Study on Porosity of Plasma Sprayed Carbon Nano Tube Reinforced Composite Coatings

Rakesh Goyal^{1*}, Vikas Chawla² and Buta Singh Sidhu³

¹Dept. of Mechanical Engineering, Chitkara University, Rajpura, Punjab, India ²F.C.E.T., Ferozshah, Ferozpur, Punjab, India ³Punjab Technical University, Kapurthala, Punjab, India * corresponding author e-mail: rakeshgoval6@gmail.com

Abstract - Oxidation of metals and alloys took place when they are heated to elevated temperatures in air or highly oxidising environments. Further, for elevated-temperature service the effect of incorporation of Carbon Nano Tubes (CNTs) into various alloy powder coatings on the morphology of the coating surface and corrosion properties has been a topic of technology concern. The present piece of work describes the effect of CNT inclusion in Al_2O_3 coatings deposited on various boiler steels. In many cases it is found that porosity is an important factor on the coating surface. Knowledge about the extent of these porosity imperfections is critical since they influence a wide range of spray coated properties and behaviors. The aim of this investigation is to find out the range of porosity of the coatings after CNT is added in the alloy powder.

Keywords: CNTs, High temperature oxidation, coatings, porosity, image analyser

I. INTRODUCTION

Surface engineering is the range of technologies that modify the surface of a component to improve its performance characteristics whether it is wear & corrosion resistance or something else. Coatings can be applied to surfaces to improve the surface characteristics over those of the bulk properties and are widely used in tribological applications [1]. Oxidation of metals and alloys took place when they are heated to elevated temperatures in air or highly oxidising environments [2].

Plasma surfacing is an excellent technology in highperformance coating applications ranging from aerospace industry to biomedical industry. Thermal spraying process implements a wide variety of materials (metal, ceramic, alloy and its composite) and processes (atmospheric plasma spraying, vacuum plasma spraying, etc.) for improving surface properties. The conventional plasma-spraying process is commonly referred to as air or atmospheric plasma spraving (APS). To generate plasma, an inert gas typically argon/argon + hydrogen mixture is superheated by a DC arc. Plasma temperatures range from approximately 6000°C to 15000°C in the power heating region, which are significantly above the melting point of any known material [24]. The powder mixture of carbon nano tubes and Al2O3 alloy powder in different compositions (size from $40\pm10\mu$ m) injected into a high-temperature plasma flame which is then rapidly heated and accelerated to a very high velocity by the plasma flame impacts the surface of the substrate material in the form of molten or semi molten state and very quickly cools to form a high-quality coating.

Nanotechnology nowadays is one of the most important trends in science, perceived as one of the key technologies of the present century. It has vast applications in industrial manufacturing processes, in the introduction of advance materials. In 1991, Sumio Iijima [5] reported the preparation of a new type of finite carbon structures. These carbon needles were made of coaxial graphitic tubes (up to about 50) ranging from 4 to 30 nm diameter, up to 1m in length and invariably closed at both ends (Fig. 1 shows the electron micrographs of the microtubules of graphitic carbon obtained in this work) [6].



Fig. 1 Electron micrographs of "microtubules of graphitic carbon" obtained in the first report of CNTs. Parallel dark lines correspond to the (0 0 2) lattice images of graphite. A cross-section of each tubule is illustrated. (a) Tube consisting of five graphitic sheets, diameter 6.7 nm. (b) Two-sheet tube, diameter 5.5 nm. (c) Sevensheet tube, diameter 6.5 nm, which has the smallest hollow diameter (2.2 nm).

Reprinted from with permission from Nature Publishing Group. [6] Carbon nanotubes (CNTs) are known to possess exceptional mechanical properties, very high thermal conductivity[7], high current carrying capacity[8]. Further studies made by researchers [9] revealed that the CNTs– Alloy powder composite coating, made on mild steel substrate, possesses higher resistance to corrosion (more than double, 42 hours as compared to 20 hours) when compared to pure alloy powder coating. Chen et al. [10] also reports that the metal surface possesses defects, cracks, gaps, crevices and micro holes. More over this micro hole behaves as active sites for dissolution of metal during corrosion. Nanoparticles i.e. CNTs can easily enter and fill these gaps and act as physical barrier to the corrosion process. Thus CNTs enhances the mechanical and tribiological behavior of composites.

