Ni-Cr Coated Alloy for Highly Corrosive High Temperature Conditions

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Abstract:

The waste-to-energy plants around the globe are still running at low efficiency as compared to fossil fuel based plants due to hot corrosion degradation failure of the heat exchanger components. The presence of mainly alkali and heavy metals along-with chlorine in the waste lowers the first melting point (FMT) of deposits on the surfaces, results in accelerated corrosion of the components. Though superalloys show better results compared to different boiler steels but still there is need of corrosion resistant coatings to improve the efficiency of the power plants. The work related to cold sprayed coating is not much reported in high temperature corrosive environments. This paper presents the results of the corrosion behavior of cold spray coated superalloy in the chlorine containing real service medical waste based incinerator plant environment.

1. Introduction

The corrosive degradation of waste incinerator components is a serious problem [1-3]. The hot corrosion of heat resistant alloys, in waste incinerators and other similar environments, accelerates by the presence of mainly chlorine, sulfur and alkali metals in the fuel combustion products or impurities [3]. Therefore, an attempt have been made to study the hot corrosion performance of cold sprayed Ni-20Cr coating on Ni- based superalloy in the highly corrosive real service environment of medical waste based incinerator. The detail of cold spray coating deposition process is reported in literature by the authors [4,5].

Experimental procedure

The Ni-based superalloy (12Fe-23Cr-1Mn-1.3Al-0.3Ti - Balance Ni) was used as substrate material for the present study. The material procured from Mishra Dhatu Nigam Limited, Hyderabad (India) in the rolled sheet form. The bare superalloy specimenswere cuts from the sheet with dimensions of 20x15x3mm. Two specimens were prepared for surface and cross-section analysis. Polishing of specimens was done using SiC emery papers of 100, 220, 400, 600 grit size.

Table 1 Cold spray process parameters

The specimens were grit blasted with alumina powders (grit 45) before the development of the coatings by cold spray process. Commercially available Ni-20Cr feedstock alloy in powder from was used coating deposition. Cold spray Kinetics 4000 system was used for depositing the coating at ASB industries, Inc., Barbeton Ohio, USA. Standard spray parameters used for coating are mentioned in Table 1. All the process parameters were kept constant throughout the coating process. After polishing the coated sample, the thickness was measured from the Back-Scattered Electron Images (BSEI) taken along the cross section.

Hot corrosion studies in waste incinerator

The hot corrosion study of cold spray coated specimen was carried out in waste incinerator plant, at Amritsar Enviro Care Systems (P) Ltd., Amritsar, Punjab, India**.** The incinerator plant is

based upon medical waste as fuel. The plant operates as per the guidelines of Fifth Amendment in 2008 of Environment Protection Rules of 1986 by Ministry of Environment and Forests, Govt. of India, New Delhi. The gasses going to the atmosphere from the incinerator should be less than or equal to the parameter-specific emission standards given in Table 2. The samples were hanged in the secondary chamber of plant using steel wire through a hole at one of the edges of samples as shown in Fig. 1. The temperature in the plant varies due to heterogeneous nature of fuel and the average temperature at the position of hanged samples was 900°C. The study was conducted for 10 cycles with each cycle consisting of 100h of exposure followed by 1 h of cooling at ambient conditions. The weight of samples was measured after each cycle of study. The samples were visually examined at the end of each cycle for any change in the colour, luster, adherence of scale to the substrate and spalling tendency. After 10 cycles of studies, the corrosion products and their distribution on the surfaces were studied with XRD and SEM/EDX analysis. For cross-sectional analysis the samples were sectioned and mounted in epoxy along cross-section. The mounted specimens were prepared by polishing, using SiC emery papers of 220, 400, 600 grit and subsequently 1/0, 2/0, 3/0, and 4/0 grades. Fine polishing was carried out using 0.3 µm diamond paste. The prepared specimenswere then analyzed by SEM/EDX techniques.

Table 2 Specific environmental emission limits for medical waste incinerator

PARAMETER	EMISSION STANDARD
Particulates	50 mg/Nm^3
HCl	50 mg/Nm^3
SO2	200 mg/Nm^3
CO	100 mg/Nm^3
	50 mg/Nm^3
Total Organic Carbon	20 mg/Nm^3
HF	4 mg/Nm^3
NOX (NO and NO_2 expressed as NO_2)	400 mg/Nm^3
Total dioxins and furans	0.1 ng TEQ/Nm^3
Cd + Th + their compounds	0.05 mg/Nm^3
Hg and its compounds	0.05 mg/Nm^3
Sb + As + Pb + Cr + Co + Cu + Mn + Ni + V + theircompounds	0.5 mg/Nm^3

Scan Speed (mm/s)	Step Size (mm)	Temperature (^{O}C)	Pressure (Bar)	Nitrogen gas flow rate (m^3/hr)	Carrier gas flow rate (m^3/hr)	Powder feed rate (RPM)
500	1.0	650	38	95	3.0	2.5

