Corrosion performance of Cr$_3$C$_2$-NiCr+0.2\%Zr coated super alloys under actual medical waste incinerator environment

Lalit Ahuja$^1$, Deepa Mudgal$^2$, Surendra Singh$^3$, Satya Prakash$^4$

$^1$Department of Mechanical Engineering, SLIET, Longwol, Sangrur, 148106, India
$^2$Department of Mechanical Engineering, Thapar University, Patiala, 147004, India
$^3$Department of Metallurgical and Materials Engineering, IIT Roorkee, 247667, India

*Corresponding author E-mail: deepamudgal01@gmail.com

Abstract. Incineration techniques are widely used to dispose of various types of waste which lead to formation of very corrosive environment. Such corrosive environment leads to the degradation of the alloys used in these areas. To obviate this problem, zirconium modified Cr$_3$C$_2$-(NiCr) coating powder has been deposited on three superalloys namely Superni 718, Superni 600 and Superco 605 using Detonation gun technique. Corrosion test was conducted in actual medical waste incinerator environment. The samples were hung inside the secondary chamber operated at 1050°C for 1000h under cyclic condition. Corrosion kinetics was monitored using the weight gain measurements and thickness loss. Corrosion products were characterized using scanning electron microscopy, energy dispersive spectroscopy and X-ray diffraction technique. It was observed that coating is found to be successful in impeding the corrosion problem in superalloys.

1. Introduction
In last 20 years, developing countries have adopted incineration technique to dispose off the high volume of industrial, medical and municipal waste because of its advantage of being one of the effective and hygienic methods of disposal. For example, in Western Europe, the number of incinerators is constantly increasing apart from having almost 600 running plants [1]. However, the degradation of boiler due to the usage of different types of waste such as biomass and solid waste fuels have been frequently encountered during the operation which is one of the major causes of unwanted shut down. The major species responsible for the corrosion problems are the presence of chlorine, sulphur, potassium and hydrogen chloride gases either as reactants, products, by-products or as contaminants. These problems generally arise in chemical and metallurgical industries such as waste incinerators, coal-fired boilers, recuperators, plastic/polymer decomposition mills and vinyl chloride monomer mills [2]. The complex and corrosive nature of the incineration environment coupled with high temperatures can lead to premature failure of various metallic components in an incinerator [3]. Hence in the present study, zirconium incorporated chromium carbide nickel chromium coating which was deposited using D-gun technique on different alloys was tested under the actual medical waste incinerators environment. The most corrosive area of incinerator was chosen for the study. The specimens were hung inside the secondary chamber of the incinerator where the temperature was 1050±50°C. The specimens were exposed for 1000 h where each cycle consists of 100h heating followed by 1h cooling.

2. Experimental details
Three superalloys viz. Superni 718, Superni 600 and Superco 605 were procured from MIDHANI, Hyderabad, in hot rolled and annealed condition in the form of plates. The specimens of size 20×15×5
mm were cut down from the plates. The specimens were coated with 0.2wt.%Zr doped Cr$_3$C$_2$-NiCr coating power using Detonation gun technique at SVX Powder M Surface, Greater Noida, India. The specimens were coated form all the six surface. The specimens were drilled so as to hung inside the incinerator using Kanthal wire. For corrosion test the specimens were hung inside the secondary chamber of medical waste incinerator where the temperature is 1050°C for 1000h under cyclic condition. Each cycle consist of 100h heating followed by 1h cooling in ambient air. After 1000h, thickness loss measurements were done to know the corrosion rate in mpy.

3. Results

3.1. Visual Analysis

Visual analysis has been reported to discuss the change in colour of the specimen, if any, occurred throughout the course of exposure. It will also cover if any type of spallation of delamination of coating observed during 1000h of exposure. Visual macro photos for Cr$_3$C$_2$-(NiCr) +0.2wt. %Zr coated Superni 718, Superni 600 and Superco 605 after hot corrosion in actual medical waste incinerator environment at 1050±50°C are shown in figure.1.