II. OXIDATION OF METALS AND ALLOYS

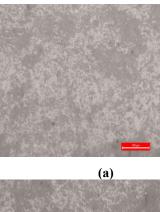
Oxidation of metal is reaction between a metal and oxygen gas and the total chemical equation is considered as,

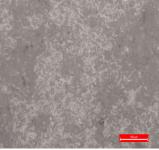
$$aM + \frac{b}{2}O_2 \rightarrow M_aO_b$$

It may seem to be the simplest chemical reaction. However, the reaction mechanisms may prove to be more complex, as the reaction path and oxidation behaviour of a metal depend on a variety of factors.

III. EXPERIMENTATION AND POROSITY EVALUATION

The micrographs have been taken at 20X value on a number of locations. The micrographs has been captured on LEICA microscope placed at IIT Ropar, Punjab.







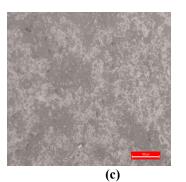
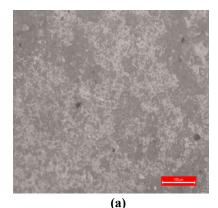
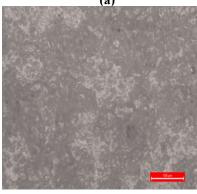


Fig. 2 Microstructures (a) T11 Al2O3 98.5% - CNT1.5% (b) T22 Al2O3 98.5% - CNT1.5% and (c) T91 Al2O3 98.5% - CNT1.5%





(b)

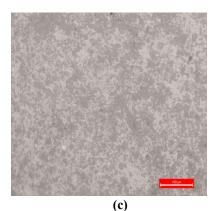
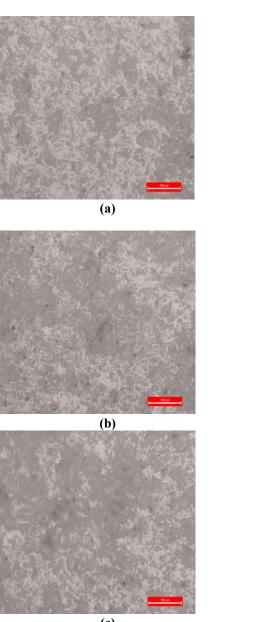


Fig. 3 Microstructures (a) T11 Al2O3 98% - CNT 2% (b) T22 Al2O3 98% - CNT 2% and (c) T91 Al2O3 98% - CNT 2%

Study on Porosity of Plasma Sprayed Carbon Nano Tube Reinforced Composite Coatings



(c) Fig. 4 Microstructures (a) T11 Al2O3 96% - CNT 4% (b) T22 Al2O3 96% - CNT 4% and (c) T91 Al2O3 96% - CNT 4%

After the porosity value has been measured on Image Analyser. The threshold limit has been selected and the porosity value has been taken at at least five points on the same substrate to increase in accuracy of porosity value as shown in figure.

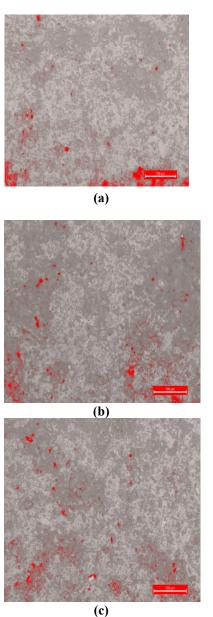
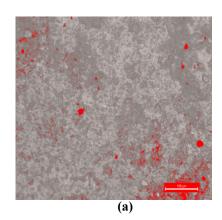


Fig. 5 Threshold selected for measuring porosity (a) T11 Al2O3 98.5% -CNT1.5% (b) T22 Al2O3 98.5% - CNT1.5% and (c) T91 Al2O3 98.5% -CNT1.5%



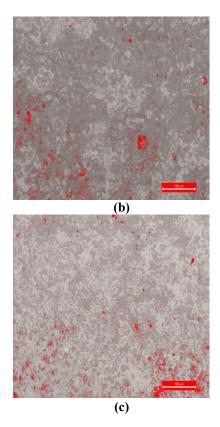
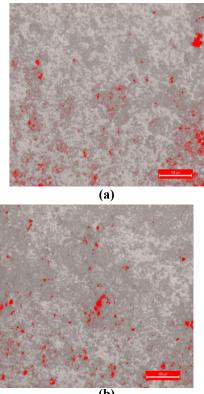


Fig. 6 Threshold selected for measuring porosity (a) T11 Al2O3 98% -CNT 2% (b) T22 Al2O3 98% - CNT 2% and (c) T91 Al2O3 98% - CNT 2%



(b)

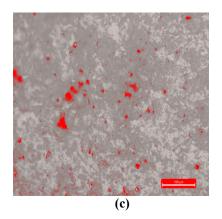


Fig. 7 Threshold selected for measuring porosity (a) T11 Al2O3 96% -CNT 4% (b) T22 Al2O3 96% - CNT 4% and (c) T91 Al2O3 96% - CNT 4%

The average of the total reading taken has been calculated for more accuracy. The porosity value is found to be as 3.69 approximately as shown in the table given.

