

Comparative study on high temperature oxidation behaviour of CoCrAlY coatings by various reinforcement composition profile analysis

In this article, high temperature oxidation behaviour of plasma sprayed carbides and oxides reinforced composite CoCrAlY coatings were investigated at 700°C. CoCrAlY was reinforced with Al_2O_3 +YSZ, CeO_2 , WC-Co, Cr_3C_2 -NiCr individually to produce four different coatings.

SEM, EDS and XRD are used to analyze the oxide scales formed during oxidation process on the coatings surface. From the results it is found that, all these coatings exhibited parabolic weight gain nature, indicating presence of protective oxide scale on coating surface, whereas changes in total weight gain is observed. CoCrAlY+ Al_2O_3 +YSZ coatings exhibited higher oxidation resistance than other coatings. The distribution of thermodynamically stable α - Al_2O_3 in the coating is shown slow-scale growth kinetics during the oxidation.

1.0 Introduction

The plasma sprayed MCrAlY coatings are commonly deposited as thick coatings on large industrial components to lengthen service life under oxidising atmosphere (Wu et al. 2001).

MCrAlY coatings (M=Co, Ni or both) is generally employed to prevent oxidation and hot corrosion up to 1100°C. However, these coatings are reported to be undesirable for the applications in wear conditions, since its lower hardness leads to severe material loss (Bolelli et al. 2015). Oxide coatings individually used for high temperature thermal cycling, corrosion and thermal barrier purpose, but more prone to severe erosion loss by brittle cracking (Amaya et al. 2009).

There are many high temperature applications such as compressor outlet blades, vanes and disks, turbine exit blades,

vanes and disks and turbine inlet disks and outer casing where high temperature oxidation, corrosion and wear problems predominate (James and Rajagopalan 2014).

In recent years attempts have been made to improve the traditional MCrAlY coatings by addition of reactive elements such as Ti, Zr, Hf, Si, Ta, Ce, Ru, Ir, and Mo (Yuan et al. 2015). However, these changes are not beneficial for critical environment like combined oxidation, corrosion wear and erosion. Further, the MCrAlY coating is reinforced with carbides and oxides to combat against both high temperature oxidation and wear degradations (Nithin et al. 2017).

Carbides such as WC and Cr_3C_2 coatings with minor amount of metallic binder are used for high temperature wear resistant applications. Although these coatings have excellent wear behaviour, they are not most preferable in high temperature oxidation and corrosion environments (Zhang et al. 2016). The addition of oxide particles to high temperature coating materials strengthens the coating and eventually increases the hardness and wear resistance. (Bobzin et al. 2008) studied wear behaviour of 10 wt.% YSZ oxide of reinforced in NiCoCrAlY coating at 700°C.

Most of the research articles published associated with hard phase reinforced composite coatings focussed on tribological behaviour and phase evolution (Ramesh et al. 2010, Nithin et al. 2018). However, the studies on high temperature oxidation behaviour of these composite coating is on high demand since these composite coatings exposed to various environment.

Hatami et al, (2018) studied the oxidation behaviour of 0, 5, 10 and 15% YSZ mixed with the commercial CoNiCrAlY powder HVOF sprayed coatings. The result reported that coating with 5% YSZ obtained the better oxidation resistance at 1000°C. Similarly, Ghadami et al, (2020) investigated the oxidation behaviour of HVOF sprayed CeO_2 -gradient NiCrAlY coatings at 1000°C. It is reported that functionally graded NiCrAlY/nano- CeO_2 coating had a better oxidation resistance as well as a lower oxide growth rate compared to the rest of the mono-layered coatings due to controlling Al and O

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diffusion due to the formation of relatively thin, dense, and sticky Al_2O_3 oxide scale.

In the present work, attempt has been made to develop four different coatings by addition of different oxides and carbides reinforcement such as Al_2O_3 , CeO_2 , WC and Cr_3C_2 with CoCrAlY coating. A comparative study on cyclic oxidation behaviour of these plasma sprayed composite coatings at 700°C have been studied and reported in this paper.

2.0 Experimentation

2.1 COATING POWDER AND DEPOSITION

The Co based composite powder of CoCrAlY (23Cr-13Al-0.65Y-bal Co) was reinforced with Al_2O_3 +YSZ (28%+2%), CeO_2 (2%), WC-Co (30%), Cr_3C_2 -NiCr (30%) exclusively to produce feedstock. The coating powders are developed by using mechanical mixing. The coating powders are CoCrAlY+28% Al_2O_3 +2% YSZ and CoCrAlY+2% CeO_2 were coated on the bond coat by plasma spray technique. The reinforcement was added in weight percentage.

