



MRS Singapore - ICMAT Symposia Proceedings

7<sup>th</sup> International Conference on Materials for Advanced Technologies

Degradation Studies of Wire arc Sprayed FeCrBSiMn alloy Coating  
in Molten Salt Environment

V. N. Shukla<sup>a\*</sup>, Nidhi Rana<sup>a</sup>, R. Jayaganthan<sup>a</sup>, V. K. Tewari<sup>a</sup>.

<sup>a</sup>Department of Metallurgical and Materials Engineering, Indian Institute of Technology, Roorkee 247667, India

Abstract

The aim of the current investigation is fabricate the FeCrBSiMn alloy coating onto 310S stainless steel substrate by wire arc spraying process and to study degradation behavior of the coating exposed to molten salt environment ( $\text{Na}_2\text{SO}_4\text{-}82\%\text{Fe}_2(\text{SO}_4)_3$ ) at 900°C under cyclic conditions after 50 cycles. X-ray diffraction (XRD) and scanning electron microscopy/energy-dispersive analysis (SEM/EDS) were used to characterize morphology of coated and uncoated samples for substantiating the degradation mechanisms. The dense and globular morphology of the coatings is observed from the SEM analysis. The maximum microhardness of coating was found to be (430-1060 HV). The coating showed superior hot corrosion resistance as compared to boiler steel due to the formation of protective scale,  $\text{Cr}_2\text{O}_3$ . The protective scale formed at high temperature prevents hot corrosion of coated boiler steel as evident from the morphological studies made by using FE-SEM/EDS. The FeCrBSiMn alloy coating showed good adherence to the 310S substrate with negligible microspalling of the scales.

© 2013 The Authors. Published by Elsevier Ltd.

Selection and/or peer-review under responsibility of the scientific committee of Symposium [Advanced Structural and Functional Materials for Protection] – ICMAT.

*Keywords:* Wire arc spray; Coating; Microhardness; Hot corrosion.

1. Introduction

Corrosion is a serious problem in superheater of coal fired boilers. Degradation of components occurs due to high temperature oxidation and hot corrosion of boiler tubes in steam generating system of power generation industry [1-8]. Huge amounts of material wastage in super heaters due to the combustion of fuels are reported [9-15]. Literature reveals the wide contribution of thermal sprayed coatings for the protection of turbine engine and boiler tubes against high temperature corrosion attack [16-21]. Recently, there has been an increasing interest in producing Fe-base alloy coatings due to their high strength and hardness, superior wear and corrosion resistance [22]. HVAS process is preferred for the deposition of FeCr base coatings on bare substrate compared to other thermal spray techniques due to its cost effectiveness (operating

\* Corresponding author. Tel.:0091-9458121041; fax: 91-1332-28-5243.

E-mail address: [metavns@gmail.com](mailto:metavns@gmail.com)

lower cost), high deposit efficiency and less applications difficulties.[23-24] The degradation mechanisms of high velocity arc sprayed FeCr based alloy coatings exposed to molten salt ( $\text{Na}_2\text{SO}_4$ -82%  $\text{Fe}_2(\text{SO}_4)_3$ ) environment at  $900^\circ\text{C}$  under cyclic conditions is scarce in the literature. Therefore, the present work has been focused to study microstructural changes and hot corrosion behavior of FeCr-based coatings after exposure of 50 hours in molten salt ( $\text{Na}_2\text{SO}_4$ -82%  $\text{Fe}_2(\text{SO}_4)_3$ ) environment at  $900^\circ\text{C}$  by using FE-SEM/EDS, XRD and X-ray line mapping, respectively.

## 2. Experimental

The austenitic stainless steel (310S) was used as substrate in the present study. The chemical composition (wt.%) of the substrate material is given in Table 1.

