

Development of Solution Precursor Plasma Spray TiO₂/Al₂O₃ Composite Coatings for Heat Exchanger Application

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ABSTRACT

Surface modification of the metal components involved in heat transfer is one of the passive methods used to enhance their heat transfer efficiency. Coatings with micro- or nano-scale features are widely employed to modify surfaces due to their enhanced surface area, which increases the number of boiling nucleation sites, leading to the generation of a higher number of bubbles. In geothermal power generation, due to the aggressive nature of the working fluid and chemistry of the geothermal brine, ceramic coatings are preferred. Along with having good compressive strength and hardness, ceramic coatings can protect the surface against corrosion, oxidation and wear. The coating deposition method has a specific impact on the coating microstructural characteristic as well as performance, which define its application. Among these, plasma-spraying has been widely used to deposit ceramic materials, due to its high jet enthalpy and the excellent corrosion and wear resistance of the obtained coatings. In this work, solution precursor plasma sprayed coatings of TiO₂/Al₂O₃ composite were developed on carbon steel for boiling heat transfer applications in geothermal heat exchangers. The effect of plasma current and stand-off distance variation on the microstructural properties of coated samples were assessed. The morphology of the final coatings was compared using SEM/EDX. Further, the surface wetting property was analyzed through a drop sample analyzer and found that with spray parameters the water contact angle and diiodomethane contact angle fluctuate.

Key words: Solution precursor plasma spray; TiO₂/Al₂O₃ composite coating; Contact angle.

INTRODUCTION

Geothermal heat exchangers, due to the continuous contact with the aggressive environment such as humidity, dissolved ions and non-condensable gases within the geothermal fluids, temperature fluctuations etc. are always at risk of corrosion and scaling. This greatly affects the lifetime and efficiency of the geothermal power plant as a whole. Hence, to protect the material and enhance the heat transfer ability, innovative coatings are used. Different active, passive and compound techniques such as flow disruption, surface roughness, out of plane mixing, fluid additives, channel curvature, etc. are used to improve the heat transfer performance [1]. Surface modification, relying on alteration of the surface chemistry and topography, is one of the extensively used heat transfer amplification method. Generally, coatings with micro- or nano-scale features are used, which multiplies the boiling nucleation sites due to the enhanced surface area [2]. Coatings deposited through thermal spray are widely favored because of being time- and cost-efficient and their robust nature. Plasma spray is one such technique that provides the flexibility to deposit a wide range of materials on different substrates such as metals, glass, fabrics, polymers, etc. Conventionally, powder-based plasma spray is used to deposit metal oxides, however, due to the issues like agglomeration, clogging, feedstock preparation, research has shifted towards liquid-based feedstocks (suspensions/solutions). Along with resolving the handling issues, liquid feedstock-based plasma spray introduces micro- and nano-features such as columns, lamellae, pores, vertical cracks, etc. into the deposited coatings [3]. The coating microstructures can be controlled by varying different parameters involved in spraying such as plasma source, injection type, solvent type, standoff distance, solid concentration, particle size, etc. [3]. Once injected, the suspension or solution precursor interacts with the plasma jet and due to kinetic and thermal energy exchange, hits the substrate into a molten or semi-molten state. Depending on the droplet size and injection velocity, liquid feedstock droplets travel into the different zones of plasma jet. Bigger droplets with good injection force reach into the core region of the plasma flame, while droplets with a smaller size and less force have a weak momentum and due to the turbulence, follow the gas trajectory, hitting the substrate at a shallow angle and deposit on asperities [4]. Sequential splats depositing onto these asperities give rise to the columnar structures. Compared to the suspension plasma spray (SPS), solution precursor plasma spray (SPPS) provides better control over the stoichiometry of the coating as target particles are in precursor form. Besides, SPPS gives rise to thin coatings. However, due to the complexity and lack of sufficient information, SPPS has not been widely researched. Therefore, in this work, we have performed a developmental study related to $\text{TiO}_2/\text{Al}_2\text{O}_3$ composite coating deposition using SPPS. Further, microstructural and surface wetting properties were compared using respectively, SEM/EDX and drop samples analyzer, where water and diiodomethane contact angles were measured.