The spraying parameters specified by the feedstock powder manufacturer were used during plasma spray deposition. METCO USA 3MB equipment was used to conduct the coating by plasma spray technique. The parameters are listed, powder feed rate of 60 g/min; Ar and H_2 flow rate of 40 L/min and 7 L/min; current of 490 A; voltage of 60V. Coating particle size is between -45+15 μm .

2.2 HIGH TEMPERATURE OXIDATION STUDIES

The oxidation behaviour of plasma sprayed CoCrAlY+ Al_2O_3 +YSZ, CoCrAlY+ CeO_2 , CoCrAlY+WC-Co and CoCrAlY+ Cr_3C_2 -NiCr. The oxidation studies was conducted in static air for 50 cycles at the temperature of 700°C . The specimens were visually examined at the end of each cycle. Thermogravimetry technique is used to study the reaction rate and kinetics of the oxidation process. The identification and structural investigation of reaction products of the oxidized specimens were made by means of the XRD and SEM/EDAX techniques. The results have been compiled in different sections of the chapter to assess the performance of each coating.

3.0 Result and discussion

The cumulative weight gain (mg/cm^2) plots of CoCrAlY+ Al_2O_3 +YSZ coatings as a function of time expressed in number of cycles are shown in Fig.1. The overall weight gain after 50 cycles of oxidation of the CoCrAlY+ Al_2O_3 +YSZ, CoCrAlY+ CeO_2 , CoCrAlY+WC-Co and CoCrAlY+ Cr_3C_2 -NiCr coatings on MDN 321 and Superni 76 alloys are shown in Table 1. The weight gain square (mg^2/cm^4) data plotted as a function of time to determine the oxidation kinetics is shown in Fig.1.

Both the coated alloys showed minimal difference in

weight gain. The rate of weight gain of the coated alloys was shown to be higher during the initial oxidation cycles which is attributed to the rapid formation of oxides of active elements. Also due to oxidation at the coating splat boundaries and the diffusion of the oxidizing species along the splat boundaries and open pores.

The parabolic rate constant value of all the coatings on both substrates are shown in Table 1 in the form of Kp in $10^{-10} \text{ g}^2\text{cm}^{-4}\text{s}^{-1}$.

3.1 PHASE ANALYSIS

XRD patterns of oxidised CoCrAlY+ Al_2O_3 +YSZ, CoCrAlY+ CeO_2 , CoCrAlY+WC-Co and CoCrAlY+ Cr_3C_2 -NiCr coated alloys at 700°C are shown in Fig.2. The major peaks of the oxidised coated alloys correspond to Cr_2O_3 , CoO, CoCr_2O_4 and CoAl_2O_4 . The minor peaks indexed to α - Al_2O_3 and AlCo. CoWO_4 and NiCr_2O_4 is the spinel oxide observed in CoCrAlY+WC-Co and CoCrAlY+ Cr_3C_2 -NiCr coatings respectively. The major phases observed in all the coatings are similar, as the base coating composition is same. Also, no peaks of the elements of substrate alloys were found in the XRD indicating that no diffusion has occurred from the substrate.

3.2 SURFACE SEM, EDS ANALYSIS, CROSS

3.2.1 Section and elemental mapping

The surface morphology of corroded CoCrAlY+ Al_2O_3 +YSZ coatings is shown in Fig.3a. The dark and light grey larger patches and globular structures have appeared on the oxidised surface. EDS analysis of dark grey patch marked as region 'A' in Fig.3a showed the dominant presence of Co with nominal O and Cr and traces of Al. The light grey layer marked as region 'B' indicates the dominant presence of O, Cr and Co with traces Al; whereas the oxide scale CoCrAlY+ CeO_2 (Fig.3b) consists of compact granules like structure with unusual dark gray patches across the oxidized coating surface. The EDS analysis on the dark gray patches marked as region 'A' indicates the presence of dominant Co and Cr elements with minimal amount of Al, Ce and O. The compact granular structure marked as region 'B' revealed the possible presence of O and Co as a major constituent with minor Cr content.

