

DEVELOPMENT OF CERAMIC COATINGS USING RED MUD—A SOLID WASTE OF ALUMINA PLANTS

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ABSTRACT

Plasma Spraying is a surface modification technique that combines particle melting, rapid solidification and consolidation in a single process. But as high cost of spray grade powders limits the adoption of this technique, exploring newer and cheaper materials suitable for plasma spray coating has drawn a lot of attention. This work reports an attempt to spray coat red mud (the waste generated in alumina producing plants) on different metal substrates. Plasma sprayed coatings of red mud have been developed at different operating power levels of the plasma gun on aluminium and copper substrates. Coating adhesion strength and deposition efficiency were studied at various operating conditions. Characterization of the coatings includes micro hardness measurement and scanning electron microscopy (SEM). It was observed that the operating power appreciably influences the coating adhesion strength and coating thickness. Coatings deposited at very low and very high power levels show poor adhesion. Maximum interface adhesion strength of ~8MPa was recorded at operating power of 12 kW. This work establishes 'red mud' as a potential coating material, which may be suitable for wear resistant applications. It also suggests a value added utilization of this industrial waste.

INTRODUCTION

Aluminium metal is commercially produced from bauxite ore through two main process steps. In the first step alumina is obtained by the Bayer's process [1] and in the second step the alumina is electrolyzed in a Hall-Heroult cell [2] to yield aluminum metal. Production of alumina from bauxite by the Bayer's process is associated with the generation of red mud as the major waste material. Depending upon the quality of bauxite, the quantity of red mud generated varies

from 55-65% of the bauxite processed. The enormous quantity of red mud discharged by industries producing alumina poses an environmental and economical problem. The treatment and disposal of this residue is a major operation in an alumina plant.

Red mud, as the name suggests, is brick red in colour and slimy having average particle size of about 80 μm . It comprises of the iron, titanium and the silica part of the parent ore along with other minor constituents. It is alkaline, thixotropic and possesses high surface area in the range of 13-16 m^2/g with a true density of 3.30g/cc. The leaching chemistry of

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bauxite suggests that the physical and chemical properties of red mud depend on the bauxite used and the manner in which the bauxite is processed. Residues from different bauxite have a wide range of composition: Fe_2O_3 20-60%, Al_2O_3 10-30%, SiO_2 2-20%, Na_2O 2-10%, CaO 2-8%, TiO_2 traces – 28%. Detailed characterization of red mud generated from NALCO aluminum refinery at Damanjodi, India is reported by Mohapatra *et al.* [3] and of some other sources by various authors [4, 5, 6]. Although a lot of research and developmental activities are going on throughout the world to find out effective utilization of red mud, almost no attempt has been made to develop plasma sprayed coatings out of it on metallic components which can have various applications. The use of red mud as yet is restricted only as building materials, paints and pigments etc. Some efforts are also made for recovery of metal values [7]. But none of these uses are aimed at processing this material for a high valued product.

Over the past three decades thermal plasmas have been used for processing various types of materials, some of which would not have been possible by conventional techniques [8]. In thermal plasma it is possible to spray all metallic and non metallic materials such as metal oxides, carbides, nitrides, silicides etc. [9]. Today plasma spray coatings find wide applications not only in research and development area but also in the industrial work places ranging from textile industries to medical applications. Plasma sprayed coatings are used mostly for erosion, corrosion or abrasion resistance in a wide variety of applications [10]. Currently, conventional coating materials e.g., carbides, oxides, metallic, etc. are available commercially. The choice of a material depends on the specific application. However, the ceramic coatings are very hard and hence on an average offer more abrasion resistance than their metallic counterparts. Amongst carbides, WC is very popular for wear and corrosion applications [11]. Metallic coatings and metal containing carbide coatings sometime are not suitable in high temperature environments in both wear and corrosion applications. Often they fail owing to oxidation or decarburization. In such case the material of choice can be an oxide ceramic coating. Chromia (Cr_2O_3) is used as a coating material when corrosion resistance is required in addition to abrasion resistance. It adheres well to the substrate and shows an exceptionally high hardness 2300 HV [8]. Zirconia (ZrO_2) is widely used as a thermal barrier coating. It is endowed with the essential qualities of a good coating material, i.e., hardness, chemical inertness, etc. and shows reasonably good wear behaviour. Titania (TiO_2) coating is known for its high hardness, density, and adhesion strength. Alumina powder (Al_2O_3) is a commonly used plasma sprayable coating material. Excellent performance of alumina-titania coatings in tribological applications has been extensively reported in the literature [12].