Table 1 Chemical composition of substrate material

Chemical composition (wt.%) of 310S									
C	Cr	Ni	Mn	Si	Cu	Mo	P	S	Fe
0.0409	25.18	19.14	1.32	0.486	0.189	0.177	0.0202	0.004	Balance

Spectrometric analysis was used to determine the chemical composition of the substrate (310S stainless steel). Specimens with dimensions of approximately  $20 \times 15 \times 5 \text{ mm}^3$  was cut from the sheets. The specimens were polished and grit blasted with alumina powders prior to coatings. The size of the alumina powder used for grit blasting the substrate specimens was  $\sim 350 \mu\text{m}$ . FeCrBMnSi alloy coating was deposited on the 310S steel substrates by using the HVAS process, at M/s Industrial Processors and Metallizers (IPM), Pvt. Ltd, New Delhi, India using the standard spray parameters. Fe-base cored wires (TAFA 95 MXC) used as feedstock. Chemical composition (wt %) is listed in Table 2

Table 2 Chemical composition (wt.%) of feedstock wire material.

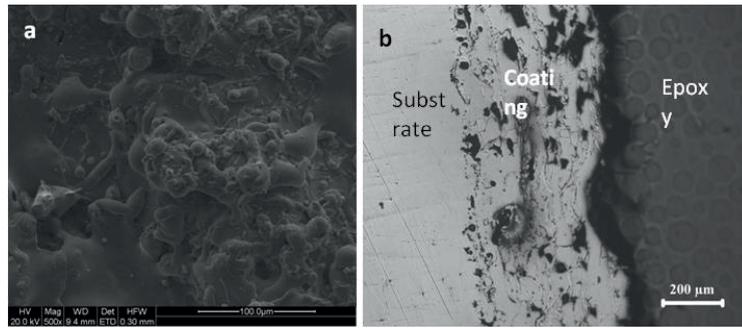
elements	Cr	B	Mn	Si	Fe
95MXC	< 29	< 3.75	< 1.65	< 1.6	Bal.

The surface of the specimens was cleaned by polishing with alumina powder followed by cleaning by acetone. To remove the moisture, polished samples were pre-heated for 1 hour at  $250^\circ\text{C}$ . A coating of uniform thickness with  $4\text{-}5 \text{ mg/cm}^2$  of  $\text{Na}_2\text{SO}_4$ -82%  $\text{Fe}_2(\text{SO}_4)_3$  was applied with a camel hair brush on the preheated sample ( $250^\circ\text{C}$ ). Bare and coated specimens were exposed to molten salt ( $\text{Na}_2\text{SO}_4$ -82%  $\text{Fe}_2(\text{SO}_4)_3$ ) environment at  $900^\circ\text{C}$  under cyclic conditions for 50 cycles. One hour heating in a SiC tube furnace, followed by 20 minutes cooling at room temperature ( $25^\circ\text{C}$ ) is adopted in each cycle. The corrosion products and cross sectional analysis of the scale were characterized by X-ray diffraction (XRD), and field emission scanning electron microscope (FESEM, FEI, Quanta 200 FEG-SEM) with EDAX Genesis software attachment; XRD analysis was carried out using a Bruker AXS D-8 Advance powder diffractometer (Germany).

