alumina while tetragonal (T) structure of zirconia.

However, by annealing the substrate, the surface morphology became smooth and the boundary between ZrO_2 and Al_2O_3 regions became ambiguous. From these results, it was proved that post heat treatment influenced the surface morphology as well as lattice structure and cross-sectional microstructure.

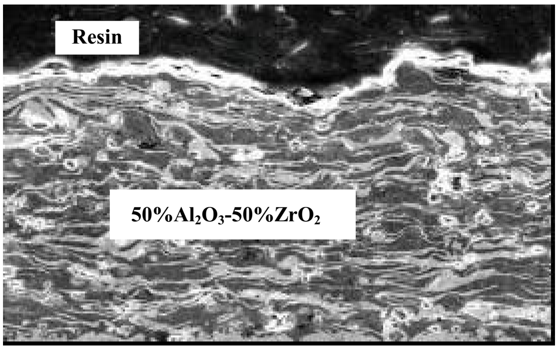
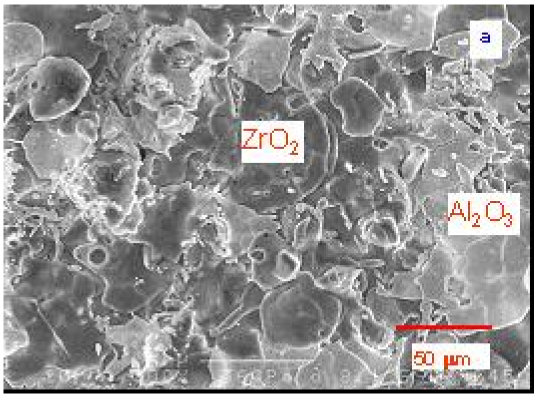
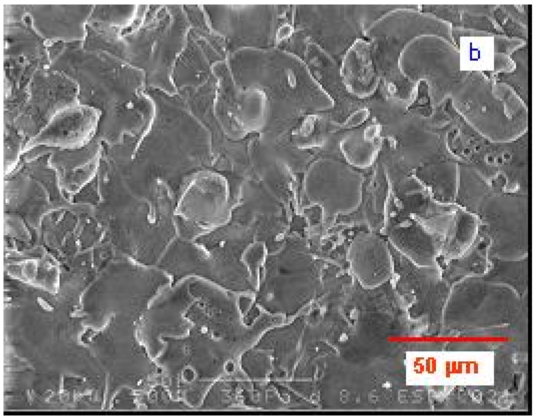


Fig.3 SEM micrograph showing the cross section of the as-sprayed 50%Al_2O_3-50%ZrO_2 coating after heat treatment at 650ºC.



a) Before heat treatment



b) After heat treatment

Fig.4 SEM micrograph showing the surface morphology of the as-sprayed 50%Al_2O_3-50%ZrO_2 coating after heat treatment at 650ºC.

3.2 Effect of the annealing on the Al_2O_3 coating at 1050℃

In order to investigate the behavior of Al_2O_3. on a practical condition, post heat treatment of the substrate at 1050 ºC for 5 hrs was carried out. After the heat treatment, the ZrO_2 coating system showed spallation from the substrate. But the Al_2O_3 coating showed no spallation, even failure occurring after exposure at the same heat treatment condition is shown in Fig.5. The delamination failure is due to large thermal stresses developing within the coating and the phase transformation of Al_2O_3. Analytical models show that plasma sprayed Al_2O_3 layers should be very thin since thicker layer would generate larger residual tensile stresses [15].

