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Plasma Spraying of Functionally Graded Yttria Stabilized Zirconia/NiCoCrAlY Coating System Using Composite Powders

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Pre-alloyed and plasma spheroidized composite powders were used as the feedstock in the plasma spraying of functionally graded yttria stabilized zirconia (YSZ)/NiCoCrAlY coatings. The ball milling parameters of the composite powders and the plasma spraying parameters for preparing functionally graded materials (FMGs) coatings were optimized to obtain the best performance for the thermal barrier coatings (TBCs). Microstructure, physical, mechanical, and thermal properties of YSZ/NiCoCrAlY FGMs coatings were investigated and compared with those of traditional duplex coatings. Results showed that the advantages of using pre-alloyed composite powders in plasma spraying were to ensure chemical homogeneity and promote uniform density along the graded layers. Microstructure observation showed the gradient distribution of YSZ and NiCoCrAlY phases in the coating, and no clear interface was found between two adjacent different layers. Oxidation occurred during plasma spray and the resultant aluminum oxide combines with YSZ in a wide range of proportions. The bond strength of functionally graded coatings was about twice as high as that of the duplex coatings because of the significant reduction of the residual stresses in the coatings. The thermal cycling resistance of functionally graded coating was much better than that of duplex coating.

Keywords thermal barrier coating, functionally graded materials, bond strength, thermal cycling resistance

1. Introduction

Functionally graded materials (FGMs) are crucial to the development of aircraft and space vehicles as the requirement for special materials to withstand severe environments such as superhigh temperatures and large temperature gradients become increasingly demanding.[1] The design of FGMs has been extended to thermal barrier coatings (TBCs). Thermal barrier coatings have been applied to turbine blades with Ni-based alloys as the oxidation resistant bond coat and heat resistant yttria stabilized zirconia (YSZ) ceramics as the top coat.[2] The TBCs concept is important because the mechanical properties of the metallic superalloy are maintained and the alloy is protected against high temperatures due to the low thermal conductivity of the ceramic top coat. Plasma spraying is a convenient method to fabricate TBCs.[3] With the further application of TBCs in the combustion chambers of diesel engines, there is a need for thick TBCs.[4] However, one problem related to such applications is the poor adhesion (due to stress buildup) in thick (>1 mm) coatings.[4] These problems can be eliminated by using a functionally graded TBC.[5,6] The FGMs concept is to prepare a new composite with a gradual compositional variation from heat resistant ceramics to tough metals.[7,8]

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There have been some studies on the mechanical and thermal properties of FGMs TBCs prepared by plasma spraying.[9,10] In this paper, NiCoCrAlY and YSZ powders were mechanically milled, plasma spheroidized, and used as feedstock to fabricate the YSZ/NiCoCrAlY FGMs coatings. The plasma spraying parameters for the different layers were optimized. Microstructure, physical, mechanical, and thermal properties of FGMs coatings were evaluated.

2. Experimental Details

2.1 Preparation of Prealloyed Powders

The composition of YSZ and NiCoCrAlY powders (Praxair, Indianapolis, IN) is listed in Table 1. The mixture of these two types of powders with different ratios of NiCoCrAlY (25, 50, and 75 wt.%) was ball milled in the P-5 Planetary Mill (Fritsch GmbH, Idar-Oberstein, Germany) using a zirconia bowl. The rotating

Table 1 Chemical composition of raw powders

(a) NiCoCrAlY powder

NiCoCrAlY (wt.%); particle size: 40 to 80 μm

Ni	Co	Cr	Al	Y
Bal	23	17	13	0.5

(b) Yttria-stabilized YSZ powder

YSZ (wt.%); particle size: 35 to 70 μm

ZrO_2	Y_2O_3	HfO_2	SiO_2
Bal	7.02	1.71	0.17

speed and duration time were varied between 100, to 200 rpm and between 0.5 to 4 h, respectively. The optimized milling parameters for these mixed powders with the particle size between 20 to 60 μm were obtained by analyzing these powders using a scanning electron microscope (SEM) and a particle size analyzer Analysette 22 (Fristch GmbH, Idar-Oberstein, Germany). The ball-milled powders were subsequently spheroidized by plasma spraying into distilled water using a 40 kW plasma torch (SG-100, Miller Thermal Inc., Baytown, TX). Table 2 shows the parameters used in the plasma spraying spheroidization.