TABLE 1 AVERAGE POROSITY VALUE OF ALUMINA COATI	NG
WITH VARIOUS COMBINATIONS OF CARBON NANO TUBE	ES

S. No.	Material	Porosity
1	T11 Al ₂ O ₃ 98.5% - CNT1.5%	3.99
2	T11 Al ₂ O ₃ 98% - CNT 2%	3.85
3	T11 Al ₂ O ₃ 96% - CNT 4%	3.77
4	T22 Al ₂ O ₃ 98.5% - CNT1.5%	3.6
5	T22 Al ₂ O ₃ 98% - CNT 2%	3.61
6	T22 Al ₂ O ₃ 96% - CNT 4%	3.38
7	T91 Al ₂ O ₃ 98.5% - CNT1.5%	3.48
8	T91 Al ₂ O ₃ 98% - CNT 2%	3.62
9	T91 Al ₂ O ₃ 96% - CNT 4%	3.64

IV. STUDIES OF CNTS INCORPORATED ALLOY **POWDERS COATINGS**

Experimental work made by Keshri et al. [22] showed that thermal spray processes provides the possibility of developing coatings of Al₂O₃-1.5 wt.% CNT on AISI 1020 steel. An increase of 15% in the microhardness value, 24% in relative fracture toughness was observed with the addition of 1.5 wt.% CNT in the reference coating (coating with Al₂O₃ powder without CNTs). Furhter Balani et al. [23] reported an improvement of 49 times in the sliding wear resistance by the addition of 8 wt.% CNT to Al₂O₃. Such improvement was attributed to a uniform dispersion of nanotubes, CNT bridging between the splats and enhanced densification by CNTs.

Experimental results of the study made by Praveen et al. [9] revealed that the CNTs-Zn composite coating, made on mild steel substrate, possesses higher resistance to corrosion (more than double, 42 hours as compared to 20 hours, during salt spray corrosion testing) when compared to pure zinc coating. CNTs inclusion reduces the porous nature of pure zinc coating. Corrosion behavior of metal deposits containing nano particles reports that the incorporation of CNTs in the deposits improved the corrosion resistance.

Experimental results of the study made by Chen et al. [10] revealed that the corrosion resistance for the CNTs– Ni coating was seven times and three times as compared to the bare and pure Ni coated samples. CNTs were embedded deeply in the nickel grains, reinforcing the nickel layer, and filled in crevices, gaps and micron holes[9]. CNTs act as inert physical barriers to the initiation and development of defect corrosion, modifying the microstructure of the nickel layer and hence improving the corrosion resistance of the coating.

V. CONCLUSION

The porosity measured for pure alumina coating powder with plasma spray method has been observed as more than 4. But in the present case studied when the coating powder has been prepared by mixing alumina with various percentages of carbon nano tubes, the average porosity value has been calculated as 3.69. It might be because the nano tubes fill in the capillaries of pores and might have been resulted for lower porosity than the earlier.