The oxide scale on CoCrAlY+WC-Co shows the existence of globular structure (Fig.3c) similar to CoCrAlY+ Al_2O_3 +YSZ coating. Also micro-porous (sponge) structures with superficial cracks are observed in Fig.3c. Porous structure indexed the presence of W rich oxides which may be tungsten-trioxide (WO_3) and cracks are observed in this defective oxide region. Whereas, the surface oxide scale of CoCrAlY+ Cr_3C_2 -NiCr coating (Fig.3d) consist of compact dense globular structure with patches of dispersed unusual dark gray regions across the oxidized coating surface. Globular structure as the major constituent of O, Cr and Co which indicates the presence of oxides of Cr and Co. Grey patches

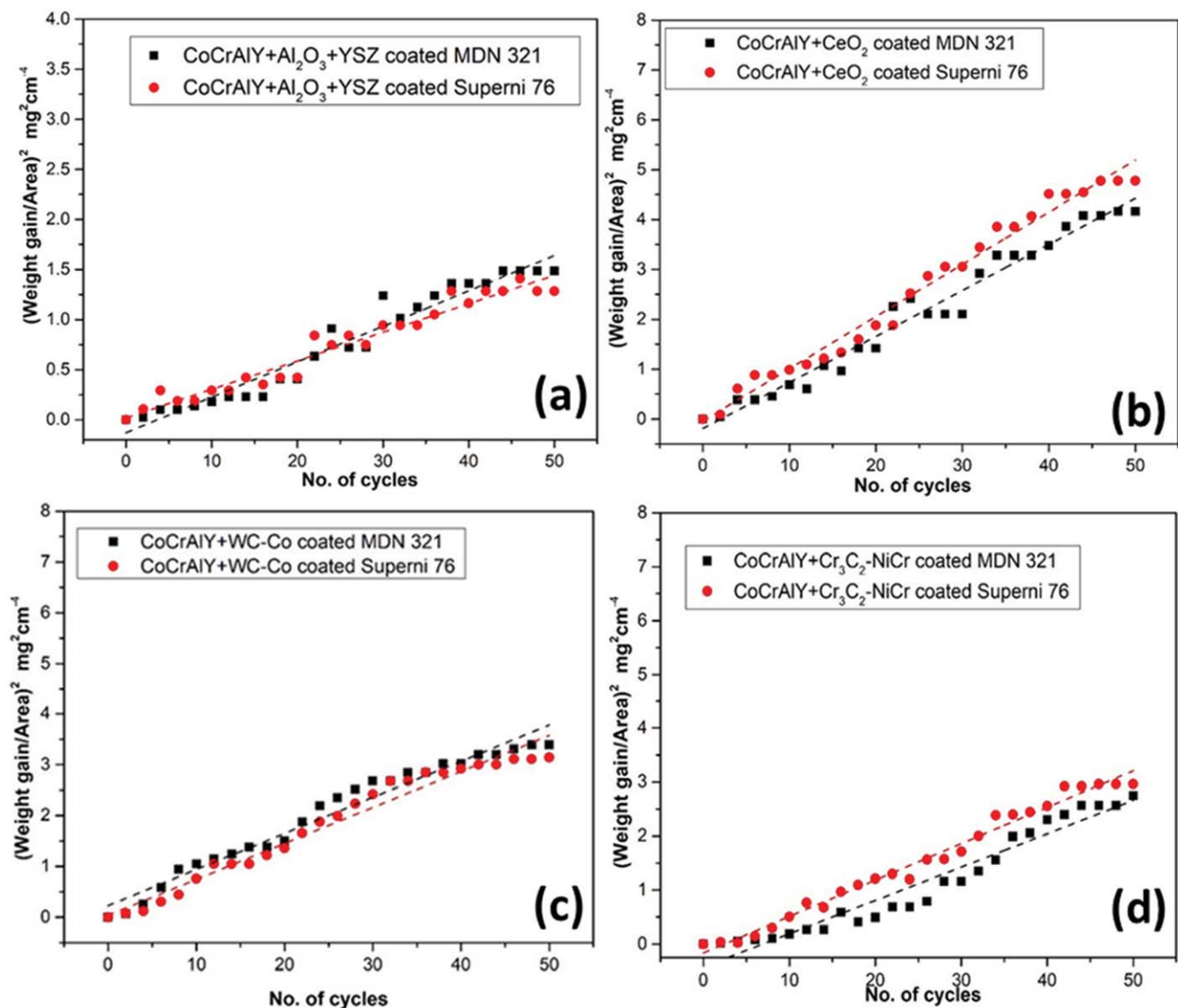


Fig.1: (Weight gain/area)² vs. number of cycles plot of (a) CoCrAlY+Al₂O₃+YSZ, (b) CoCrAlY+CeO₂, (c) CoCrAlY+WC-Co and (d) CoCrAlY+Cr₃C₂-NiCr coatings after oxidation

consist of Co and Ni with Al and O which may indicate the presence of oxides Co and Ni.

