

A Study of Nanostructured CeO₂ Oxidation Barrier Film on Superalloy

Larub Younis Khan *, Saima Sheikh², Urba Afnan,
Shafaq Lone and Atikur Rahman

Department of Metallurgical and Materials Engineering,
National Institute of Technology Srinagar,
Hazratbal Srinagar-190006, India
E-mail: *laraib985@gmail.com

Abstract—The high temperature oxidation behaviour of bare and nanostructured cerium oxide coating on nickel-based superalloy at 900°C for 100 cycles in air has been studied in present work. The film has been deposited with the intention to improve the oxidation resistance of the superalloy by acting as a diffusion barrier to cations and anions. The microstructural and morphological features of the scales formed on bare as well as coated samples were characterized by SEM/EDAX, Raman Spectroscopy. Thermogravimetric technique was used to investigate the oxidation behaviour of the coatings. The growth kinetics of oxide layers was studied from the weight changes on the bare and coated samples. It was found that the corrosion rate of nanostructured Cerium oxide coated superalloy was lower than that of uncoated superalloy due to formation of dense, adherent and protective oxide over the surface of coatings. Among the various coatings applied in this study at different concentrations of cerium acetate (0.1, 0.2 and 0.3) on superalloy, 0.3M proved to be the best, indicating a better protection among the coated superalloys. The morphological features and phases present in the coating were used to elucidate the mechanism of high temperature oxidation. A continuous thin layer of protective oxide films has formed over the cerium oxide coating exposed to air at high temperature, 900°C.

1. INTRODUCTION:

Corrosion is process in which a refined metal is converted to its stable form which can be its oxide, hydroxide or sulphide. It necessitates the gradual debilitation of the material by chemical or electrochemical reaction. It causes depletion of the properties of materials. The loss in properties can be in the form of their strength, appearance, permeability to liquids, gases, etc. Superalloys are the alloys which exhibit superior mechanical strength, creep resistance at high temperatures, good surface stability, corrosion and oxidation resistance. Super alloys find applications in chemical, petrochemical industries, power plants, oil and gas industries, aerospace, in the turbine blades, jet/ rocket engine, nuclear reactors, etc. at the same time, these are exposed to high temperatures and high sulphur, chlorine, carbon-containing compounds, water vapours, alkali and alkaline-earth metal salts due to which the superalloys experience corrosion. Superalloys are broadly of three types: Fe, Co, Ni-based superalloys. Higher amount of

alloying elements cannot be added because they cause embrittlement and decrease the melting point the refore, the nanostructured coatings must be applied to provide protection against aggressive environments. The purpose of coating is to create a dense oxide layer and to impede the diffusion of metals from the substrate. The coating must be appurtenant with the substrate. Although there are various methods of deposition of coating on the superalloys, some are costly, some are time and labour consuming. In the present work, nanostructured CeO₂ coating has been deposited on Superni-750 using electroless process. Electroless process involves the presence of a chemical reducing agent in

Table 1: Composition of Superni-750

Midh ani grade	Fe	Ni	Cr	Ti	Al	C	Mo	Nb
Super ni-750	-	73.02	16.45	1.70	-	-	-	1.20

solution to reduce metallic ions to the metal state. There are no external electrodes present, but there is electric current (charge transfer) involved. Instead of a cathode to reduce the metal, a substrate serves as the cathode, while the electrons are provided by a reducing agent. The process is easy to handle and cheap. Good adherence between film and substrate is obtained with the help of this process. In the present work, cerium oxide coating was deposited on the super alloy. The cerium oxide formed acts as barrier for the diffusion of metals from the substrate, which inturn is due to the reason that size of cerium is larger as compared to the metals present in the substrate.

