Oxidation Behavior of D-Gun Spray Ni-20Cr Coated ASTM A213 347H Steel at 900°C

G. Kaushal[1], N. Kaur[2], H. Singh[2] and S. Prakash[3]
[1]*RIMT-Institute of Engineering & Technology, Mandi Gobindgarh, Punjab, India*
[2]*Indian Institute of Technology Ropar, Rupnagar, Punjab, India*
[3]*Indian Institute of Technology Roorkee, Roorkee, Uttarankhand, India*
E-mail: gagankaushal@rimt.ac.in

Abstract—*Detonation-gun (D-gun) spray technology provides the possibility of producing high quality coatings because of high kinetic energy and low thermal energy involved in the process. In this study, D-gun spray technique was used to deposit Ni-20Cr coating on a boiler steel ASTM A213 347H. The specimens with and without coating were subjected to cyclic oxidation testing at an elevated temperature of 900°C to ascertain usefulness of the coating. Mass change data was recorded to formulate the kinetics of oxidation for the specimens. The exposed specimens were characterized by X-ray diffraction (XRD) and field emission-scanning electron microscopy/energy dispersive spectroscopy (FE-SEM/EDS). It was observed that Detonation gun sprayed Ni-20 Cr coating was suitable to provide oxidation resistance to the given steel in the air environment.*

Keywords: *D-Gun, High temperature oxidation, Protective coating, Ni-20Cr, Oxide scales*

Introduction

It is accepted that coatings can improve the surface characteristics over those of the substrate bulk properties and are widely used in tribological applications either to reduce wear or to modify friction during contact [1]. One among the various coating techniques is Detonation gun (D-gun) spray technique. The essence of D- gun spraying is the use of energy of the gas mixture detonation to heat and relay high kinetic energy to the particles of powdered coating material [2]. The D-gun deposited coatings are formed by collision with the substrate material and deformation of grains of the powder which together with detonation products, form metallic spray. This is very promising technique to achieve high abrasion, high erosion and corrosion resistance, thermal shocks, good adhesion and low porosity [3]. High kinetic energy and low thermal energy in the two phase metallic spray are energy sources of bonds between the deposited powder, substrate and coating layers [4-6].Furthermore, the D-Gun spray process can reach top temperatures as high as 3850 ºC in the combustion process, and accelerate powder particles up to a speed of 600m/s to 1200 m/s, which is much higher than that of Low Pressure Plasma Spraying (about 400 m/s) and High-Velocity Oxy-Fuel spraying (at maximum 500m/s) [7]. As a result, the detonation spray coating produces a denser microstructure.

The focus of the paper is to explore the oxidation resistance of the D-gun deposited Ni-20Cr coating on a ASTM A213 347H (347H) boiler steel. The behaviour of D-gun sprayed Ni-20Cr coating on same steel in molten salt environment and actual boiler environment has already been reported by the authors in their earlier publications [8, 9]. The outcome of the present study will provide an improved understanding and possibly endorse the beneficial performance of the D-gun sprayed Ni-2Cr coating even for oxidation environment.

Experimental Procedure

Development of Coating

Substrate Material

347H boiler steel tube material, with chemical composition C - 0.04-0.1, Mn - 2.0, P - 0.04 max, S - 0.03 max, Si - 0.75, Cr -17-19, Ni - 9.0-13.0 and Fe - 65.08 (mass%), has been used as a substrate material in this current study. The specimens each measuring 20mm x 15mm x 5mm, approximately, and were made from the new boiler tubes. The specimens were polished down to 180 grit SiC paper finish and then were grit blasted with Al_2O_3 (grit 60) before the deposition of the coating.

Coating Formulation

The Ni-20Cr coating (DC1) was coated on the steel sample using the commercially available detonation-gun spray process at M/S Sai Surface Coating Technologies, Hyderabad, India. The flame temperature was 3900°C and the maximum spray rate was 3kg/h. The gas flow rate was $11m^3/h$ and particle impact velocity was 600-1200m/s. The coating parameters are listed in Table 1[8].

