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Optimization of Mullite Based Coating Using Slurry Spray Technique

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ABSTRACT

Ceramic-metal functionally graded materials (FGMs) have been attracting a great deal of attention as environmental barrier coatings (EBCs) for aerospace structures and turbine blades working under elevated temperatures and chemically harsh environment. A relatively new, simple and low cost manufacturing method of environmental barrier coatings based on the slurry spray technique (SST) has been developed. In this research, it is desired to develop this technique to achieve the coating quality comparable to the existing manufacturing methods, which are often expensive. This paper describes the development and optimization of mullite-nickel based coating using Slurry Spray Technique analysing the effect of MgO as liquid phase sintering (LPS) additive. Taguchi's experimental design based on L9 orthogonal array was employed for optimizing the technique and analyzing the effect of selected process parameters (sintering temperature, sintering time and percentage of additives). The response parameter of the coating so produced is measured in terms of coating interface adhesion strength. The test results have been used to downselect the significant process parameters and help demonstrate the feasibility of coatings produced by slurry spray technique. The test results demonstrate satisfactory adhesion strength of the developed coating, which is comparable with that produced from traditional techniques such as flame spray method.

1. INTRODUCTION

Environmental barrier coatings (EBCs) have been developed to improve the stability in aggressive environments. Non-oxide and oxide ceramic coatings are well suited to improve the resistance against corrosion and oxidation of metals due to their superior properties at elevated temperatures and in chemically harsh environments [1]. The application of EBCs can significantly increase the operating temperatures up to 1400-1500°C, increase efficiency and improve the durability of the components such as in oxidizing environment. Functionally Graded FG-EBCs can significantly reduce the thermal mismatch and, therefore, largely reduce thermal stresses as well as the possibility of fractures caused by these thermal stresses and, as a result, drastically improve the service life. There are many applications, which have benefited from adopting EBCs. These include the aeronautical, aerospace, automotive and nuclear industries and heavy duty utilities such as diesel trucks [2-4].

There are many fabricating methods for depositing ceramics or other coating materials on a metal substrate which have been developed over the past three decades [5]. All fabricating techniques can be categorised in three main groups: bulk processes, flame spray techniques and deposition techniques; each technique differing from each other greatly, in terms of physical principal used, cost and simplicity. However, the main obstacle in the widespread application of these techniques is a relatively high cost of manufacture and equipment. Moreover, many of these techniques are not applicable to cover large or curved areas. All these drawbacks form the motivation for the development of slurry spray technique. This method is not as highly utilised as the other techniques and it is desirable to determine whether it can produce EBC coatings of comparable quality [6]. The developed technique for fabrication of mullite based environmental barrier coating using slurry spray technique is briefly outlined in this paper.

Mullite is a high melting crystalline alumino-silicate material which has long been used in heavy-duty refractories pertaining to its several remarkable physico-chemical properties [7]. These properties include low thermal expansion and thermal conductivity, good thermal and chemical stability, high melting point, low creep rate, reasonable toughness and strength, good thermal shock resistance, adequate infrared transparency etc [8-11]. For theses beneficial properties Monolithic mullite ($3Al_2O_3 \cdot 2SiO_2$) is widely studied and used in the production of heat resistant material applications like heat insulation, refractories, heat exchanger, turbine blades, spacecraft components, computer chips etc. [12,13].

Despite its excellent properties, the widespread usage of mullite has been restricted due to the difficulty of sintering mullite in its pure form from powder because of the low interdiffusion rates of Si^{4+} and Al^{3+} within the mullite lattice [14,15]. In response to this, liquid phase sintering (LPS) additives such as titanium dioxide (TiO_2) [16], ferrous oxide (Fe_2O_3) [17], Y_2O_3 [18] and magnesium oxide (MgO) [19] have been utilised in an attempt to reduce the sintering temperature. Whilst oxide-based compounds have been the most widely utilized sintering aids, attempts have also been made to incorporate fluoride-based sintering aids.

Taguchi's experimental design based on L9 (3^4) orthogonal array (OA) was employed for conducting the experiments. The effect of various process parameters (percentage of additives, sintering temperature and sintering time) on the adhesion strength of the coating is discussed in view of the quality, fracture and durability. The optimum process parameters are predicted on the basis of analysis (ANOVA) of the raw data and signal-to-noise (S/N) ratio.