2.2 Fabrication of FGMs Coatings

A computerized plasma spraying system 4500 (Miller Thermal Inc., Baytown, TX) was used in the optimization of plasma spraying parameters for the three layers in the FGMs coatings. All the process parameters of plasma spraying for different layers are listed in Table 3. The parameter of argon gas flow rate was changed to obtain the optimized parameters. Optimization of parameters was evaluated using ASTM C633-79 to measure the bond strength between coating and substrate.[11] The bond strength was the average tensile strength of five samples measured using an Instron 4302 tester (Instron Corp., MA) at a crosshead speed of 1 mm·min^{-1}. The detailed optimization procedures were as follows: first, a NiCoCrAlY layer with 150 μm was sprayed on a nickel stub using the given optimized parameters; then, 75 NiCoCrAlY + 25% YSZ powders were sprayed on a NiCoCrAlY layer with a thickness of 200 μm at different plasma net energy levels and argon gas flow rate. The so-formed coatings were used to test the bond strength. The parameters that determine the highest bond strength of the coatings are chosen as the optimized ones. After this procedure, a third layer of 50% NiCoCrAlY with 200 μm thickness was sprayed onto the optimized two-layer coating using different process parameters and the optimized parameters can be obtained from the bond strength results. The optimized parameters for 75% YSZ were also obtained using this method.

Table 2 Plasma spheroidization parameters

Primary, gas pressure/flow rate	Argon/345 kPa/2.32 m^3 h^{-1}
Auxiliary gas pressure/flow rate	Helium/345 kPa/0.74 m^3 h^{-1}
Carrier gas pressure/flow rate	Argon/50 kPa/0.34 m^3 h^{-1}
Atmosphere	Ambient
Arc current	800 A
Arc voltage	50 V
Spray distance	120mm
Powder feed rate	30 g min^{-1}

2.3 Analysis of Physical, Mechanical, and Thermal Properties

A JEOL JSM5310 scanning electron microscope (SEM, Japan Electron Optics Ltd., Tokyo) attached with an energy dispersive X-ray spectrometer (EDS) was used to study the microstructure of both powders and coatings. The microhardness profile of FGMs coatings was obtained using a Matsuzawa DMH-1 microhardness tester (Matsuzawa Seiki Co. Ltd., Tokyo) with an applied load of 300 g. The results of microhardness were the average of ten readings. A high-temperature dilatometer was used to measure the thermal cycling resistance of duplex coatings and FGMs coatings. The specimens were heated and cooled cyclically between 1300 °C and room temperature with both the heating rate and cooling rate of 50 °C/min. The shrinkage and dilatation of the specimen were used to identify the thermal cycles of the coatings. The sharp drop or increase in shrinkage or dilatation was considered as coating failure.

3. Results and Discussion

3.1 Characterization of Composite Powders

The optimum parameters of ball milling at which the average size of the powders was between 20 to 60 μm were as follows: 2 h at 100 rpm for 75% YSZ/25% NiCoCrAlY, 3 h at 100 rpm for 50% YSZ/50% NiCoCrAlY, and 2 h at 200 rpm for 25% YSZ/75% NiCoCrAlY powders.

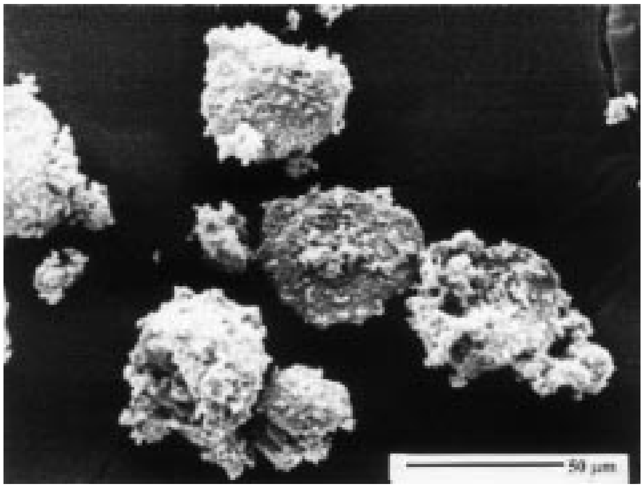
The SEM morphologies of the mixed powders before and after plasma spheroidization are shown in Fig. 1(a) and (b), respectively. Figure 2 shows the particle size distribution of the powders after plasma spheroidization. The powders after spheroidization are spherical and have a uniform particle size around 20 to 60 μm, which is optimized for plasma spraying.[12] Higher deposition rates, more uniform melting characteristics, and better coating consistency can be achieved using these spheroidized powders in plasma spraying. The spherical powders flowed smoothly, while the as-milled powders were found to choke occasionally when fed with the powder hopper.