Table 1: Spray Parameters Employed for the D-gun Coating [8]

Parameter	Related Value
Oxygen flow rate [kg/cm^2]	2640
C_2H_2 flow rate[kg/cm^2]	2240
N_2 flow rate [kg/cm^2]	960
Spray distance [mm]	140
Frequency of shots [s]	3

Characterization of As-Sprayed Coating

The coated samples were wheel polished and then subjected to X-ray diffraction (XRD), Field emission scanning electron microscope (FE-SEM, FEI, Quanta

200F Company) with EDAX Genesis software attachment; made in Czech Republic is used to characterize the surface cross-sectional morphology and X-ray mapping. The morphology of the Ni-20Cr coatings exhibits splat like morphology and very low porosity, the details regarding characterization of the coating have been discussed in our earlier publication [9].

High Temperature Oxidation Experiments

All the specimens were polished down to 1 µm alumina wheel before being subjected to accelerated oxidation runs. Each cycle consisted of 1 hour heating at 900 °C in Silicon Carbide tube furnace followed by 20 minutes cooling at room temperature. A cyclic study of 50 cycles was performed as the duration of 50 hours is considered to be adequate for attaining a steady state oxidation for a material [10]. The temperature of study was deliberately kept high at 900°C similar to the earlier studies reported [11, 12]. The specimens were kept in alumina boats and inserted in the furnace. The studies were performed for the uncoated and coated specimens for the purpose of comparison. The mass change measurements were taken at the end of each cycle with the help of Electronic Balance Model 06120 (Contech) with a sensitivity of 1 mg. Mass change data was analyzed to approximate the kinetics of corrosion. After the exposure, all the exposed samples were analyzed for the characterization of oxide scales. The corroded samples were subjected to the XRD and FE-SEM/EDS analyses for the surface as well as the cross-sectional analysis as per the procedure mentioned in Section 2.3.

Results

High Temperature Oxidation Tests Kinetics

Mass change (mg/cm^2) versus number of cycles plots for the uncoated and Ni-20Cr coated 347H steel oxidized at 900°C in air upto 50 cycles have been shown in Fig. 5.2. The mass change data is usually used to establish the kinetics of the oxidation process. A higher mass gain represents higher rates of oxidation. Therefore, the oxidation rates of various materials can be compared with the help of mass change data. It is perceptible from the plots that the uncoated 347H steel showed mass gains for the first 14 cycles followed by gradual mass losses till the end of the exposure**.** There was an overall mass loss of 16.632 mg/cm^2 by the end of oxidation study. On the other hand the DC1 coated steel showed overall mass gain which was not significant. The oxidation rate was slightly low in the earlier hours of study followed by a slight rate of oxidation by end of cyclic studies. The overall mass gain in DC1 coating was 3.379 mg/cm^2. Hence, it can be concluded that the DC1 coating is better as compared to the uncoated steel.

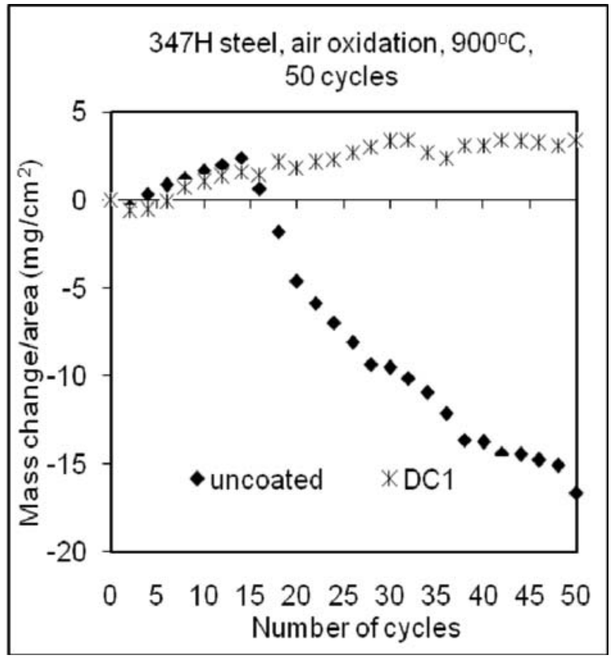


Fig. 1: Mass Change vs. Number of Cycles Plot for the Uncoated and D-gun Spray DC1 Coated 347H Steel Subjected to Cyclic Oxidation in Air at 900°C for 50 Cycles