2. EXPERIMENTAL

2.1 Material and coating formulation:

The Nickel based Superalloy viz., Superni-750 was procured from Mishra Dhatu Nigam Limited, Hyderabad (India) in annealed and cold rolled sheet form. The chemical composition of the substrate material is shown in table 1. Specimens of dimensions of usable size were cut from the sheet, ground on belt grinder and emery papers upto 320 grit size. The samples were then polished on polishing disc using alumina powder. The dimensions of the specimens were measured carefully with the help of digital Vernier caliper. Samples were hung in the scaffolds and then the scaffold along with the samples were placed in three beakers containing 0.1, 0.2 and 0.3 molar solutions of cerium acetate. The solutions were then heated on hotplate. The important parameters of the process like temperature (90°C), concentration of triethylamine (5 ml), time (2hrs) were kept constant.[figure 1]

2.2 Post coating treatment:

The samples along with the boats were preheated (annealed) at 250°C and the temperature of the furnace was increased upto 500°C and it was maintained for about 2hrs. The furnace was then turned off and the samples were allowed to cool in the furnace atmosphere.

2.3 Cyclic oxidation studies:

Cyclic oxidation studies were performed in air at 900°C for 100 cycles in muffle furnace. Each cycle consisted of 1hr heating followed by 20min cooling at room temperature. The weight change measurements of four samples were done with the help of electronic balance. The purpose of creating cyclic conditions was to mimic the hot corrosion conditions which the superalloys face during applications.



Figure 1: Picture of as coated sample.

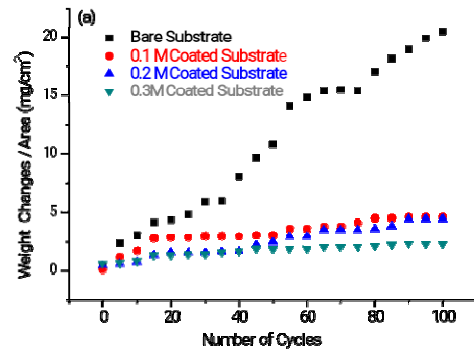


Figure 2: Plot between weight change /area (mg/cm²) and number of cycles

2.4 Characterization of coating:

The morphology and chemical composition of bare as well as coated CeO₂ samples was carried out with the help of SEM/EDAX (Hitachi-3600N) and Raman spectroscopy.

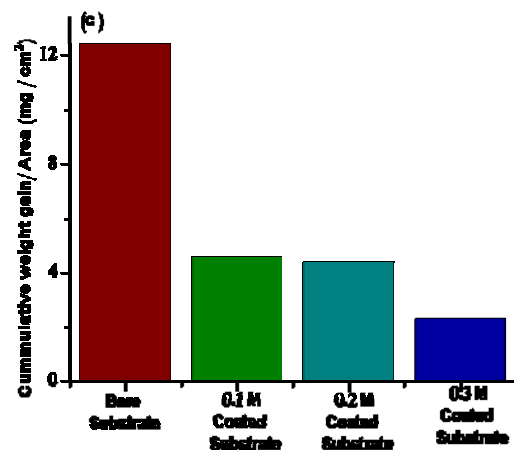


Figure 3. Graph of cumulative weight change.

3. RESULT AND DISCUSSION:

3.1 Visual observations:

When the samples were subjected to thermal cycles, samples lost their lusture, colour of scales changed, and the surface became rougher. In case of bare sample the colour of scale changed from greenish grey (at around 5th cycle) to dull grey (at around 100th cycle). In case of 0.1M coated sample, the colour changed from tan-brown (initial) to yellowish (upto 40th cycle). At the end of 100th cycle, the sample colour changed to grey with non uniform light brown coating. In 0.2M coated sample, the sample changed its colour from light

tan to dark grey due to spalling of coating. In case of 0.3M coated sample, the colour changed from light brown to golden brown and then to creamish with least grey spots till last cycle.

3.2 Cyclic oxidation:

The weight change data for all the four superalloys is plotted in figure 2. It indicated that three coated samples follow parabolic rate law while as bare sample showed huge deviation from the same. In case of bare sample, the deviation is evident particularly after 5th and 90th cycle while in case of coated sample, 0.1M and 0.2M coated samples showed slight deviation at around 50th cycle. In case of 0.3M coated sample, there is no particular deviation. The value of parabolic rate constant (K_p value) was obtained from the ratio of the slope of the curve graph with R^2 . The parabolic rate constant of the bare sample was found to be greater than the coated one. The cumulative weight gain for bare and coated samples is given in figure 3. The overall weight gain for bare, 0.1M, 0.2M and 0.3M oxidized superalloys was calculated as 12.43243, 4.56989, 4.40205, 2.29508 mg/cm^2 , respectively. These results indicate that coated superalloys are resistant to corrosion than bare one.

