

High Temperature Oxidation Behavior of Nano-structured CeO₂ Coatings on Superalloy

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Abstract—Nanostructured CeO₂ coatings on superalloy substrate were deposited by electroless process in the present work. Microstructure and cyclic high temperature oxidation behavior of nanostructured CeO₂ coatings on superalloy substrate were investigated. Cyclic high temperature oxidation tests were conducted on uncoated and coated samples at peak temperatures of 900°C for up to 50 thermal cycles between the peak and room temperature. The results showed that coated sample has higher oxidation resistance as compared to bare substrate at 900°C. The external scale of coated sample exhibited good spallation resistance during cyclic oxidation testing at both temperatures. The improvement in oxide scale spallation resistance is believed to be related to the fine-grained structure of the coating. The oxidation results have shown improved oxidation resistance of the CeO₂ coating on superalloy as compared to bare substrate up to 50 cycles. The relevant oxidation mechanisms are discussed.

1. INTRODUCTION

Metallic materials used in high temperature environments are usually iron, nickel or cobalt based alloys. The oxides formed on these metals are not sufficiently protective above 500°C and are therefore alloyed with chromium, aluminum or silicon to establish more protective oxides (scales) of chromia, alumina or silica respectively. Protective oxide scales should be non-volatile, stoichiometric to maintain low ionic transport, stress free at operating high temperatures to reduce scale failure, adherent, free of defects like pores and cracks to prevent short circuit transport of reactants. In practice, it is almost impossible to form such ideal scales. The use of reactive elements, especially rare earths to improve high temperature oxidation resistance of superalloy (chromia and alumina forming alloys) is well known. The improvements are in the form of reduced oxidation rates and increased scale adhesion [1, 2]. The rare earths have been added to the alloy bulk in the form of elements or as oxide dispersions. Addition of rare earths to the alloy surface by ion implantation or as oxide coatings, have the same effect on alloy oxidation resistance as bulk additions [3-4]. Rare earths oxide coatings have the advantage of not affecting adversely the mechanical properties of the alloy and the potential of being used on

metallic components in service and exposed to high temperature oxidizing environments. Nanostructured coatings have been identified as potential materials for providing good resistance against high temperature oxidation and hot corrosion [5-14] as compared to conventional coatings due to the formation of dense, continuous, non-porous and adherent alumina and/or chromia scales over the coatings [15-17]. The size effect of nanostructured coatings facilitates the enhanced diffusivity of atoms to form the continuous protective scales, which is normally discontinuous in the conventional coatings as reported in the literature [18]. C.T. Nuguen et al. [19] have reported that cerium oxide coatings on FeCrAl alloys exhibited improved oxidation resistance in air environment at 1100°C. Various processes, such as Chemical Vapor Deposition [20], Electron beam physical vapour deposition (EB-PVD) [21] and R.F. Magnetron Sputtering [22] are used for the development of cerium oxide films. The PVD deposition of thin film process is complex process as it requires high vacuum and costly target materials. Also, size of the sample deposited is limited. The literature on high temperature oxidation behavior of electroless cerium oxide films on superalloy is scarce. Therefore, in the present research work, nanostructured rare earth oxide coatings on nickel base superalloy were deposited by electroless process. Electroless deposition process is simple, cheap, easy to handle and no sophisticated elements or instruments are required [23-26]. Good adherence of the films can be obtained by this deposition technique. The dopant additions can be easily controlled by altering composition of inorganic precursors. Also, there is flexibility in size and shape of the sample for deposition of the film by electroless.

Rare earth oxide coatings on superalloy could be used as oxidation barrier coating for high temperature application. Generally, thermal barrier coatings (TBC) are applied on superalloy for high temperature oxidation and hot corrosion resistance. The TBC is the combination of bond coat and top layer of the ceramic coating provided on superalloy used in turbine engines. In addition to high temperature oxidation and hot corrosion resistance, the prime requirement of bond

coating is to serve as diffusion barrier for the substrate element. Without diffusion barrier, it could weaken the adherence of the thermally grown oxide as they diffuse into the bond coat, which would accelerate the premature spallation failure of TBC. In order to improve the high temperature oxidation and hot corrosion resistance of TBC, nanostructured rare earth oxide coatings on superalloy (as a first coat before TBC) could be used as oxidation barrier coating. Superni-718 (Inconel 718) has been chosen as the substrate material in the present study. It is used for

fabrication of turbine blade of jet engine and high speed airframe parts, such as wheels, buckets, spacers, high temperature bolts and fasteners. This nickel based superalloy exhibits high yield, tensile and creep rupture properties up to 800°C. Therefore, the present work has been focused to study the high temperature oxidation behavior (at 900°C) of nanostructured CeO₂ coated samples at different concentration of cerium acetate (0.1M, 0.2M and 0.3 M) on Superni-718 and bare Superni-718 and assess the protective efficiency of the coated super alloy.