XRD Analysis of the Corroded Samples

XRD analysis for the uncoated steel after exposure to air at 900°C for 50 cycles has been compiled in Fig. 2. As is clear from the diffractograms, the formation of Fe_2O_3 and NiO phases has been confirmed alongwith a spinel $NiCr_2O_4$ phase. The D-gun-sprayed DC1 coating after exposure to air environment has been shown in Fig. 3 on reduced scale. NiO is observed as strong phase whereas Cr_2O_3 and Fe_2O_3 as medium intensity phases. $NiCr_2O_4$ is also observed as a low intensity phase.

FE-SEM/EDS of the Corroded Samples

The SEM micrograph of the surface scale developed on the oxidized 347H boiler steel consists of an upper sub-layer, the sub-layer is in the form of patches, which are surrounded by low-lying channels, showing tendency to align along a particular direction in the form of streaks. The EDS analysis indicates that the scale is mainly consisting of Fe, Cr and O showing the possibility of formation of oxides of Fe and Cr in the scale. Presence of significant quantities of Ni is also revealed, Fig.4. A dense fine grained nodular scale can be seen for the oxidized D-gun-spray DC1 coated 347H boiler steel as shown in Fig. 5. The scale has Cr and Ni as its main constituents alongwith significant amounts of O.

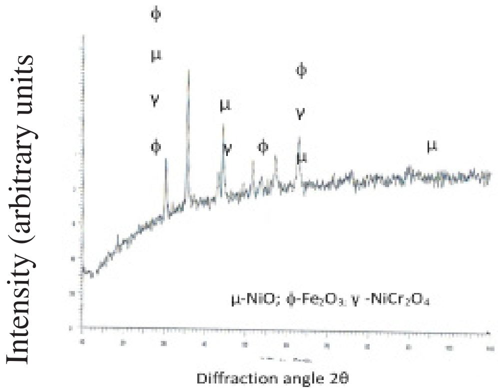


Fig. 2: X-ray Diffraction Profiles of the 347H Steel Boiler Steel Subjected to Cyclic Oxidation in Air at 900°C for 50 Cycles

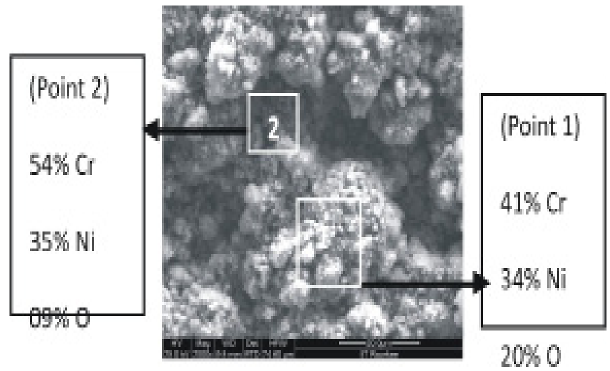


Fig. 5: Surface Scale Morphology and EDS Analysis of D-gun Sprayed Ni-20Cr (DC1) Coating on 347H Boiler Steel Subjected to Cyclic Oxidation in Air at 900°C for 50 Cycles

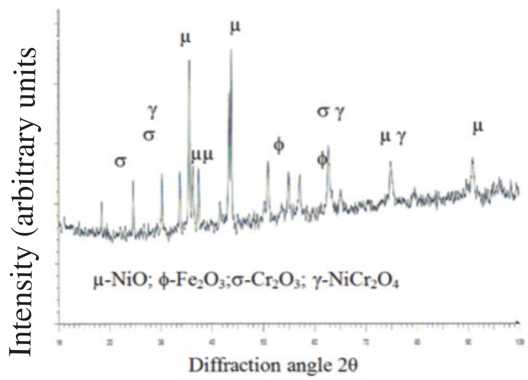


Fig. 3: X-ray Diffraction Profiles of the D-gun Spray Ni-20Cr (DC1) Coated 347H Boiler Steel Su Diffraction angle 2q in Air at 900°C for 50 Cycles.