![Figure 1. Macrophoto for Cr$_3$C$_2$-25(NiCr) +0.2wt.% Zr coated (a) Superni 718, (b) Superni 600 and (c) Superco 605 after hot corrosion in actual medical waste incinerator at 1050±50°C for 1000hours.](attachment:macrophoto.jpg)

It was observed that the colour of Cr$_3$C$_2$-(NiCr) +0.2wt.% Zr coated Superni 718 (figure.1 (a)) changes to greenish oxide with dark grey background after 100h of exposure. The green colour on the dark grey background got intensified and spread throughout the surface after 200h of exposure. Some yellowish white ash was found to be deposited at the edges. Deposition of mustard brown colour ash was observed from 300h which continued till 1000h. But the intensity of deposition of ash seemed to diminish after 700h of exposure. In case of Cr$_3$C$_2$-(NiCr) +0.2wt.%Zr coated Superni 600 (figure.1(b)), colour of the specimen changed to greenish oxide on dark grey background. Green colour on the surface of the coating intensified and spread throughout the surface. After 500h of exposure deposition of mustard brown colour was observed which continued till 1000h. In case of Cr$_3$C$_2$-(NiCr) +0.2wt.%Zr coated Superco 605 (figure.1(c)), green colour patches were formed on the
dark grey background. The shape and size of the patches started increasing which continued till 500 h. After 600 h of exposure deposition of mustard brown colour ash was seen. This continued till 1000 h.

3.2. **Average thickness loss and corrosion rate in mpy**

Difference of average thickness loss before corrosion and after the 1000 h of exposure for Cr$_3$C$_2$-NiCr+0.2wt.% Zr coated superalloys after corrosion under actual medical waste incinerator was 0.064 mm, 0.071 mm and 0.080 mm respectively. Based on these values, mpy for all the three coated superalloys was calculated and is shown in figure. 2.

![Figure 2](image_url)

**Figure 2.** Bar chart showing corrosion rate for the Cr$_3$C$_2$-(NiCr) +0.2wt.% Zr coated Superni 718, Superni 600 and Superni 605 after 1000 hours exposure in actual medical waste incinerator environment.

3.3. **SEM/EDS**

Scanning electron microscopy analysis showed the morphology of oxide on the surface of the coating. EDS has been done to know the elements present in the oxide scale. In case of Cr$_3$C$_2$-(NiCr) +0.2wt.% Zr coated Superni 718 (figure.3), spongy type massive oxide was observed on the surface of corroded specimen. EDS analysis indicated the existence of chromium and oxygen in major amount along with minor amount of sodium, sulphur, calcium, iron and zinc. Traces of aluminium, chlorine and potassium were also detected. Whereas in case of Cr$_3$C$_2$-(NiCr)+0.2wt.%Zr coated Superni 600 (figure.4), dense and compact oxide was seen along with the melted regions having cracks. EDS analysis indicated the presence of chromium, nickel and oxygen throughout the surface of the corroded coating. EDS analysis detected the presence of chlorine at the sites of melted particles. In case of Cr$_3$C$_2$-(NiCr)+0.2wt.%Zr coated Superco 605 (figure.5), two different types of morphology were observed. White colour clusters showed the presence of sodium, sulphur, calcium, chromium and oxygen. Whereas platelet like spongy morphology indicated the presence of chromium and oxygen in major amount with minor amount of nickel and zinc. Traces of sulphur were also detected.
Figure 3. SEM micrograph along with EDS for Cr$_3$C$_2$-(NiCr) +0.2wt.%Zr coated Superni 718 after hot corrosion in actual medical waste incinerator at 1050°C±50°C for 1000h.

Figure 4. SEM micrograph along with EDS for Cr$_3$C$_2$-(NiCr) +0.2wt.%Zr coated Superni 600 after hot corrosion in actual medical waste incinerator at 1050°C±50°C for 1000h.
Figure 5. SEM micrograph along with EDS for Cr$_3$C$_2$-(NiCr) +0.2wt.%Zr coated Superco 605 after hot corrosion in actual medical waste incinerator at 1050°C±50°C for 1000h.