The polished cross section of the plasma spheroidized powders is shown in Fig. 3(a). A layer of YSZ normally attached to the Ni alloy powder. The formation of the pre-alloyed composite powders can be explained as follows. Some YSZ powders are crushed into small pieces during the ball milling process. These small, hard, crushed YSZ powders are pressed into the ductile NiCoCrAlY powder forming a composite powder. When these composite powders are used in plasma spraying, the

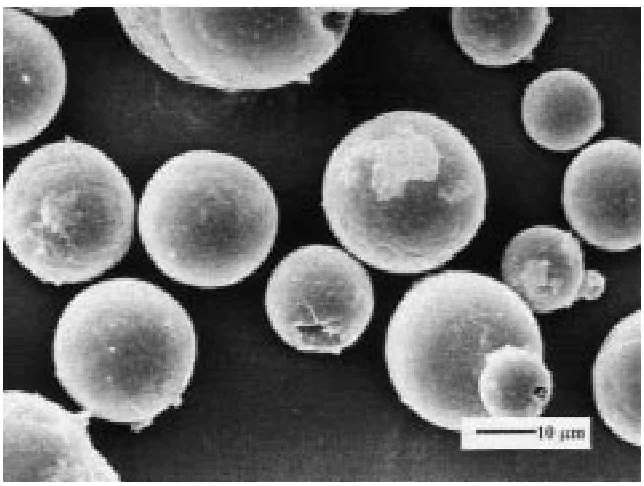
Table 3 Ranges of plasma spraying parameters for functionally graded coatings

	N	75% N + 25% Z	50% N + 50% Z	25% N + 75% Z	Z
Net energy (kW)	17.7	17.2, 17.6	17.2, 17.6	17.2, 17.6	17
Argon gas (m^3 h^{-1})	2.32	1.70, 1.98, 2.27	1.70, 1.98, 2.27	1.70, 1.98, 2.27	1.53
Helium gas (m^3 h^{-1})	1.13	1.19	1.19	1.19	1.25
Carrier gas (m^3 h^{-1})	0.34	0.34	0.34	0.34	0.34
Feed rate (g min^{-1})	35	35	35	35	40

N = CoAlY and Z = YSZ.



(a)



(b)

Fig. 1 SEM micrograph of powders: (a) before spheroidization and (b) after spheroidization.

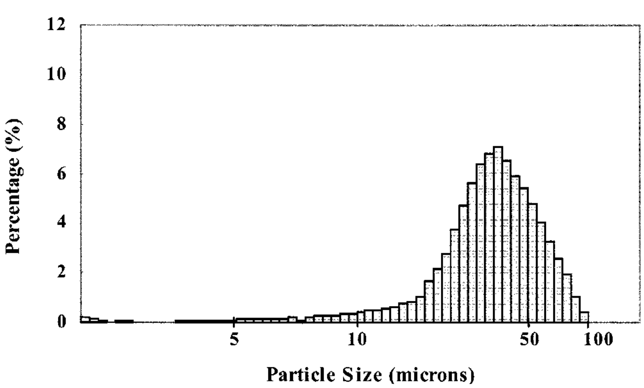
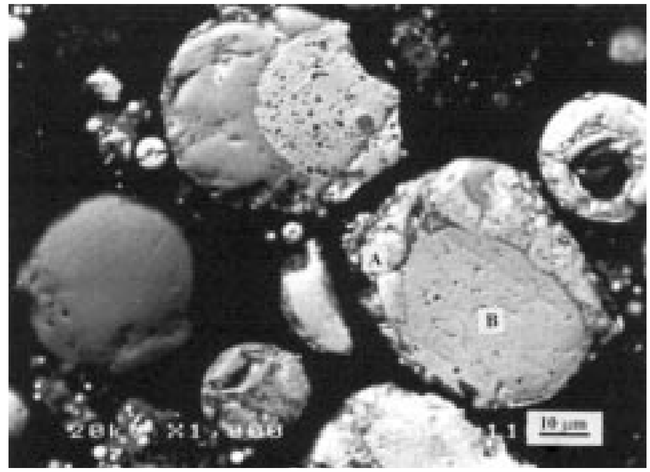
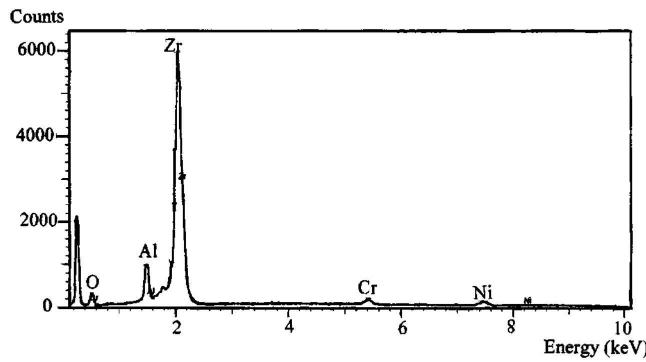