Cross-sectional Analysis

The scale formed on the surface of uncoated 347H steel has a dense appearance with a nearly smooth substrate-scale interface as shown in Fig. 6. The scale consists mainly of iron along with small amounts of chromium and nickel. Presence of oxygen has been indicated throughout the scale. However, the concentration of the

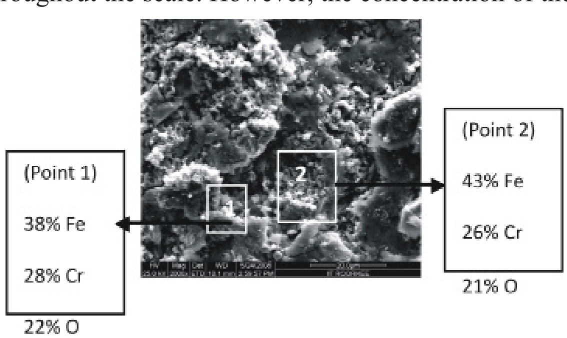
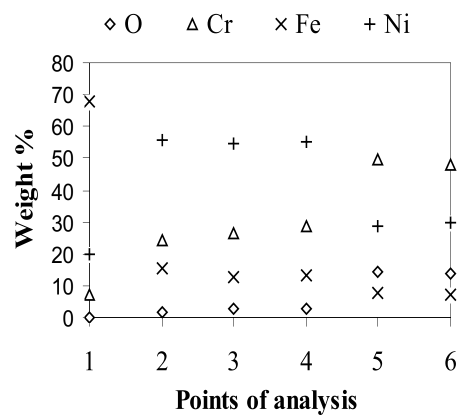


Fig. 4: FE-SEM along with EDS Analysis of Boiler Steel Subjected to Cyclic Oxidation in Air at 900°C for 50 Cycles: 347H Steel



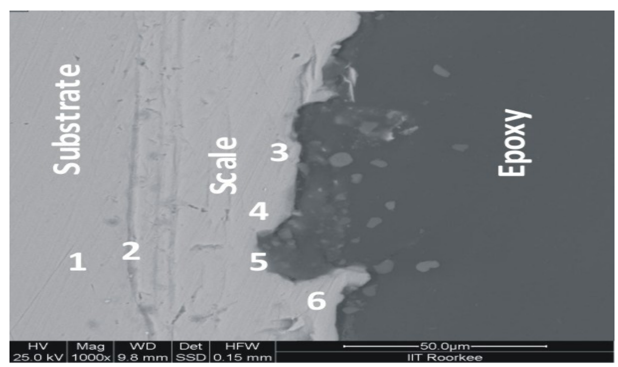


Fig. 6: Oxide Scale Morphology and Variation of Elemental Composition Across the Cross-section of Uncoated 347H Boiler Steel Subjected to Cyclic Oxidation inAir at 900°C for 50 Cycles

same is only marginal at all the points of analysis. The oxide scale for the D-gun-sprayed DC1 coated 347H steel seems to be dense and strongly bonded to the substrate steel even after the oxidation study for 50 hours in the air environment Fig. 7. The oxide scale mainly contains chromium along with some amounts of nickel and oxygen. The concentration of chromium is increasing from point 3 to point 5 in a linear fashion, whereas the amount of nickel is uniform from point 2 to point 4; it shows a dip at points 5 and 6. The outermost layer (point 6) of the scale mainly comprises chromium alongwith good amounts of nickel and oxygen. This seems to have diffused throughout the thickness of the oxide scale.