2. SLURRY SPRAY TECHNIQUE

The Slurry Spray technique for manufacturing environmental barrier coating utilises traditional wet powder spraying methods to deposit sinterable coating materials onto target substrates. The process involves suspending the coating material within a fluid to form a slurry mixture that can be applied to a surface using common gravity fed air pressurised spray guns. Successive layers are then sprayed onto the substrate and dried using varying slurry compositions to produce a functional coating. The optimal thickness of the layers to deter surface cracking during the drying process is approximately 250 µm and the drying time is approximately an hour, depending on ambient conditions [6]. After the desirable number of layers of the EBC is deposited the multilayered coating is loaded in a compression chamber to form a densified layer before being sintered in the furnace. The applied pressure varies depending on the number of coating layers, typically between 10 and 40 MPa. The fabrication in the slurry spray and sintering process consists of the following steps:

Mixing: the slurry is prepared from a mixture of ceramic and metal powders, binder, dispersant and distilled water.

Spraying: the slurry mixture is then sprayed onto the substrate to form a wet coating. Spraying is effected using a normal gravity fed spray gun.

Drying: The coated substrates is left to dry at ambient conditions to let the solvent evaporate. Steps 2 and 3 are repeated for each subsequent layer to produce a functionally graded coating (figure 1).

Pressure Stamping: The dried coatings are then pressure stamped to compact the layers at 30 MPa.

Sintering: The green substrate is finally sintered using a muffle furnace.

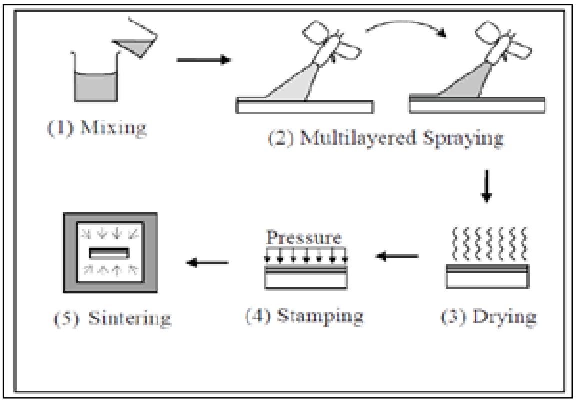

Figure 1: Slurry Spray and Sintering Technique

3. COATING FABRICATION

3.1 Slurry preparation

Tetra Sodium Pyrophosphate as dispersant is added to a volume of distilled water (solvent) and stirred continuously to mix [20,21]. Hydro soluble polyvinyl alcohol binder crystals are added to the slurry mixture to complete the slurry [22]. The slurry mixture composes of a ceramic and metal powder (Mullite and Nickel), binder and a dispersant, with the remaining percentage being distilled water. MgO is added to the slurry mixture as a liquid phase sintering (LPS) additive. Table 1 below summarizes the composition of the slurry mixture for the intermediate layer (comprising 50% pure nickel powder and 50% mullite, with 1 % additive).

Table 1, optimum composition of the slurry mixture

Mullite +Ni powder	LPS additive	Binder	Dispersant	Mix agent
44 %	1 %	3 %	0.4 %	51.6 %

3.2 Spraying and Stamping

A gravity fed paint spray gun is connected to an air compressor and used to spray the slurry mixture fed from a top mounted paint hopper. The gun is directed to the surface to deposit the slurry particles in a uniform layer. The spraying technique used to spray the TBC onto the substrate involves using several quick passes of the spray jet over the substrate surface to form an even coating. The spray nozzle is kept a moderate distance (150 mm) from the surface to allow a large cone shaped spray stream and prevent rapid deposition of the slurry on the surface. The pressure of the spray stream is varied from 4-6 bars, depending on the desired coating thickness. A diagram of the graded composition can be seen in Figure 2.

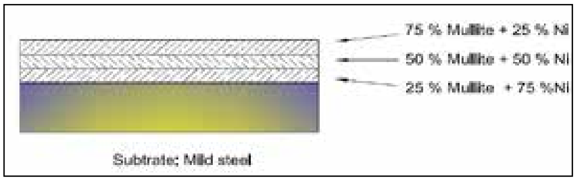

Figure 2, multilayer Functionally Graded Coating.

