Influence of CNTs in protecting Air Plasma Sprayed Al$_2$O$_3$-3wt\%TiO$_2$ Coated Surface

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Abstract. The Al$_2$O$_3$-3wt\%TiO$_2$ powders reinforced by Carbon nanotubes (CNTs) were used to prepare composite coatings by Air Plasma Spraying (APS) process. The coatings derived from APS process were varied in the percentage proportion of CNTs such as 2wt\%, 4wt\%, and 6wt\% respectively. The coated surfaces were evaluated by means of scratch testing. The SEM micrographs of scratched samples showed the intensity of penetration during scratching gets reduced due to the presence of CNTs film over the surface. Also, the CNT reinforced coated samples showed a significant improvement in mechanical and microstructural properties such as microhardness, porosity as well as surface roughness.

1. Introduction

The coatings derived from Air Plasma Spraying process were widely functional for wear resistance applications such as surface of turbine blades, nozzle for pumps, coating of aircraft engines etc., [1-2]. Coatings derived from Plasma spraying process possess various splats to attain the requisite thickness [3]. The Alumina-Titania coatings acquired from plasma spraying process exhibits superior hardness of 1000-1200 VHN and worthy wear resistance [4, 5]. However, the ceramic coating materials still have their brittleness and moderate microhardness characteristics which makes them weak for profitable applications [6-8]. Due to this reason, only ceramic material used for coatings is not desirable. Hence, the addition of a second phase provides a solution to reduce the brittleness. In recent times, the coatings have been produced by nanostructured ceramic powders, cermet (ceramic+metal) powders and powders doped with some rare earth oxides [9]. The Multiwalled Carbon nanotubes (MWCNTs) were gaining popularity recently due to its involvement in improving mechanical properties of coatings obtained from thermal spraying process [10]. However, carbon nanotubes (CNTs) are considered as an exceptional choice for the reinforcement of ceramics with their superior properties such as physical microstructure and mechanical strength. CNTs were having a high elastic modulus of 1000 GPa, a high tensile strength of 60 GPa and thermal conductivity of 3000 W/mK [11]. It also possess unique mechanical features due to the geometry and size.

This examination is carried out to identify the crack formation phenomenon on the APS sprayed coatings obtained from conventional Al$_2$O$_3$-wt\%TiO$_2$ powders mixed with CNTs. Also, the interpretation of toughening mechanism on the coated samples can be acquired through CNT bridging. The impact of CNT bridging on the coating microstructure and number of pores present on the as-sprayed coating while conducting scratch test, were also analyzed. The purpose of varying percentage proportion of CNTs in the coatings by 2wt\%, 4wt\% and 6wt\%, is to evaluate the scratch resistance of coatings and to analyze the influence of CNT percentage in the scratch track.
2. Experimental Methods and Materials

In this present work, the thermal sprayed coating method used was Air Plasma Spraying process for the deposition of powder particles. The conventional Al$_2$O$_3$-3wt%TiO$_2$ powders were used for coating purpose. These powders were mixed with CNTs by varying the percentage proportion in the order of 2wt%, 4wt% and 6wt%, respectively. The scratch analysis and microstructural characterization of scratch tracks were investigated on the varied proportion of coatings mixed with CNTs. The spray parameters used for deposition of coatings is shown below in Table 1.

Table 1. Parameters for Air Plasma Spraying Process

| Parameters                  | Air Plasma Spraying (APS) |
|-----------------------------|---------------------------|
| Gun                         | Metco 3MB                 |
| Nozzle Type                 | GH                        |
| Powder Feed rate            | 40-50 g/min               |
| Current                     | 490 A                     |
| Spray Distance              | (76-127 mm)               |
| Flow rate of Primary gas (Ar)| 50-60 lit/min             |
| Flow rate of carrier gas (H$_2$)| 8-10 lit/min           |