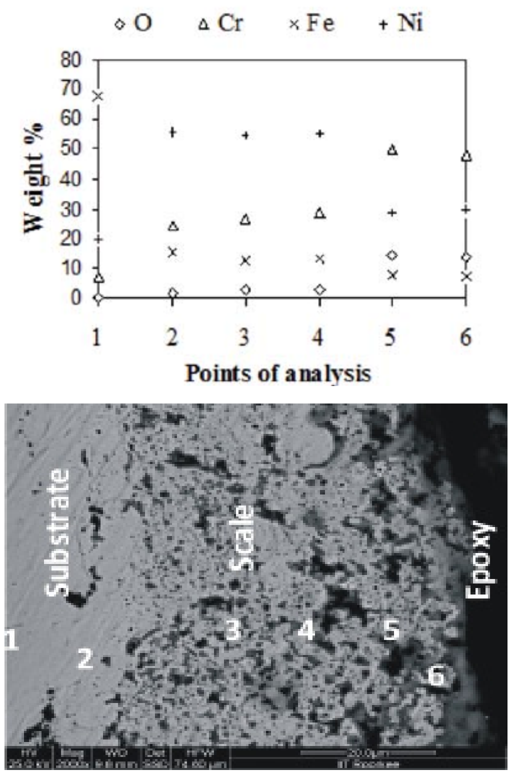


Fig. 7: Oxide Scale Morphology and Variation of Elemental Composition across the Cross-section of D-gun Sprayed Ni-20Cr (DC1) Coating on 347H Boiler Steel Subjected to Cyclic Oxidation in Air at 900°C for 50 Cycles

X-ray Mappings Analysis

Analysis for the oxidized 347H, [Fig. 8] shows that the oxide scale has a dense appearance, in general, and has a nearly uniform thickness. From the elemental maps, it is clear that the scale consists mainly of Fe and Cr. Both these elements are found to co-exist in the scale. Oxygen is found to be higher in concentration in the outer layers of the oxide scale alongwith Fe and Cr, thereby indicating formation of oxides of Fe and Cr. The composition image and elemental mappings for the exposed cross-section of D-gun spray DC1 coated 347H steel are shown in Figure 9. The scale is found to be intact and strongly bonded. The oxide scale consists mainly of Cr alongwith significant amounts of Ni. Iron is mainly confined to the substrate only.

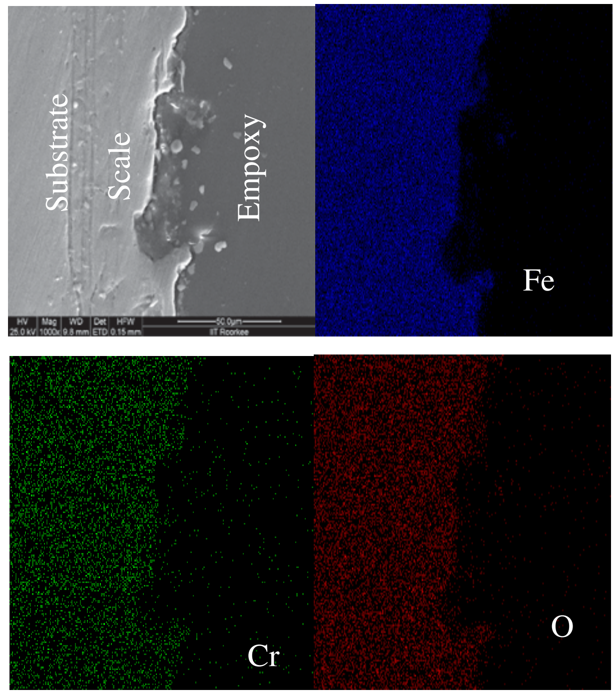


Fig. 8: Composition Image (SEI) and X-ray Mappings Across the Cross-section of Uncoated 347H Boiler Steel Subjected to Cyclic Oxidation in Air at 900°C for 50 Cycles