The SEM image of oxidised coatings cross section after 50 cycles is shown in Fig.4. All the remaining coatings have shown compact, adhered oxide scale on the top surface, whereas in CoCrAlY+CeO₂ coating cracks and delamination of oxide is observed (Fig.4b). The marking of 1, 2, 3 and 4 on the cross-section image indicated the EDS analysis at different regions and the corresponding elemental weight percentage is recorded in Table 2.

4.0 Comparative discussion

The total weight gain (mg/cm²) of all coatings subjected to oxidation is shown in Fig.5. CoCrAlY+Al₂O₃+YSZ coated alloys showed considerably lower weight gains than other

TABLE 1: WEIGHT GAIN AND PARABOLIC RATE CONSTANT VALUES OF OXIDISED COATINGS

Coatings	Weight gain in mg/cm ²		Parabolic rate constant K _p in 10 ⁻¹⁰ g ² cm ⁻⁴ s ⁻¹	
	on MDN 321	on superni 76	on MDN 321	on superni 76
CoCrAlY+Al ₂ O ₃ +YSZ	1.68	1.56	0.16	0.13
CoCrAlY+CeO ₂	2.35	2.56	0.31	0.35
CoCrAlY+WC-Co	2.97	3.15	0.46	0.50
CoCrAlY+Cr ₃ C ₂ -NiCr	1.65	1.69	0.42	0.38

coatings. All the coatings have experienced parabolic weight gain nature during oxidation cycles. Based on the thermogravimetric data, the relative oxidation resistance of the various coatings are shown in the following sequence and

