Thermal stability studies of plasma sprayed yttrium oxide coatings deposited on pure tantalum substrate

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Abstract. Plasma sprayed Yttrium oxide is used for coating of crucibles and moulds that are used at high temperature to handle highly reactive molten metals like uranium, titanium, chromium, and beryllium. The alloy bond layer is severely attacked by the molten metal. This commonly used layer contributes to the impurity addition to the pure liquid metal. Yttrium oxide was deposited on tantalum substrates (25 mm x 10mm x 1mm thk and 40 mm x 8mm x 1mm thk) by atmospheric plasma spray technique with out any bond coat using optimized coating parameters. Resistance to thermal shock was evaluated by subjecting the coated specimens, to controlled heating and cooling cycles between 300K to 1600K in an induction furnace in argon atmosphere having \( \leq 0.1 \text{ppm} \) of oxygen. The experiments were designed to examine the sample tokens by both destructive and non-destructive techniques, after a predetermined number of thermal cycles. The results upto 24 thermal cycles of 25 mm x 10mm x 1mm thk coupons and upto 6 cycles of 40 mm x 8mm x 1mm thk coupons are discussed. The coatings produced with the optimized parameters were found to exhibit excellent thermal shock resistance.

1. Introduction

Over the years, plasma spray coating has been accepted as an established technique to produce ceramic coatings for protection against heat, corrosion and wear. Plasma spray coating is highly versatile and almost all materials that can be melted without decomposition can be deposited on substrates, which are required to have only reasonable heat resistance. The main limitation of the plasma spray coating is the inferior mechanical strength of the coatings in comparison with the corresponding ceramic monolithic materials [1].

Yttrium oxide has excellent thermal stability up to its melting temperature and also possesses superior resistance to aggressive chemical attack by molten metals and salt mixtures at high temperatures. Because of the thermodynamic stability, yttrium oxide exhibits better corrosion resistance to liquid metal corrosion and is used in the form of sintered shapes and protective coatings in several applications associated with high temperature corrosion [2, 3]. Thermodynamic analysis based on free energy minimization principle suggests that yttrium oxide is chemically more stable in comparison to \( \text{ZrO}_2 \) and \( \text{Al}_2\text{O}_3 \) against attack by uranium up to 3000 K [10-12]. The yttria coatings on metallic materials used at high temperatures are also required to have good thermal shock resistance because the peeling of a coated layer leads to serious problems during operation, apart from enhanced...
corrosion due to the failure of the coating. Typical plasma coated coatings have a two-layered structure consisting of a bond coat and chemically resistant and thermally insulating ceramic topcoat. However, when the coating is serving as a chemical barrier and simultaneously as a thermal barrier, the bond coat is required to be chemically inert to the corrosive media as the substrate metal. The bond layer commonly used (Ni-Cr-Al-Y alloy) is severely attacked by the molten uranium and also the oxidation of the bond layer develops interface stress, which deteriorates the coating performance. Hence the Y₂O₃ protective coating on Tantalum should be without a bond layer. However, there is not enough reported literature available on production methods and performance evaluation of plasma spray coatings on substrates without a bond coat.

In the present work, Yttrium oxide was deposited on tantalum substrates (25 mm x 10mm x 1mm thk and 40 mm x 8mm x 1mm thk) by atmospheric plasma spray technique after conducting series of experiments for optimization of coating parameters. Resistance to thermal shock was evaluated by subjecting the coated specimens, to controlled heating and cooling cycles between 300K to 1500K in an induction furnace. The experiment was designed to examine the sample tokens by both destructive and non-destructive technique, after a pre-determined number of thermal cycles. The results upto 26 thermal cycles of 25 mm x 10mm x 1mm thk coupons and upto 6 cycles of 40 mm x 8mm x 1mm thk coupons are discussed.

2. Experimental procedure

2.1. Preparation of plasma spray grade Y₂O₃ Powder

Two kinds of powders have been utilized in preparation of Y₂O₃ coatings. Inhouse sintered and prepared powder was made from the raw material supplied by IRE Ltd that has a size range of 5-10 micron. The powder was subjected to Cold Isostatic Pressing (CIP) at 30,000 PSI to obtain green density of ~ 50%. Sintering of the compact was done at 1600°C for 4 hours. Microhardness test was conducted on the sintered blocks to evaluate the sintering process. Sintered block was crushed to chunks followed by reduction to smaller size fraction in a planetary Ball mill with alumina balls each weighing 20g. Ground powder was then sieved to separate powders of size range 38-75µm and 76 - 106µm.