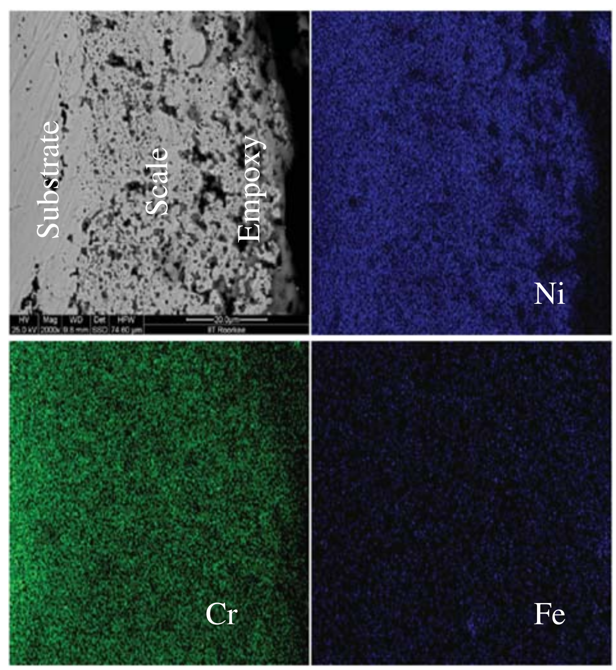


Fig. 9: Composition Image (SEI) and X-ray Mappings of the Across the Cross-section of D-gun Sprayed Ni-20Cr (DC1) Coating on 347H Boiler Steel Subjected to Cyclic Oxidation in Air at 900°C for 50 Cycles

Discussion

During oxidation studies the uncoated 347H steel showed mass gains for the first 14 cycles followed by gradual mass losses till the end of cyclic studies. The mass loss in this case may be attributed to the formation of some volatile phases during the oxidation studies.The behaviour of the uncoated steel was not protective and thus non-parabolic (Fig. 1). On the contrary, the Ni-20Cr (DC1) coated 347H steel showed only slight mass gain, moreover, the coated steel was observed to follow a parabolic rate of oxidation, which indicates that a protective oxide has formed, which has the capability to act as diffusion barrier to the corroded species during longer durations of usage. Initial mass gain maybe attributed to higher oxidation rate of the coated specimen due to air which is entrapped during D-gun deposition and sheltered in the pores, since the cooling of the coating was rapid; there is shortage of time for the residual air to react with the surrounding coating alloys [13]. The coating underwent in-situ reaction during high temperature oxidation (900 °C) and was partially oxidized, during the subsequent cycles, the formation of oxides has blocked the pores and acted as diffusion barriers to the inward diffusion of corrosive species as per the opinion of Kamal et al [14]. This leads to a slow oxide scale growth; consequently the mass gain is low. Overall the DC1 coating, in general, showed good adherence to the boiler steel during exposure to the air oxidation with no spallation of their oxide scales from their major surfaces areas, which indicates the effectiveness of the coatings under study to protect the substrate steel as the cyclic-oxidation behavior of an alloy is dictated mainly by the scale spallation resistance as per the opinion of Stott [15].

The Fe_2O_3 phase was revealed as strong intensity phase in the scales of 347H steel by the XRD analysis. The surface FE-SEM/EDS of the scales mainly revealed Fe and Cr. The cross-sectional FE-SEM/EDS and X-ray mapping analyses further endorse these results. In the DC1 coated 347H boiler steel (Fig. 3), formation of NiO as strong phase has been revealed. Cr_2O_3 and Fe_2O_3 are found as medium intensity phases and $NiCr_2O_4$ is identified as the weak intensity phases. The phases formed have also been confirmed by the FE-SEM/EDS and elemental mapping techniques. These chromium containing oxides are protective as reported by Ul-Hamid [16] and Sundararajan et al [17]. The surface EDS analysis of the coated steel further confirms the formation of these oxides (Fig. 5). The results are well endorsed by the cross-sectional analysis which shows that the coating is mainly composed of Ni and Cr with only slight penetration of O (Fig. 7). The X-ray mappings of the exposed coated steel (Fig. 9) further confirm that the oxide layer mainly consists of NiO, although with a significant presence of Cr. The outermost layer of the exposed coating contains mainly Cr along with O, thereby indicating the possibility of formation of Cr_2O_3. The presence of Cr_2O_3 phase in the oxide scales of the coated steel provides a shield to the base metal against any diffusion of oxidizing species through the oxide scale. This is visible from the cross-sectional EDS and X-ray mapping analysis where the penetration of O has been found to be only marginal. The chromium oxide phase is thermodynamically stable [18] up to very high-temperatures due to its high melting point. As well, it forms dense, continuous and adherent layers that grow relatively slowly [19]. A scale of this type forms a solid diffusion barrier that inhibits the interaction of oxygen of underlying coating.

Conclusion

Based upon the results reported herein, and the studies already published by authors it is interpreted that D-gun spray Ni-20Cr (DC1) coating could be successful in imparting high temperature corrosion [8], erosion-corrosion [9] as well as oxidation resistance to the ASTM A213 347H steel.