But one major limitation of all these currently used conventional coating materials is their relatively high price. In a coating industry, the cost of plasma sprayable powder accounts for nearly 55% of the total spraying cost. This makes plasma spraying an expensive deposition process. On the contrary, an industrial waste like red mud is not only free of cost but also is abundantly available. Being rich in metal oxides it has tremendous potential to be used as a coating mate-

rial. It does not belong to the so called plasma sprayable category and being a waste, is cheap. [13]

EXPERIMENTAL DETAILS

The raw material (red mud) collected from National Aluminium Co. in the state of Orissa was sieved to obtain a particle size of about 60-100 micron. Experiments were carried out using a 40kW plasma spray system at the Laser and Plasma Technology Division, BARC, India. This is a typical atmospheric plasma spray system working in the non-transferred arc mode. The major sub-systems of the set up include the plasma spray torch, power supply, powder feeder, plasma gas supply, control console, cooling water and spray booth. A current regulated DC supply was used. A four stage centrifugal pump at a pressure of 10kg/cm^2 supplied cooling water for the system. Argon and Nitrogen taken from normal cylinders at an outlet pressure of 4kg/cm^2 , were used as plasma gas and carrier gas respectively. Plasma spray red mud coatings are thus deposited over aluminium, copper, mild steel and stainless steel substrates of dimensions $50 \times 20 \times 3$ mm. Prior to coating all the substrates were sand blasted to get the required surface roughness. The powder feed rate was kept constant at about 10 gm/min. The operating parameters used in the experiments are given in Table 1.

RESULTS AND DISCUSSION

Composition Analysis

After sieving the received material i.e. red mud, chemical composition analysis was carried out again. The variation in the percentage of the major constituents in the composition of the material available from the site and that of after sieving is presented in Table 2.

Coating Thickness

The variations of coating thickness obtained at different operating power levels are plotted in Figure 1. From the figure it is found that maximum thickness of about 210 micron is obtained in case of copper substrate at 12kW power level. With increase in power level the coating thickness is increased in case of all substrates but is showing a decreasing trend at very high operating power level. This implies that the deposition rate is affected by operating power. The deposition efficiency may be low at higher power level due to flying off of the sprayed powder at that condition. That is why coating thickness is less at 16 kW operating power.

Coating Adhesion Strength

The first requirement of any coating mainly depends on its adhesion on to the substrate. The values of adherence strength of various coatings are measured using coating pull

TABLE 1
Operating parameters for plasma spraying of red mud

| <i>Parameters</i> | <i>Range</i> |
|---|--------------|
| Operating Power (kW) | 6-16 |
| Current (Amps) | 200-400 |
| Voltage (V) | 30-50 |
| Primary Plasma gas (Argon) flow rate (Lpm) | 20 |
| Secondary gas (Nitrogen) flow rate (Lpm) | 2 |
| Torch to base distance (mm) | 100 |
| Powder feed rate (gm/min) | 10 |
| Powder carrier gas (Argon) flow rate (Lpm) | 7 |

TABLE 2
Composition of the raw material

| <i>Constituents</i> | <i>Composition of red mud as collected from site (in wt percent)</i> | <i>Red mud (after sieving) used for coating (in wt percent)</i> |
|--------------------------------|---|---|
| Al ₂ O ₃ | 5.4 | 4.5 |
| Fe ₂ O ₃ | 65.2 | 63.7 |
| TiO ₂ | 6.8 | 2.5 |
| SiO ₂ | 12.4 | 2.81 |
| Na ₂ O | 0.5 | -- |
| CaO | 0.02 | 0.20 |
| MgO | -- | -- |
| LOI | 6.5 | 6.3 |
| P ₂ O ₅ | 0.4 | ---- |

out method and are plotted in Figure 2. It is found that with the increase in input power of the plasma gun there is an increase in the adherence strength up to a certain level of operating power and then it decreases with further increase in the power level. Although this trend is observed for all types of substrates the magnitude differs. For copper substrates the strength has varied from 5.6 MPa having a maximum of 6.84 MPa at the power level of 12 kW. For aluminum substrate, this value ranges from 6.21 MPa to 6.95 MPa with the maximum at 12 kW power level. The maximum adhesion of 8 MPa was recorded for mild steel substrate at 12 kW power level.

