Chapter 7

COMPREHENSIVE DISCUSSION

This chapter includes comprehensive discussion for the results obtained in molten salt and actual boiler environment. Comparative corrosion resistance of different coatings in similar environments has also been discussed. Some of the common phenomenons observed during the studies have also been mentioned.

HVOF spraying process has been successfully used to deposit NiCr and Cr$_3$C$_2$-NiCr coatings on T91 boiler steel substrates. The coatings exhibit a dense, adherent and uniform splat like microstructure, with splats oriented parallel to the substrate surface. The splats parallel to the substrate provides a necessary protection against corrosive species penetrating into the coating (Kamal et al, 2009B). The coatings possess some voids and oxide inclusions that are typical characteristics of the HVOF sprayed coatings. Sidhu et al (2006L) also observed the similar features of HVOF sprayed coatings. The porosity of the coatings lies in the range of 1.5–2.5%. The measured value of porosity for as-sprayed NiCr and Cr$_3$C$_2$–NiCr coatings are almost in agreement with the finding of Sahraoui et al (2003); Lih et al (2000) and Sidhu et al (2006F). After post treatment of coatings by method of heat treatment and sealing, decrease in the porosity has been found, which is consistent with the results reported by Bolelli et al (2008) and Wang et al (2003B).

The bar charts showing the overall weight gain of the uncoated and coated steel subjected to molten salt (Na$_2$SO$_4$-60%V$_2$O$_5$) environment for 50 cycles at three different temperatures i.e. 600, 750 and 900 °C are presented in Fig. 7.1. It is evident from the data that the weight gain for the bare steel got reduced significantly at all the three temperatures after the application of HVOF spray NiCr and Cr$_3$C$_2$-NiCr coatings in both as-deposited and post treated coatings. It can be perceived from the Fig. 7.1 that the gain in weight for the bare and coated T91 steel increased drastically with the
increased in corrosion temperature from 750 °C to 900 °C in comparison to increase in temperature from 600 °C to 700 °C. This behaviour can also be immediately inferred from the weight gain data, where corrosion rate increased unbeatably high with the increase in corrosion temperature from 750 °C to 900 °C.

HVOF sprayed NiCr and Cr$_3$C$_2$-NiCr coatings in both as-deposited and post treated condition were found useful in providing necessary resistance to T91 boiler steel against molten salt (Na$_2$SO$_4$–60%V$_2$O$_5$) corrosion at 600 °C and 750 °C under cyclic conditions. At 600 °C temperature of hot corrosion, both the coatings in as-deposited and post treated condition performed well and remained intact with the substrate without any visible defects till the end of cyclic study. However, for 750 °C temperature of hot corrosion, cracks were observed in the oxide scale perpendicular to the substrate surface for both the coatings. Cracks in the coatings perpendicular to the coating surface may be attributed to the combined effect of thermal fatigue damage experienced by the coatings due to cyclic hot corrosion studies and thermal stresses generated due to differences in the thermal-expansion coefficients of the coatings and substrate (Sidhu et al, 2006Q; Sidhu et al, 2005A and Portinha et al, 2005). Further, the formation of cracks may also be attributed to formation of greater specific-volume oxides at the coating-substrate interface due to the penetration of corroding species to the coating-substrate interface through the interconnected porosity in the coating. These cracks may result in exfoliation of the coating in long term studies due to the penetration of corroding species through these cracks to the coating-substrate interface and formation of greater specific-volume oxides (Chatha et al, 2012A). In the present investigation mainly iron oxide (Fe$_2$O$_3$) from beneath appeared through cracks in the coating. Further these cracks may have provided easy path to the corroding species to reach the substrate, which might have accelerated the corrosion process. Oxide protrusion and pimples from inside those have relatively higher specific volume were also observed by Bornstein et al (1975). Both the coatings post treated by the method of heat treatment and sealing, provided adequate protection to the substrate steel and remained adherent to the substrate till the end of cyclic study.
At 900 °C temperature of hot corrosion study overall weight-gain values for the steel have reduced significantly after the deposition of the coatings. However, NiCr and Cr$_3$C$_2$-NiCr coating in as-deposited condition were not able to provide necessary protection to the substrate steel for 50 cycles of study as the thickness of the samples reduced significantly till the end of 50 cycles. As-deposited NiCr and Cr$_3$C$_2$-NiCr coating experienced two stages of hot corrosion i.e. initiation stage and propagation stage. Once the coatings entered the propagation stage, the protective scale (scale rich in oxides of Ni and Cr) rendered ineffective and substrate became vulnerable to hot corrosion, thereby resulting in intense spalling, sputtering and peeling-up of its oxide scale. During initiation stage, coatings have provided adequate protection to the substrate steel. Cracks appeared on the surface of samples. The phenomena of cracking of the scale as well as the coating may be the result of mismatch in coefficient of expansion between the substrate and coating and due to penetration of corroding species to the substrate material through interconnected porosity/intersplat boundaries of the coating (Sidhu et al, 2006Q; Sidhu et al, 2005A and Chatha et al, 2012A). Further, cracking may be due to the presence of Mo in the substrate steels, which contains 0.87%Mo. As suggested by Lai (1990) and Chatterjee et al (2001), Mo forms MoO$_3$ that has melting point of 795 ºC, which is significantly lower than the temperature of investigation i.e. 900 ºC. The oxide protrusions appeared from beneath through the cracks is perhaps of greater specific-volume oxides, which is consistent with the observations of Sidhu and Prakash (2006C). After the initiation stage, the coated samples experienced the propagation stage, in which the salts got access to the unprotected metal and corrosion continued unabated at exceeding high rates.