## 3. Results and discussion

### 3.1 Coating Characterization

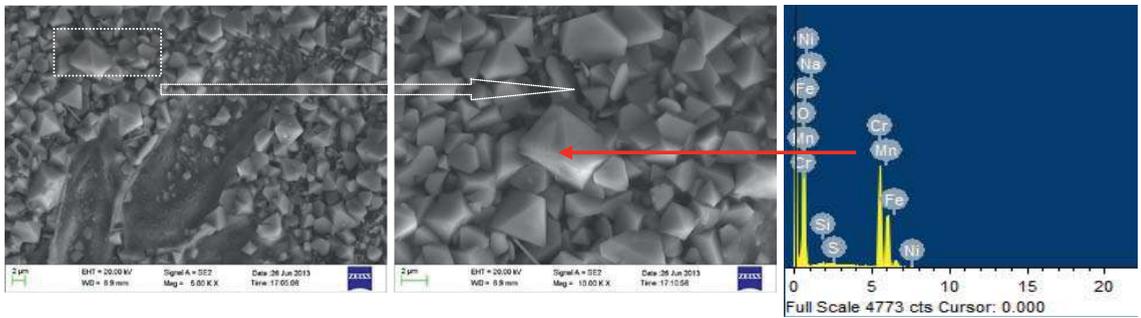
The dense and globular morphology of the coatings is observed from the SEM analysis. The microstructures revealed that coating consist of irregular shaped splats which are interconnected (Fig 1a). The coated samples were cut in cross-section, mounted in transoptic powder and subjected to mirror polishing. Optical microscopy image of cross-section of coated specimen is shown in Fig. 1b. Micro hardness of the coating was determined across the cross-sectioned samples. The micro hardness of the as sprayed coatings was measured by using Micro hardness Tester (VHM-002 Walter UHL, Germany) using 300 grams (2.941N) load applied for a dwell time of 15 sec. The maximum microhardness of as sprayed coating was found to be 1060 Hv.



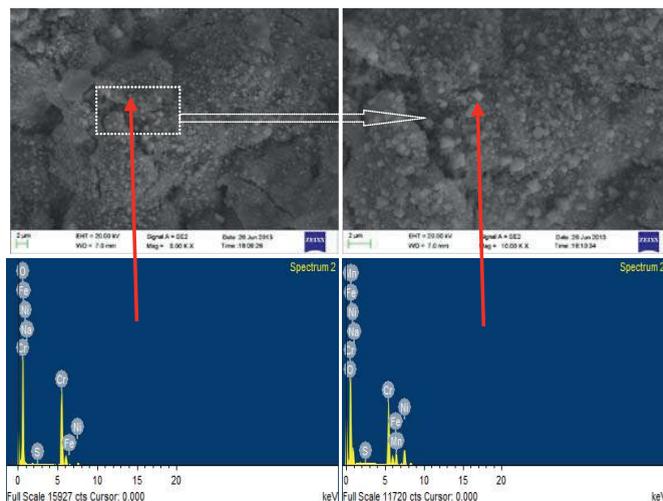
**Fig 1:** (a) FE-SEM micrograph showing the morphology of as-sprayed coating, (b) Optical microscopy image of the cross-sectional view of the as-sprayed coating.

### 3.2 Surface morphology

FE-SEM micrographs with EDS analysis for the bare and coated specimens exposed to molten salt ( $\text{Na}_2\text{SO}_4$ -82%  $\text{Fe}_2(\text{SO}_4)_3$ ) environment at  $900^\circ\text{C}$  under cyclic conditions for 50 hours are shown in Fig. 2 and Fig. 3, respectively. The scale formed on alloy substrate was porous and less adherent.