Table 1: Chemical composition in wt-% of Superni-718.

Midhani Grade	Fe	Ni	Cr	Ti	Al	Mo	Mn	Si	Co	Nb	P	C	S
Superni-718	19.8	Bal	17.6	0.96	0.53	3.23	0.02	0.03	0.01	4.91	0.005	0.02	0.007

2. EXPERIMENTAL PROCEDURE

2.1 Preparation of plating bath

The electroless bath solution was prepared using Cerium (III) Acetate Hydrate [(CH₃COO)₃.xH₂O] (Sigma Aldrich, purity 99.99%), and Diethanolamine (Analytical Grade). CeO₂ coatings with different concentration of cerium acetate (0.1M, 0.2M and 0.3M) were prepared in the laboratory using electroless process. The above chemicals are used without any further purification. Initially, appropriate amount of Cerium Acetate and Diethanolamine are dissolved in distilled water and was stirred at 60°C for 2 hr, which served as bath solution after cooling to ambient temperature.

2.2 Electroless Deposition of Coatings

Ni-based superalloy namely Superni-718 has been chosen to deposit electroless CeO₂ coatings in the present work. The superalloy was procured from Mishra Dhatu Nigam Limited, Hyderabad, India in annealed and cold rolled sheet form and its chemical composition is shown in **Table 1**. Each specimen measuring approximately: 18 mm(L) × 15 mm(W) × 3 mm(T) were cut from the rolled sheet and ground by using 220, 320, subsequently down to 1000 grit of SiC emery papers. Subsequently, it was polished on cloth polishing disc by using alumina powder followed by diamond. Before deposition of film, sensitization and activation of the samples were done by dipping into the 20 % hydrochloric acid (5 minutes), 10 % nitric acid (5 minutes) and mixture of SnCl₂ (0.62 gram) + 5ml hydrochloric acid + 95 ml of distilled water for 10 minute followed by water rinsing. Finally, clean and activated substrate was dipped into the prepared electroless bath at 90°C for 2 hr. The wet deposited samples were dried in air at room temperature. Samples were kept in the horizontal position to avoid draining and blending of the just deposited wet-coatings, which could lead to irregularities in the layer thickness and to surface inhomogeneties. The deposited coatings were annealed in a muffle furnace for 2 hr in air environment at 500°C temperature. Samples are prepared with different

concentration of cerium acetate (0.1M, 0.2M and 0.3M). Standard conditions for synthesizing of CeO₂ coatings with different concentration of cerium acetate are shown in **Table 2**. The electroless CeO₂ coatings (before and after oxidation) were subjected to SEM analysis. SEM (LEO 534) has been used to characterise the microstructures of the CeO₂ coatings at an acceleration voltage of 20 kV.

2.3 Cyclic oxidation studies

The cyclic high temperature oxidation studies on the bare (uncoated) and CeO₂ coated superalloy samples were conducted for 50 thermal cycles each at 900 °C. Each thermal cycle consisted of 1 hr of heating at the particular peak temperature followed by 30 min of air cooling at room temperature. For thermal cyclic exposure, the samples were placed in the alumina boats and then inserted into the silicon carbide (SiC) tube furnace which was maintained at the desired peak (soaking) temperature. After every 1 hr of holding (soaking) in the furnace, the samples were removed and then cooled in air for 30 min at the room temperature. The weight change measurements during the thermal cyclic tests were made at the end of each thermal cycle to calculate the oxidation rate of the sample. An electronic balance Model CB-120 (Contech, Mumbai, India) and having a sensitivity of 1 × 10⁻⁵ g was used to measure the weight changes. The necessary care was taken to include the spalled scale (if any) in the weight change measurements. The results of the weight changes were documented as a function of the number of thermal cycles to explain the oxidation mechanism. The kinetics of cyclic oxidation of coated and bare superalloy samples was determined using the thermo gravimetric analysis and by evaluating the parabolic rate constants. After oxidation studies, the oxidized samples were analyzed by XRD and SEM to elucidate the oxidation mechanisms.

Table 2: Standard conditions for synthesizing of CeO₂ coatings with different concentration of cerium acetate.

Cerium-Acetate-Hydrate	X	Diethanolamine	Bath Temperature (°C)	Deposition Time (Minute)
0.1		0.5	90	120
0.2		0.5	90	120
0.3		0.5	90	120

