

Synthesis and Characterization of Nanostructured CeO₂ Coatings on Superalloy

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Abstract—In the present work, nanostructured coatings of ceria have been synthesized by electroless process on superalloy Superni-750. The coatings are intended to increase the life of the thermal barrier coatings by acting as a diffusion barrier to the outward diffusion of cations. Nanostructured coatings lead to formation of a protective scale faster and the ceria particles enhance the properties of the scale by the reactive element effect. The microstructure of the synthesized nanostructured CeO₂ coatings on substrate has been investigated by SEM-EDS and XRD analysis. Cyclic high temperature oxidation tests were conducted on uncoated and coated samples at peak temperatures of 900 °C for up to 100 thermal cycles between the peak and room temperature. The coated samples have shown a higher oxidation resistance as compared to bare substrate at 900 °C. The external scale of coated sample exhibited good spallation resistance. The CeO₂ coating on superalloy showed an improved oxidation resistance as compared to the bare substrate.

1. INTRODUCTION

Superalloys are used in high temperature applications since they are able to maintain their mechanical properties at elevated temperatures. They have a good oxidation resistance due to the formation of oxide scale. For an oxide scale to be protective, it should be adherent, non-volatile, and defect-free and should allow low ionic transport. However such ideal scales are never formed that exhibit all the desired properties [1].

In order to increase the life of the superalloys, thermal barrier coatings have been applied on these alloys. The TBCs have been studied from a long time and their properties are further tailored by additions of reactive elements like the rare earths. The rare earth elements can be added to the surface of alloy as oxide dispersions or in the form of elements. Rare earth oxide coating has shown improvement in the oxidation resistance and scale-adherence without having an adverse effect on the mechanical properties [2, 3].

The rare earth oxide films can be applied on the base materials by various techniques such as chemical vapour deposition, electron-beam physical vapour deposition, RF magnetron sputtering. However all these processes have certain limitations like the cost involved, complexity of the process or the size and shape of the substrate [4-6].

The literature on the microcrystalline coatings is well established. However the nano-structured coatings have shown improvement in the oxidation resistance properties and thus the nano-structured coatings on superalloy are potential materials in high temperature applications to provide high temperature oxidation and hot corrosion resistance [7-10].

2. RESEARCH SIGNIFICANCE

Considering the above mentioned facts, our present work has been focussed on developing the nano-structured cerium oxide coatings on Superni-750 which is a nickel-based superalloy by electroless method, and to study the high temperature degradation behaviour of the coated and the bare substrate at 900 °C for 100 thermal cycles where each cycle consists of heating at 900 °C for 1 h followed by cooling for about 20 minutes. Cerium oxide coating has been chosen as when applied on Fe-Cr-Al alloys, it has shown improved oxidation resistance in air at 1100 °C [11].

Electroless process is simple, economical and easy to handle as compared to other methods of coating. The dopant additions are easily controlled and the limitation of size and shape of the substrate is also eliminated [12-15].

3. MATERIALS AND METHODS

Preparation of Plating Bath

The electroless bath solution was prepared using Cerium (III) Acetate Hydrate [(CH₃COO)₃.xH₂O] (Sigma Aldrich, purity 99.99%), and Triethanolamine (Analytical Grade), used without any further purification. 0.1 M, 0.2 M and 0.3 M solutions of Cerium Acetate and an appropriate amount of triethanolamine was dissolved in distilled water and stirred at 60 °C for 2 h. This bath solution was used to produce CeO₂ by electroless process.

Deposition of Coatings

CeO₂ coating was deposited on Ni-based superalloy, Superni 750. The superalloy was procured from Mishra Dhatu Nigam Limited, Hyderabad, India in annealed and cold rolled sheet form and its chemical composition as provided by the

manufacturer, is shown in **Table 1**. Each specimen measuring approximately: 18 mm (L) \times 15 mm (W) \times 3 mm (T) was cut from the rolled sheet and polished up to 1000 grit of SiC emery paper and subsequently on cloth polishing disc by using alumina powder. Before deposition of the coating, the substrate was activated. The sensitization and activation of the sample was done by dipping into 20 % hydrochloric acid for 5 minutes then in 10 % nitric acid for 5 minutes and in a mixture of SnCl₂ (0.62 gram), 5ml hydrochloric acid, 95 ml of distilled water for 10 minutes, followed by water rinsing. Finally, clean and activated specimen was dipped into the prepared electroless bath at 90 °C for 2 h. The wet sample was then dried in air at room temperature. The deposited coating was annealed in a muffle furnace for 2 h in air at 500 °C temperature. Standard conditions for synthesizing of CeO₂ coatings with different concentration of cerium acetate are shown in **Table 2**. The electroless CeO₂ coated substrate were subjected to SEM and XRD analysis before and after oxidation.