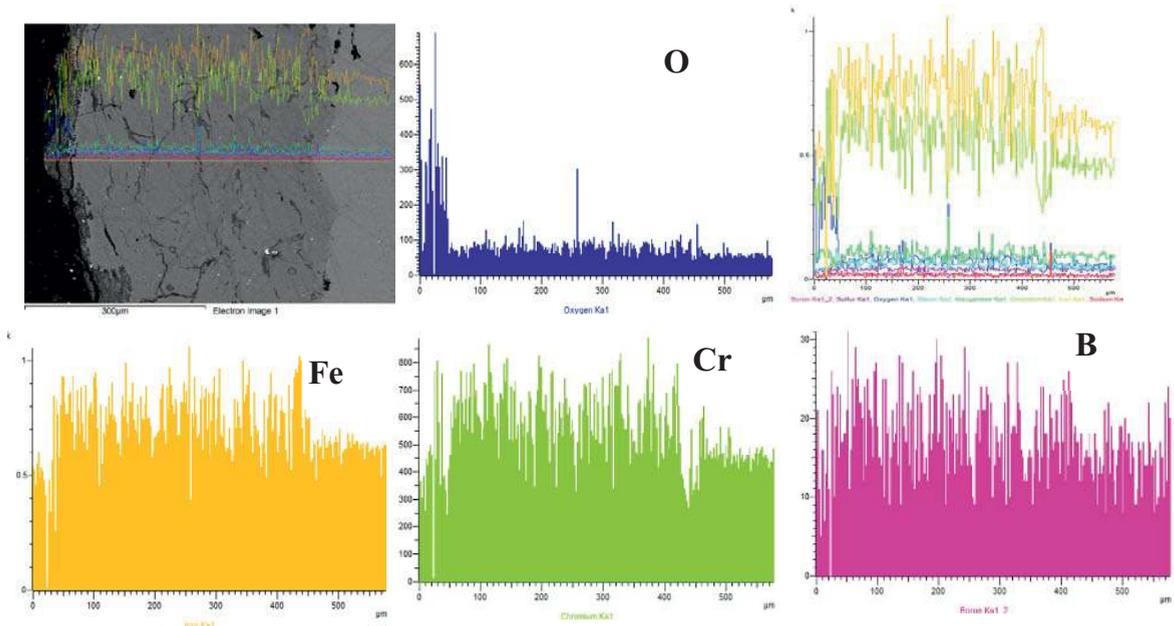
**Fig 2:** FE-SEM/EDS surface analysis of bare substrate exposed to molten salt ( $\text{Na}_2\text{SO}_4$ -82%  $\text{Fe}_2(\text{SO}_4)_3$ ) environment at  $900^\circ\text{C}$  under cyclic conditions for 50 hours.



**Fig 3:** FE-SEM/EDS surface analysis of coated substrate exposed to molten salt ( $\text{Na}_2\text{SO}_4$ -82%  $\text{Fe}_2(\text{SO}_4)_3$ ) environment at  $900^\circ\text{C}$  under cyclic conditions for 50 hours.

The scale consists mainly of Cr, Ni, Fe and O. Spalling and cracking were observed in case of alloy substrate as shown in Fig 3. Wang also observed severe spalling of the oxide scale during cyclic study of 2.25Cr-1Mo steel at 740<sup>o</sup> C in coal-fired boiler [25]. The FeCrBMnSi alloy coating deposited on 310S by the high-velocity arc spraying process behaved very well in molten salt environment. The oxide scale of the coated specimen appears as consisting of spongy nodules. EDS analysis of surface indicates Cr, O, Fe, B. Minor amount of Mn, Na, S and Si are detected in the oxide scale. The scale was adherent and minor spalling observed at the edges of the coated specimen.

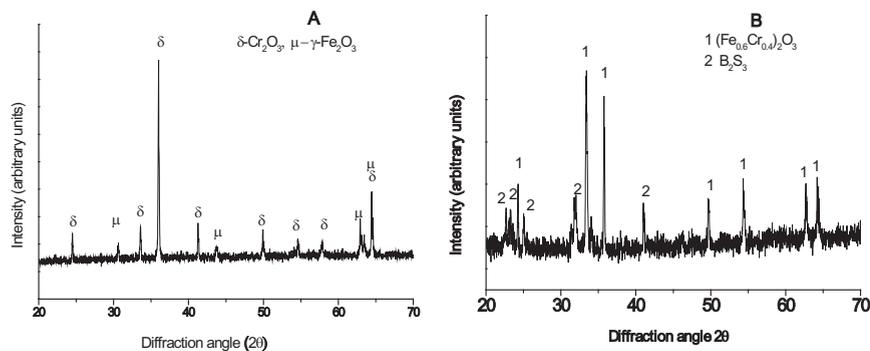
### 3.3 Cross-sectional analysis



**Fig 4:** X-ray line mapping of the cross section of coated substrate exposed to molten salt ( $\text{Na}_2\text{SO}_4$ -82%  $\text{Fe}_2(\text{SO}_4)_3$ ) environment at 900<sup>o</sup>C under cyclic conditions for 50 hours.