3.4. XRD
The XRD profiles for the scale of Cr$_3$C$_2$-(NiCr) +0.2wt.%Zr coated Superni 718, Superni 600 and Superco 605 are shown in figure 6. In case of Cr$_3$C$_2$-(NiCr)+0.2wt.%Zr coated Superni 718 and Superni 600, the common major peaks identified after hot corrosion under incinerator environment were Cr$_2$O$_3$, ZnCr$_2$O$_4$, K$_2$ZnCl$_4$, NiCr$_2$O$_4$, CaAl$_2$SiO$_6$, NiCl$_2$ and CaSO$_4$. Whereas in case of Cr$_3$C$_2$-(NiCr) +0.2wt.%Zr coated Superco 605, the peaks identified after hot corrosion run under actual incinerators environment were Cr$_2$O$_3$, NiCr$_2$O$_4$, CaAl$_2$SiO$_6$ and NiCl$_2$.

Figure 6. X-ray diffraction analysis for Cr$_3$C$_2$-(NiCr)+0.2wt.%Zr coated (a) Superni 718, (b) Superni 600 and (c) Superco 605 after hot corrosion in actual medical waste incinerator environment at 1050±50°C for 1000h.
3.5. Cross Sectional Analysis
Cross sectional analysis for Cr$_3$C$_2$-(NiCr)+0.2wt.%Zr coated Superni 718, Superni 600 and Superco 605 are shown in figure 7. In case of Cr$_3$C$_2$-(NiCr)+0.2wt.%Zr coated Superni 718 (figure 7(a)), about 60µm thick oxide was observed on the surface. EDS analysis at point 1 shows the presence of basic elements of the substrates which are nickel, iron, chromium, niobium and titanium. This indicates that during the hot corrosion run in the incinerators environment the substrate remains unaffected from the corrosive species. At the coating substrate interface (point 2), presence of oxygen, niobium, chromium, aluminium and iron was observed along with nickel. The concentration of nickel decreases relatively as present in the substrate. Presence of chromium and oxygen indicated the formation of oxide which might be acting as a diffusion barrier for the cation and anion diffusion after some cycle. Points 4 and 5 which were taken at the dark grey region of the coating showed the presence of chromium along with oxygen. The presence of oxygen at point 4 indicates that this grey phase is chromium oxide, suggesting that the coating has partially oxidized along the splat boundaries. At point 6, chromium and oxygen were indicated while point 7 indicated the existence of chromium, oxygen and calcium with minor amount of sulphur. In case of Cr$_3$C$_2$-(NiCr)+0.2wt.%Zr coated Superni (figure 7(b)), about 65 µm thick porous oxide was observed on the surface. Point 1 shows the presence of only basic elements of the substrate. At point 2 the presence of 8 percent of iron indicates the diffusion of iron from the substrate towards the interface. At point 3 which lies on the dark grey region of the coating, presence of chromium and oxygen was observed thereby indicating the formation of chromium oxide along the splat boundaries. Light grey region that was point 4 shows the absence of oxygen and presence of nickel which reveals that the nickel rich splats remain unaffected from the corrosion.

3.5. X-Ray Mapping
In case of Cr$_3$C$_2$-(NiCr)+0.2wt.%Zr coated Superni 718 (figure 8), a top scale was consists of chromium with oxygen and there was unreacted nickel encapsulated in the Cr$_2$O$_3$ scale. The Cr from the substrate has migrated into the coating thereby leaving a thick band along the coating substrate boundary. On the surface of the scale there was a presence of calcium and aluminium indicating the ash deposition. There was a thin band of chromium oxide just above the interface of substrate and coating. In case of Cr$_3$C$_2$-(NiCr)+0.2wt.%Zr coated Superni 600 (figure 9), a top scale consisting of chromium was formed. The reacting species have further permeated into the coating and chromium oxide has been formed along the unreacted nickel. Silicon and magnesium were seen on the surface of the scale which pertain to ash getting embedded on the scale surface. In the case of Cr$_3$C$_2$-(NiCr)+0.2wt.%Zr coated Superco 605 (figure 10), dense layer of chromium and oxygen can be seen thereby indicating the formation of chromium oxide. Unreacted metal was also present throughout the oxide and oxygen has permeated into the bulk of the coating and got partially oxidized. Presence of calcium on the surface of the coating indicates the deposition of ash.