3. RESULTS AND DISCUSSIONS

3.1 Structural Properties

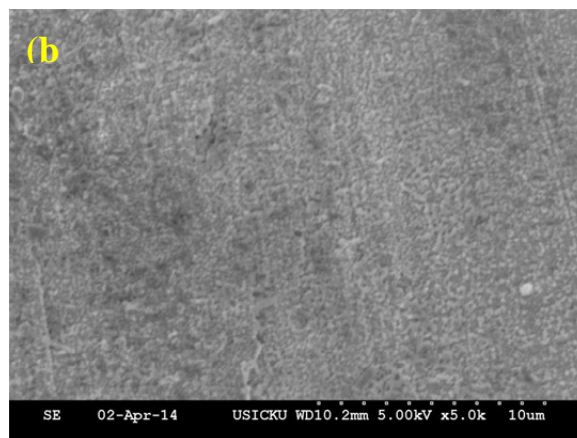
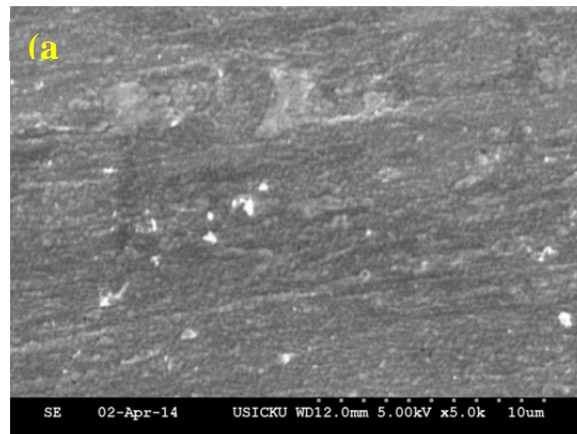
XRD (Bruker AXS, D8 Advance) measurements were made using CuK_α radiation to characterize the as deposited CeO₂ coatings (annealed at 500°C in air atmosphere) on Superni-718 substrate. The scan rate and the scan range used were 0.1 step/sec and from 10° to 70° respectively. **Fig. 1(a)** shows the X-ray diffraction patterns of CeO₂ coated samples on superalloy substrate at different concentration of cerium acetate (0.1M, 0.2M and 0.3M) before oxidation. XRD pattern of CeO₂ coated samples consists of three main reflections on the 2θ scale, 29.54°, 48.52° and 57.34° corresponding to (111), (220) and (311) planes, respectively. The diffraction peaks are characteristic of the cubic ceria phase with fluorite structure (JCPDS card number 34-394). CeO₂ coated samples of 0.3M concentration of cerium acetate has the highest (111) diffraction peak intensity (**Fig.1 (a)**). Moreover, the peak intensities of CeO₂ coated samples increased with increasing the cerium acetate concentrations higher than 0.1 M, which indicates that an increase in concentration increases the crystallinity of coatings. An average grain size of the CeO₂ coated sample was determined applying Scherrer's equation [27], calculated from the full width at half maximum intensity (FWHM) of the mean reflection (111). It was found to be in the range of 20-35 nm and 21.8 nm, 23.4 nm and 25.7 nm coated sample at different concentration of cerium acetate (0.1 M, 0.2M and 0.3 M), respectively. The XRD results of CeO₂ coated samples on superalloy substrate at different concentration of cerium acetate (0.1M, 0.2M and 0.3M) after 50 hours of cyclic oxidation in air at 900°C are shown in **Fig.1 (b)**. The XRD patterns reveal that dominant as well as minor peaks of Cr₂O₃, Fe₂O₃, NiO and CeO₂ phases are present in the CeO₂ coated samples on superalloy substrate at different concentration of cerium acetate (0.1M, 0.2M and 0.3M) after 50 hr of cyclic oxidation in air at 900°C.

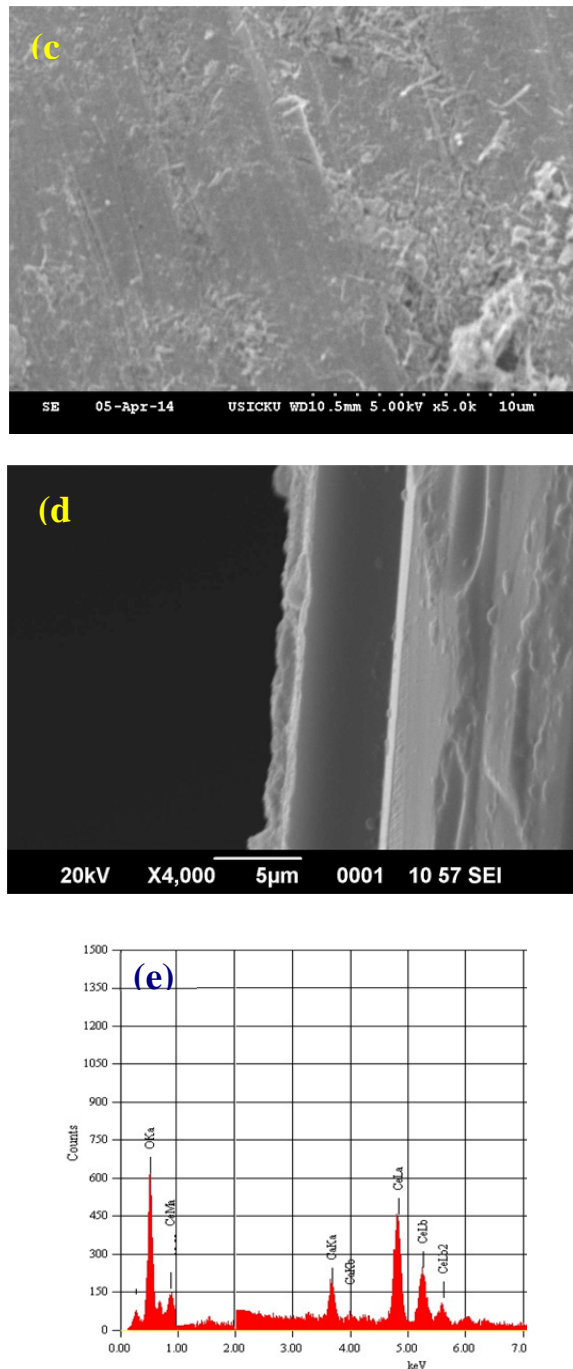
3.2 Microstructures of Coating before Oxidation

