Cyclic Oxidation Behaviour of D-gun sprayed Cr_3C_2 -25(NiCr) coating for High Temperature Applications

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Abstract:

Addition of small amount of rare earth material greatly enhance the coating property at high temperature. Cr_3C_2-(NiCr) is well known for its corrosion and erosion resistance property at high temperature. The present paper describe the high temperature oxidation of chromium carbide nickel chromium on Ni based superalloy at 900°C under cyclic condition and the effect of adding 0.2%wt Zr in chromium carbide nickel chromium coating on high temperature oxidation resistance has been studied using thermogravemtric technique. Characterization of Oxide scale has been done using FESEM, XRD, EDAX, X-ray mapping and cross sectional analysis

Keyword: Rare earth, Superalloy, Oxidation, FESEM, XRD.

Introduction:

Power plant boiler, turbines, chemical industries are facing corrosion problem due to the presence of high temperature and pressure. Although superalloys are widely used in such applications but these materials also start deteriorating after some time. Hence, coatings are generally used to protect the surface of an alloy that has been developed for strength but does not have sufficient intrinsic resistance to high temperature corrosion [1]. Thermal spray processes have been used successfully to produce varieties of protective coatings for wear, corrosion and heat resistance [2]. There are several different thermal spray technologies to apply coatings to substrates including conventional plasma, vacuum plasma, wire arc metalizing, and high velocity oxyfuel (HVOF) and gas detonation processes [3]. Among thermal spray methods, detonation spraying has always been characterized by the best quality of the coatings it produces [4]. It can be considered that D-gun coating is the best technique from the viewpoint of coating density and coating exhibits lamellar structure [2]. In the present study, chromium carbide nickel chromium coating has been sprayed using D-gun technique. Ni and Cr based coatings containing CrC particles dispersion (hard phase), are very attractive due to their excellent oxidation resistance [5]. It has been reported that more than 20% of Cr in substrate provide best corrosion resistance but Nickel alloys containing more than 20 percent chromium are extremely difficult to fabricate by conventional hot working processes because of the development of a brittle alpha chromium phase. In addition, high-chromium nickel- based alloys are susceptible to a decrease in ductility after exposure to elevated service temperature [6]. Hence chromium carbide nickel chrome coating is found to be beneficial for high temperature oxidation resistance. Adding rare earth elements provide additional benefits to the coating. Various mechanisms have been proposed to explain the effect of rare earth elements on improving oxidation resistance. The mechanism most widely accepted explains the improvements observed in high temperature oxidation of alloy containing RE, as being due to the diffusion of the RE ions to oxide scale grain boundaries and blocking of alloy cation diffusion along these paths[7]. The present paper describe the high temperature oxidation behaviour of D-gun sprayed chromium carbide nickel chromium coating on Ni based superalloy at 900°C under cyclic condition and the effect of adding 0.2%wt Zr in chromium carbide nickel chromium coating on high temperature oxidation resistance has been studied using thermogravemetric curve. Oxide scale characterization has been done using FESEM, XRD, EDAX, X-ray mapping and cross sectional analysis.

2. Experimental Details:

2.1 Substrate materials

Ni based superalloy Superni 600 (Cr -15.5, Fe-10max, Mn-0.5, C-0.2 Ni-Bal.) has been procured from Mishra Dhatu Nigam Ltd, Hyderabad, in the form of rectangular sheets in hot rolled and annealed condition.

2.2 Coating powder

Commercially available Cr_3C_2-25(NiCr) coating of particle size 10µm to 45µm has been used to spray on the substrate using D-gun technique.

2.3 Formulation of coating

Ni based superalloys Superni 60 has been used in present investigation which has been procured from MIDHANI, Hyderabad, India in rolled and annealed form. The specimen of size 20x15x5(mm) were from the sheet and polished using 220, 320, 400, 600 and 800 grit size emery paper followed by cloth polishing using alumina of 0.3micron. Then, the samples were degreased with acetone and grid blasted to rough the surface of the specimen using alumina powder just before coating the substrate using D-gun technique. A commercially available chromium carbide nickel chromium powder has been used for depositing on the substrate. The particles are of spherical shape with an average size varying from 10µm-35µm. Detonation gun process was used to deposit the coating powder at SVX powder M Surface Pvt. Ltd, Greater Noida, India. Parameters set by the firm for coating are shown Table1. All the process parameters, including the spray distance, were kept constant throughout the coating process. Around 200µm thick coating was deposited with a detonation gun.

Table 1. Parameters of Detonation gun.