Table 1: Chemical composition of superalloy used in study

	Chemical composition, Wt-%			
Midhani Grade	Ni	Cr	Ti	Nb
	73.02	16.45	1.70	1.20

Table 2: Standard conditions for synthesis of CeO₂ coating with different concentration of cerium acetate (0.1M, 0.2M, and 0.3M)

Synthesis precursors		Parameters	
Cerium Acetate-X-Hydrate	Triethanol-amine	Bath Temperature (oC)	Deposition Time (Hours)
0.1 M	5 ml	90	2
0.2 M	5 ml	90	2
0.3 M	5 ml	90	2

Cyclic oxidation studies

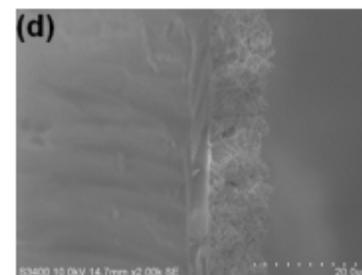
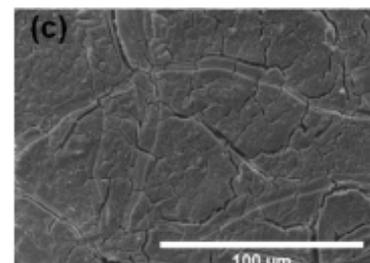
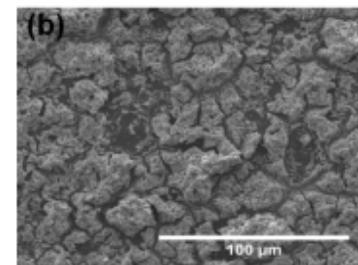
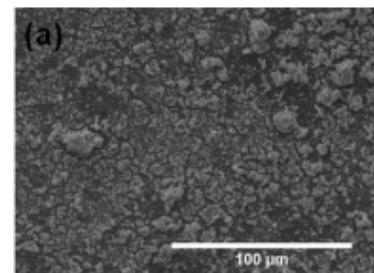
The cyclic high temperature oxidation studies on the uncoated and CeO₂ coated superalloy specimens were conducted for 100 thermal cycles at a temperature of 900°C. Each thermal cycle consisted of heating the specimens at 900°C followed by air cooling at room temperature for about 30 minutes. For thermal cyclic exposure, the specimens 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. 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) having sensitivity of 1×10^{-4} 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 plotted as a function of the number of thermal cycles. 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 SEM/EDS to elucidate the oxidation mechanisms.

4. RESULTS AND DISCUSSION

Microstructures of the Coating before oxidation

Figure 1 a-c shows the surface morphology of the oxide coatings on the Superni 750 substrate. It can be clearly observed that 0.1 M (Fig 1 a) coated substrate does not cover the surface completely where as the 0.2 M and 0.3 M (Fig 1 (b-c)) cover the surface completely. The 0.3 M coated surface has dense and uniform coating. The chemical composition of the as-deposited coating was determined by EDAX Genesis software with SEM/EDS attachment. The result (Fig 1 e) shows the presence of cerium and oxygen.



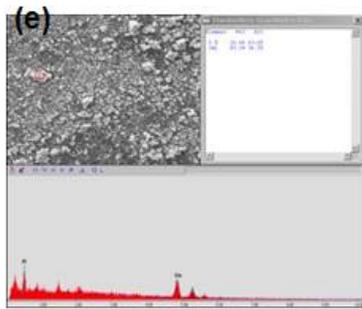


Figure 1: (a-c) SEM surface morphology of CeO₂ coated samples at different concentration of cerium acetate (0.1M, 0.2M and 0.3M) before oxidation. (d) Cross-sectional SEM image (e) EDS spectra obtained for CeO₂ coating on the substrate, showing the presence of cerium.