REFERENCES

- Goyal Rakesh, Chawla Vikas, Sidhu Buta, "State of Art: Thermal Spraying and Performance of Hard Coatings: A Review", International Journal of Research in Mechanical Engineering and Technology, 2011, 22-26.
- [2] Lai, G.Y., 'Oxidation-Chapter 3', High Temperature Corrosion of Engineering Alloys, Pub. ASM International, 1990, 15-46.
- [3] Li, M.H., Sun, X.F., Li, J.G., Zhang, Z.Y., Jin, T., Guan, H.R., Hu, Z.Q., 'Oxidation Behaviour of a Single-Crystal Ni-Base Superalloy in Air-I: At 800 and 9000C', Oxid. Metals, 2003, Vol. 59 (5-6), 591-605.
- [4] Eliaz, N., Shemesh, G. and Latanision, R.M., 'Hot Corrosion in Gas Turbine Components', Engineering Failure Analysis, 2002, Vol. 9, 31-43.
- [5] S. Iijima, Nature (London) 354 (1991) 56.
- [6] Lidia M. Ravelo-Pérez, Antonio V. Herrera-Herrera, Javier Hernández-Borges, Miguel Ángel Rodríguez-Delgado, "Carbon nanotubes: Solid-phase extraction", Journal of Chromatography A, 1217 (2010) 2618–2641
- [7] Zhidong Han, Alberto Fina, "Thermal conductivity of carbon nanotubes and their polymer nanocomposites: A review", Progress in Polymer Science 36 (2011) 914–944.
- [8] [8] Pallab Barai, George J. Weng, "A theory of plasticity for carbon nanotube reinforced composites", International Journal of Plasticity 27 (2011) 539–559.
- [9] B.M. Praveen, T.V. Venkatesha, Y. Arthoba Naik, K. Prashantha, "Corrosion studies of carbon nanotubes–Zn composite coating", Surface & Coatings Technology 201 (2007) 5836–5842.
- [10] X.H. Chen, C.S. Chen, H.N. Xiao, F.Q. Cheng, G. Zhang, G.J. Yi, "Corrosion behavior of carbon nanotubes–Ni composite coating", Surface & Coatings Technology 191 (2005) 351–356.
- [11] Kofstad, P., 'Chapter 1-General Introduction', High Temperature Oxidation of Metals, John Wiley & Sons Inc. USA, 1966, 1-20.
- [12] Haugsrud, R., 'On the High-Temperature Oxidation of Nickel', Corros. Sci., 2003, Vol. 45 (1), 211-35.
- [13] Yedong, H. and Stott F. H., 'The Selective Oxidation of Ni-15%Cr and Ni-10%Cr Alloys Promoted by Surface-Applied Thin Oxide Films', Corros. Sci., 1994, Vol. 36 (11), 1869-84.

- [14] Bittel, J.T., Sjodahl, L.H. and White, J.F., 'Oxidation of 304L Stainless Steel by Steam and by Air', Corrosion, 1969, Vol. 25 (1), 7-14.
- [15] Seal, S., Bose, S. K. and Roy, S. K., 'Improvement in the Oxidation Behaviour of Austenitic Stainless Steels by Superficially Applied, Cerium Oxide Coatings', Oxid. Metals, 1994, Vol. 41 (1-2), 139-78.
- [16] Roy, K., Bottino, C., Rakesh, V. R., Kuiry, S. C. and Bose, S. K., 'Improved High Temperature Oxidation Behaviour of AISI 347 Grade Stainless Steel by Superficial Coating of CeO₂', ISIJ Int., 1995, Vol. 35 (4), 433-42.
- [17] Pettit, F. S. and Meier, G. H., 'Oxidation and Hot corrosion of Superalloys', Superalloys, Eds. Gell, M., Kartovich, C. S., Bricknel, R. H., Kent, W. B., Radovich, J. F., The Met. Soc. of AIME, Warrendale, Pensylvania, 1984, 651-687.
- [18] Chatterjee, U. K., Bose, S. K. and Roy, S. K., 'Alloy Oxidation-Chapter-6', Environmental Degradation of Metals, Pub., Marcel Dekker Inc., New York, 2001, 287.
- [19] Levy, M., Huie, R. and Pettit, F., 'Oxidation and Hot Corrosion of Some Advanced Superalloys at 1300 to 2000^oF (704 to 1093^oC)', Corrosion, 1989, Vol. 45 (8), 661-74.
- [20] Hussain, N., Shahid, K.A., Khan, I.H. and Rahman, S., 'Oxidation of High-Temperature alloys (Superalloys) at Elevated Temperatures in Air:I', Oxid. Metals, 1994, Vol. 41 (3-4), 251-269.
- [21] Li, M.H., Sun, X.F., Jin, T., Guan, H.R., Hu, Z.Q., 'Oxidation Behaviour of a Single-Crystal Ni-Base Superalloy in Air-II: At 1000, 1100, and 1150°C', Oxid. Metals, 2003, Vol. 60 (1-2), 195-210.
- [22] Anup Kumar Keshri, Virendra Singh, Jun Huang, Sudipta Seal, Wonbong Choi, Arvind Agarwal, "Intermediate temperature tribological behavior of carbon nanotube reinforced plasma sprayed aluminum oxide coating", Surface & Coatings Technology 204 (2010) 1847–1855.
- [23] K. Balani, S.P. Harimkar, A. Keshri, Y. Chen, N.B. Dahotre, A. Agarwal, Acta Mater. 56, (2008), 5984.