Parameters	Cr3C3-NiCr coating
Oxygen/acetylene flow rate	1:1.21
Carrier gas flow rate N_2(m^3/hr)	0.96
Frequency (shots/s)	3
Diameter of spot (Shot size)mm	20
Spraying distance from Nozzle	165
Powder flow rate (gram/shot)	1-2

2.4 Experimental

The specimens of size 20 x 15 x 5 (mm) were polished using 220, 400, 600 and 800 grit size emery paper followed by cloth polishing using alumina (1µm) for mirror finish. After that the dimensions of the sample were taken using sylvac digital vernier calliper (swiss make, resolution 0.01mm) to calculate the surface area of the substrate. The substrates were washed with distilled water and cleaned with acetone. The uncoated and coated samples were exposed to cyclic oxidation in a silicon carbide Horizontal tube furnace at 900˚C for 1 hr followed by 20 min cooling in ambient air. All these prepared samples were subsequently subjected to the cyclic hot corrosion tests for 100 cycles at 900˚C. During the experimentation, each sample was kept in alumina boat and the weight of the boat and specimen was measured, which was taken as the initial weight for the concerned sample at the start of experiment. Weight measurements were done after every cycle using weighing balance of 1mg accuracy to find out the corrosion kinetics using thermogravemetric technique.

3. Results

3.1 Visual observation

The coated superalloys during oxidation in air at 900°C exibits good oxidation resistance. The greenish scale appeared on the surface of coated superalloys. During initial cycles the colour was dark grey with green patchs which intensified with progressive cycles.

3.2 Thermogravemtric analysis

The kinetics of oxidation was determined from weight change (mg/cm^2) versus time plots for the coated four superalloys subjected to oxidation in air environment at 900°C upto 100 cycles is shown in Figure 1(a). The curves shows an initial weight gain in all cases. During the initial period, oxidation of the free surface of the coated superalloys resulted in high oxidation rate. While (Weight gain/area) ^{2} Vs. Number of cycles curve plotted as shown in Figure 1(b) to calculate the parabolic rate constant.