SEM surface morphology of CeO₂ coated samples at different concentration of cerium acetate (0.1M, 0.2M and 0.3M) before oxidation can be seen in **Fig. 2(a-c)**. In the present work, the CeO₂ coated sample at 0.1M concentration shows uniform small spherical shape grains (**Fig.2 (a)**). The CeO₂ coated superalloy sample at 0.2M concentration depicts uniform coating and have mixture of small spherical and rod type

grains (**Fig.2 (b)**). **Fig.2(c)** represents the CeO₂ coated sample at 0.3M concentration and has the fine needles, rod type grains. According to the micrographs, the coating morphology **Fig. 1** X-ray diffraction patterns of CeO₂ coated samples on superalloy substrate at different concentration of cerium acetate (0.1M, 0.2M and 0.3M) (a) before oxidation (b) after oxidation.

Shows a dependence on the bath concentration. In general, the grain shape and size change with the bath concentrations, although a meticulous observation, allows us to see as the fine and long needle shape grains present in CeO₂ coated sample at 0.3M concentration (**Fig.2. (c)**). Thickness of the coating (sample at 0.3M) was calculated from its cross-sectional SEM image (**Fig.2 (d)**) and it is found to be approximately 4 μm. The chemical composition of as deposited CeO₂ coating on the Superni-718 substrate was analysed from its surface and cross-sectional SEM/EDS micrographs (**Fig.2 (a-d)**) and **Fig.2 (e)** shows EDS spectra obtained for CeO₂ coating on the Superni-718 substrate, showing the existence of cerium within the samples.





Element	KeV	Atom%
O	0.525	47.82
Ce	4.839	52.18
Total		100

Fig. 2 (a-c) SEM surface morphology of CeO₂ coated samples at different concentration of cerium acetate (0.1M, 0.2M and 0.3M) before oxidation. **(d)** Cross-sectional SEM image **(e)** EDS spectra obtained for CeO₂ coating on the Superni-718 substrate, showing the existence of cerium within the samples.

3.3 Cyclic high temperature oxidation kinetics

The Superni-718 superalloy exhibits high yield, tensile and creep rupture properties at 750 °C. The cyclic oxidation study of coated and bare substrate in air at 900° C for 50 hrs of thermal cycles was performed and the results are shown in **Fig.3 (a-c)**. It shows that the bare substrate has the highest weight gain/ area (mg/cm²) and prone for oxidation. The cyclic oxidation behavior of the CeO₂ coated samples deposited at different concentration of cerium acetate (0.1M, 0.2M and 0.3M) at the peak temperature of 900°C as a function of thermal cycles is also shown in **Fig.3 (a)**. The plots of the mass-change/area, mg/cm² (**Fig.3 (a)**) data exhibited two distinct oxidation stages with a rapid oxidation in the initial stage followed by a slower/ steady oxidation. The durations required to reach the steady oxidation and to maintain this stage are important indexes, besides the oxidation resistance for evaluating coating/alloy oxidation resistance [28]. In case of bare Superni-718, substrate weight increases continuously up to 25th cycles and then rapidly increases up to 30th cycles and finally shows very little weight gain, a constant weight variation, whereas CeO₂ coated sample shows very less mass change in the whole test run. In CeO₂ coated sample deposited at 0.1M concentration of cerium acetate, weight has increased up to 20th cycle and after 20th cycle, weight variation is constant, where as CeO₂ coated sample prepared at 0.2M concentration of cerium acetate, weight has increased up to 15th cycle and after 15th cycle weight variation is constant, On the other hand, CeO₂ coated sample at 0.3M concentration of cerium acetate, shows the weight gain up to 15th cycles and subsequently in the following cycles, weight change is very less and remains constant. The overall weight gain in CeO₂ coated sample is lower as compared to bare Superni-718 substrate. Among them, CeO₂ coated sample at 0.3M concentration of cerium acetate, shows the least weight gain. The weight change curve reveals that the CeO₂ coated substrate is found to be more oxidation resistant than the bare superalloy. The CeO₂ coated substrate obeys a parabolic rate law and exhibit the tendency to act like diffusion barriers to the oxidizing species. In other words, the duration required to reach the steady oxidation of CeO₂ coated sample is very low (15 hr to 20 hr) as compared to bare substrate (25 hr to 30 hr). The high temperature oxidation kinetic behavior of the bare Superni-718 substrate and CeO₂ coating on Superni-718 at different concentration of cerium acetate (0.1M, 0.2M and 0.3M) was further examined and shown in **Fig. 3(b)** as (weight gain/area)² versus time plots. The parabolic rate (**Fig. 3(b)**) constant K_p was calculated by a linear least-square algorithm to a function in the form of (W/A)² = K_p t, where W/A is the weight gain per unit surface area (mg/cm²) and 't' indicates the number of cycles represents the time of exposure[29]. The parabolic rate constants here are termed by k_p^{1st} for the initial oxidation stage and k_p^{2nd} for the later stage/ steady stage oxidation, respectively [30]. The parabolic rate constant k_p^{1st} corresponds to the initial oxidation stage between 1 and 25 hr in case of bare Superni-718 substrate, whereas for CeO₂ coated sample at 0.1M concentration of cerium acetate was between 1 and 20