References

[1] Wang, J. Sun, B. Guo, Q. Nishio, M. and Ogawa, H. (2002), “Wear Resistance of a Cr3C2-NiCr Detonation Spray Coating” J. Therm. Spray Technol, Volume 11(2) pp. 261-265.

[2] Senderowski, C. and Bojar, Z. (2009), “ Influence of Detonation Gun Spraying Conditions on the Quality of Fe-Al Intermetallic Protective Coatings in the Presence of NiAl and NiCr Interlayers”, J. Therm. Spray Technol, Volume 18(3), pp. 436-447.

[3] 3.J.K.N. Murthy, B. Venkataraman, Surf. Coat. Technol. 200 (2006) 2642.

[4] E. Kadyrov and V. Kadyrov, (1995), “Gas Detonation Gun for Thermal Spraying”, Adv. Mater. Processes, Volume, 8, pp. 21-24.

[5] E. Kadyrov and V. Kadyrov, (1995), “Gas Dynamical Parameters of Detonation Powder Spraying” , J. Therm. Spray Technol., Volume, 4(3), pp. 280-286.

[6] E. Kadyrov, Gas-Particle Interaction in Detonation Spraying Systems,(1996), J. Therm. Spray Technol., Volume, 5(2), pp. 185-195.

[7] Zhang, Y.J., Sun, X.F., Zhang, Y.C., Jin, T., Deng, C.G., Guan, H.R. and Hu, Z.Q. (2003) Mater. Sci. Eng., A360, 65.

[8] Kaushal, G. Singh, H. and Prakash, S., (2011), “Surface Engineering of ASTM A213 TP 347H Steel to Enhance its High Temperature Corrosion Resistance by Detonation-Gun Spray Coating,” Materials at High Temperatures, Vol. 28, No. 1, pp.1-11

[9] Kaushal, G. Singh, H. and Prakash, S., (2012) “Performance of detonation gun sprayed Ni-20Cr coating on ASTM A213 TP347H steel in a boiler environment” Journal of Thermal Spray Technology, DOI: 10.1007/s11666-012-9770-1, Available Online, March 2012.

[10] H. Singh, D. Puri, S. Prakash., Surf. Coat. Technol., 2005, 192, 1, 27-38.

[11] R.A. Mahesh, R. Jayaganthan, S. Prakash., Surface Engineering, 2011, 27, 5, 332-339.

[12] A. Rahman, V. Chawla, R. Jayaganthan, R. Chandra, V.K. Tewari, R. Ambardar, R., Surface Engineering, 2012, 28, 4, 249-256.

[13] Yu-Juan Zhang, Xiao-Feng Sun, Heng-Rong Guan, Zhuang-Qi Hu, Surf. Coat. Technol. 161 (2002) 302.

[14] Kamal, S. Jayaganthan, R., Prakash, S. and Kumar, S., "Evaluation of cyclic hot corrosion behaviour of detonation gun sprayed Cr3C2–25%NiCr coatings on nickel- and iron-based superalloys", Surface & Coatings Technology, Vol. 203,pp. 1004–1013.

[15] Stott, F.H., (1992), "Developments in Understanding the Mechanisms of Growth of Protective Scales on High-Temperature Alloys," Mater. Charact., Vol. 28, No. 3, pp. 311-325.

[16] Ul-Hamid, A., (2003), "Diverse Scaling Behavior of the Ni-20Cr Alloy," Maters. Chem. Phys., Vol. 80, pp. 135-142.

[17] Sundararajan, T., Kuroda, S., Itagaki, T. and Abe, F., (2003B), "Steam Oxidation Resistance of Ni-Cr Thermal Spray Coatings on 9Cr-1Mo Steel. Part 2: 50Ni-50Cr," ISIJ Int., Vol. 43, No.1, pp. 104-111.

[18] Kamal, S. Jayaganthan, R. Prakash, S. and Kumar, S., J Alloys Comp., Vol.463, No.1–2, (2008), 358.

[19] 19.Stott, F.H., Principles of growth and adhesion of oxide scales, The Role of Active Elements in the Oxidation Behaviour of High Temperature Metals and Alloys., Lang, E., (editor). Elsevier Applied Science, London, (1998).