Coating Hardness

The hardness of the coating is an important parameter for recommending its use for wear resistance purpose. The polished cross sections of the coated samples were subjected to micro hardness measurement using a Leitz Micro-hardness Tester. The hardness measurement [HV] was done with a load of 0.5 N along the coating and substrate cross-section.

Maximum hardness of 560 HV has been recorded on the coating.

Coating Interface

Some typical interface microstructures of coatings deposited at 6, 9 and 12 kW on copper substrates are shown in Figures 3, 4 and 5 respectively. The interface morphologies for coatings deposited at different power levels are found to be smooth and no crack is observed at the interface even for higher operating power levels. Longitudinal cracks seen at the inter-particle layers of coating deposited at 12kW on copper substrate, as shown in Fig. 5, which affect the adhesion strength. The interface homogeneity may be due to the higher thermal conductivity of copper that had helped in faster rate of conduction of heat from the sprayed powders to the substrate.

Development of plasma spray coatings depends on various parameters to obtain a good quality coating and better adherence with the substrates. The coating efficiency also depends on particle shape, size and the distribution, flow rate,

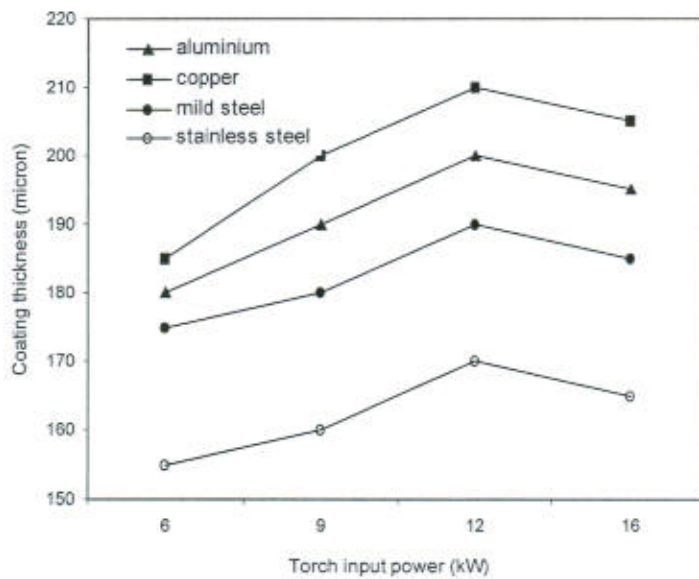


FIGURE 1
Thickness of red mud coatings made at different power level

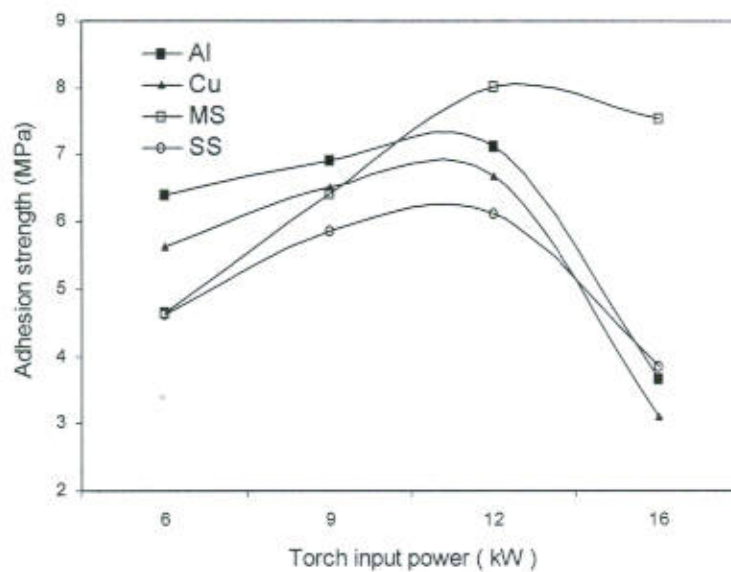


FIGURE 2
Thickness of red mud coatings made at different power level

torch to substrate distance and operating power level etc. In the present study the optimum coating thickness are observed at a power level between 9 to 12 kW with a maximum of 210 microns in case of copper substrate. This indirectly indicates that within this power level the deposition efficiency is maximum. At higher operating power, due to high temperature and high enthalpy, more particles are fragmented into smaller sizes and fly off causing less deposition. The coating morphology is homogenous at the intermediate power level, which may be the cause for good adhesion to the substrate.