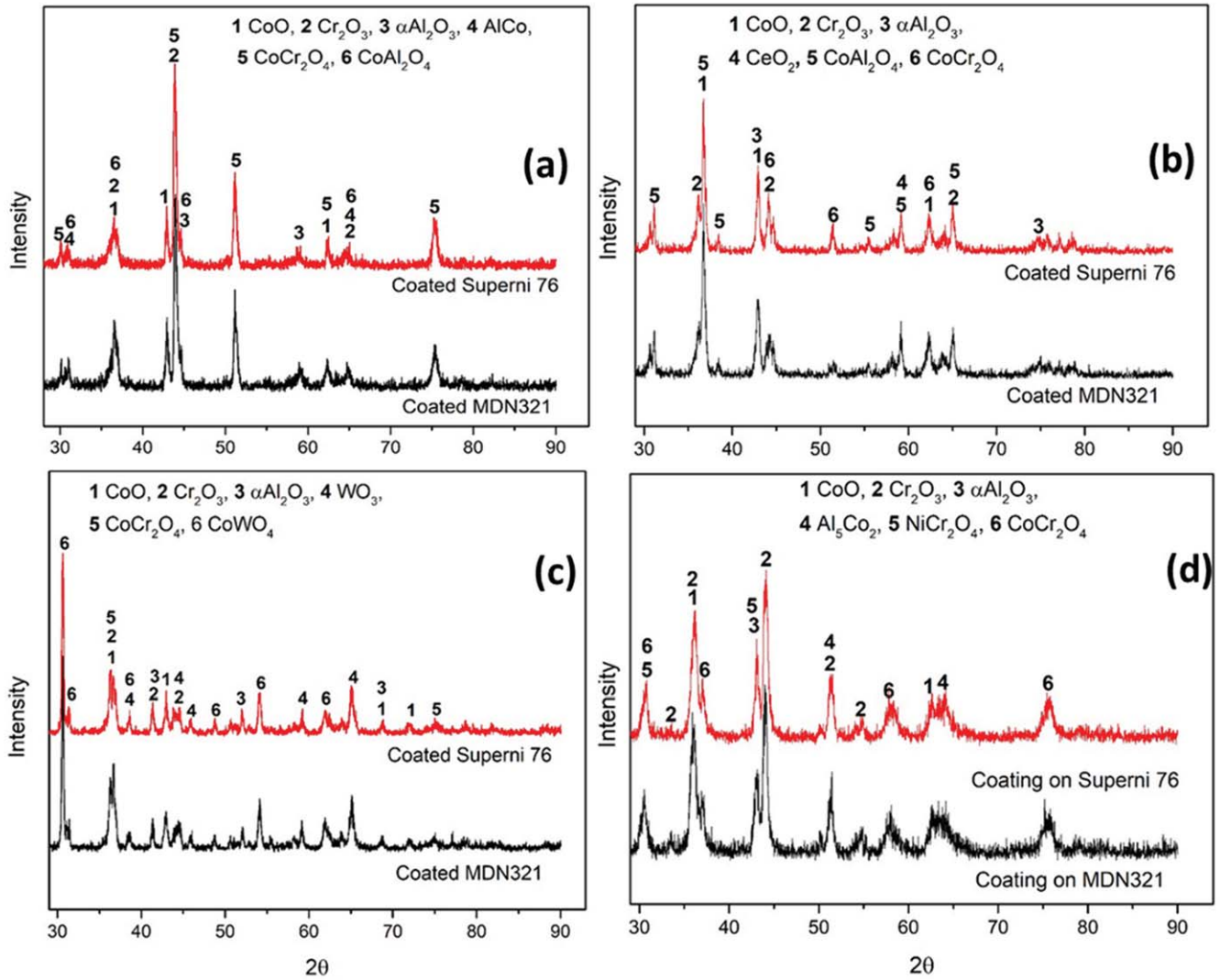


Fig.2: XRD patterns for (a) CoCrAlY+Al₂O₃+YSZ, (b) CoCrAlY+CeO₂, (c) CoCrAlY+WC-Co and (d) CoCrAlY+Cr₃C₂-NiCr coated alloys subjected to oxidation

TABLE 2: EDS ANALYSIS OF OXIDISED COATINGS CROSS SECTION.

Element (wt. %)	CoCrAlY+Al ₂ O ₃ +YSZ				CoCrAlY+CeO ₂				CoCrAlY+WC-Co				CoCrAlY+Cr ₃ C ₂ -NiCr			
	1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4
O	18.5	8.6	10	5	23.4	20.5	11	11.3	18.9	3.6	12	6.1	25.5	14.1	11.2	5.1
Al	10.8	9.7	8.1	6	2.5	9.5	7.2	10.9	5.3	-	5.9	26.8	7.5	8	15.2	2.5
Cr	47.2	18.4	17.8	14.5	14.5	13.5	12.7	17.1	11.1	1.5	10.1	17	24.6	29.5	19.2	38.2
Co	23.3	62.7	59.2	72.1	50.2	47.2	61	29.1	36.7	11.6	36.7	24.6	15.8	19.5	25.6	4.6
Ce	-	-	-	-	-	7.7	1.7	28.4	-	-	-	-	-	-	-	-
W	-	-	-	-	-	-	-	-	7	36.9	0.3	3.6	-	-	-	-
C	-	-	-	-	-	-	-	-	7	34.6	0.7	2.7	8	7.7	-	8.5
Ni	-	-	-	-	-	-	-	-	-	-	-	-	18.3	21.2	-	23.6

discussed in the same order: CoCrAlY+Al₂O₃+YSZ> CoCrAlY+Cr₃C₂-NiCr> CoCrAlY+WC-Co> CoCrAlY+CeO₂

Considering the upper limit of total weight gain of coatings on two substrates, CoCrAlY+Al₂O₃+YSZ coating

approximately experience 28%, 34% and 44% lesser weight gain than CoCrAlY+Cr₃C₂-NiCr, CoCrAlY+WC-Co and CoCrAlY+CeO₂ coatings respectively. The major phases observed on coatings on both the substrate are same and the