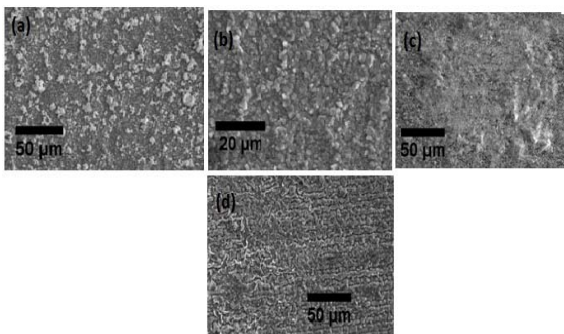


Figure 4. SEM micrographs at Lower Magnification (600X)

3.3 SEM/EDAX

SEM micrographs of coated Superni-750 (0.1, 0.2, and 0.3) and bare Superni-750 after 100 cycles at 600X and 1800X are shown in figure 4 and 5, respectively. The light grey regions represent the coated surface and dark grey regions, the surface of sample. From the micrographs it is clear that the coating is dense and continuous in case of 0.3M coated sample and least dense in 0.1M coated sample. In the micrographs of bare sample, pits, rough surface is observed since it lacks any protective coating and the scale formed has spalled off and had exposed the substrate to corrosive environment. EDX of the oxidized coated samples showed the presence of cerium, oxygen and some amount of titanium, cobalt and chromium. The cerium oxide formed acts as a barrier for the diffusion of metals from the substrate.

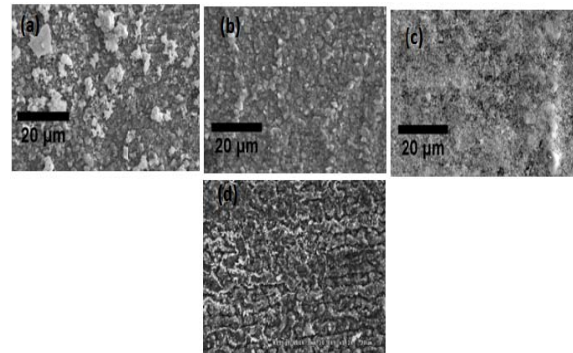


Figure 5. SEM micrograph at 1800X

While the EDX of bare oxidized sample showed presence of oxygen, nickel, chromium, titanium, etc on the surface which indicates that the uncoated samples were least resistant to corrosion. Hence this diffusion of substrate metals in case of bare sample was responsible for its higher corrosion rate.

3.4 Raman spectroscopy:

The Raman spectrum for CeO_2 coated Superni-750 at 0.1, 0.2, 0.3M concentrations after 100 cycles is given in figure 6. From the figure, it is clear that the highest peaks are around 450 cm^{-1} and 500 cm^{-1} . All the coated samples show a peak at 462 cm^{-1} [Neil J. Lawrence, Marcella Ihring, et al.] This confirms the presence of ceria (CeO_2) in the coated samples.