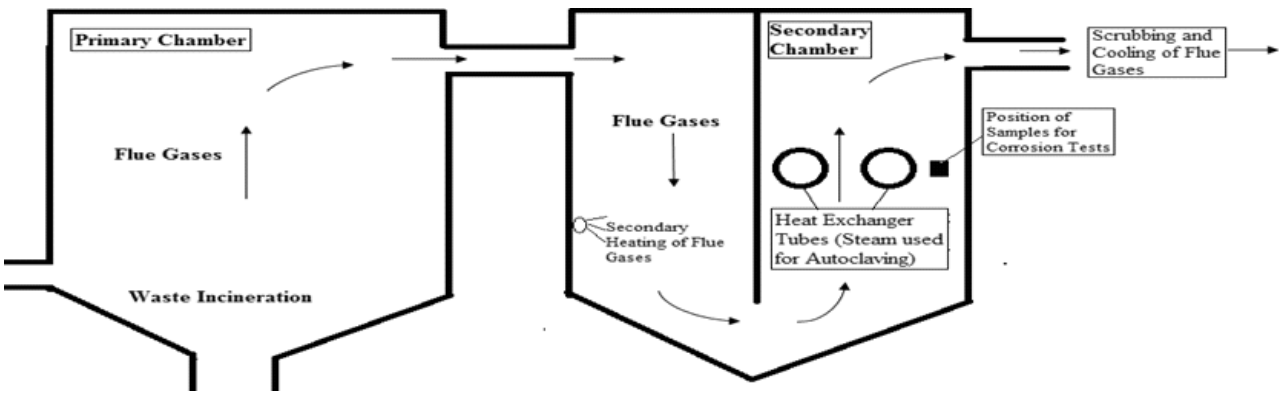


Figure l: Schematic diagram showing the position of specimens in waste incinerator plant.

Results

Corrosion kinetics

The weight change per unit area (mg/cm^2) for the hot corroded coated superalloy for 1000 h exposure to the medical waste based incinerator environment follows parabolic law of rate an d the parabolic rate constants k_p ($g^2cm^{-4}s^{-1}$) found to be: 22.27. The average scale thickness for found to be: 217 μm and the cold spray coated superalloy showed no indication of internal corrosion attack.

SEM/EDX and XRD surface analysis

The diffraction patterns for the corroded coated specimen shows the presence of Cr_2O_3 as major phase along with presence of NiO, Fe_2O_3 and Al_2O_3. The SEM micrograph and EDX analysis on the surface scale formed on uncoated and cold spray coated Superni 601 superalloy after 1000 h exposure to the waste incinerator environment shown in figure 2.

The SEM/EDX analysis shows that the oxide scale formed on the surface of the specimens is interacting with the condensed phases of the ash. The scale is uniform and adherent after 1000 h exposure in waste incinerator environment. There is no indication of cracks and EDX analysis indicates that the white phase (point 2) has composition similar to ash from the surrounding environment. The compact and adherent surface scale has small concentration of Fe and Ni, however, scale is rich in Cr, and oxygen. The presence of Fe in the surface scale can be attributes to the diffusion from the substrate or from deposited ash.

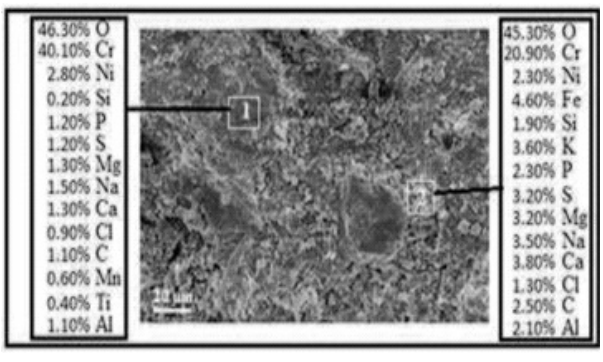


Figure 2: SEM/EDX of surface analysis of corroded coated specimen

SEM/EDX cross-section analysis

The back scattered electron images (BSEI) and EDX analysis of the scale formed on specimen at some selected point of interest across the cross-section after 1000 h exposure to medical waste incinerator environment is shown in figure 3. There is minor diffusion of the elements from the deposits along the cross section of the scale of specimens. BSEI across the cross- section shows that there is formation of oxide scale layer at top surface of the coating, which is directly exposed to the waste incinerator environment, and the remaining coating is adhered to the substrate. The EDX analysis across section shows mainly the presence Cr and oxygen elements with small concentration of Ni at the topmost scale layer of the specimen (point 1 and 2). There is diffusion of Mn and Ti in the coating from the superalloy substrate. Oxygen is found throughout the coating but is restricted (upto point 5) to the scale-substrate interface. EDX analysis also almost confirms the concentration of Ni and Cr in the Ni-20Cr coating especially at point 3 where oxygen concentration is very less. At point 4 there is preferential oxidation of Cr at the splat (point 3) boundary.