Structural Properties before oxidation

The XRD analysis of the as-deposited coating was done to confirm the formation of cerium oxide on the surface of the substrate. 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). The scan rate and the scan range used were 0.1 step/sec and from 10° to 90° respectively. Fig. 2 shows the X-ray diffraction patterns of CeO₂ coated samples on substrate at different concentration of cerium acetate (0.1M, 0.2M and 0.3M) before oxidation.

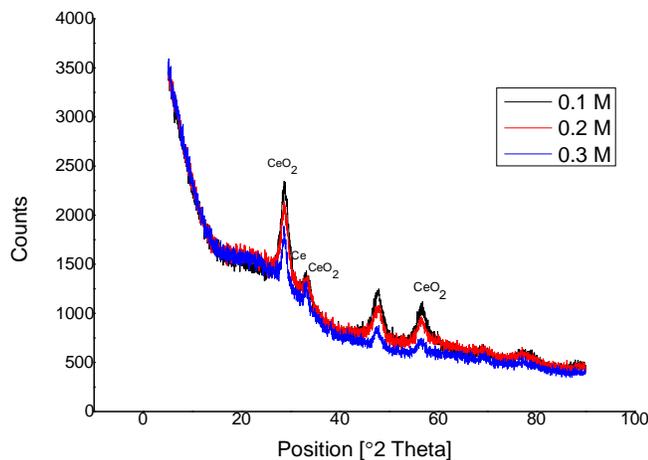


Figure 2: XRD of 0.1 M, 0.2 M and 0.3 M coating before oxidation.

Oxidation Mechanism

The cyclic oxidation study of coated and bare substrate in air at 900° C for 100 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 is prone to oxidation as compared to the coated specimens. 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 three 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 weight gain for evaluating coating/alloy oxidation resistance [16]. In case of bare Superni-750, substrate weight increases continuously up to 40th cycle and then again increases up to 80th 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-750 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 h to 20 h) as compared to bare substrate (40 h). The high temperature oxidation kinetic behavior of the bare Superni-750 substrate and CeO₂ coating on Superni-750 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 [17]. The calculated K_p value for bare is 43.166×10⁻¹¹ g²cm⁴s⁻¹, for 0.1 M is 5.777×10⁻¹¹ g²cm⁴s⁻¹, 0.2 M is 5.611×10⁻¹¹ g²cm⁴s⁻¹ and 0.3 M is 1.416×10⁻¹¹ g²cm⁴s⁻¹.

Fig 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-750 substrate subjected to cyclic high temperature oxidation in air at 900 °C for 100 cycles. 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 100 cycles. CeO₂ coating on Superni-750 substrate at 0.3M concentration has been found to be successful in reducing the

overall weight gain as compared to bare substrate. Whereas, CeO₂ coating on Superni-750 substrate at 0.1M and 0.2M concentration also have reduced the overall weight gain as compared to bare substrate.

Morphology of scale

Surface morphology and chemical composition of scale on bare as well as CeO₂ coated samples was studied by Scanning Electron Microscopy/Energy Dispersive Spectroscopy SEM/EDAX(Hitachi-3600N) after having undergone 100 thermal cycles at 900 °C (Fig 4 (a-d)). The scale on CeO₂ coated sample at 0.1 M concentration of cerium acetate after oxidation at 900 °C (Fig 4(a)) has light grey regions showing that coating is not dense and continuous. The scale on CeO₂ coated sample at 0.2 M concentration of cerium acetate after its oxidation at 900 °C Fig 4(b) is uniform and covers the substrate well. However, there are still some fine uncoated regions (dark spots). The scale on CeO₂ coated sample at 0.3 M concentration of cerium acetate after its oxidation at 900 °C Fig 4(c) is uniform, evenly spread and covers the entire substrate, which means spalling was minimum. This explains the lowered oxidation rate in the case of 0.3 M coated specimen. In bare substrate the scale formed has spalled, exposing the substrate to corrosive environment after 100 thermal cycles and hence is not protective (Fig 4 d). 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.5(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 (30.36 at.%) as compared to CeO₂ coated sample at 0.1M concentration (5.37 at.%) and 0.2 M concentration (11.70 at.%) of cerium acetate oxidized at 900°C after 100 h 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 superni-750 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 100 h.