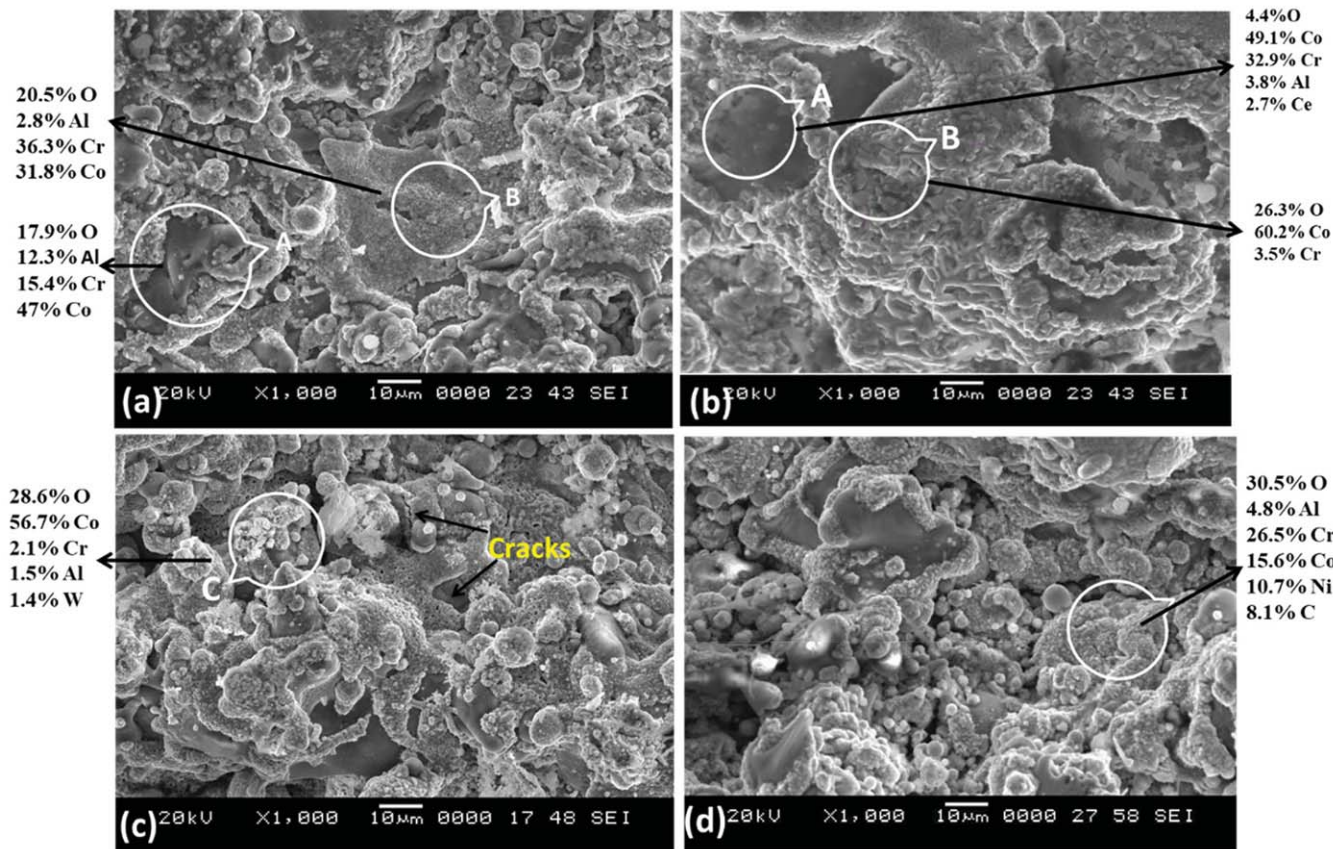


Fig.3: Surface morphology of oxidised (a) CoCrAlY+Al₂O₃+YSZ, (b) CoCrAlY+CeO₂, (c) CoCrAlY+WC-Co and (d) CoCrAlY+Cr₃C₂-NiCr coated alloys subjected to oxidation

major substrate elements are not identified on oxidised coatings surface shows the absence of substrate effect on the growth of oxide scale.

The surface morphology of oxidised CoCrAlY+Al₂O₃+YSZ coating comprises closely packed continuous globular structure. The cross section of oxidised coating in Fig.4a shows the thin, dense, non-porous and well adhered oxide scale on the coating surface. These are the characteristic features of protective oxides on the coating surface.

During the initial stages of oxidation, the oxygen penetrates into the coatings through the open porosities located along the splat boundaries until all the accessible internal surfaces have been oxidized. Further Al and Cr are partially oxidized reduced the additional oxygen ingress into the coating. The distribution of thermodynamically stable α -Al₂O₃ in the coating is shown slow-scale growth kinetics during the oxidation (Zhu et al. 2013). Also the α -Al₂O₃ is a pre-oxidised phase which further will not undergo any oxidation is one of the reasons for lower weight gain. As a result, the oxidation event occurs solely on the coating's external surface. Cr gets oxidized to Cr₂O₃ with CoAl₂O₄ and CoCr₂O₄ spinels which further retards the oxide growth and results in a lower oxide scale thickness as observed in the present study. (Sidhu and Prakash 2006A), (Singh et al. 2005),

Niranatlumpon et al. (2000), also reported the internal oxidation via open pores during the early stages of oxidation for thermal-sprayed MCrAlY coating substantiating the observations in the present work. The XRD analysis of oxidized surface reveals presence of Cr₂O₃, CoCr₂O₄ and CoAl₂O₄ as the major phases which are thermodynamically stable, having close-packed globular structure.

Whereas, in CoCrAlY+Cr₃C₂-NiCr coating, the total Cr percentage present in coating including the Cr present in Cr₃C₂-NiCr reinforcement is 36%. The higher Cr content in the coating leads to the fast transformation of Cr to Cr₂O₃ during the early stage. The presence of Cr₂O₃ as a dominating phase is responsible for this.