2.1. Sample Preparation

In this present work, the powder used for deposition of coatings was Al$_2$O$_3$-3wt%TiO$_2$. The powders were coated using Air Plasma Spraying (APS) process. The microstructural characterization and properties related to scratch analysis of the coatings were examined by varying the percentage composition of CNTs with 2wt%, 4wt% and 6wt%, respectively. The mild steel substrate of AISI 1020 (60x50x5) mm were used for the deposition of coatings. The Alex NH 500 surface grinder was used to remove excess dirt and unwanted oxide layers from the surface and also to maintain the surface roughness of sample to be 0.2 μm. The work samples were grit blasted using alumina grits of size 32 at an air pressure of 120 psi. Then the samples are to be kept in iso-propanol solution for 5-10 min to remove the foreign particles. Finally, the substrates were preheated at 200°C using Plasma Gun. Sulzer Metco 3MB plasma gun is used to deposit the coatings. Argon is used as the primary gas for generating plasma whereas hydrogen is used as the secondary and carrier gas. The mixture of Ni-5wt%CrAlY is used as the bond coating of thickness ranging from 130-150 μm were deposited first for further deposition of Al$_2$O$_3$+TiO$_2$ top coat mixed with various percentage proportions of CNTs. The thickness of ceramic top coating is ranging from 300-350 μm. The process parameters used for the deposition of coatings are shown in Table 1. For examination purpose, the specimens of 10 x 5 x 5 mm size were cut from coated samples, using a low speed diamond saw. For metallographic examinations, hot mounts with specimen inserts were prepared using Bakelite powder hot mounting process. The hot mounted samples, with coatings cross-section, were polished using Silica-Carbide abrasive papers of various grades such as 220, 400, 600, 800 and 1000. The process of polishing was carried out for a period of 15 minutes on each grade of abrasive paper and disc polishing was done for period of 20 minutes.
2.2. Characterization Procedure

Coatings microstructures were analyzed using a Zeiss Evo 60 scanning electron microscope (SEM). For a given CNT percentage, three SEM images were taken at variable magnifications of range 100X to 10,000X. X-ray diffraction studies were carried out using a PANalytical X’pertPRO PW1070 instrument with CuKα radiation, operating at 40 kV voltage and 30 mA current, scanning step of 0.01670 and step time of 0.13 s. The scratch tests were carried out using a scratch tester (Model: TR-101-M5, Made: Ducom Instruments, Bangalore, India). The scratch tester integrated with an indenter of Rockwell C type with 120° apex angle and 200 µm tip radius was used. Three scratches were made on the as-sprayed coating for microstructural investigation as well as examination of coating failure. The table 2 provides the detailed standard parameters used for scratch test [12]. Also, the most familiar technique to evaluate the porosity of a coating system i.e. preparing metallographic sample and then taking multiple micrographs for analysis was done. The image analysis was carried out by means of contrast difference between voids i.e., pores to estimate percentage of porosity [13].

Table 2. Detailed Parameters used for Scratch Test

| Parameters          | Scratching test |
|---------------------|-----------------|
| Indenter type       | Rockwell C      |
| Variable Load       | 30-100 N        |
| Scratching speed    | 0.1 mm/s        |
| Scratch distance    | 7 mm            |
| Number of Scratches | 3               |

3. Results and Discussion

3.1. Microstructural Characterization

The powder morphologies of Al₂O₃-3wt%TiO₂ were examined by using SEM. The characterization was carried out without CNT and after adding CNT in the proportion of 2wt%, 4wt% and 6wt%. The CNTs were consistently detached throughout the powders. It can be seen that Alumina-Titania powders are regular, wedge-shaped, and also contain pores in it whereas CNTs are looking like bundle-shaped structure (See Figure 1a and 1b) [14]. The presence of CNTs in Alumina-Titania composition can be visible at higher magnification (see Figure 1b). The XRD analysis of Al₂O₃-3wt%TiO₂ powder shows the presence of α-Alumina and Anatase Titania phases in it as shown in Figure 2a. When CNTs were added to Al₂O₃-3wt%TiO₂ powder, the carbon phase gets included. It was also found that the presence of α-alumina in the coating powder provides the resistance to high temperature and very little amount of anatase titania with tetragonal crystal structure provides stability to α-alumina.