The weight gain by the duplex coating systems having Cr$_2$O$_3$/Al$_2$O$_3$ as top coat and NiCr/Cr$_3$C$_2$-NiCr as the interlayer is almost identical to the weight gain by the as-deposited NiCr/Cr$_3$C$_2$-NiCr coatings. Therefore based upon the weight gain data, the application of Cr$_2$O$_3$/Al$_2$O$_3$ as top coats on NiCr/Cr$_3$C$_2$-NiCr coating may not be much useful in improving hot corrosion resistance of the NiCr/Cr$_3$C$_2$-NiCr coating on T91 steel in the given environment. Whereas, the post treatment of the NiCr and Cr$_3$C$_2$-NiCr
coating on T91 steel by the means of heat treatment and sealing proved useful in improving hot corrosion resistance of NiCr/Cr$_3$C$_2$-NiCr coating on T91 steel in the given environment at all the three temperatures i.e. 600, 750 and 900 °C, as the weight gain values for the heat treated and sealed coating are significantly smaller than the weight gain by the as-deposited NiCr and Cr$_3$C$_2$-NiCr coating on T91 steel.

At 900 °C temperature of testing in Na$_2$SO$_4$-60%V$_2$O$_5$ environment, duplex coating systems consisting of Cr$_2$O$_3$/Al$_2$O$_3$ as top coat and NiCr/Cr$_3$C$_2$-NiCr as the interlayer experienced internal corrosion, cracking and oozing out of material from beneath for both NiCr and Cr$_3$C$_2$-NiCr coatings. Internal oxidation attack may be better revealed from X-ray mappings of NiCr coating with Cr$_2$O$_3$/Al$_2$O$_3$ as top coat. X-ray mapping reveals the deep penetration of corroding species (Na, V and O) into the substrate. Oozing out of substrate material (Fe) may also be revealed from Fe map. The oozed-out material is believed to be greater specific volume oxides. Oxide protrusions produced as a result of this oozing-out phenomenon were also observed by Bornstein et al (1975); Singh (2003) and Bala et al (2009B). Internal corrosion attack of coatings might be attributed to the porosity of coatings (NiCr/Cr$_3$C$_2$-NiCr) and top coats (Cr$_2$O$_3$/Al$_2$O$_3$). So due to porous nature, top coats are not able to enhance the life of coatings in the given environment. Minor decrease in weight gain by the duplex coating systems than the as-deposited coatings may be attributed to increase in coating thickness due to deposition of top coats. The appearance of cracks in the oxide scale as well as across the coatings may be the result of mismatch in coefficient of expansion and due to penetration of corroding species to the substrate material through interconnected porosity/intersplat boundaries of the coatings in view of the results reported by Niranatlumpong et al (2000) and Evans and Taylor (2001).