Pressure is applied to the dried multi-coating layers to promote contact between powder particles, which in turn decreases the time and applied temperatures required for sintering [23]. The lower applied temperatures and reduced times of sintering are very beneficial for the load-carrying substrate structure by reducing thermal damage to the substrate material during the coating process.

3.3 Debinding and Sintering

To debind the EBC specimens the furnace is first preheated to 300°C while the EBC specimen dries after spraying. Once dry the EBC is placed in the heated oven for debinding for 30 minutes. Over this time period the hydrosoluble polyvinyl alcohol begins to be vaporised at 230°C to form carbon dioxide and water vapour which do not react with the ceramic powder coating.

The furnace temperature is further raised to the sintering temperature i.e. 800°C [6]. The coating coupons are allowed to sinter for respective sintering time. After the sintering the coupons are allowed to cool in ambient atmosphere.

4. BOND ADHESION TEST

From the mechanical point of view, adherence can be estimated by the force corresponding to interfacial fracture and is macroscopic in nature [24]. It has been stated that the fracture mode is adhesion if it takes place at the coating-substrate interface and that the measured adhesion value is the value of practical adhesion, which is strictly an interface property, depending exclusively on the surface characteristics of the adhering phase and the substrate surface condition [25,26].

In this work, evaluation of coating interface adhesion strength is done using coating pullout method, conforming to ASTM C-633-79 standard [27]. The test method determines the degree of adhesion (bonding strength) of a coating measured in tension normal to the substrate. One surface of a cylindrical specimen, which acts as the test substrate, is coated. The coating is bonded to a counterpart specimen with a suitable adhesive, such as epoxy. The adhesive used in this study is Araldite 2014 two component epoxy paste with tensile strength more than 30MPa. The glued cylinders are assembled in a self-aligning fixture which is mounted on a tensile test machine and pulled in a plane normal to that of the coating at a constant cross head speed between 0.013 mm/s and 0.021 mm/s until failure occurs. Once rupture occurs, the maximum load is recorded. The adhesion strength can be calculated using the following equation:

Adhesion strength = maximum load / cross-sectional area of the specimen

The purpose of this test was to investigate the effect of the composition versus the adhesion strength of the fabricated coating.

5. TAGUCHI EXPERIMENTAL DESIGN

The experimental design was according to the L9 (34) orthogonal array (OA) based on the Taguchi method as this array is most suitable to provide the minimum degrees of freedom as 9 [= 1 + 4 x (3–1)] required for the experimental exploration. The levels of each coating parameters were set in accordance with the L9 orthogonal array, based on the Taguchi experimental method. The process parameters and the range used, on the basis of good quality coating achieved in the selected range in the pilot experiments are given in Table 2. Feasible limits of the process parameters were chosen in such a way that the coating produced should be free from any visible defects like cracking, spallation and delamination. Moreover, the significant coating parameters associated with the adhesion strength were determined by ANOVA based on S/N ratio.

Table 2, coating parameters and their range.

Parameters	Units	Labels	Level 1	Level 2	Level 3
Sintering temperature	°C	A	750	800	850
Sintering time	Min.	B	30	45	60
Sintering additive	%	C	1	3	5

The response characteristic data is provided in Table 3. The standard procedure is employed to analyze the data based on S/N ratio, as suggested by Taguchi. The average values of the S/N Ratio of the response characteristics for each parameter at different levels are calculated from experimental data. The response parameter viz. adhesion strength, is of "higher the better" type of coating quality characteristics, hence the S/N ratio for these type of responses is given below.

$$\left(S/N\right)_{HB} = -10 \log\left(MSD_{HB}\right)$$

$$MSD_{B} = \frac{1}{R}\sum_{j=1}^{R}(1/y_j^2)$$

Where y_j is the output response and R is the repeating number of trails in each group. Where is the output response and R is the repeating number of trails in each group. The main effects of process parameters for S/N ratio for each response were plotted by calculating the average values of response characteristics for each parameter at different levels. Analysis of Variance (ANOVA) is performed to identify the significant process parameters and to quantify their effect on the response characteristics.