The phases present in Al₂O₃-3wt%TiO₂ coatings after adding CNTs are shown in Figure 2b. In Alumina-Titania coatings with CNTs, the main phase observed was α-alumina which is present in the coatings without adding CNTs also. The anatase titana phase is transferred to Rutile Phase and Magneli phase after adding CNT [15]. Rutile phase is the most stable form of TiO₂ than anatase phase at all temperatures. Magneli phase is obtained due to the reduction (i.e. removal of oxygen) of titania at high temperatures. Since the phases are common in 2wt%, 4wt% and 6wt% CNT added coating systems, the XRD patterns for only 6wt% CNT coatings are shown in Figure. 2c.
Figure 1. Powder Morphology of (a) Conventional Al$_2$O$_3$-3wt%TiO$_2$ Powders, (b) Conventional Al$_2$O$_3$-3wt%TiO$_2$ Powders with 6wt% CNTs.
Figure 2. XRD peaks of (a) Conventional Alumina-Titania Powders (b) Powders mixed with 2wt% CNT (c) Coatings with 6wt% CNTs
3.2. Coating Scratch Characterization

The various test parameters used for performing scratch test using scratch tester have been shown in Table 2. The SEM micrographs of Alumina-Titania coating system after conducting scratch test were shown in Fig.3, Fig.4, and Fig.5. The variation of CNT percentage in the coating system were 2, 4 and 6 percent respectively. Three sets of images were taken and analyzed after the scratches are done on the coating. In that, location of failure and intensity of penetration for the percentage proportion of CNTs were examined. The back scattered electron images (BSE) were taken to interpret location of spots that initiate cracks. The brighter and darker intensity of BSE images provide meaningful information regarding greater and lower dispersion of CNTs in the coating system. In Fig. 3, the 2wt% of CNTs mixed with Al$_2$O$_3$-3wt%TiO$_2$ powders were coated and scratch test was performed on as-sprayed coatings. The Fig.3 (a) shows SEM image of scratch track in which an intense penetration was clearly visible due to less percentage of CNTs i.e., 2wt%. But, the intensity of penetration gets reduced with increasing percentage of CNT as shown in Fig. 4 (a) and Fig. 5 (a). The scratching failure mechanism is mainly attributed to tensile cracks. The location of failure in each percentage of CNTs can be visible in Fig. 3 (b), 4 (a) and 5 (c). The failure occurs early when the scratch starts, whereas the location of failure can be observed far from the start of scratch.

![Figure 3. SEM Morphology of Alumina-Titania coatings with 2wt%CNT (a) Scratch track (b) Location of failure and (c) Back Scattered Image of scratch track](image-url)

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[Image of SEM morphology with labels: (a) Scratch debris, (b) Presence of internal cracks, (c) Less penetration due to presence of CNTs]
Figure 4. SEM Morphology of Alumina-Titania coatings with 4wt% CNT (a) Location of failure, (b) Scratch Track and (c) Back scattered Image of scratch track

Figure 5. SEM Morphology of Alumina-Titania coatings with 6wt% CNT (a) Intensity of scratch, (b) Location of failure and (c) Back scattered Image of scratch track
3.3. Porosity Analysis

The porosity percentage has been calculated from the obtained SEM micrographs using Image J software. It can be observed from Figure 6 that the percentage of porosity decreases with the increase of CNTs percentage. It can also be noted that the porosity percentage for conventional coatings without adding CNTs was measured 7.4±0.4 percent whereas for the coatings with 6wt% of CNT, the porosity was observed as 2.4±0.5 percent. This reduction in porosity can be attributed to filling of pores with CNT bundles in the coating microstructure.

![Figure 6. Porosity of Alumina-3wt%Titania coatings with different CNT percentage](image)

4. Conclusion

The scratch tests were performed on the coatings obtained from conventional Al₂O₃-3wt%TiO₂ powders mixed with various percentage of CNTs like 2wt%, 4wt% and 6wt% respectively. The intensity of penetration during scratch test was high for 2wt% CNT mixed coating system due to the presence of maximum number of pores. The intensity of penetration was less due to the reduction in percentage of porosity, i.e., 2.4±0.5 in coating system mixed with 6wt% CNTs. Also, the location of failure which is due to tensile cracks were initiated early from starting of scratch at 2wt% CNT, whereas, the crack initiation in 6wt% CNT were delayed due to the toughening of coating microstructure. Hence, it can be concluded that by increasing the percentage of CNTs, the intensity of penetration was reduced due to CNT bridging between the splats in the coating microstructure.
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6. References

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