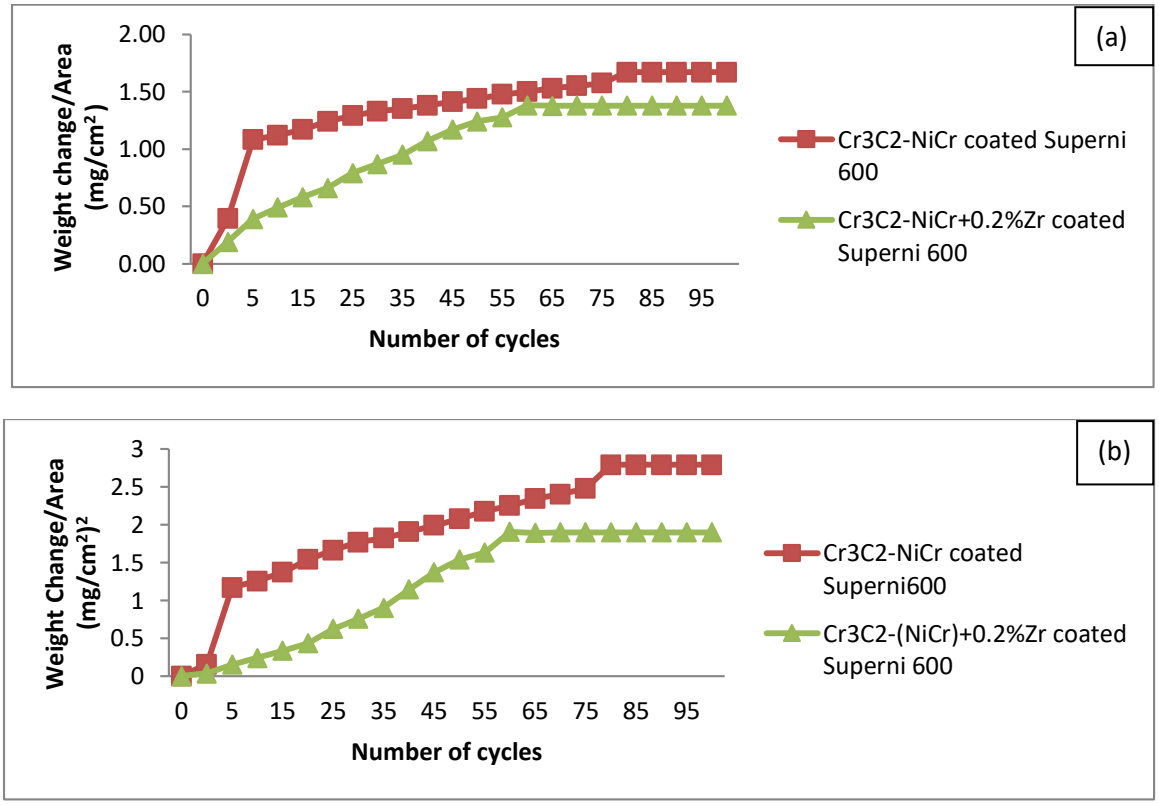

Figure1 (a) (Weight gain/area) vs. Number of cycles plot for and (b) (weight gain/area) ^{2} Vs. Number of cycles plot for specimens subjected to cyclic oxidation at 900˚C after 100 cycle.

Table1. Parabolic Rate Constant

Sample	**Parabolic Rate Constant (gm^2 cm^{-4} sec^{-1})**
Cr_3C_2-NiCr Coated SN 600	0.31 x 10^{-10}
Cr_3C_2-NiCr+ 0.2%wtZr coated SN 600	0.28 x 10^{-10}

3.3 FESEM/EDAX

FESEM micrographs (Figure2) reveal the surface morphology of the Cr_3C_2-NiCr coated substrate superalloys specimens after cyclic oxidation in air environment for 100 cycles at 900°C.

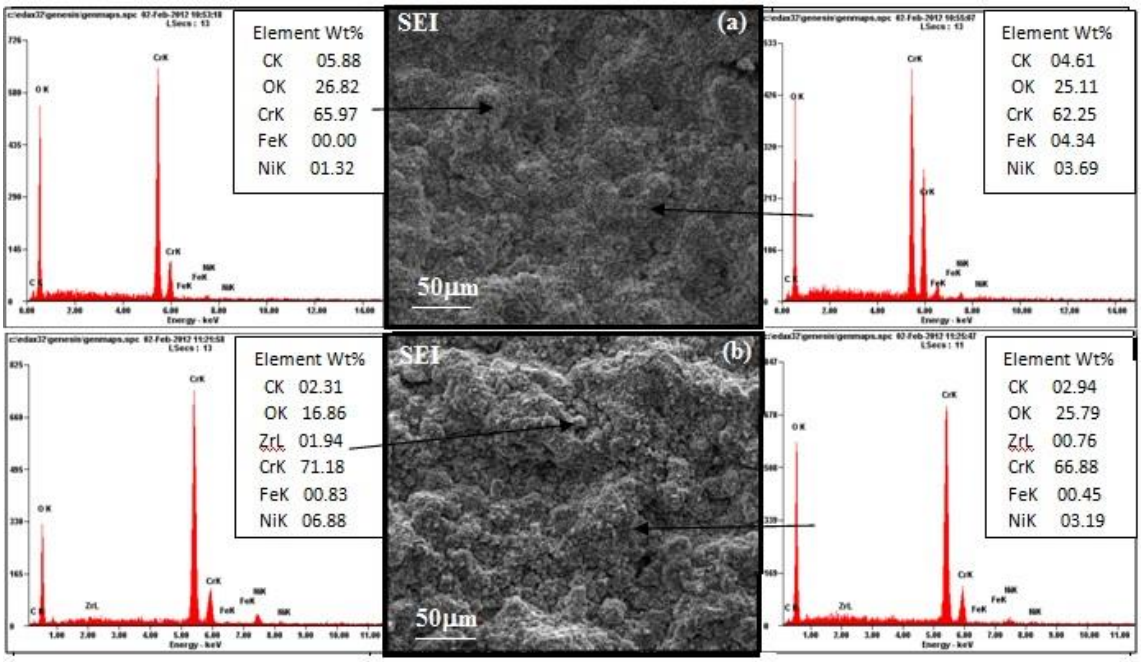

Figure2 FESEM/EDS of (a) Cr3C2-25(NiCr) coated SN 600 and (b) Cr_3C_2-25(NiCr)+0.2%wtZr coated SN600 subjected to cyclic oxidation at 900C for 100 cycles in air environment.

3.4 XRD analysis

The X-ray profiles for the scale of D-gun sprayed Cr_3C_2-25(NiCr) coated and Cr_3C_2-25(NiCr)+0.2wt%Zr coated Superni 600 after cyclic oxidation for 100 cycles at 900°C are shown in Figure3 (a) and (b) respectively. The phases detected at the coated specimens are Cr_2O_3, Cr_7O_3, $Cr_{23}C_6$, NiO and $NiCr_2O_4$ spinel. An extra peak of ZrO_2 was observed in case of Cr_3C_2-25(NiCr)+0.2wt%Zr coated Superni 600.