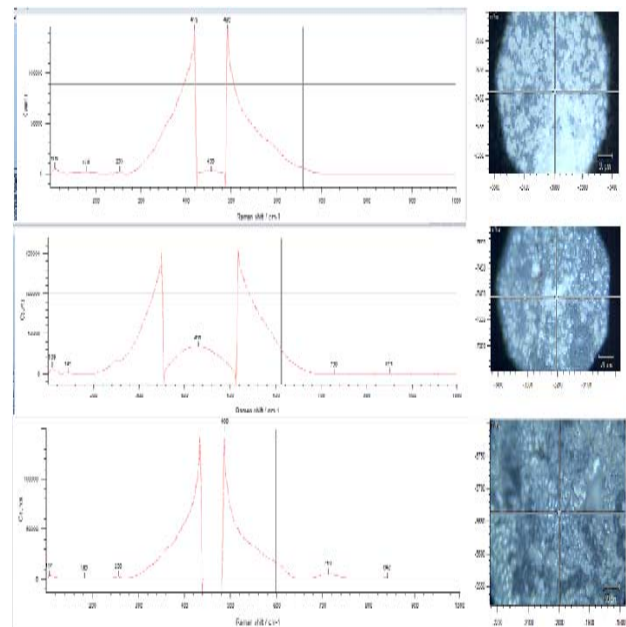


Figure 6. Raman spectrum for CeO_2 coated samples at 0.1M, 0.2M and 0.3M concentration of cerium acetate Superni-750 after 100 thermal cycles

4. CONCLUSIONS :

In the present work , four samples of Superni-750 were taken ,three of these were coated with CeO₂ at different concentration of cerium acetate(0.1M, 0.2M and 0.3M) bath and one sample has been kept bare and the degradation behaviour of CeO₂ coated sample at different concentration of cerium acetate(0.1M, 0.2M and 0.3M) on superni-750 exposed to air environment at 900 °C has been investigated. The high temperature oxidation kinetics of CeO₂ coated samples were compared with that of the bare Superni-750 and it was found:

There was a marked difference between weight gain due to high temperature oxidation at 900°C of bare Superni-750 and CeO₂ coatedSuperni-750.

Further it was 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.

1. The continuous mass gain of Superni-750 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.
2. Among the various coatings applied in this study at different concentration of cerium acetate(0.1M, 0.2M and 0.3M) on superni-750, 0.3M proved to be the best.
3. This was further proved by the morphological features of oxidized, coated and bare samples as characterized by SEM. It was shown that the scales formed on the surface of CeO₂ coated sample at different concentrations were having minimum defects.
4. 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
Surface scale morphology on oxidized CeO₂ coating was fine, dense and uniform.

Therefore, such coatings could enhance the high temperature oxidation resistance and improve the scale-metal adherence, but the mechanism of this improvement needs further investigation.

REFERENCES

- [1] Matthew J Donachie, Stephen j. Donachie, “ Superalloys: A Technical Guide”, 2nd Edition, DOI:10.1361/stgs2002p001
- [2] –McGraw Mars G Fontana-“ Corrosion Engineering”, Hill Book Company-1986- Pg.-304-309; 505,524
- [3] Atikur Rahman, R. Jayaganthan, “Effect of pH values on nanostructured Ni–P films” ,Appl Nanosci DOI 10.1007/s13204-014-0342-1
- [4]Deepa Mudgal, Pawn K.Verma, Surendra Singh, Satya Prakash, “High temperature degradation of Co based superalloy in incinerators environment”, Advanced Materials Research , Vol 585, 2012 .
- [5] A. Mahesh, R & Rengaswamy, Jayaganthan & Prakash, satya. . “Oxidation behaviour of selected Ni- And Fe- based Superalloys in air at 900°C under cyclic conditions.” ,Transactions of the Indian Institute of Metals.,2012, 61.10.1007/s12666-008-0064-8. (3)
- [6] Atikur Rahman, Vidin Chula, R. Jayaganthan, Ramesh Chandra, R. Ambardar , “Evaluation of High Temperature Oxidation Behaviour of Nanostructured Cr/Co–Al Coatings”- Springer Science-Oxide Met ,2010 ,74:341–358 DOI 10.1007/s11085-010-9217-3 (4)
- [7] Subhash Kamal, R. Jayagantha, S. Prakash ,Journal of Alloys and Compounds 472 (2009) 378–389- “High temperature oxidation studies of detonation-gun-sprayed Cr₃C₂–NiCr coating on Fe- and Ni-based Superalloys in air under cyclic condition at 900 °C” –
- [8] Atikur Rahman, R. Jayaganthan,, Ramesh Chandra b, R. Ambardar -Applied Surface Science 265 (2013) 10–23 - “High temperature degradation behaviour of sputtered nanostructured Co–Al coatings on superalloy.”-
- [9] Surface & Coatings Technology 260 (2014) 23–27- “Oxidation resistance of low-velocity.