To evaluate phase transformation of Al_2O_3 due to plasma spray process, a free standing Al_2O_3 layer was oxidized at 1050 ºC for 5hrs. X-ray diffraction was conducted to examine phases of the sprayed layers. A comparison of diffraction patterns of the as-sprayed and heat-treated Al_2O_3 is summarized in Fig.6. The α-Al_2O_3 that was formed during plasma spray undergoes a phase

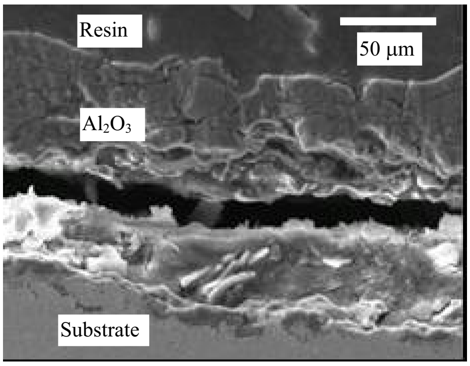


Fig.5 Spallation failure of Al_2O_3 coating after oxidation at 1050ºC for 5hs, showing the crack path leading to complete delamination.

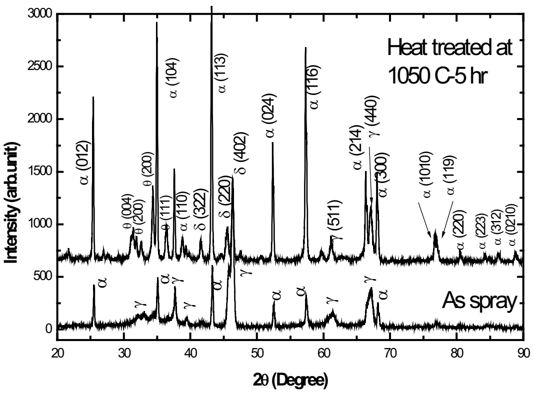


Fig.6 XRD patterns of Al_2O_3 coatings in the as sprayed state and after oxidation at 1050 ºC for 5 hr.

transformation to a more stable α-Al_2O_3 during heat treatment, although some fraction of γ phase was retained in the coating. Other phases, namely δ-, θ- Al_2O_3 were also identified. It is noted that the transformation of γ had never been direct, such that δ and θ phases can be regarded as the intermediate phases, suggesting that the transformation of γ to (δ,θ) occurred in the annealed coating [16,17]. The phase transformation to γ involves a volume change, resulting in additional residual stresses. Density values of coated samples indicated that an additional volume change could be attributed to the porosity closing during heating.

This observation shows that the higher surface roughness of alumina resulted in higher bond strengths in comparison with bond strengths of Al_2O_3/ZrO_2 composite coatings. Further improvement by applying a graded region between bond coat and topcoat will be developed in future. Such increase of bond strength in the system containing metal-ceramic graded region could be expected since interfacial thermal stresses generated during the deposition process were lower compared to those generated in a TBC. Despite phase transformation of the plasma sprayed Al_2O_3 interlayer during high temperature exposure and a higher thermal diffusivity of Al_2O_3, it is believed that Al_2O_3 material is effective in suppressing the oxidation of TBC system. Hence, it increases the lifetime of the coated component and improves its reliability.

4. Conclusion

The feasibility of functionally graded Al_2O_3/ZrO_2 thermal barrier coating prepared via atmospheric plasma spray had been evaluated. The following results were obtained:

(1) The phase composition of as-sprayed zirconia/alumina composite coatings by gas tunnel type plasma spraying using premixed Al_2O_3 and ZrO_2 powders mainly consisted of the non-transformable tetragonal phase of ZrO_2; no monoclinic and cubic zirconia phases of ZrO_2 were observed.

(2) The γ -Al_2O_3 that was formed during plasma spray undergoes a phase transformation to a more stable α-Al_2O_3 during heat treatment, although some fraction of γ phase was retained in the coating. The high temperature oxidation behavior of the functionally graded TBCs showed the effectiveness of the Al_2O_3 layer functioning as an oxidation barrier.

(3) The residual stress that is induced by the phase transformation of γ-Al_2O_3 to α-Al_2O_3 will be minimized at the interlayer, which results in maintaining structural integrity and reliability of the TBC systems.

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