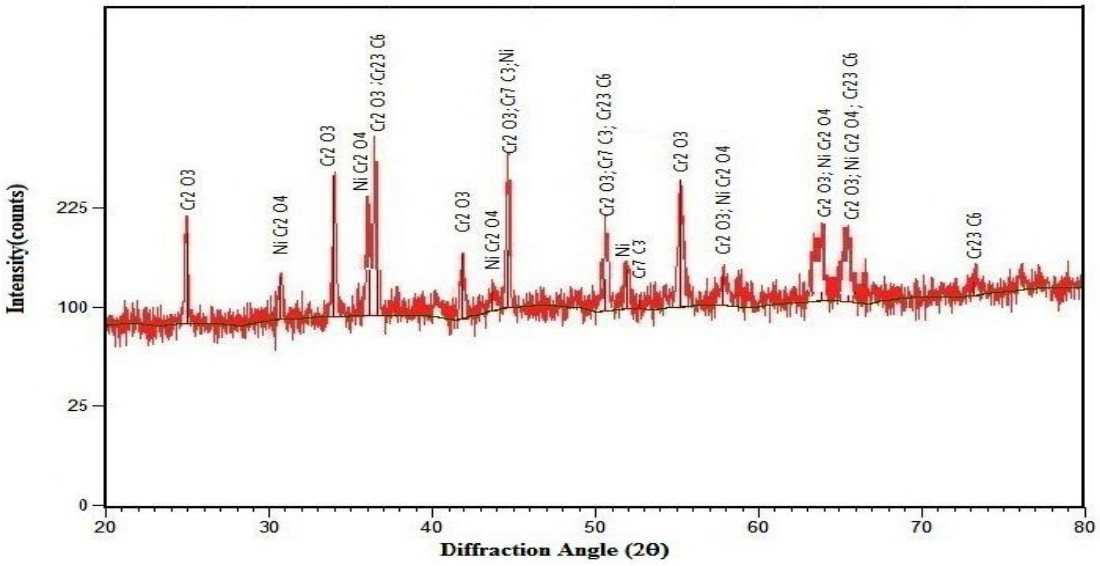

Figure.3 (a) XRD pattern of Cr_3C_2-25(NiCr) coated Superni 600 subjected to cyclic oxidation in air for 100 cycles at 900ºC

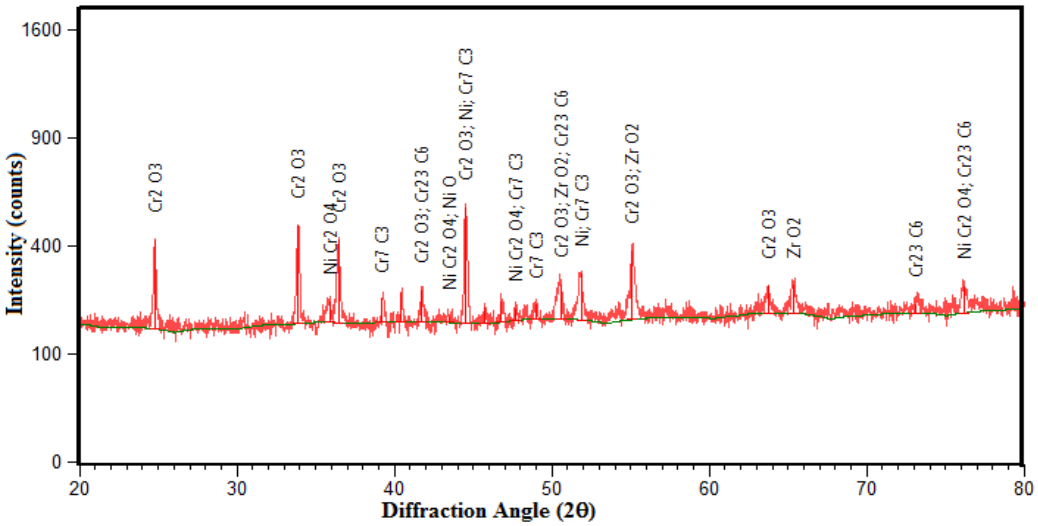

Figure. 3(b). XRD analysis of Cr_3C_2-25(NiCr) +0.2%Zr coated Superni 600 subjected to cyclic oxidation at 900˚C in air after 100 cycles.