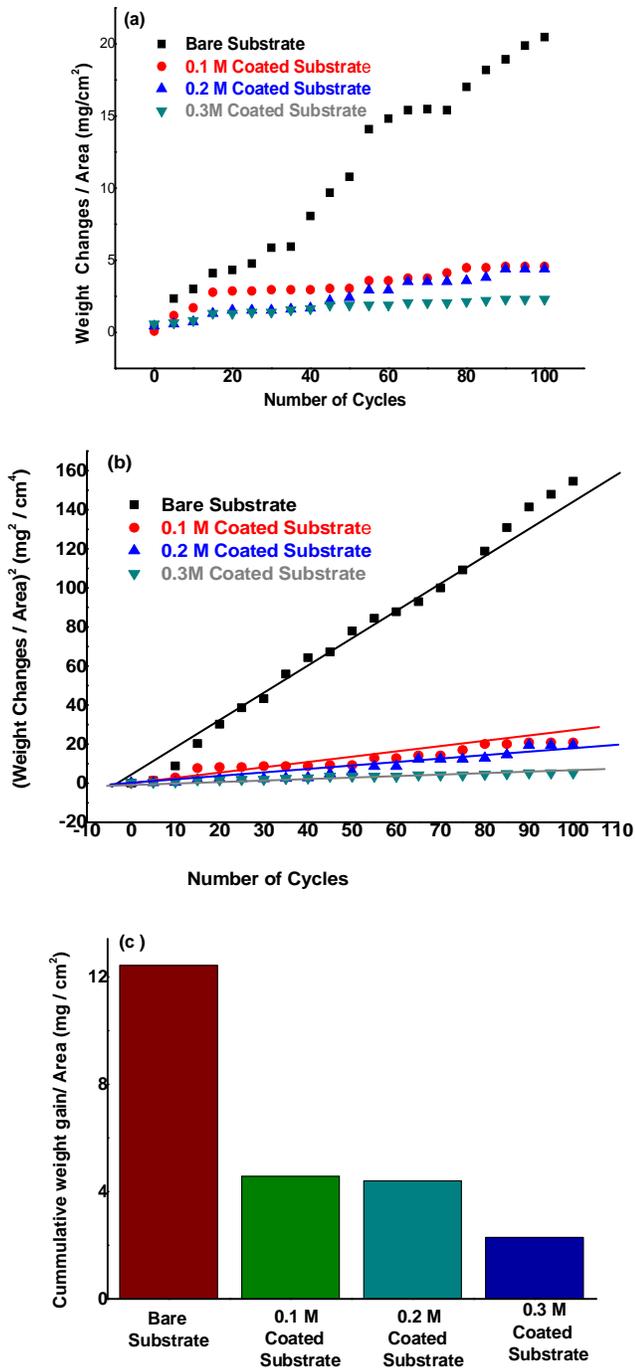
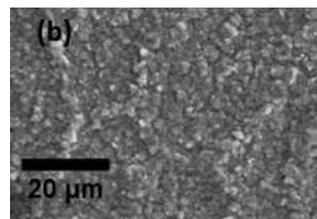
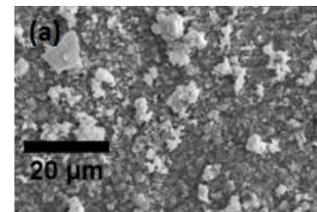


Figure 3:(a) Weight changes/area (mg/cm²) versus number of cycles and (b) parabolic rate constant, Kp (weight change/area)², mg²/cm⁴ versus number of cycles, for bare and coated samples oxidized in air at 900 °C, and (c) cumulative weight gain/area (mg/cm²) versus number of cycles, for bare and coated samples oxidized in air at 900 °C for 100 cycles.



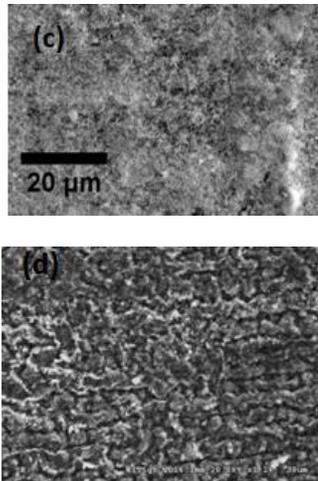


Figure 4: (a-c) SEM surface morphology of CeO₂ coated samples at different concentration of cerium acetate (0.1M, 0.2M and 0.3M) after oxidation for 100 h at 900 °C. (d) SEM surface morphology of bare after oxidation for 100 h at 900 °C.