The cross-sectional analyses and X-ray line mapping of different elements of the coated specimens exposed to molten salt ( $\text{Na}_2\text{SO}_4$ -82%  $\text{Fe}_2(\text{SO}_4)_3$ ) environment at 900<sup>o</sup>C under cyclic conditions after 50 cycles are shown in Fig. 4. The Scale mainly consists of Fe, Cr and O along with significant amounts of B, Si, Ni, Na and S. The coating is intact with the substrate and there is no sign of crack at the interface.

### 3.4 X-ray diffraction (XRD) analysis



**Fig 5:** (a) The XRD patterns of the scale formed on (a) bare substrate, and (b) coated substrate, exposed to molten salt ( $\text{Na}_2\text{SO}_4$ -82%  $\text{Fe}_2(\text{SO}_4)_3$ ) environment at 900<sup>o</sup>C under cyclic conditions for 50 hours.

The XRD patterns of the scale formed on bare and coated specimens exposed to molten salt ( $\text{Na}_2\text{SO}_4$ -82%  $\text{Fe}_2(\text{SO}_4)_3$ ) environment at  $900^\circ\text{C}$  under cyclic conditions after 50 cycles are shown in Fig. 5a and Fig. 5b. XRD analysis of the surface of the bare specimen after 50 cycles at  $900^\circ\text{C}$  revealed the presence of  $\text{Cr}_2\text{O}_3$  and  $\gamma\text{-Fe}_2\text{O}_3$ , whereas the XRD diffractograms for the coated specimen revealed the presence of  $(\text{Fe}_{0.6}\text{Cr}_{0.4})_2\text{O}_3$  and  $\text{B}_2\text{S}_3$ .

#### 4. Conclusion

FeCrBMnSi alloy coatings were deposited successfully on 310S by the high-velocity arc spraying process. Coating consisted of very dense structure. The maximum microhardness of as sprayed coating was found to be 1060 Hv. FeCrBMnSi alloy coatings exhibited excellent oxidation and wear/spallation resistance. The oxide scale of coated specimen showed the presence of mainly oxides of Cr and Fe which might be responsible for better corrosion resistance. There is perceptible diffusion of some elements from the substrate to the coating.

#### Acknowledgments

The authors would like to express their thanks to M/s Industrial Processors and Metallizers (IPM), Pvt. Ltd., New Delhi, India for providing the powders and coating facilities.