hours. For CeO₂ coated sample deposited at 0.2M and 0.3M concentration of cerium acetate, it was between 1 and 15 hr. Similarly, k_p^{2nd} represents the later stage or steady stage of oxidation between 30 hrs to 50 hrs in case of bare Superni-718 substrate, whereas, for CeO₂ coated sample at 0.1M concentration of cerium acetate was between 25 hr and 50 hr, CeO coated sample at 0.2M and 0.3M concentration of cerium acetate was between 20 hr and 50 h, respectively. The oxidation obeyed a parabolic rate law throughout the temperatures. The calculated k_p^{1st} for the CeO₂ coatings deposited at different concentration of cerium acetate (0.1M, 0.2M and 0.3M) on superalloy is found to be $1.6879 \times 10^{-9} \text{ g}^2 \text{ cm}^{-4} \text{ s}^{-1}$, $1.07325 \times 10^{-9} \text{ g}^2 \text{ cm}^{-4} \text{ s}^{-1}$ and $0.47806 \times 10^{-9} \text{ g}^2 \text{ cm}^{-4} \text{ s}^{-1}$ respectively. It is very less as compared to the k_p^{1st} value of $8.01666 \times 10^{-9} \text{ g}^2 \text{ cm}^{-4} \text{ s}^{-1}$ obtained for the bare Superni-718 substrate. Similarly, the calculated k_p^{2nd} for the CeO₂ coatings deposited at different concentration of cerium acetate (0.1M, 0.2M and 0.3M) on superalloy is found to be $0.1301 \times 10^{-9} \text{ g}^2 \text{ cm}^{-4} \text{ s}^{-1}$, $0.04353 \times 10^{-9} \text{ g}^2 \text{ cm}^{-4} \text{ s}^{-1}$ and $0.03722 \times 10^{-9} \text{ g}^2 \text{ cm}^{-4} \text{ s}^{-1}$ respectively. It is also very less as compared to the k_p^{2nd} value of $0.3204 \times 10^{-9} \text{ g}^2 \text{ cm}^{-4} \text{ s}^{-1}$ obtained for the bare Superni-718 substrate.

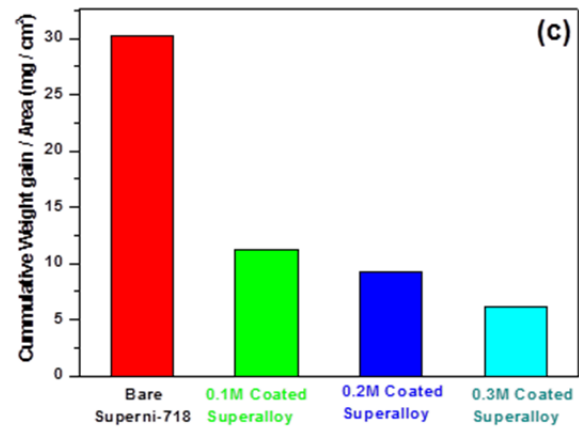
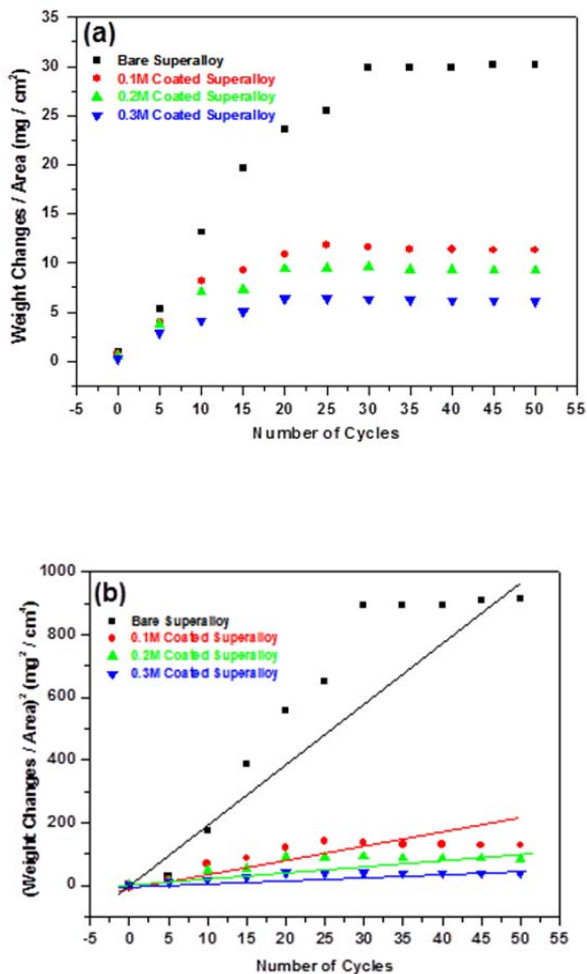