3.5 Cross sectional analysis

The D-gun coated Cr_3C_2-25(NiCr) coated superalloy samples after air oxidation for 100 cycles at 900°C, were cut across the cross-sections and mounted in transoptic mounting resin. The samples were mirror-polished. Before inserting inside the SEM, silver paste was applied between samples and stub in order to have conductivity. After that gold coated to facilities FESEM/EDS of the different elements across the scale. FESEM/EDS analysis was carried out at different points of interest along the cross-section of oxidised coated Superni 600 and the results are shown in Figure 4(a) and (b). In all the cases, a dense and adherent oxide scale has formed on the coated superalloys, which has retained its dense structure. FE-SEM micrograph across the cross section of Cr_3C_2-25(NiCr) coated Superni 600 alloy after 100 cycles at 900°C in air indicates an oxide layer on the top surface (Figure 4 point1) mainly consisting of chromium and nickel rich oxides, further in the subscale region at points 2, 3, 4 and 5 the presence of Cr and Ni rich elements was observed in the coating.

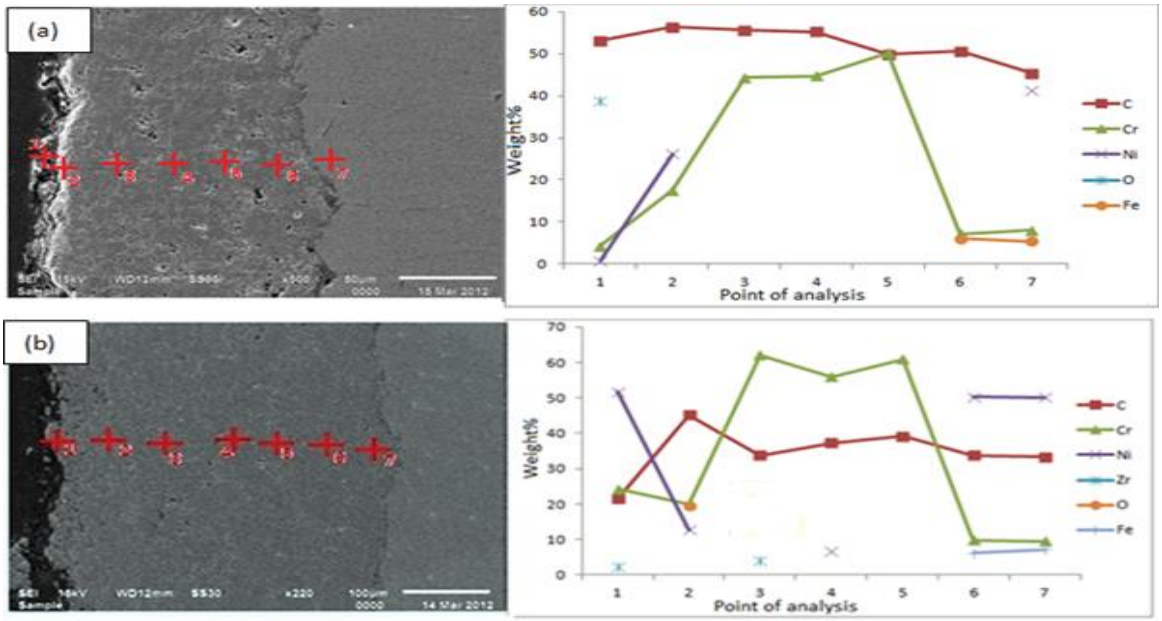

Figure.4 Cross sectional microstructure of (a)Cr_3C_2-25(NiCr) coated SN600 and (b) Cr_3C_2-(NiCr)+0.2%wtZr coated SN600 subjected to cyclic oxidation at 900°C for 100 cycles in air environment.

3.6 X-ray Mapping

X-ray mapping of air oxidised Cr_3C_2-25(NiCr) coated Superni 600(Figure 5) shows very thin oxide scale mainly consisting of chromium in the top scale, in the sub scale region, Ni-rich splats are found mostly at places where Cr is depleted. Oxygen penetration is restricted to the top surface of the coating but its presence at the coating-substrate interface may be either due to the in-flight oxidation of coating material or oxygen might have penetrated during initial cycles of air oxidation run along the intersplat boundaries. The X-ray mappings for Cr_3C_2-25(NiCr)+0.2%Zr coated superni600 after 100 cycles of oxidation in air environment at 900°C (Figure 6.) indicated that only top layer of the coating has been oxidised. The oxide scales mainly consist of Cr_2O_3