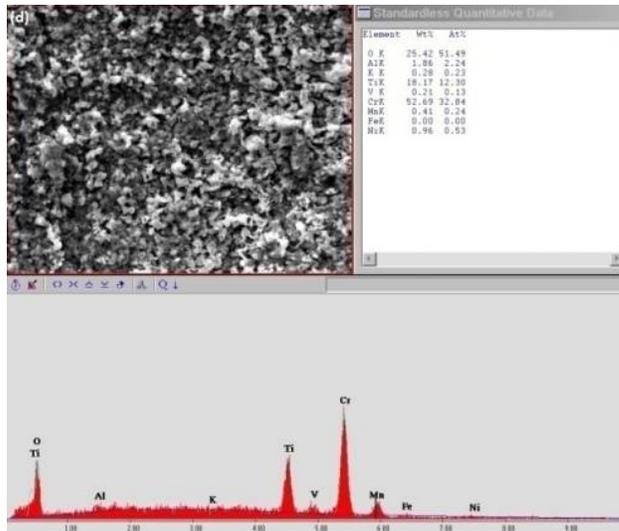
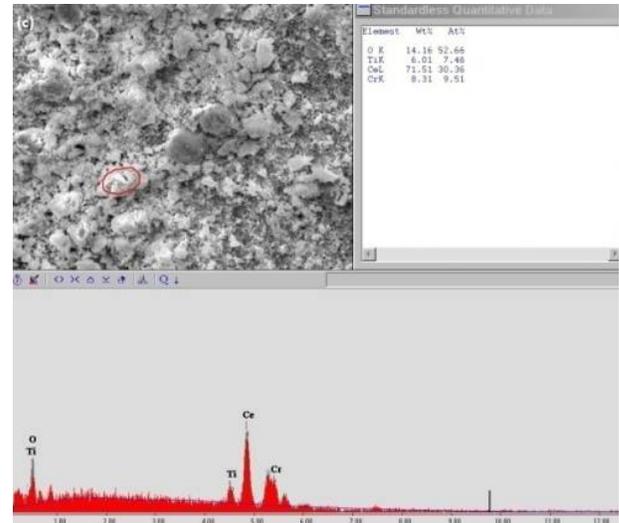


Figure 5: (a-c) SEM/EDS micrographs of the CeO₂ coated samples, prepared at different concentration of cerium acetate (0.1M, 0.2M and 0.3M), exposed to 900 °C for 100 h of thermal cycles. (d) SEM/EDS micrographs of the bare substrate exposed to 900 °C for 100 h of thermal cycles.

Oxidation Mechanism

CeO₂ coated superalloy at different concentration (0.1M, 0.2M and 0.3M) was oxidized at 900 °C for 100 h in air. CeO₂ oxide gets incorporated in the growing scale as confirmed by SEM/EDS analysis (Fig.5 (a-c)). 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 [18]. 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 CeO_2 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. Inhibition of the outward transport of alloy cations also results in a reduction in the parabolic rate constant as observed in the present work [19].

Particularly, CeO_2 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 as a 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 CeO_2 oxide is incorporated in the scale, Ce^{+4} ions might segregate in to grain boundaries in the oxide scale and block all possible paths, which in turn increase oxidation resistance of the coated sample.

It may be concluded from the present study that nanostructured CeO_2 coating can be used as an oxidation barrier (first layer of TBC coating i.e. first layer of CeO_2 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 CeO_2 coated superalloy has lower cumulative weight gain/area as compared to uncoated superalloy. The lower oxidation rate of nanostructured CeO_2 coatings on superalloy observed in the present work is in accordance with the results of F. Czerwinski and J.A. Szpunar [20]. The similar observations were made by Sundararajan et al. [4], where nano ceria coated 9Cr-1Mo ferritic steel showed a higher oxidation resistance when compared to the uncoated steel under similar conditions.

5. CONCLUSION

The high temperature oxidation kinetics of CeO_2 coated samples were compared with that of the bare Superni-750 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 bare substrate is due to the renewal of fresh surface of the materials. CeO_2 coatings on superalloy at 0.3M concentration, showed a lower oxidation rate as compared to CeO_2 coating at 0.1M and 0.2M concentration and bare substrate. It is due to the dense and adherent coating. 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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