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Electrophoretic Deposition of Mullite Nano Coating by using Low Voltage DC

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Abstract

Electrophoretic Deposition (EPD) of ceramic materials on metallic substrates is a promising technique to improve the surface properties like, wear resistance, corrosion resistance, heat resistance and mechanical strength. So far, researchers have applied a high DC voltage of above 200 volts to coat various ceramic materials on metallic substrates. In this paper an attempt was made to use a low voltage DC of 30 to 35 volts to coat mullite($3Al_2O_3$-$2SiO_2$)ceramic powder of 200 nm average particle size on mild steel substrate to enhance the mechanical, thermal and corrosion resistance properties of the base metal. The electrolyte comprised of organic compounds, 2-Butanone and n-Butylamine, and Polyvinylbutyral was used as the binding agent to improve the adhesion of the coated material. The electrolyte being non-aqueous in nature served only as a carrier of the suspended ceramic particles. The DC power source of laboratory model was used during the study. A magnetic stirrer was used to prevent suspension of the ceramic powder particles. The experiment was conducted for a long duration of 3 hours. Visual examination showed the coating of a thin layer of ceramic material on the substrate. The coating thickness was measured using electronic weighing balance and confirmed by analytical method. The samples were tested in a particle size analyser Horiba nanopartica SZ 100 of USA. Particle size is measured using dynamic light scattering (DLS) principle. XRD conducted on the coated samples using reports showed the mullite phase. X-ray diffraction (XRD) reports were generated using PanalyticalXpert Pro Powder Diffraction unit.EDS studies were conducted in Jeol SEM and the composition of mullite was confirmed.

Keywords: *EPD, low voltage DC, non-aqueous solution, nanomullite, particle analyzer.*

1. Introduction

Electrophoretic Deposition (EPD) technique is gaining importance in the domain of advanced ceramic coatings. Applications of EPD are diverse due to its cost effectiveness and user friendly apparatus. In the 1980's, it was applied for advanced ceramics and Hamaker [1] first studied the method for ceramic materials. Work is being carried out by many researchers to understand the basic principles of EPD and to optimize the operating variables in order to have a bigger reach of the process. Many mechanisms of EPD have been explained by many researchers' and they claim that the process cannot be restricted to one type of mechanism as per Jonathan J. Van Tassela and Clive A. Randall [2]. EPD is one of the methods in ceramic production with short processing time where ceramic particles are suspended in a solution and inter particulate forces come into play; use of use friendly apparatus with no restriction on the shape of the substrates. The process can be modified for any given application. For use of EPD in ceramic coatings, time of deposition of the coating and applied potential are the two important parameters used to control the thickness and morphology of the coating.

In EPD, when a DC electric field is applied suspended powder particles carry a charge in a aqueous or non-aqueous medium and due to forces of attraction are deposited into a conductive substrate of opposite charge. In comparison to electroplating process, EPD involves charged suspended particles whereas electroplating process involves ions of salts in a solution (electrolyte).

Advanced ceramics like Mullite, Zirconia are used in advanced aero engines, stationery gas turbines, heat exchangers, radiant burners, heat

treatment furnaces, nuclear fusion reactors, automobiles and biological implants. Mullite is a ceramic with attractive high temperature resistance properties. It can act as a good thermal barrier to protect the substrates exposed to high temperature, though its fracture toughness is low and cannot be used for structural applications. Also it is used widely in diverse fields: fuel cells, thermal barrier coatings, electronics, catalysis and optical devices [3-11].

An attempt has been made in this paper to conduct coating trials using low voltage DC power of 30 Volts and extending the duration of the process to 3 to 4 hours. The objective of the study was to obtain a nano layer coating of nano mullite on mild steel substrate.

2. Materials and Methods.

2-Butanone is an organic compound (C_4H_8O). It acts as a medium through which the EPD process takes place.

n-Butylamine is an organic compound with the formula $CH_3(CH_2)_3NH_2$. It acts as the buffer compound and a template to carry the ionized particles. It helps in maintaining the pH at 12.6 (alkaline).

Polyvinyl butyral is a resin used for applications that require toughness and flexibility, strong binding, optical clarity and adhesion to many surfaces. It is prepared from polyvinyl alcohol by reaction with butyraldehyde.

The constituents of fused mullite are Al2O3 (78%), SiO2 (21.6%), Fe2O3 (0.05%) and Na2O (0.35%).

The mild steel plates were machined to 50×50×5 mm. The surface was sand blasted using copper slag, aluminum oxide, river sand and stainless steel grit to have a surface roughness of 50 microns.