Cr₂O₃ protects against oxidation and corrosion by preventing oxygen from diffusing inward below 800°C. Cr₂O₃ begins to evaporate at temperatures above 800°C, forming volatile chromium oxide (CrO₃), which is ineffective in resisting oxidation (Seo et al. 2008).

The CoCr₂O₄ spinel oxide which is also a major phase as observed from XRD analysis due to nucleation of CoO and Cr₂O₃. The presence of small amount of Ni in Cr₃C₂-NiCr reinforcement oxidised to NiO and nucleation of NiO and Cr₂O₃ results in the formation of NiCr₂O₄.

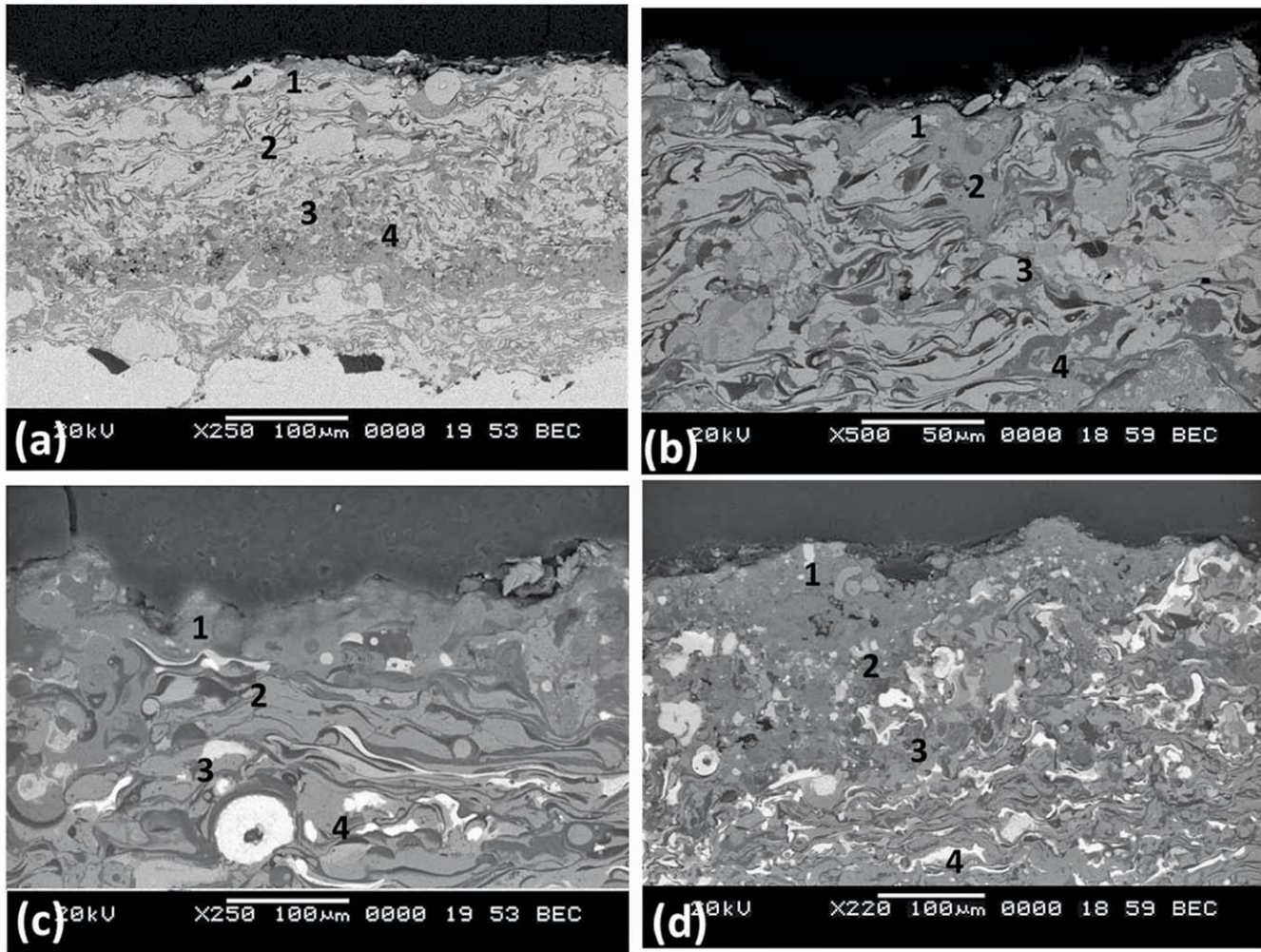


Fig.4: Oxidised coating cross section of (a) CoCrAlY+Al₂O₃+YSZ, (b) CoCrAlY+CeO₂, (c) CoCrAlY+WC-Co and (d) CoCrAlY+Cr₃C₂-NiCr coated alloys subjected to oxidation