Table 3: The L9 (34) OA with Experimental Results of Various Response Characteristics

Exp No.	Run Order	Parameter level				Response for adhesion strength			
		1	2	3	4	Raw data for bonding strength (MPa)			S/N Ratio (dB)
		A	B	C	e	R1	R2	R3	
1	1	1	1	1	1	13	15	14	22.92
2	3	1	2	2	2	14.5	15	15	23.42
3	2	1	3	3	3	14	13	13.5	22.60
4	4	2	1	2	3	17.5	18.5	17.5	25.02
5	6	2	2	3	1	18	16.5	15.5	24.43
6	5	2	3	1	2	16.5	13.5	15	23.52
7	9	3	1	3	2	17	18	15.5	24.52
8	7	3	2	1	3	15.5	16.5	14	23.71
9	8	3	3	2	1	16	15	17.5	24.17
Total						142	141	137.5	214.34
						Overall mean of Bonding strength =			15.57

R1, R2, R3 represent response value for three repetitions of each trial. The 1's, 2's, and 3's represent levels 1, 2, and 3 of the parameters. (e) represents no assignment in the column.

6. RESULTS AND DISCUSSION

The average values and main effect (S\N Data) of respective process parameters on adhesion strength is shown in figure 3, figure 4 and figure 5 respectively. The results of ANOVA for Raw Data and S/N Ratio associated with adhesion strength obtained from the L9 OA based on Taguchi method is shown in table 4 and table 5.

Figure 3, Effect of sintering temperature on adhesion strength

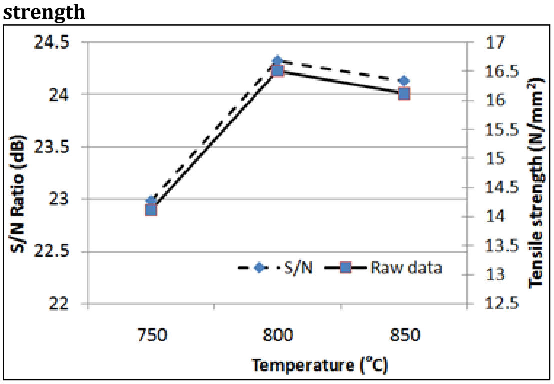

Figure 4, Effect of sintering time on adhesion strength

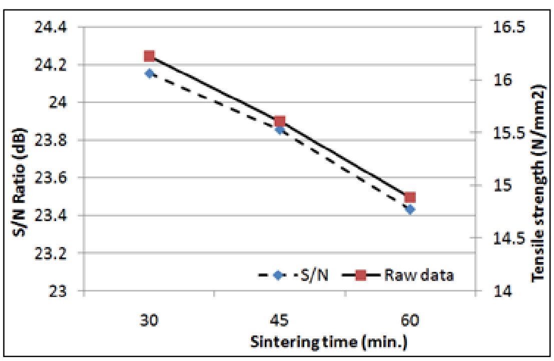

Figure 5, Effect of sintering additive on adhesion strength

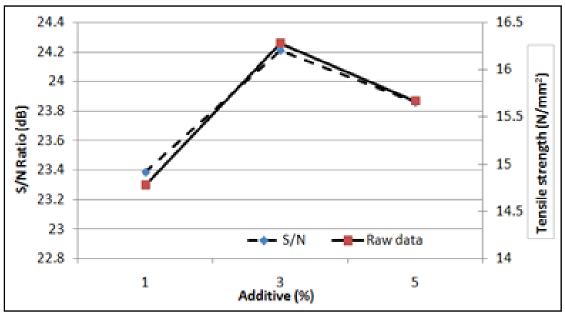

Table 4: ANOVA (Raw Data, adhesion strength)

SOURCE	SS	DOF	V	P %	F-Ratio
A	29.57	2	14.78	43.26	14.41*
B	8.01	2	4.00	11.73	3.9*
C	10.24	2	5.12	14.98	4.99*
e	-	-	-	-	-
ERROR	20.51	20	1.02	30.01	
Total (T)	68.35	26	*	100	
* Significant at 95 % confidence level. Fcritical=3.49 SS –Sum of Squares, DOF–Degree of Freedom, V–Variance					