4. Discussion
Cr$_3$C$_2$-(NiCr)+0.2wt.%Zr coating was successfully sprayed on Superni 718, Superni 600 and Superco 605 using Detonation gun technique. All the three coated superalloys tested under actual medical waste incinerators at 1050°C for 1000 h provide adequate protection to the substrate. Visual analysis clearly (figure 1) shows that the coating remains intact to the substrate even after 1000 h of exposure. Brownish layer observed on the surface indicates the presence of ash deposition on the coated alloys because of the sticky behaviour of the fly ash. SEM micrograph of all the three coated substrates indicated the formation of irregular morphological structure. SEM micrograph of Cr$_3$C$_2$-(NiCr)+0.2wt.%Zr coated Superni 600 (figure 4) showed the presence of cracked oxide mainly consisting of chromium, nickel, oxygen and chlorine.
Figure 7. Oxide scale morphology and variation of elemental composition across the cross section for Cr$_3$C$_2$-(NiCr)+0.2wt.%Zr coated (a) Superni 718, (b) Superni 600 and (c) Superco 605 after hot corrosion in actual medical waste incinerator environment at 1050±50°C for 1000h.
Figure 8. BSEI and X-ray mapping of the cross section for Cr$_3$C$_2$-(NiCr)+0.2wt.%Zr coated Superni 718 after hot corrosion in actual medical waste incinerator environment at 1050°C±50°C for 1000h.
Figure 9. BSEI and X-ray mapping of the cross section for Cr$_3$C$_2$-(NiCr)+0.2wt.%Zr coated Superni 600 after hot corrosion in actual medical waste incinerator environment at 1050°C±50°C for 1000h.
Figure 10. BSEI and X-ray mapping of the cross section for Cr$_3$C$_2$-(NiCr)+0.2wt.%Zr coated Superco 605 after hot corrosion in actual medical waste incinerator environment at 1050°C±50°C for 1000h.
EDS analysis of the surface morphology of three coated superalloys showed almost similar elemental composition present on the surface. Chromium, nickel and oxygen were found in major amount which shows that Cr₂O₃ and NiCr₂O₄ might have formed on the surface of the coated specimen which may protect the coating from degradation. Presence of various elements such Na, Mg, Al, Si, S, Cl, Ca, K and Zn was indicated by EDS analysis. As these elements neither present in the coating nor in the substrate. Hence it was assumed that these elements found because of the deposition of fly ash present in the secondary chamber of the incinerator. Composition of the fly ash depends upon the type of fuel burnt in the incinerator in primary chamber. The most abundant elements found in Municipal waste incinerator are Si, Al, Fe, Ca, Mg, K, Na and Cl along with heavy metal such as Pb and Zn [4].

X-ray diffraction analysis (figure.6) for all the three coated superalloys showed the formation of Cr₂O₃ and NiCr₂O₄. The oxides of chromium and spinel were mainly responsible for providing protection to the coating. Presence of NiCl₂ was also seen which might have formed because of the reaction between the chlorine and Nickel. Deb et al.[5] reported the hot corrosion attack by 75%Na₂SO₄-25%NaCl where NaCl reacts with the oxides releasing chlorine, which in turn reacts with the oxides to form volatile chlorides. Reactions are given below from equation (1)-(2).

\[ 2Cr_2O_3(s) + 6Cl_2(g) = 4CrCl_3(g) + 3O_2(g) \] .................................(1)
\[ NiO(s) + Cl_2(g) = NiCl_2(g) + 1/2O_2(g) \] .................................(2)
\[ Cr(s) + 3/2Cl_2(g) = CrCl_3(g) \] .................................(3)
\[ Ni(s) + Cl_2(g) = NiCl_2(g) \] .................................(4)

Existence of NiCl₂ was seen because of its high melting point as compared to chlorides of other protective elements. Chang et al. [2] reported the melting point of all the possible chlorides formed in presences of chlorine and indicated that meting point of NiCl₂ is 1050°C as can be seen from Table.1.