Post treatment of coatings by the method of heat treatment and sealing proved to be effective and rendered adequate protection to the substrate steel for 50 cycles of study in Na$_2$SO$_4$-60%V$_2$O$_5$ environment at all the three different temperatures i.e. 600, 750 and 900 °C. Sealed coatings have shown better corrosion resistance in molten salt and actual boiler environment among all the investigated cases. Better protection
provided by the sealed coatings to the substrate steel may be associated with the formation of a barrier layer by the sealant over the top surface of the coatings by filling the surface pores. Once the open pores are closed by the sealant, the diffusion of corrosive species to the internal portions of the coating gets desolate. Both the NiCr and Cr$_3$C$_2$-NiCr sealed coatings showed neither scale initiation at the coating-substrate interface nor the de-lamination in the coating. Better protection by the sealed coating is also reported by Zeng et al (2008) during corrosion studies on High-velocity air fuel sprayed sealed 316L stainless steel (SUS316L) coatings on carbon steel substrate. Authors opined that when sealing treatment is applied, the porosity at the particle boundaries is filled by the sealant.

Heat treated coatings provided better protection to the substrate steel than the as-deposited coatings in both molten salt and actual boiler environment; however, its performance is less than the sealed coating. Better hot corrosion resistance of heat treated coating may be attributed to the rapid formation of oxides at the coating splat boundaries and within open pores due to penetration of the oxidising species along the splat boundaries/open pores during heat treatment of the coated sample in an oxidising environment. Guilemany et al (2002A) reported the formation of Cr$_2$O$_3$ by treating the Cr$_3$C$_2$-NiCr coating at 880 °C for 1 h in an oxidising atmosphere. Formation of intersplat oxides during heat treatment of HVOF sprayed Cr$_3$C$_2$-NiCr in air have also been observed by Matthews (2004B). Once the oxides are formed at splat boundaries and places of porosity, the coating becomes dense; as a result the diffusion of corroding species to the internal portions of the coatings gets slowed down and the growth of the oxides becomes limited mainly to the surface of the specimen (Mahesh et al, 2008B). This in turn improved the corrosion resistance of the coating. Better performance of heat treated coating in the given environment has also been attributed for its tendency to form protective dense oxides of chromium, nickel and their spinels.

The bar charts indicating the erosion-corrosion rate and thickness change of the uncoated and coated steels subjected to actual boiler environment is represented in Fig. 7.2. It can be inferred from the bar chart that, in general, both the coatings in as-
deposited and post treated condition performed appreciably well during exposure to boiler environment and significant resistance to the degrading species has shown by the coatings on T91 steel in the given environment. The sequence of the erosion-corrosion resistance based upon thickness loss data (mpy) in the given environment is as follows:

Sealed NiCr > Sealed Cr$_3$C$_2$-NiCr > Heat treated NiCr > Heat treated Cr$_3$C$_2$-NiCr > as-deposited NiCr > as-deposited Cr$_3$C$_2$-NiCr > NiCr with Al$_2$O$_3$ top coat > Cr$_3$C$_2$-NiCr with Al$_2$O$_3$ top coat > NiCr with Cr$_2$O$_3$ top coat > Cr$_3$C$_2$-NiCr with Cr$_2$O$_3$ top coat > Bare T91 steel

Heat treatment of NiCr and Cr$_3$C$_2$-NiCr coatings also proved beneficial to enhance the erosion-corrosion resistance in actual boiler environment. The higher erosion-corrosion resistance shown by the heat treated NiCr and Cr$_3$C$_2$-NiCr coatings might be due to the formation of oxides at the coating splat boundaries and within open pores due to penetration of the oxidising species along the splat boundaries/open pores during heat treatment of the coated sample in an oxidising environment. The presence of oxides along the grain boundaries and at the places of porosity in the coating might have helped in providing shield against diffusion of the corrosive species towards the substrate, thereby leading to better protection of the base steel. Also the existence of a protective Cr$_2$O$_3$ rich layer along with additional spinel phase of NiCr$_2$O$_4$ at the outermost region of the scale as depicted by the X-ray mappings might have been useful in protecting the base steel. For both the coatings diffusion of alloying elements from the substrate to the oxide scale has been revealed by EDS and X-ray mapping analysis. These results of diffusion of alloying elements to the coating are in good agreement with the findings of Sidhu et al (2006J); Mahesh et al (2009A) and Sidhu et al (2006F).
Fig. 7.1 Bar chart showing cumulative weight gain per unit area for bare and coated T91 steel subjected to molten salt environment at 600, 750 and 900 °C for 50 cycles.
Fig. 7.2  Bar chart indicating the thickness change in mils per year (mpy) by the bare and coated steel exposed to a platen superheater of the coal fired boiler for 1500 h at 900 °C.