Fig.3 a (a) Weight changes/area (mg/cm²) versus number of cycles (b) parabolic rate constant, K_p (weight change/area)², versus number of cycles. **3(c)** Cumulative weight gain per unit area for CeO₂ coated sample at different concentration of cerium acetate (0.1M, 0.2M and 0.3M) and bare Superni-718 substrate subjected to cyclic high temperature oxidation in air at 900°C for 50 cycles.

3(c) shows the cumulative weight gain per unit area for CeO₂ coated sample at different concentration of cerium acetate (0.1M, 0.2M and 0.3M) and bare Superni-718 substrate subjected to cyclic high temperature oxidation in air at 900°C for 50 cycles. **Fig.3(c)** indicated that CeO₂ coating at 0.3M concentration of cerium acetate shows minimum cumulative weight gain per unit area as compared to bare substrate and CeO₂ coating at 0.1M and 0.2M concentration of cerium acetate in air at 900°C for 50 cycles. CeO₂ coating on Superni-718 substrate at 0.3M concentration has been found to be successful in reducing the overall weight gain by 79.6 % with reference to bare superni-718 substrate (**Fig.3(c)**). Whereas, CeO₂ coating on Superni-718 substrate at 0.1M and 0.2M concentration have reduced the overall weight gain by 62.6 % and 69.4% with reference to bare superni-718 substrate (**Fig.3(c)**).

3.4 Morphology of scales

The cross-sectional SEM/EDS micrograph of the oxidised bare substrate at 900°C for 50 hr in air atmosphere is shown in **Fig.4 (d)**. The cross-sectional micrograph shown in **Fig.4 (d)** reveals that many pores are present in the scale formed on the bare substrate at 900°C. The possible reason for the presence of these pores in the scale could be due to the formation of volatile Mo-oxide (MoO₃), the melting point of which is 795°C. Due to the presence of pores in the scale, the chemical elements present in the substrate material come in direct contact with the air leading to their oxidation and hence results in the higher weight gain of the bare substrate. This is indicative of the fact that the bare Superni-718 substrate has poor oxidation resistance at 900°C under the present

experimental conditions. The very low presence of Aluminum in the chemical composition (**Table 1**) of the Superni-718 substrate material could be the reason for the poor oxidation resistance shown by the bare superalloy at 900°C. The above observations suggest that the Superni-718 substrate may need a protective coating when used at 900°C [16]. The overall cross-sectional EDS analysis of the uncoated Superni-718 substrate is presented in **Fig.4 (d)**. EDS result revealed that the scale formed on the bare substrate comprises mainly oxides such as Cr_2O_3 , Fe_2O_3 , NbO_2 and NiO .

The SEM/EDS cross-sectional micrograph of the CeO_2 coated samples prepared at 0.1 M and 0.2 M concentration of cerium acetate oxidised at 900°C in 50 hr of thermal cycles are seen in **Fig.4 (a-b)**. It reveals the coarse morphology of oxide scale formed on the coatings. For performing the cross-sectional analysis, the