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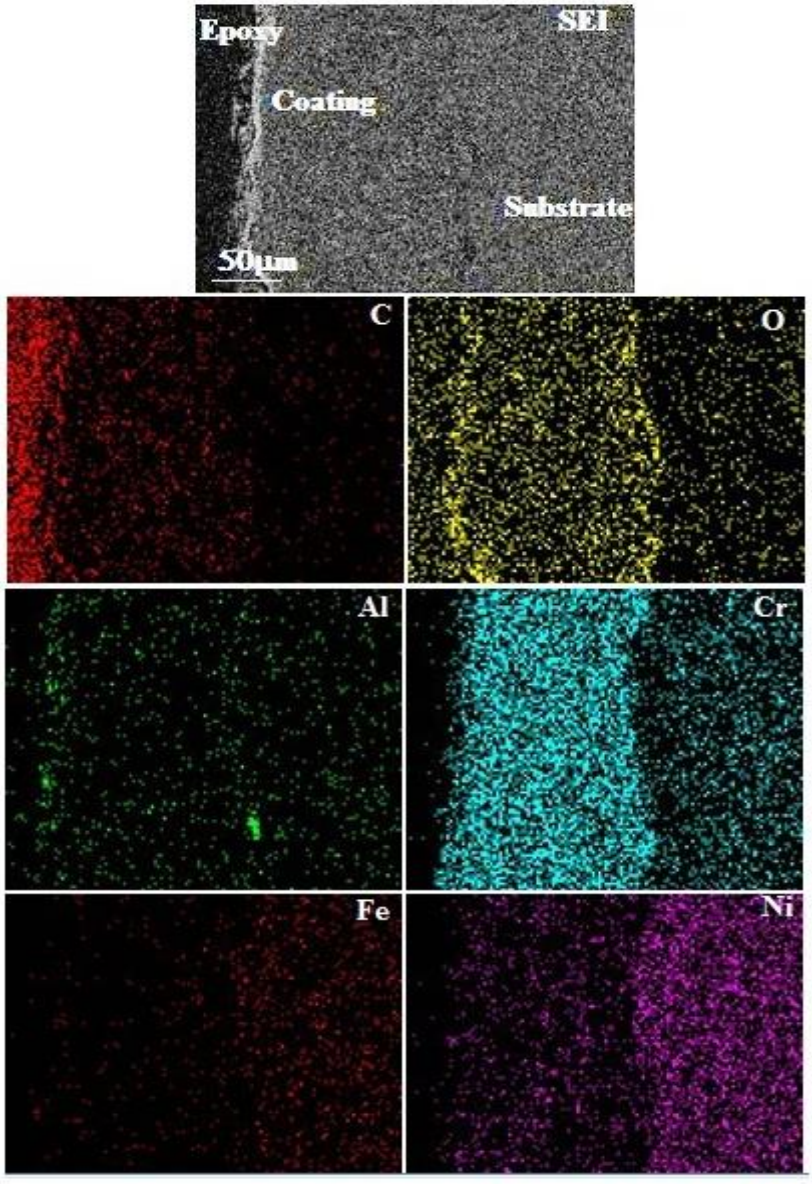

Figure. 5 X ray mapping of of Cr_3C_2-25(NiCr) coated SN600 subjected to oxidation at 900°C for 100 cycles in air environment.

3.7 Discussion

Figure 1(a) shows the graph of Weight change/ surface area vs. number of cycles. The weight gain of both the specimens are relatively high during first few cycles of oxidation, but subsequently increase in weight gain is found to be gradual and become constant after some cycles. The initial high weight gain of coated specimens might be attributed to air which is entrapped during D-gun deposition and sheltered in pores, since the cooling of the coating was rapid, there is shortage of time for residual air to react with the surrounding coating alloys [8]. In comparison, Zr added coating shows lesser gain in weight. Higher weight gain was observed in case of Cr3C2-25(NiCr) coated superalloy as can be inferred from the histogram shown in Figure 7. This may be due to the effect of Zr (rare earth) which increases