2.1. Experimental

The sand blasted samples were cleaned in acetone and dried in an oven for 2 hours before taking up for the deposition. The electrolyte, the binder and the ceramic material was mixed in a glass beaker in the proportions of 20 g of mullite, 180 ml of 2- butanone, 20 ml of n- butylamine and 0.4 g of polyvinyl butyral**.** The pH was maintained about 12.6 at 25°C. Experiments were also conducted on aluminum sheets. The experimental setup of EPD is shown in Fig. 1. The electrophoresis experiment was carried out for 3-4 hours

2.2. Characterization

The coating thickness was measured using electronic weighing balance and confirmed by analytical method. The samples were tested in a particle size analyser Horiba nano partica SZ 100 of USA. Particle size is measured using dynamic light scattering (DLS) principle. XRD conducted on the coated samples using reports showed the mullite phase. X-ray diffraction (XRD) reports were generated from 10° to 80° using PanalyticalXpert Pro Powder Diffraction unit (Cu Kαradiation, λ_1 = 1.540; λ_2 = 1.544) at 40 kV and 30 mA. EDS studies were conducted in Jeol SEM and the composition of mullite was confirmed. Studies were also conducted on aluminum sheet and the visual examination showed the layer of mullite coating formed.

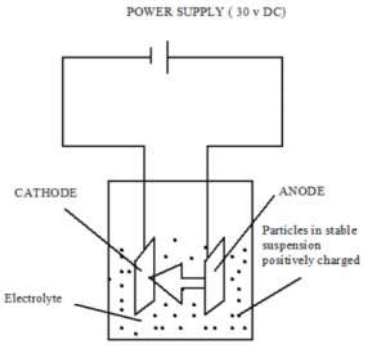


Fig. 1. *EPD setup*

Table 1. *Thickness measurement.*

Time (sec)	Weight of deposit (mg)	Thickness of deposit (microns)
600	0.00152304	2.175771
1200	0.00304608	4.351543
1800	0.00456912	6.527314
2400	0.00609216	8.703086
3000	0.0076152	10.87886
3600	0.00913824	13.05463
4200	0.01066128	15.2304
4800	0.01218432	17.40617
5400	0.01370736	19.58194
6000	0.0152304	21.75771
6600	0.01675344	23.93349
7200	0.01827648	26.10926
7800	0.01979952	28.28503
8400	0.02132256	30.4608
9000	0.0228456	32.63657
9600	0.02436864	34.81234
10200	0.02589168	36.98811
10800	0.02741472	39.16389
12600	0.03198384	45.6912
14400	0.03655296	52.21851

3. Results and discussions

3.1. Thickness of deposit

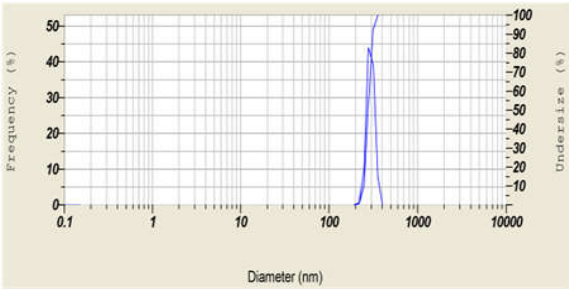
Table 1 shows the thickness of the deposit calculated from experimental results. Measuring thickness directly by instrumental techniques may be done, but the costs involved are high due to the nano size of the layer. Hence a simple method was adopted. The amount of particles deposited is expressed as given below

$$W = \frac{2C\varepsilon_0\varepsilon_r\xi Et}{3\eta L} \quad (1)$$

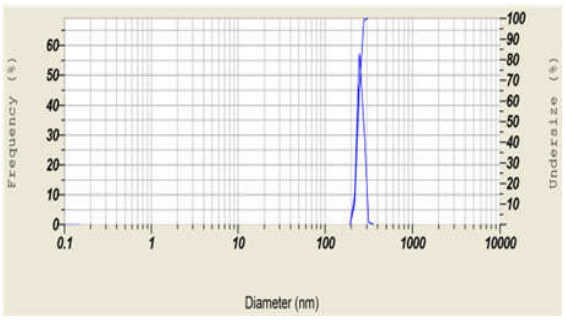
Where W is the amount of particles coated during EPD in milligrams / unit area of electrode, C is the particle concentration in the solvent, ε_0 is permittivity of vacuum, ε_r is the relative permittivity of the solvent, ξ is the zeta potential of the particles, η is the solvent viscosity, E is the potential applied in volts, L is the distance between electrodes in cm and t is the time of deposition in min [12, 13].

3.2 Particle size analysis

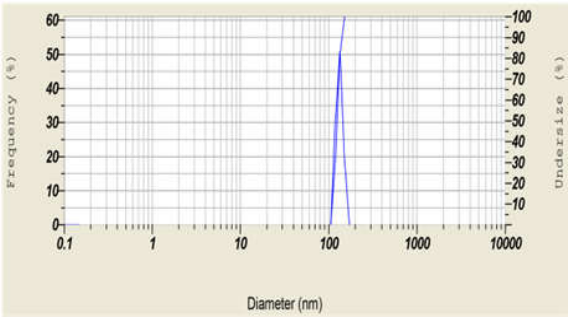
The particle sizes measured for sample 1 is 278 nm, 2- 240 nm, 3- 124.6 nm in diameter. The size distributions of the mullite powders obtained by milling in the attrition mill appear as shown below in Fig. 2. These powders show a Gaussian particle size distribution. The powder milled in the attrition mill reaches an average size of around 278 nm, but has a very narrow size distribution ranging from 200 nm up to 400 nm for the first sample.