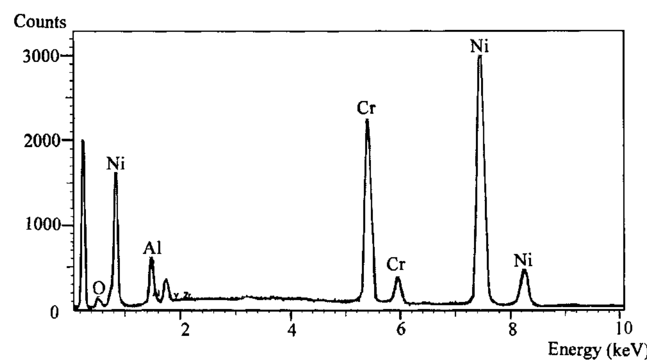
Fig. 2 Particle size distribution after plasma spheroidization



(a)



(b)



(c)

Fig. 3 Cross section of a composite powder: (a) cross section of the composite powder, (b) Al_2O_3 + YSZ mixture, and (c) Ni-based alloy

oxidation of the NiCoCrAlY powder can probably be reduced due to the encapsulation of YSZ. In addition, these powders can ensure chemical homogeneity and promote uniform density along the graded layers. The EDS results of point A in Fig. 3(a) indicate that some aluminum elements in NiCoCrAlY alloy are oxidized during plasma spray spheroidization, as shown in Fig. 3(b).

3.2 Optimization of Plasma Spraying Parameters for Different Interlayers

Figure 4 shows that the argon gas flow rate has a significant effect on the bond strength of different adjacent layers. To spray

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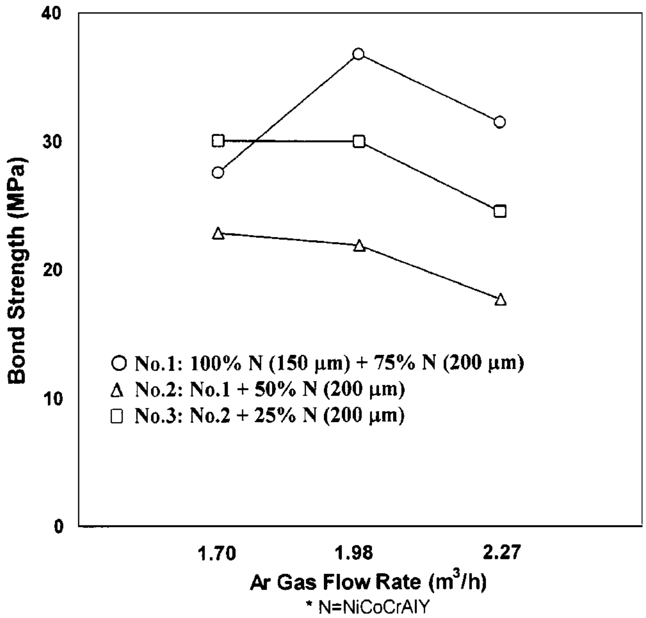