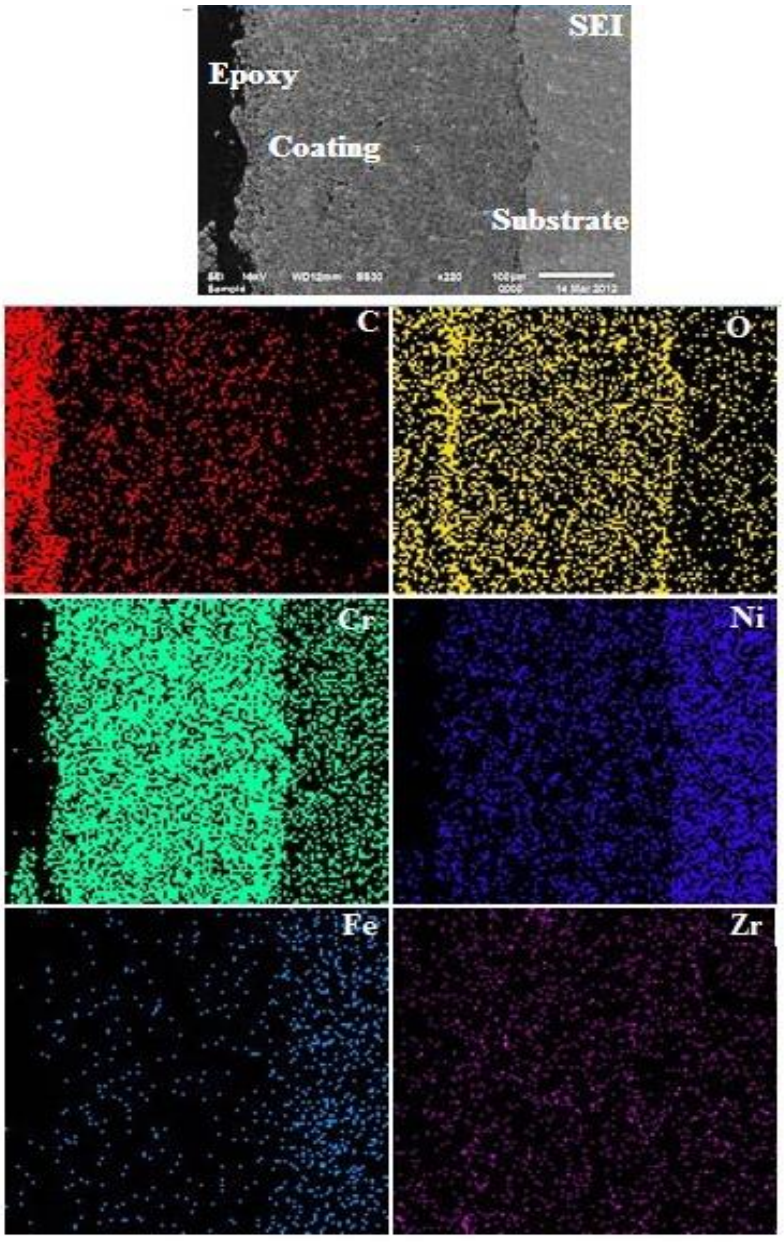

Figure .6 X-ray mapping for Cr_3C_2 (NiCr) +0.2wt%Zr coated SN600 subjected to cyclic oxidation at 900°C for 100 cycles

25Cr20Ni alloy at 950˚C under low oxygen partial pressure was investigated which concluded that small amount of Ce promoted oxidation resistance [9]. It was also discussed in the literature that the increase in oxidation resistance of chromia forming alloys in the presence of REEs is due to changes in the cation diffusion process. This is brought about by segregation of REEs to the grain boundaries of the scale, and consequent variations in ionic defect concentrations [10]. Both the coatings behave in same manner during oxidation and found to be adherent. FESEM images (Figure 2) shows that the oxide formed on the surface of the coating were compact, adherent and non porous.

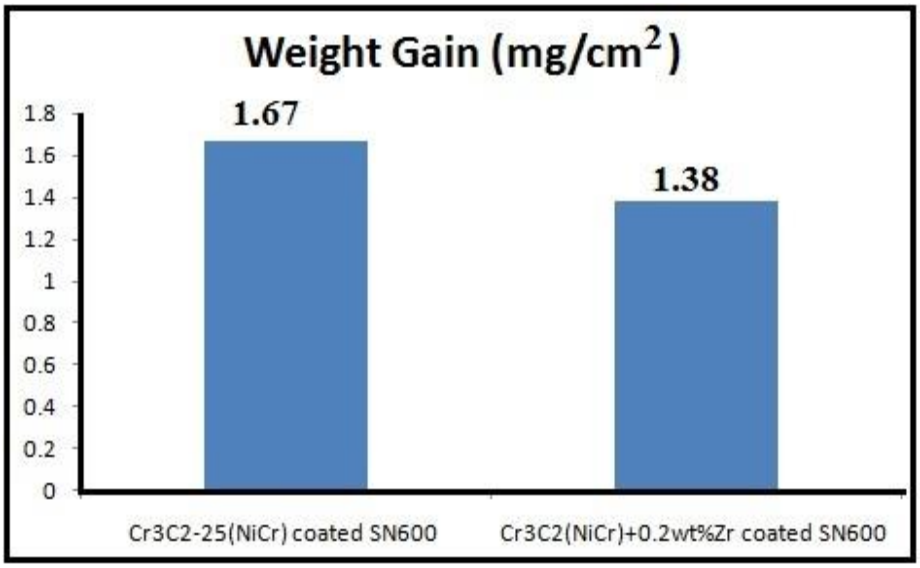

Figure 7. Cumulative weight gain for Cr_3C_2(NiCr) and Cr_3C_2(NiCr)+0.2wt%Zr coated SN600 subjected to cyclic oxidation at 900°C for 100 cycles.