CONCLUSIONS

Red mud, the industrial waste can be used for depositing plasma spray coatings on metals. Characterization of the coatings is highly relevant in the context of coating developmental studies as well as process optimization. A maximum coating thickness of about 210 micron is obtained. Coating - interface adhesion strength of ~ 8MPa is observed with the coating deposited on mild steel substrate. The optimum

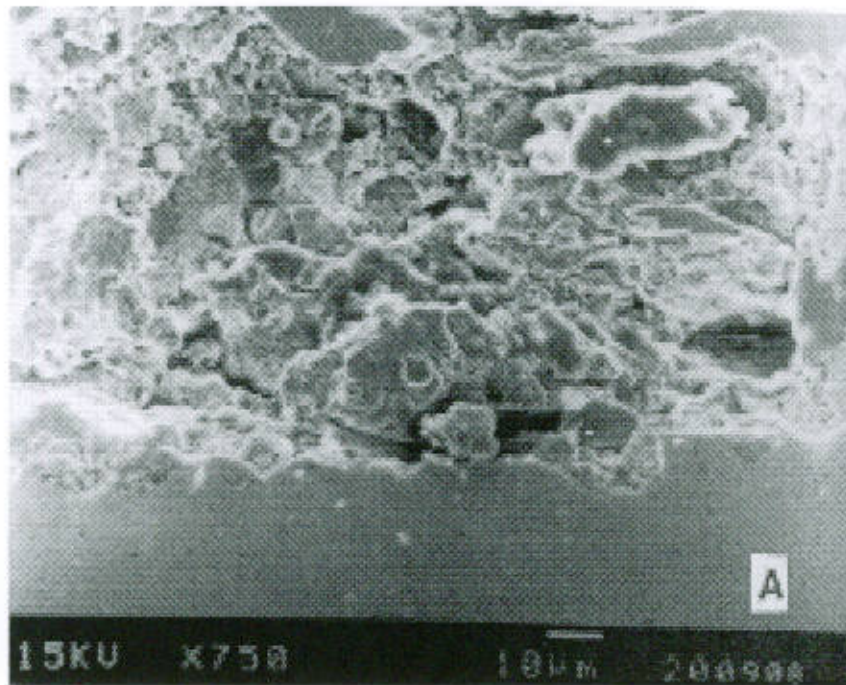


FIGURE 3
Interface microstructure of coatings made at 6 kW power level

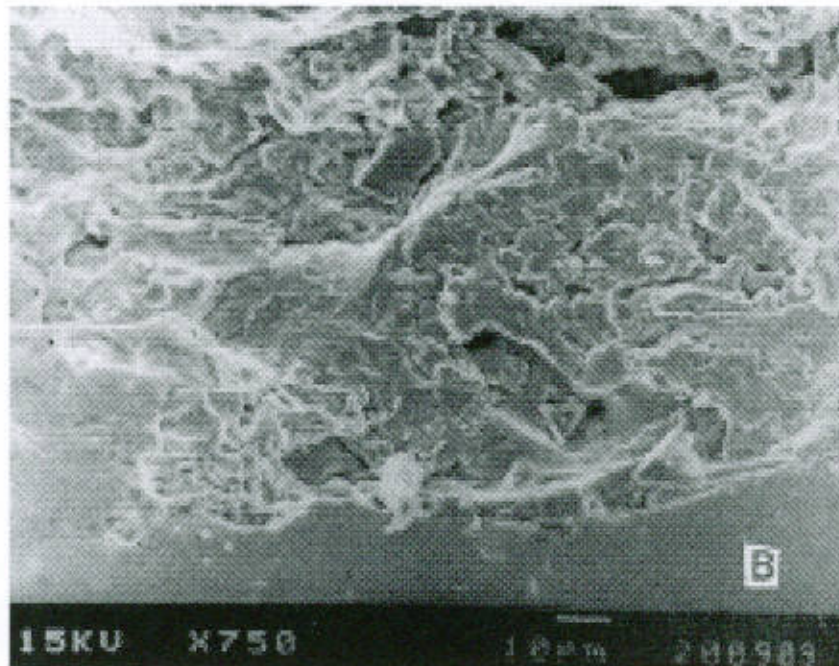


FIGURE 4
Interface microstructure of coatings made at 9 kW power level

strength is observed at operating power of 12 kW. The coating interface morphology reveals that the coating is homogeneous at intermediate power level. The study shows that coating properties vary widely with operating conditions. Red mud coatings possess high hardness of about 560 HV. It im-

plies that these can be used in wear resistance (tribological) applications. The performance assessment of these coatings with respect to currently used conventional coatings can be made later after further investigation.