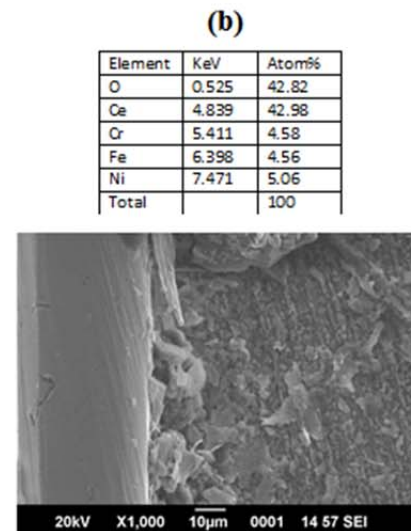
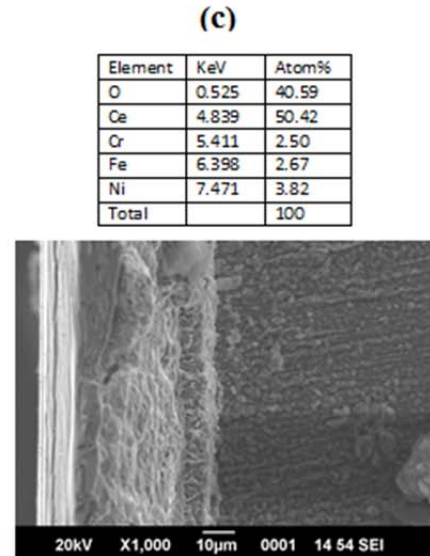
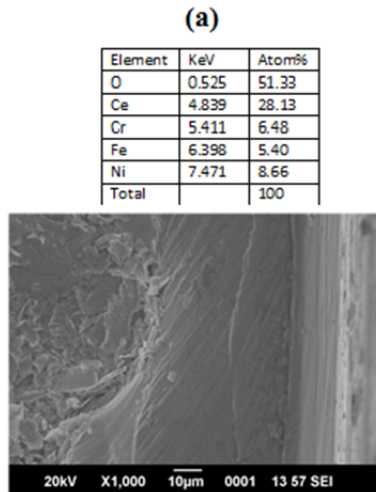
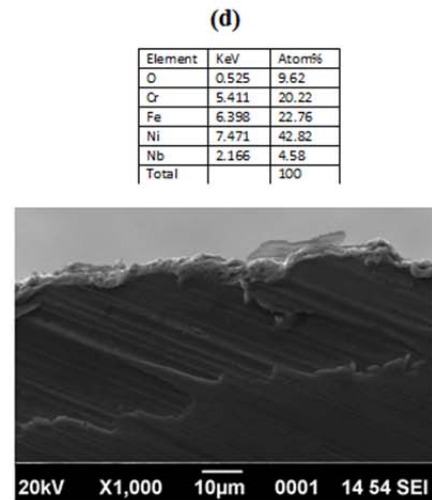


Fig.4 (a-c), shows the cross-sectional SEM/EDS micrographs of the CeO_2 coated samples, prepared at different concentration of cerium acetate (0.1M, 0.2M and 0.3M), exposed to 900°C for 50 hr of thermal cycles.



oxidised sample was cut by a diamond cutter operating at a very low speed of 80 rpm. All possible necessary precautions were taken during cutting to avoid any damage to the oxide scale formed on the coated sample. The delamination of the scale from the coating-substrate interface is seen in the SEM micrographs shown in **Fig.4 (a-b)**. This could be due to the damage caused to the oxide scale during sectioning of the sample for cross-sectional analysis. Fine layers of oxide scale are clearly seen in the SEM/EDS cross-sectional micrograph (**Fig.4(c)**) of the CeO₂ coated samples at 0.3 M concentration of cerium acetate after its oxidation at 900°C. The scale formed is almost uniform, continuous and dense. In general, the oxidized scale formed on the CeO₂ coated samples at 0.3 M concentration of cerium acetate is more dense, compact, and adherent as compared to the scale formed on the CeO₂ coated samples at 0.1 M and 0.2 M concentration of cerium acetate after its oxidation at 900°C. The above observation suggests that the CeO₂ coated samples at 0.3 M concentration of cerium acetate exhibit highest resistance to oxidation at 900°C in 50 hours of thermal cycles than the CeO₂ coated samples prepared at 0.1 M and 0.2 M concentration of cerium acetate.

EDAX Genesis 32 software was used to calculate the composition of the oxidized products, mainly, oxides using elemental composition. The results of the EDS analysis carried out at various locations along the cross-sections of the CeO₂ coated samples at different concentration of cerium acetate (0.1M, 0.2M and 0.3M) is shown in **Fig.4(a-c)**. In case of the CeO₂ coated sample, at 0.3M concentration of cerium acetate, oxidized at 900°C, the EDS results reveal that the CeO₂ content in the oxide scale formed is high (50.42 at.%) as compared to CeO₂ coated sample at 0.1M concentration (28.13 at.%) and 0.2 M concentration (42.98 at.%) of cerium acetate oxidized at 900°C in 50 hr of thermal cycles. It is evident that Cr, Fe and Ni content in oxide scale have decreased in CeO₂ coated samples prepared with 0.3 M to 0.1 M concentration of cerium acetate. It shows that CeO₂ coating on superalloy substrate serves as an oxidation barrier coating for anions as well as cations. Hence, CeO₂ coated samples (0.1 M, 0.2M and 0.3M) have shown lower weight gain/cm² as compared to bare superalloy at 900°C for 50 hrs.