#### References

- [1] Matthews, S., James B., Hyland M., 2013. High temperature erosion-oxidation of Cr<sub>3</sub>C<sub>2</sub>-NiCr thermal spray coatings under simulated turbine conditions, *Corrosion Science* 70, p. 203.
- [2] Kaur, M., Singh, H., Prakash, S., 2011. Surface engineering analysis of detonation-gun sprayed Cr<sub>3</sub>C<sub>2</sub>-NiCr coating under high-temperature oxidation and oxidation-erosion environments, *Surf Coat Technol.* 206, p. 530.
- [3] Rhys-jones, T. N., 1989. Coatings for blade and vane applications in gas turbines, *Corrosion Science* 29 (6), p. 623.
- [4] Mayoral, M., C., Andre's, J., M., Belzunce, J., Higuera, V., 2006. Study of sulphidation and chlorination on oxidized SS310 and plasma-sprayed Ni-Cr coatings as simulation of hot corrosion in fouling and slagging in combustion, *Corrosion Science* 48, p. 1319.
- [5] Guo, H., Li, D., Peng H., Cui, Y., Gong, S., 2011. High-temperature oxidation and hot-corrosion behaviour of EB-PVD b-NiAlDy coatings, *Corrosion Science* 53, p. 1050.
- [6] Krishnarao, V., Agrawal, M., 2008. Evaluation of arc sprayed coatings for erosion protection of tubes in atmospheric fluidised bed combustion (AFBC) boilers, *Wear* 264, p. 139.
- [7] Matthews, S., James, B., Hyland, M., 2009. The role of microstructure in the high temperature oxidation mechanism of Cr<sub>3</sub>C<sub>2</sub>-NiCr composite coatings, *Corrosion Science* 51, p. 1172.
- [8] Matthews, S., James, B., Hyland, M., 2008. Erosion of oxide scales formed on Cr<sub>3</sub>C<sub>2</sub>-NiCr thermal spray coatings *Corrosion Science* 50, p. 3087.
- [9] Priyantha, N., Jayaweera, P., Sanjurjo, A., Lau, K., Lu, F., Krist, K., 2003. Corrosion-resistant metallic coatings for applications in highly aggressive environments, *Surf. Coat. Technol.* 163-164, p. 31.
- [10] Sidhu, B., S., Prakash, S., 2006. Studies on the behaviour of stellite-6 as plasma sprayed and laser remelted coatings in molten salt environment at  $900^\circ\text{C}$  under cyclic conditions, *Journal of Materials Processing Technology*, 172, p. 52.
- [12] Collins, S., 1997. Biomass-fired plants face down near-term challenges, *power* 137, p. 51.
- [13] Wang, B., Q., 1996. Effect of alkali chlorides on erosion-corrosion of cooled mild steel and Cr<sub>3</sub>C<sub>2</sub>-NiCr coating, *wear* 199, p. 268.
- [14] Wang, B., 1996. Erosion-corrosion of thermal sprayed coatings in FBC boilers, *Wear* 199, p. 24.
- [15] Nielsen, H., P., Dam-Johansen K., Baxter, L., L., 2000. Progress in Energy and Combustion, *Science* 26, p. 283.
- [16] Huang, H., Liu, C., Ni, L., Zhou, C., 2011. Evaluation of microstructural evolution of thermal barrier coatings exposed to  $\text{Na}_2\text{SO}_4$  using impedance spectroscopy, *Corrosion Science* 53, p. 1369.
- [17] Guo, R., Q., Zhang, C., Chen, Q., Yang, Y., Li, N., Liu, L., 2011. Study of structure and corrosion resistance of Fe-based amorphous coatings prepared by HVOF and HVOF, *Corrosion Science* 53, p. 2351.
- [18] Wang, Y., Tian, W., Zhang, T., Yang, Y., 2009. Microstructure, spallation and corrosion of plasma sprayed Al<sub>2</sub>O<sub>3</sub>-13%TiO<sub>2</sub> coatings, *Corrosion Science* 51, p. 2924.
- [19] Rhys-Jones, T., N., 1990. Thermally Sprayed Coating Systems for Surface Protection and Clearance Control Applications in Aero Engines, *Surf Coat Technol.* 43/44, p. 402.
- [20] Saha, G., C., Khan, T., I., Zhang, G., A., 2011. Erosion-corrosion resistance of microcrystalline and near-nanocrystalline WC-17Co high velocity oxy-fuel thermal spray coatings *Corrosion Science* 53, p. 2106.
- [21] Murthy, J., K., N., Murthy, B., 2006. Abrasive wear behavior of WC-CoCr and Cr<sub>3</sub>C<sub>2</sub>-20(NiCr) deposited by HVOF and detonation spray processes, *Surface and Coatings Technol.* 200, p. 2642.
- [22] Jandin, G., Liao, H., Feng, Z., Q., Coddet, C., 2003. Correlations between operating conditions, microstructure and mechanical properties of twin wire arc sprayed steel coatings, *Materials Science and Engineering A* 349, p. 298.
- [23] Cheng, J., Liang, X., Xu, B., 2009. Microstructure and wear behavior of FeBSiNbCr metallic glass coatings, *J. mater Sci Technol.* 25, p. 687.
- [24] Wielage, B., Pokhmurska, H., Student, M., Gvozdeckii, V., Stupnyckyj, T., Pokhmurskii, V., 2013. Iron-based coatings arc-sprayed with cored wires for applications at elevated temperatures, *Surface & Coatings Technology* 220, p. 27.
- [25] Wang, D., 1988. Corrosion Behaviour of Chromized and/ or Aluminized 21/4Cr-1Mo Steel in medium-BTU Coal Gasifier Environments, *Surf. Coat. Technol.* 36, p. 49.