Fig. 4 Bond strength vs argon gas flow rate.
No. 1 (two-layer): [100% NiCoCrAlY (150 μm)] + [75% NiCoCrAlY + 25% YSZ (200 μm)]
No. 2 (three-layer): No. 1 + [50% NiCoCrAlY + 50% YSZ (200 μm)]
No. 3 (four-layer): No. 2 + [25% NiCoCrAlY + 75% YSZ (200 μm)]

the layers with high content of NiCoCrAlY, the optimized gas flow rate is relatively large, whereas for the layer with high content of YSZ, the optimized gas flow rate is relatively low. The gas flow rate can affect the energy density and temperature of the plasma flame. The higher the gas flow rate, the lower the energy and temperature of the plasma flame. For the powders with high content of NiCoCrAlY, the temperature should be low to avoid the oxidation of the metal powders. Too low a flow rate of argon gas will cause severe oxidation of the metal powder and, therefore, decrease the bond strength, whereas for the powders with high content of YSZ, in order to melt the YSZ powder, the energy should be relatively high. Then, the flow rate of argon gas should be low.[13] From the above analysis, the optimum plasma spraying parameters for the five different layers are listed in Table 4.

3.3 Microstructure of FGMs Coating

Figure 5 shows the SEM micrograph of the polished cross section of a five-layer YSZ/NiCoCrAlY graded coating, in which the dark phase is YSZ and the white phase is NiCoCrAlY. From the NiCoCrAlY layer to the YSZ layer, NiCoCrAlY gradually changes in morphology from a lamellar pattern to a dispersed pattern, while YSZ distributes gradually from a dispersed pattern to a porous pattern. No clear interface between two adjacent different layers can be found. The gradient distribution of the two phases in the coating can significantly eliminate the sharp interface of the conventional duplex ceramic/metal coating and decrease the high thermal stress.

Backscattered electron (BSE) images of cross sections of FGMs coating revealed the lamellar structure with different gray levels, as shown in Fig. 6. It is likely that selective oxidation of aluminum, yttrium, and chromium in the nickel alloy occurred during the high-temperature plasma spraying. The resultant oxides mixed with zirconia rapidly at the molten state. The EDS analyses show that the white particles and lamellae are YSZ and NiCoCrAlY alloy, respectively. Al_2O_3 + YSZ mixtures and sometimes with addition of $Cr_2O_3 + Y_2O_3$ are also observed covering several intermediate gray levels in BSE images from light gray to black, which is due to different percentages of metal oxides in YSZ.

Table 4 Optimum plasma spray parameters for different layers

	Argon gas flow rate (m^3 h^{-1})	Plasma net energy (kW)
No. 1	1.98	17.2
No. 2	1.70	17.2
No. 3	1.70	17.2

No. 1 (two-layer): [100% NiCoCrAlY (150 μm)] + [75% NiCoCrAlY + 25% YSZ (200 μm)]
No. 2 (three-layer): No. 1 + [50% NiCoCrAlY + 50% YSZ (200 μm)]
No. 3 (four-layer): No. 2 + [25% NiCoCrAlY + 75% YSZ (200 μm)]

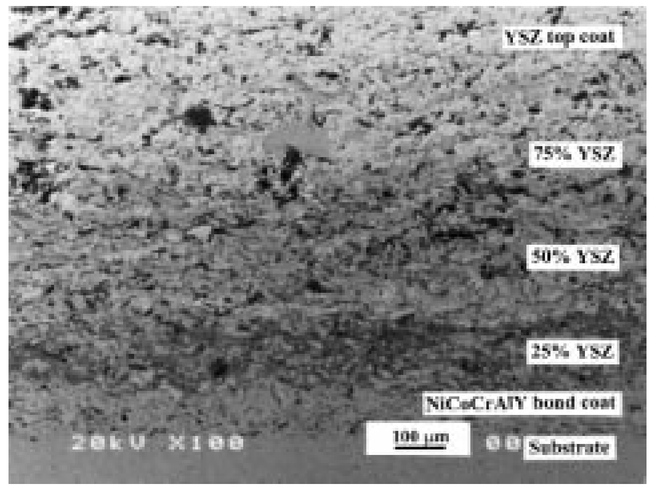

Fig. 5 BSE micrograph of the polished five-layer YSZ/NiCoCrAlY graded coating

3.4 Physical, Mechanical, and Thermal Properties of FGMs Coatings

Microhardness distribution. Figure 7 shows the microhardness distribution of YSZ/NiCoCrAlY five-layer functionally graded coating. The gradient distribution of the microhardness can reduce the large difference of the elastic modulus between ceramic and metal layers, which is better for the bond strength between coating and substrate under bending or tensile stress.