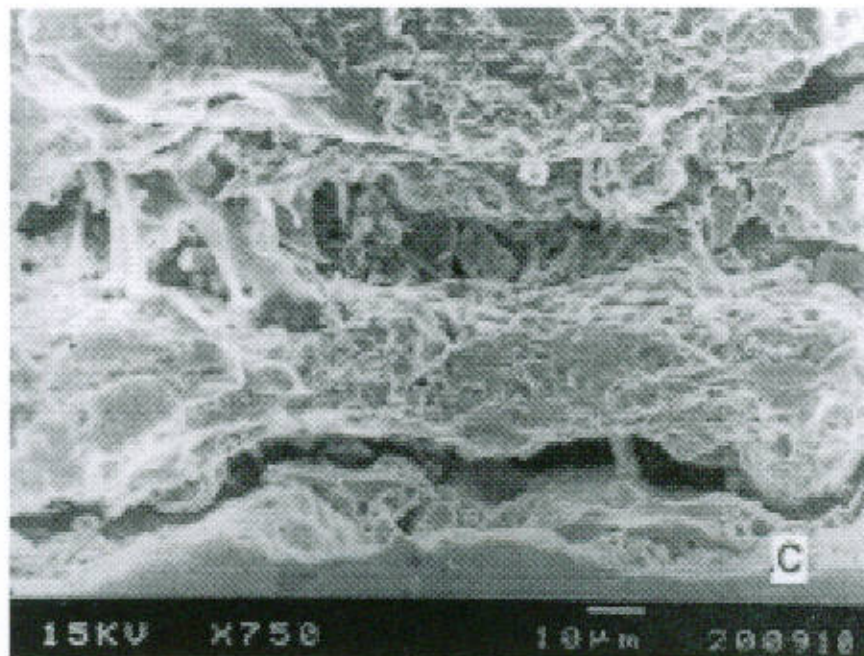


FIGURE 5
Interface microstructure of coatings made at 12 kW power level

REFERENCES

1. Chinloy, D.R. and R.K. Holzwarth, 1984, "Steady state simulation of the bayer Process," *Light Metals*, pp. 13-26.
2. Hall, C. M., 1889, US Patent 400766.
3. Mahapatra, B.K., M.B.S. Rao, R. Bhima Rao, and A.K. Paul, "Characteristics of red mud generated at NALCO refinery, Damanjodi, India," *Light Metals*, 2000, pp. 161-165.
4. Solimar, K., I. Sajo, J. Steiner, and J. Zoldi, 1992, "Characteristics and separability of red mud," *Light Metals*, pp. 209-223.
5. Sahin S, 1998, "Correlation between silicon-dioxide and iron-oxide contents of red mud samples," *Hydrometallurgy*, Volume 47, pp. 371-376.
6. Wang, Q, S. Gu, Z. Han, and D. Li, "Irreversible thixotropic behaviour of red mud slurry and exploitation in dry disposal process Nonferrous Metals (China)," Volume 50, No. 2, 1998, pp. 85-91.
7. Thakur R.S. and S.N. Das – 'Red Mud- Analysis and Utilization' –Publication & Information Directorate, New Delhi & Wiley Eastern Limited, New Delhi, India (1994).
8. Robert B. Hiemann–Plasma-Spray Coating-Principles and Applications, VCH Publishers Inc., New York, NY, USA, (1996)
9. Lech Pauloski–The Science and Engineering of Thermal Spray Coatings, John Wiley and Sons, New York (1995).
10. Westergard R., L.C. Erickson, N. Axen, H.M. Hawthorne and S. Hogmark– The erosion and abrasion characteristics of alumina coatings plasma sprayed under different spraying conditions *Tribology International*, Volume #1, Issue %, May 1998, Pages 271 – 279.
11. M. Codenas, R. H.J. Montes Vijande, and J.M. Sierra, 1997, *Wear*, Volume 212, p. 244.
12. Bandopadhyaya P.P. – Processing and Characterization of Plasma Sprayed Ceramic Coatings on Steel Substrate–Ph.D. Thesis, IIT, Kharagpur, India (2000).
13. Satapathy Alok –Thermal Spray Coating of Red Mud on Metals– Ph.D. Thesis , NIT, Rourkela, India (2006).