X-ray diffraction technique reveals the presence of phases namely Cr_7C_3 and $Cr_{23}C_6$, Cr_2O_3 and NiC_2O_4 in major amount on Cr_3C_2-25(NiCr) coated super alloy subjected to cyclic oxidation at 900°C after 100 cycles as shown in Figure 3(a). While no peak of Cr_3C_2 was found which inferred that Cr_3C_2 was converted into either $Cr_{23}C_6$ or Cr_7C_3. Out of these phases, $Cr_{23}C_6$ is the most stable compound while Cr_3C_2 is the least stable at high temperature [11].

The stability of $Cr_{23}C_6$ can be determined by the enthalpy and temperature graph in which Gibbs free energy is shown at different temperature (Figure 8). Clearly, it can be seen from the graph that at high temperature Cr_3C_2 phase has positive Gibbs free energy and $Cr_{23}C_6$ has negative free energy which prove that at high temperature, formation of $Cr_{23}C_6$ phase is feasible [12].

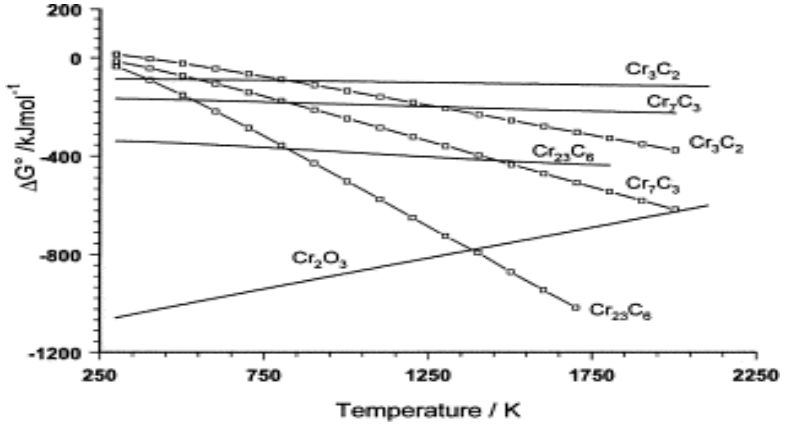

Figure.8 Evolution of the standard free enthalpy of formation for various chromium compounds and of the standard free enthalpy of reaction between chromium and methane to form various chromium carbides [12].

Also, it was discussed in the literature that the oxidation of Cr_3C_2 (orthorhombic structure) leads to decarburization and results the formation of Cr_7C_3 (orthorhombic crystal structure) and $Cr_{23}C_6$ (FCC) can be observed from XRD analysis [13]. Another major phase which seems to be existing in the oxide layer is Cr_2O_3 which is due to the affinity of chromium towards the oxygen to form such phase [14] [15] [16] [17].An extra phase of ZrO_2 was observed in Cr_3C_2-25(NiCr)+0.2wt%Zr as shown in Figure 3(b). Cross sectional analysis given in Figure 4 also confirms the presence of chromium and oxygen throughout the coating which inferred that the chromium oxide phase is formed predominantly in the coating with some chromium carbide. In both the cases oxides layer formed is found to be very thin. Around 7µm of oxide was formed on both the coatings. X-ray mapping (Figure6) shows that chromium and oxygen along with nickel are uniformly distributed throughout the coatings. While at the top of the oxide and at the coating substrate interface chromium and oxygen are present in higher amount, which shows that chromium oxide gives protection at the substrate coating interface as well as top of the coating.

3.8 Conclusions

1. 0.2%wtZr+Cr_3C_2-NiCr coating showed 17.3% lesser gain in weight as compared to Cr_3C_2-NiCr coating.
2. Oxide layer formed after oxidation was compact and adherent.
3. Major phases formed after cyclic oxidation was $Cr_{23}C_6$, Cr_7C_3, Cr_2O_3 and $NiCr_2O_4$.
4. Thin oxide layer of about 5µm approx was formed on the surface of the coated specimens subjected to oxidation at 900˚C after 100 cycles.

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