2.2 Preparation of coatings

The specimens used for testing of coatings were cut from pure tantalum sheet into coupons of rectangular shapes having dimensions 25 mm x 10 mm x 1mm thk, and 40 mm x 8 mm x 1mm thk respectively. In order to reduce the stress raising points, the corners of the rectangular tokens were rounded. A series of coating experiments were conducted by producing coatings of yttria with variation of powder size, plasma power, primary glass flow and powder feed rate. Other coating factors that were maintained constant were torch to base distance (TBD), auxiliary gas flow, feed gas flow and surface roughness. Adhesion test was used as response parameter for obtaining the optimum coating parameters. The results of the parametric experiments conducted are listed in table 1. The optimized parameters which were selected and used for plasma spray coating are given in table 2.

2.3 Testing of coatings

Prior to thermal cycling test of coated coupons, visual inspection and optical micrography was conducted to evaluate the coating. Plasma sprayed Y₂O₃ coupon was heated with 24 kW plasma flame to red hot condition and cooled to RT by putting off the flame, to qualify the coating for thermal cycling tests. Microhardness evaluation of coatings was also done to study the nature of deposited material. Table 3 presents the microhardness values measure on sintered blocks and coupons.
Table 1 List of parametric studies conducted

| Coupon no | Carrier gas Ar lpm | TBD mm | Powder Feed g/min | Substrate Material | Substrate Quantity | Powder Size μm | Power kW | Primary Gas lpm | Secondary Gas lpm | Coating Thickness (μm) | Adh. strength M Pa | Avg strength |
|-----------|-------------------|-------|-------------------|--------------------|--------------------|-----------------|-----------|-----------------|------------------|---------------------|------------------|--------------|
| I A       | 12                | 100   | 13                | SS Adh. Ta coupon  | 1                  | 38-75          | 29.4      | Ar. 30          | N₂ 3             | 250                 | 7.276            | 6.257        |
| I B       |                   |       |                   | SS Adh. Ta coupon  | 1                  |                |           |                 |                  |                     |                  |              |
| I        |                   |       |                   | SS Adh. Ta coupon  | 1                  |                |           |                 |                  |                     |                  |              |
| II A      | 12                | 100   | 13                | SS Adh. Ta coupon  | 1                  | 38-75          | 29.9      | Ar. 25          | N₂ 3             | 250                 | 4.178            | 4.535        |
| II B      |                   |       |                   | SS Adh. Ta coupon  | 1                  |                |           |                 |                  |                     |                  |              |
| II       |                   |       |                   | SS Adh. Ta coupon  | 1                  |                |           |                 |                  |                     |                  |              |
| III A     | 12                | 100   | 13                | SS Adh. Ta coupon  | 1                  | 38-75          | 24.6      | Ar. 30          | N₂ 3             | 250                 | 8.051            | 7.5415       |
| III B     |                   |       |                   | SS Adh. Ta coupon  | 1                  |                |           |                 |                  |                     |                  |              |
| III      |                   |       |                   | SS Adh. Ta coupon  | 1                  |                |           |                 |                  |                     |                  |              |
| IV A      | 12                | 100   | 13                | SS Adh. Ta coupon  | 1                  | 38-75          | 24.4      | Ar. 25          | N₂ 3             | 250                 | 6.013            | 60.33        |
| IV B      |                   |       |                   | SS Adh. Ta coupon  | 1                  |                |           |                 |                  |                     |                  |              |
| IV       |                   |       |                   | SS Adh. Ta coupon  | 1                  |                |           |                 |                  |                     |                  |              |
| V A       | 12                | 100   | 14                | SS Adh. Ta coupon  | 1                  | 76-106         | 29.9      | Ar. 30          | N₂ 3             | 280                 | 5.605            | 5.829        |
| V B       |                   |       |                   | SS Adh. Ta coupon  | 1                  |                |           |                 |                  |                     |                  |              |
| V C       |                   |       |                   | SS Adh. Ta coupon  | 1                  |                |           |                 |                  |                     |                  |              |
| VI A      | 12                | 100   | 14                | SS Adh. Ta coupon  | 1                  | 76-106         | 29.9      | Ar. 25          | N₂ 3             | 280                 | 4.280            | 3.801        |
| VI B      |                   |       |                   | SS Adh. Ta coupon  | 1                  |                |           |                 |                  |                     |                  |              |
| VI C      |                   |       |                   | SS Adh. Ta coupon  | 1                  |                |           |                 |                  |                     |                  |              |
| VII A     | 12                | 100   | 14                | SS Adh. Ta coupon  | 1                  | 76-106         | 24.6      | Ar. 30          | N₂ 3             | 280                 | 4.994            | 5.5425       |
| VII B     |                   |       |                   | SS Adh. Ta coupon  | 1                  |                |           |                 |                  |                     |                  |              |
| VII C     |                   |       |                   | SS Adh. Ta coupon  | 1                  |                |           |                 |                  |                     |                  |              |
| VIII A    | 12                | 100   | 14                | SS Adh. Ta coupon  | 1                  | 76-106         | 24.6      | Ar. 25          | N₂ 3             | 280                 | 4.076            | 3.8825       |
| VIII B    |                   |       |                   | SS Adh. Ta coupon  | 1                  |                |           |                 |                  |                     |                  |              |
| VIII C    |                   |       |                   | SS Adh. Ta coupon  | 1                  |                |           |                 |                  |                     |                  |              |