EXPERIMENTAL PROCEDURE

Solution precursor preparation

To form TiO_2 and Al_2O_3 composite particles, butyl titanate ($\text{Ti}(\text{OC}_4\text{H}_9)_4$, Sigma Aldrich, UK) and aluminium isopropoxide ($\text{C}_9\text{H}_{21}\text{O}_3\text{Al}$, Sigma Aldrich, UK) were used as Ti and Al sources. For TiO_2 precursor formulation, butyl titanate (1.7 ml), acetylacetone (0.25 ml; Sigma Aldrich, UK) and ethanol (100 ml; Sigma Aldrich, UK) were mixed as a precursor, stabilizer and solvent. The alumina precursor was prepared by mixing 2 g of aluminium isopropoxide (AIP) with one liter of DI water followed by stirring for 2 h at 80 °C. Further, while, a few drops of diluted nitric acid (3 ml nitric acid in 50 ml DI water) were added to the aqueous suspension of AIP. The solution was continuously stirred at room temperature until a clear solution is formed. The final pH of the solution was ~2.5. In the end, both the TiO_2 precursor solution and Al_2O_3 precursor solutions were mixed. The final molar ratio of Al_2O_3 and TiO_2 was 9:5.

Plasma spray

In the SPPS process, a commercial plasma torch Praxair®SG-100 was used, both with argon only or argon-hydrogen as primary and secondary plasma gases. A syringe pump (ISCO® 260D) was used to feed the feedstock to the external nebulizer, which injected the solution into the plasma zone in form of droplets. A constant feedrate of 10 ml/min was used along with a carrier gas (Ar; 3 lpm) throughout the work. S275JR, EN 10025-2 25x25x6 mm carbon steel plates were used as substrate. Before deposition, substrates were grit blasted (100 mesh Al₂O₃) and degreased with acetone. The plasma torch, attached to a 6-axis robot, was moved at 450 mm/s traverse speed and 5 mm step increment for a total of 20 passes. Since SPPS is a very complex process in comparison to the powder or suspension plasma spray, preliminary trials to optimize the spray parameters were performed. The different sets of spray conditions used are reported in Table 1.

Table 1: Spray parameters for different TiO₂/Al₂O₃ composite coatings

Samples	Plasma gas	Plasma gas flowrate	Plasma current	Standoff distance (SOD)
Ar_50	Ar	49 lpm	450 A	50 mm
Ar_80	Ar	49 lpm	450 A	80 mm
Ar_100	Ar	49 lpm	450 A	100 mm
Ar_120	Ar	49 lpm	450 A	120 mm
Ar/H ₂ _80	Ar/H ₂	49/0.9 lpm	700 A	80 mm
Ar/H ₂ _100	Ar/H ₂	49/0.9 lpm	700 A	100 mm
Ar/H ₂ _120	Ar/H ₂	49/0.9 lpm	700 A	120 mm

Characterization

The surface morphology of different deposited coatings was analyzed through Scanning Electron Microscopy (SEM), coupled with Energy Dispersive X-ray spectroscopy (EDX) analysis. Optical microscopy was also used to analyze the cross-sectional images of the as-deposited coatings. Further, surface wetting properties were compared by using a drop sample analyzer, using and 2 µl volume of both water and diiodomethane.

RESULTS

Figure 1 represents the SEM images of the surface morphology before (a & b) and after (c & d) plasma spray (Ar_80). However, due to the low deposition efficiency of SPPS, even after 20 passes, deposited coatings were very thin, and hence, we could not observe any characteristic columnar or cauliflower-like morphology. From the top-view (Figure 2), it can be noticed that all coatings look different, visually, which could be due to the different chemistry of the material deposited. The presence of coating on the surface is demonstrated by the EDX data for all the coatings, which shows the presence of both aluminium and titanium peaks. Interestingly, it was found that for both cases of Ar only and Ar/H₂ deposition, the aluminium and titanium peaks become weaker with increasing standoff distance. Since a longer standoff distance implies a longer flight time and a decreasing plasma jet temperature, it is possible that the particles start re-solidifying before impacting the substrate at the higher standoff distance employed.