(a)



(b)



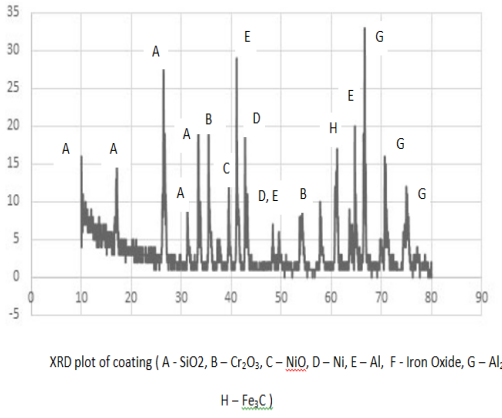
(c)

Fig. 2. *EDS spectra of (a) sample 1, (b) sample 2 and (c) sample 3*

For the second sample, the average size is around 240 nm and the size ranges from 200 to 300 nm and for the third sample it is of the order of 125 nm, with the size ranging from 100 to 180 nm. The narrow size distribution in the samples proves the efficacy of the ball milling method.

3.3 XRD analysis

The XRD plot is shown in Fig. 3. Considering the XRD plot in figure, peaks of higher intensity generally refer to mullite with peaks at 35°, 37°, 43°, 52° and 68° which correspond to corundum phase (Al_2O_3) and 26°, 58°, 67°, 68° and 78° which correspond to the quartz phase (SiO_2) as per JCPDS reports for mullite, corundum and quartz. Almost all the peaks refer to mullite phase and note the difference in intensities for the three samples. The reason for this variation is the particle size and the volume content of the samples. The intensity is lower in the third sample due to lower particle size (125 nm). The sharp narrow diffraction peaks seen in the figure imply the good crystalline nature of the as-synthesized mullite powder with little (note the hump in the plots between 10° and 20°, corresponding the amorphous content.



XRD plot of coating (A - SiO2, B – Cr_2O_3, C – NiO, D – Ni, E – Al, F - Iron Oxide, G – Al_2O_3 H – Fe_3C)

Fig. 3. *X-ray diffraction pattern*

The average crystalline size (D) of the nano-sized mullite particles was estimated from the half-height width of the diffraction peak of XRD pattern using the Debye-Scherrer equation as follows

$$D = \frac{K\lambda}{\beta\cos\theta} \quad (2)$$

Where D = crystalline size, Å, K = crystalline-shape factor, λ = X-ray wavelength, θ = observed peak angle, degree, β = X-ray diffraction broadening in radian [14]. The average crystalline size of the nano-sized mullite particles is about 2.13, 2.04 and 2.40 nm.

3.4 EDS studies

Quantitative chemical analysis by EDS confirmed the presence of all elements in the mullite powder-aluminum, silicon, oxygen and traces of nickel and chromium. The results of the observation are shown in Fig. 4 and Table 2. The signals generated seem to be weak. Nevertheless, the elements are visible in the plot.

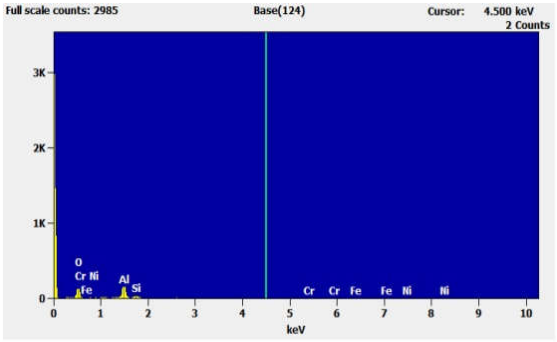


Fig. 4. *EDS plot*

Table 2. *Percentage of chemical composition in sample 1, sample 2 and sample 3 by EDS studies. (El-Element, Tot-Total)*

El.	Sample 1		Sample 2		Sample 3	
	Mass %	Atom %	Mass %	Atom %	Mass %	Atom %
O	26.19	37.56	12.97	20.25	-	-
Al	68.3	58.09	73.08	67.65	73.51	74.43
Si	5.12	4.18	13.24	11.78	26.07	25.36
Cr	0.24	0.1	0.24	0.11	0.16	0.08
Ni	0.16	0.06	0.48	0.2	0.27	0.13
Tot.	100	100	100	100	100	100

4. Conclusions

The electrophoretic deposition of nano synthesized mullite has been successfully demonstrated on mild steel and aluminum substrates using low voltage DC of 30-35 V in a laboratory. The raw materials used for the suspension/carrier and binder namely Butanone, n-Butylamine, polyvinyl butyral have served the purpose in successfully forming the deposit. The XRD and EDS studies confirm the presence of mullite on the metal surface after coating. The particle size measurement confirms the nano size range of the ceramic powder. The trials can be further done in a commercial setup to confirm the usefulness of this method for many applications. Mullite being a good ceramic with excellent wear and thermal barrier properties can be applied for many metallic surfaces. The process is very simple and cost effective and not many sophisticated equipment's are involved. Coating adhesion tests can be conducted to determine the adhesive strength of the coating.

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