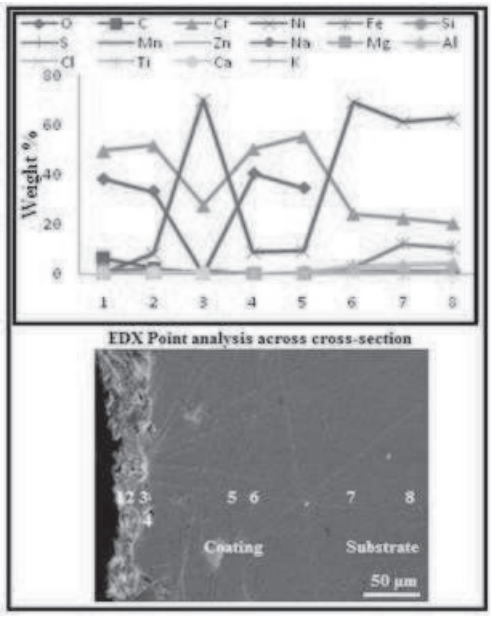


Figure 3: SEM/EDX cross-sectional analysis of corroded coated specimen

Discussion

Despite of the presence of high concentration of Ni compared to Cr in Ni-20Cr coated specimen there is formation of oxide of chromium during exposure of the coated specimen. Though there are various factors, which influence the scale development, but the preferential formation of oxide of chromium as compared to Ni might be due to higher affinity of Cr for oxygen than Ni, and Cr forms more stable oxide and NiO is less stoichiometric oxide than Cr_2O_3.

The Ni-20Cr coating proves to be effective in imparting the necessary protection to all the Ni-based supernisuperalloys, as the weight gain data of specimen follows parabolic rate law. There is no sign of oxidation of substrate superalloy, and there is no adherence loss of coating visible in BSEI micrograph. The SEM micrographs also show the formation of continuous, compact and adherent surface scale though with the presence of embedded ash particles after 1000 h exposure to waste incinerator environment. Therefore, it is conclude that the cold sprayed Ni-20Cr coating is able to provide effective and necessary protection to superalloy in the real service environment of medical waste incinerator.

This can be attributes to the dense structure of the cold sprayed coatings due to the high impact velocity of the particles during cold spray process as compared to other thermal spray processes. In addition, there is no oxidation of the coating particles in the cold spray coating, due to low operating temperature involved. This is the desired structure when the coatings have to perform in corrosive environment at higher temperature since corrosive species mostly propagate through the pores and voids and corrosion usually activates from the oxidized grain boundaries present during thermal sprayed coating processes.

Conclusions

1. The Ni-20Cr coating successfully deposited on superalloy by cold spray process.
2. The dense and strongly adhered coating structure developed is suitable for application in corrosive environment.
3. The protective scale layer of Cr_2O_3 formed on the exposed coated specimen in the waste incinerator environment.
4. The cold spray coating tested in this study is able to increase the life of boiler tubes in incinerator and other similar high temperature and corrosive environments.

Acknowledgment:

Author 'Harminder Singh' and Henna Khosla thankfully acknowledge the research grant sanctioned by the Science and Engineering Research Board, Department of Science and Technology, New Delhi, Govt. of India, under 'Fast Track Young Scientist-Engineering Science Scheme' vide No. SB/FTP/ETA-0366/2012, dated: 17.08.2015.

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Journal of the Electrochemical Society of India

Vol. No. 67 -1 - January - 2018

CODEN - JESIA 67 [1] 1 - 50, 2018 ISSN:0013-466X

Email : ecsiiisc@gmail.com

FROM IV

See Rule VIII

1. Place of publication	:	Bangalore
2. Periodicity of its publication	:	Quaterly
3. Printer name	:	Sri Rajeeva Deekshit, Secretary
Whethe Citizen of india	:	YES
Address of the printer	:	M/s. Print Hut Bangalore - 560 040.
4. Publishers Name	:	Sri Rajeeva Deekshit, Secretary
5. Editor's Name	:	Prof. E.S. Dwarakadasa
Whether Citizen of India	:	Yes
Address	:	**The Electrochemical Society** Indian Institute of Science Bangalore - 560 012
6. Name and Address of Individuals who own the newspaper/holders and partners and shareholders holding more than 1% of the total capital.	:	**The Electrochemical Society** Indian Institute of Science Bangalore - 560 012

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PUBLISHED BY THE SECRETARY FOR THE ELECTROCHEICAL SOCIETY OF INDIA, BANGALORE
PRINTED BY : M/S. PRINT HUT, GOVINDARAJANAGAR, BANGALORE - 560 040