Table 5: ANOVA (S/N Ratio, adhesion strength)

SOURCE	SS	DOF	V	P %	F-Ratio
A	3.16	2	1.58	63.52	518.18*
B	0.79	2	0..39	15.89	129.68*
C	1.01	2	0.50	20.45	166.82*
e	-	-	-	-	-
ERROR	0.006	2	0.003	0.122	
Total (T)	4.98	8	*	100	

* Significant at 95 % confidence level. Fcritical=19.33
SS –Sum of Squares, DOF–Degree of Freedom, V–Variance

As shown in the table 4 and 5, all the selected parameters of sintering temperature (A), sintering time (B) and percentage of additives (C) significantly affect both the mean and the variation in the adhesion strength values. The percentage contribution of sintering temperature on adhesive strength is highest (61.81%) followed by percentage of additives (21.36%) and sintering time (16.80%).

However in comparison with existing coating techniques such as the flame spray method, with adhesion strength of approximately 21 MPa, the adhesion strength of the produced coating (16.8 MPa) by slurry spray technique is comparable to the flame spray method [28].

Effect of sintering temperature

It is evident that adhesion strength increases from 14.11 MPa to 16.5 MPa, with increase in sintering temperature from 750°C (level 1) to 800°C (level 2), however slight decrease in adhesion strength is recorded beyond 800°C. Thus 850°C is found to be the optimal sintering temperature for mullite-nickel system with the aid of MgO as sintering additive, which is lower than the conventional sintering temperature of mullite i.e. 1350°C [29] which might be attributed to the effect of liquid phase sintering additive (MgO).

Effect of sintering time

The average values and main effect (S\N Data) of sintering time on adhesion strength is shown in figure 4. The maximum value of adhesion strength (i.e. 16.2 MPa) of the coating is achieved at 30 minutes (level 1) however with the increase in sintering time from 30 minutes to 60 minute there is constant decrease in adhesion strength. However, sintering time is not the largest contributing factor as evident from the percentage contribution of the sintering time i.e. 16.8%, considering the given parameters and conditions.

Effect of sintering additive (MgO)

The average values and main effect (S\N Data) of sintering additive on adhesion strength is shown in figure 5. It is evident that adhesion strength increases from 14.7 MPa to 16.2 MPa, with increase in percentage of MgO from 1% (level 1) to 3% (level 2), however there is decrease in adhesion strength recorded beyond 3% addition of MgO. Thus 3% MgO as liquid phase sintering additive is found to be the optimal amount of sintering additive for mullite-nickel system. The increase in MgO increases the grain size of mullite. Moreover, when a larger amount of MgO powder was added during the pilot experiments, the large defects appeared as the large amounts of glassy phase concentrated at grain boundaries. The large defects in ceramic materials play a main role on the mechanical properties [30].

The optimum levels of the parameters for the higher adhesion strength are the, second level of sintering temperature (A2), first level of sintering time (B1) and second level of percentage of additives (C2), corresponding to sintering temperature of 850°C, sintering time of 30 minutes, and percentage of additives of 3%.

7. CONCLUSIONS

The following conclusions have been made from the above investigation:

1. The slurry spray technique has been demonstrated to be capable of producing durable coating of satisfactory adhesion strength, which is comparable with that produced from traditional techniques such as flame spray method.
2. All the three selected parameters viz. sintering temperature, sintering time, and percentage of additives significantly affect the coating bonding adhesion strength.
3. With the increase in sintering temperature, coating bonding adhesion strength increases upto 800°C and a slight decrease on adhesion strength is recorded for sintering temperature of 850°C. Moreover, sintering temperature is found to be the most dominating factor for coating adhesion strength, having the highest contribution of the order of 61.81%.
4. As the sintering time is increased from 30 minutes to 45 minutes and further to 60 minutes slight decrease in coating adhesion strength is observed.
5. The optimal percentage of liquid phase sintering additive i.e. MgO, is found to be 3% for improved coating bonding adhesion strength.
6. An optimized value of the coating bonding adhesion strength for a 95% confidence interval was predicted as 16.8 MPa.

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