\[ \Sigma_v = 19.055 \]
\[ \Sigma = 24.366 \]
\[ \Sigma_v = 1.328 \]
\[ \Sigma = 18.252 \]
\[ \Sigma_v = -0.65 \]
\[ \Sigma = 1.73 \]
Table 2. Optimized coating parameters

| S.no | Parameter                   | Value   |
|------|-----------------------------|---------|
| 1.   | Power                       | 24.6 KW |
| 2.   | Primary Argon gas flow      | 30 lpm  |
| 3.   | Secondary gas flow          | 3 lpm   |
| 4.   | Powder size                 | 38-75 µm|
| 5.   | Powder feed rate            | 13 g/min|
| 6.   | Carrier gas flow            | 12 lpm  |
| 7.   | TBD                         | 100 mm  |
| 8.   | Average coating thickness   | 240-270 µm|

Table 3. Microhardness values of sintered blocks and coated coupons

| Component              | unit | Set-1 | Set-2 | Set-3 |
|------------------------|------|-------|-------|-------|
| Sintered block         | HV   | 543   | 508   | 538   |
| Plasma coated coupon   | HV   | 462   | 466   | 473   |

2.4 Thermal cycling test procedure

The thermal cycling tests were performed at 1250°C in with continuous purging of purified argon having oxygen \(\leq 0.1\)ppm. Each cycle consists of heating the coupons to 1250°C in a controlled way, and soaking at that temperature for 2 hours, followed by controlled cooling. The heating and cooling rates used for cycling experiment are shown in figure 1. The weight changes of the coated samples were measured to a precision of 0.01 mg. At least two samples were tested in identical conditions so that the average weight gain/loss of the samples can be obtained. The samples were considered as failed when cracks were observed at 100X magnification in an optical microscope.

| Time, mins | Temperature, °C |
|------------|-----------------|
| 0          | 0               |
| 200        | 200°C/hr        |
| 400        | 600             |
| 600        | 1000            |
| 800        | 1200            |
| 1000       | Soaking         |
| 1200       | Natural cooling |

Figure 1: Heating and cooling cycle for thermal cycling experiments.

2.5 Equipment

Thermal cycling tests were conducted using a 10 KW induction furnace with a graphite susceptor used for heating the coupons held in an alumina tube having dimensions of 80 mm OD and 800 mm long. The coupons were hung using Kanthal wire of 0.5 mm diameter, and were shielded from direct heating from the coil using a grounded graphite cylinder. The general assembly of the experimental setup is shown in figure 2. Leica DMI 5000 optical microscope was used for optical microscope investigations.
3. Results and Discussion

Figure 3 and 4 show the microstructure of the yttria coating on tantalum substrate. Two different kinds of morphologies in coatings were observed. As observed in figure 3, the surface is relatively rough when compared to the microstructure in figure 4. This feature was observed in the entire set of coupons, and the rough structure was always obtained on the side rectangular coupon coated last. This could be attributed to the slight oxidation that would occur on the uncoated surface during the coating of metal surface. This oxide layer must have increased the surface roughness and hence the resulting coating surface obtained is also rough.

Fig 3. Yttria coating on tantalum rectangular token, as coated surface micrograph at 100X

Fig 4. Yttria coating on tantalum rectangular token, as coated surface micrograph at 100X
Figures 5 and 6 show the micrographs of the tantalum and yttria coating interface, and figure 7 shows the yttria coating. It can be observed that the coating is uniform, and absence of large open/closed pores show that the coating quality is good.

It was observed that the coatings produced by the in-house sintered and prepared powder did not develop any cracks when viewed at 100X magnification upto 26 cycles. Further testing was not done as the process requirement criterion was satisfied upto 4 times the required number of cycles. In the case of procured powder, thermal cycling of coupons was conducted upto 6 cycles, and no failures were obtained.

Environmental influence on the performance of the coating was studied by introducing air and moisture leaks into the system. Both oxygen and moisture introduction have resulted in reaction with the substrate and peeling of the coating. In case of moisture entry it was observed that oxide along with TaC formation has taken place by reaction of hydrocarbon gases / CO produced by reaction of moisture with graphite at high temperature. Oxygen leak into the system resulted in oxidation and tantalum coupons and peeling of the coating.

4. Conclusions
The primary objective of the experimental program was to produce durable coatings of yttria on tantalum substrate without the use of any bond coating. This was accomplished by establishing the optimized plasma spray coating parameters, which were qualified by adhesion test.

Coatings prepared with the selected parameters can with stand thermal loads upto 26 cycles and 6 cycles with the in-house powder and procured powder respectively. In addition, it is observed that moisture and oxygen have a deleterious effect on the performance of the coating. The coatings have now qualified for study of corrosion by liquid metal.

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