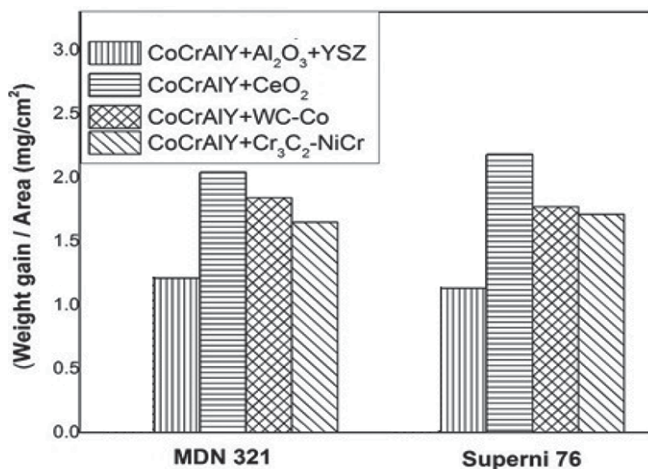


Fig.5: Total weight gain (mg/cm²) of uncoated and Plasma coated alloys subjected to oxidation

During high temperature exposure of CoCrAlY+WC-Co coating, the active elements of the coating such as W, Cr, Al and Co have undergone oxidation to form WO₃, Cr₂O₃, CoO and Al₂O₃. With subsequent oxidation cycles formation of

CoWO₄ as a strong phase with Cr₂O₃ and CoCr₂O₄ forms a dense, non-porous oxide scale which provide oxidation resistance. Similarly, Jafari et al. (2016) and (Singh et al. 2016) have been reported that the presence Cr₂O₃, CoWO₄ and CoCr₂O₄ as a strong phase during oxidation studies of W based coatings. The WO₃ seen as a porous structure which allows the inward diffusion of oxygen until it transforms into CoWO₄.

In case of CoCrAlY+CeO₂ coating, the oxidation of active elements Co, Cr and Al resulting in the formation of oxide scale on the coating surface. Ce ions blocks the outward diffusion of Co due to the segregation of CeO₂ at the grain boundaries of oxide scale, as a result oxide scale growth is primarily controlled by inward diffusion of oxygen. But, the segregation of CeO₂ occurs at slow rate, which resulting higher weight gain and cracks.

5.0 Conclusions

- CoCrAlY+Al₂O₃+YSZ coatings exhibited higher oxidation resistance than other coatings. Based on the

thermogravimetric data, the relative oxidation resistance of the various coatings is arranged in the following sequence: $\text{CoCrAlY}+\text{Al}_2\text{O}_3+\text{YSZ} > \text{CoCrAlY}+\text{Cr}_3\text{C}_2-\text{NiCr} > \text{CoCrAlY}+\text{WC-Co} > \text{CoCrAlY}+\text{CeO}_2$

- The protection offered by $\text{CoCrAlY}+\text{Al}_2\text{O}_3+\text{YSZ}$ coatings can be attributed to the oxide layer of Al_2O_3 , Cr_2O_3 and CoCr_2O_4 formed on the outermost surface, resulting in slow scale growth kinetics during oxidation. The preferential oxidation of Al and Cr along the cobalt rich splat boundary blocks the transport of oxygen into the coating through pores and voids, thereby making the oxidation rate to reach steady state.
- $\text{CoCrAlY}+\text{Cr}_3\text{C}_2-\text{NiCr}$ coating having the higher Cr content than the other coatings leads to the fast transformation of Cr to Cr_2O_3 during the early stage of oxidation. The Cr_2O_3 with spinel oxides of CoCr_2O_4 and NiCr_2O_4 as a thin oxide layer could limit the inward diffusion of oxygen there by slowing down the oxidation rate.
- The higher weight gain of $\text{CoCrAlY}+\text{WC-Co}$ coating is due to rapid oxidation of W into WO_3 , seen as a porous structure which allows the inward diffusion of oxygen until it transforms into CoWO_4 . With subsequent oxidation cycles formation of dense, non-porous oxide scale Cr_2O_3 , CoO and Al_2O_3 provide oxidation resistance.

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