3.5 Oxidation Mechanism

CeO₂ coated superalloy at different concentration (0.1M, 0.2M and 0.3M) was exposed to 900°C for 50 hours in air environment. CeO₂ oxide gets incorporated in to the growing scale as confirmed by cross-sectional SEM/EDS analysis (**Fig.4 (a-c)**). Once CeO₂ oxide gets incorporated in to the Cr₂O₃, Fe₂O₃, NiO scale, the Ce⁺⁴ ions may segregate to grain boundaries in the oxide scale and inhibit normal outward short-circuit transport of alloy cations along the scale grain boundaries. The slow moving Ce⁺⁴ ions block or impede the movement of Cr, Fe and Ni ions (substrate elements) along the grain boundaries in super alloy.[31]. The lower weight gain/area of CeO₂ coated superalloy at different concentration

(0.1M, 0.2M and 0.3M) at 900°C as compared to uncoated superalloy (**Fig.3(a)**) confirms the effective role of segregation of Ce⁺⁴ ion into the grain boundaries in the oxide scale. The transport of oxygen ion is the new rate limiting step due to the blocking of grain boundaries by Ce ions. The time taken to form the limiting oxide scale layer thickness on the CeO₂ coated superalloy is significantly longer. During this period, the scale formed is thin, more plastic; adherent to the alloy, and therefore it is capable of withstanding thermal and scale growth stresses. Due to these reasons, defects free scale is formed on CeO₂ coated superalloy as compared to uncoated superalloy. Inhibition of the outward transport of alloy cations also results in a reduction in the parabolic rate constant as observed in the present work [32].

Particularly, CeO₂ coated sample at 0.3M concentration of cerium acetate exhibits a high temperature oxidation resistance and provided the best protection as compared to that of the coatings deposited at 0.1M and 0.2M concentration of cerium acetate due to the following reasons:

- i. As deposited CeO₂ coated sample at 0.3M concentration shows fine needles, rod type grains as shown in SEM surface micrograph (**Fig. 2(c)**). It may be mentioned that the diffusivity of cations through needles type structure is slow, which results in the formation of thin fine, dense and defect free scale as confirmed by cross-sectional SEM micrograph shown in **Fig.4 (c)**. Therefore, the CeO₂ coated superalloy at 0.3M concentration shows thin oxide scale, which results into more plastic, more adherent to the alloy, which is capable of withstanding thermal and scale growth stresses.
- ii. Higher concentration (0.3M) as compared to 0.1M and 0.2M means large amount of Ce⁺⁴ ions in coating. It is believed that increased in Ce⁺⁴ ions at grain boundaries in the oxide scale acting as a barrier and blocking the transport of cations and anions, which leads to decrease in oxidation rate, thereby increasing high temperature oxidation resistance of the coated superalloy at 900°C for 50 hr in air environment. Once sufficient amount of CeO₂ oxide is incorporated in to the Cr₂O₃, Fe₂O₃, NiO scale, Ce⁺⁴ ions might segregate in to grain boundaries in the oxide scale and block all possible paths, which in turn increases oxidation resistance of the coated sample.

It may be concluded from the present study that nanostructured CeO₂ coating can be used as an oxidation barrier (first layer of TBC coating i.e. first layer of CeO₂ coating followed by bond coating and top layer of ceramic coating) on nickel based superalloy. It increased the oxidation resistance of superalloy by reducing the overall weight gain, as has been seen in **Fig.3(c)** that CeO₂ coated superalloy has lower cumulative weight gain/area (6-11 mg/cm²) as

compared to uncoated superalloy (30 mg/cm²). The lower oxidation rate of nanostructured CeO₂ coatings on superalloy observed in the present work is in accordance with the results of F. Czerwinski and J.A. Szpunar [33]. The similar observations were made by Sundararajan et al. [20], where nano ceria coated 9Cr-1Mo ferritic steel showed a higher oxidation resistance when compared to the uncoated steel under similar conditions.

4. CONCLUSION

The high temperature oxidation kinetics of CeO₂ coated samples were compared with that of the bare Superni-718 and found that the parabolic rate constant is very less for the former, which is due to the formation of continuous, nonporous, adherent and protective oxide scale over the surface of the coated sample. The continuous mass gain of Superni-718 is due to the renewal of fresh surface of the materials, and the pores resulting from the evaporation of volatile impurities in the alloy at high temperature. CeO₂ coatings on superalloy at 0.3M concentration, showed a lower oxidation rate as compared to CeO₂ coating at 0.1M and 0.2M concentration and bare substrate. It is due to the dense coating, and surface micrograph of as deposited coating showed needle, rod type the morphology of grains. Therefore, nanostructured coatings could enhance the high temperature oxidation resistance and improve the scale-metal adherence as observed in the present work.

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