Bond Strength. The results of the bond strength of the FGMs coatings and duplex coating with the same thickness of 1 mm are 17.8 and 9.3 MPa, respectively. The bond strength of the YSZ/NiCoCrAlY FGMs coating is almost twice as high as that of the duplex coating. An important factor, which affects

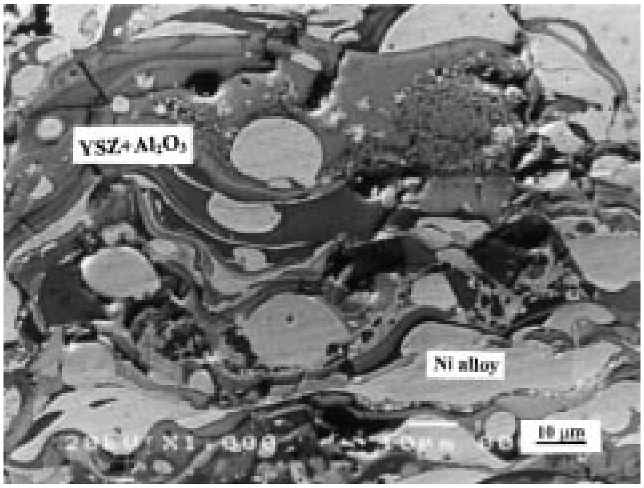

Fig. 6 BSE micrograph of the coating with 25% YSZ

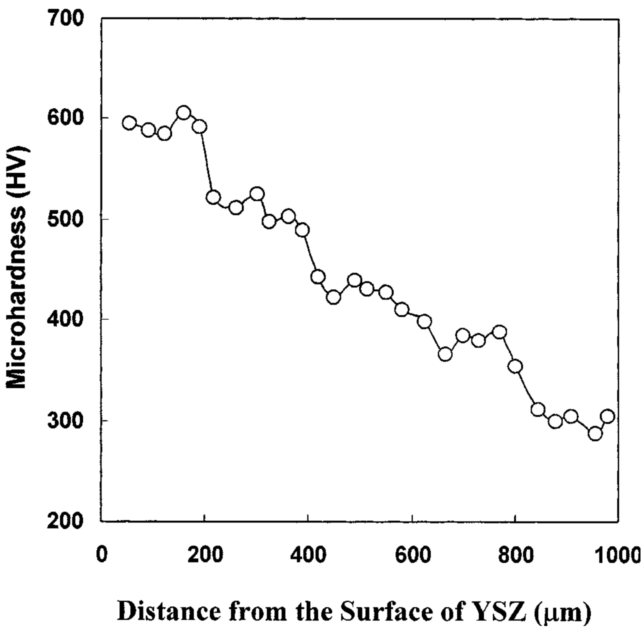

Fig. 7 Microhardness distribution of functionally graded YSZ/NiCoCrAlY coatings

the bond strength of the as-sprayed coating, is the residual stresses.[14,15] The thermal stress can be decreased significantly by using graded layers in FGMs coatings;[16] therefore, the bond strength can be improved significantly. The increase of bond strength is a reflection of the microstructure where there are no sharp interfaces between layers since the YSZ, Al_2O_3, and Ni alloy phases are dispersed within the FGMs coatings.

Thermal Cycling. The results of thermal cycles to failure for the duplex coating and FGMs coating are 15 and 90, respectively. Compared with duplex coating, it is found that the thermal cycling resistance of FGMs coating has been improved significantly and the resistance of the FGMs coating to the thermal changes is much better than that of the duplex coating. The reason for the improvement in thermal cycling of FGMs coating can be attributed to the decrease in residual stresses, the decrease in difference of thermal expansion coefficient between ceramic layer and metal layer, and the increase in bond strength.[17]

4. Conclusions

- The pre-alloyed composite powders were suitable for the preparation of functionally graded coating by plasma spraying. These powders could be used to form the interlayers leading to a FGMs coating. The advantages of using the composite powders are to ensure chemical homogeneity and promote uniform density within each of the graded layers.
- Plasma spray parameters of different interlayers were optimized through bond strength test to achieve the best performance and avoid delamination of the FGMs coatings.
- The microstructure and the microhardness were found to change gradually in the coating from the metallic (NiCoCrAlY) side to the ceramic (YSZ) side.
- The bond strength of the FGMs coating was twice as high as that of the duplex coating. Thermal cycling resistance of the FGMs coating is five times better than that of the duplex coating.

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