Table 1. Melting point (Tm) and temperatures (T4) at which the chloride vapour pressure is equal to 10⁴ atm [2].

| Chloride | Tm(°C) | T4(°C) |
|----------|--------|--------|
| FeCl₃    | 676    | 536    |
| FeCl₂    | 303    | 167    |
| NiCl₂    | 1030   | 607    |
| CrCl₂    | 820    | 741    |

The chlorine present in the form of either Cl₂ or hydrogen chloride might have formed metal chlorides after reacting with metal as per the eq (5). Direct reaction of metal with hydrogen chloride has been given in reaction (6). Because of the higher vapour pressure of the metal chlorides at the substrate-oxide interface, it will change the state and convert into gaseous as shown in eq (7).

\[ M(s) + Cl_2(g) = MCl_2(s) \] .................................(5)
\[ M(s) + 2HCl(g) = MCl_2(g) + H_2(g) \] .................................(6)
\[ MCl_2(s) = MCl_2(g) \] .................................(7)

where \[ M\{Fe,Cr,Ni\} \]

\[ Ni + Cl_2 = NiCl_2 \] .................................(8)

The oxidation of nickel to nickel chloride has a positive Gibbs free energy implying that it will not occur spontaneously. Thus if nickel is converted to nickel chloride, it is more likely to be detected within the corrosion products where the partial pressure of chloride is relatively high [2]. Formation of CaSO₄, Na₂SO₄, CaAl₂SiO₆, K₂ZnCl₄ and ZnCr₂O₄ was also indicated from XRD (figure.6).
Cross sectional analysis (figure 7) for all the three superalloys showed the formation of thick oxide on the top of the coating. Although the oxide formed was found to be porous from the subscale region because of the presence of highly corrosive species in the environment. But there was no indication of internal oxidation within the substrate which shows that the coating was successful in protecting the substrate. Addition of zirconium in the coating was found to enhance the corrosion resistance. Rare earth elements help in forming the layer of chromium oxide at early stage and do not allow any further diffusion of the corrosive species. As rare earth elements have tendency to segregate on the particle boundary, thus blocking the boundaries against any penetration of the corrosive salt species. It was also noticed that oxygen was found on the top of the oxide layer as well as along the coating substrate interface. At coating substrate interface the oxygen was found with aluminium and chromium, thereby indicating the formation of either Cr₂O₃ or Al₂O₃. Oxygen might have come during the in-flight of coating powder particles at the time of deposition. This oxygen combined with chromium after exposed at high temperature and formed a thin layer of chromium oxide at the coating substrate interface. The oxide so formed will not allow any further inter diffusion between the coating and substrate. It is also assumed the oxide on the coating substrate interface might be some Al₂O₃ which might have come from the preserve particles of alumina which were grit blasted before coating deposition [6].

Figure 11. Possible corrosion mechanism for Cr₃C₂-(NiCr)+0.2wt.%Zr coated Superco 605 after hot corrosion in actual medical waste environment for 1000 hours at 1050±50°C.

X-ray mapping for Cr₃C₂-(NiCr)+0.2wt.%Zr coated Superni 600 (figure 9) clearly showed the presence of magnesium and silicon at the top of the oxide scale on the surface of the coating. Bankiewicz et al. [7] reported that presence of calcium and silicon in the ash does not add to the corrosion enhancement as compound of calcium and silicon remain inert. X-ray mapping for Cr₃C₂-(NiCr)+0.2wt.%Zr coated Superni 718 (figure 8) and Superco 605 (figure 10) also indicated the presence of calcium on the top of the oxide scale. Presence of sodium, sulphur, calcium and magnesium showed the deposition of fly ash on the corroded coated superalloys. Possible corrosion mechanism for Cr₃C₂-(NiCr)+0.2wt.%Zr coated Superco 605 after hot corrosion in actual medical
waste environment for 1000 hours at 1050°C has been shown in figure 11. Chromium oxide and spinels have formed just above the coating. The ash was deposited on the top of this protective oxide scale.

5. Conclusion
1. Cr$_3$C$_2$-NiCr+0.2wt.%Zr coating deposited on three superalloys was found to be successful in providing adequate corrosion protection to the substrates in aggressive environment
2. XRD analysis showed the presence of Cr$_2$O$_3$, ZnCr$_2$O$_4$, K$_2$ZnCl$_4$, NiCr$_2$O$_4$, CaAl$_2$SiO$_6$, NiCl$_2$ and CaSO$_4$ phases in case of all the three coated substrates indicating the deposition of ash on the surface.
3. X-ray mapping showed the existence of Mg and Si together thereby indicating the presence of magnesium silicate.
4. Cross sectional analysis indicated the presence of chromium and oxygen on the surface of all the three substrates

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