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# Oxidation Performance Study of Nano structured Fe-18Cr-8Ni-5Al Coating Obtained By Plasma Enhanced Magnetron Sputtering Process

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**ABSTRACT: Nanocrystalline coatings are developed to meet the high temperature oxidation requirements of the water walls and superheater/reheater sections of ultra-supercritical (USC) boilers. In the present work Plasma Enhanced Magnetron Sputtering (PEMS) process was used to deposit nanocoating of Fe-18Cr-8Ni-5Al on 304L stainless steel. The as-sprayed coating was analysed using XRD and SEM/EDAX analysis. The as-deposited Fe-based nano-crystalline coatings exhibited ultra-fine grain structure. The long-term oxidation behaviour of uncoated and coated steel was evaluated through cyclic oxidation tests. The weight change for the exposed samples was measured followed by microstructural characterization. Exposed samples were characterized by SEM/EDAX analysis to identify the oxidation-product phases in the specimen scales. The results showed that the fine grain structure improved the oxidation resistance and promoted selective oxidation of Cr or Al.**

**Keywords:** Nanocrystalline coating, 304L stainless steel, oxidation.

## I. INTRODUCTION

Coal-fired power plants are an important part of the nation's power generating capacity. High thermal efficiency can be achieved primarily through the use of ultra- supercritical steam conditions (USC), which involves operation at higher steam temperatures and pressures above critical point [1]. Power plants incorporating USC technology can achieve higher cycle efficiency, and lower emissions of sulphur dioxide, oxides of nitrogen, and carbon dioxide than current coal-fired power plants. Consequently, a need arises to use advanced materials, such as austenitic stainless steels, ferritic steels, and nickel- base alloys that have adequate strength at high temperatures and pressures prevailing in USC boilers. Ferritic and austenitic alloys are excellent for advanced power generation applications because of the formation of Cr-containing oxides. On the other hand, these alloys become less protective at higher temperatures and in steam environments, as they are prone to accelerated attack by oxidation, sulfidization, and carburization usually resulting in rigorous metal loss leading to catastrophic failure. Thus, the poor oxidation and corrosion resistance, in using advanced materials systems such as Fe- and Ni-base alloys at such higher temperatures in USC system environments, where sulphur and water vapour are present, becomes a matter of concern [2, 3]. Oxidation protection of materials can be improved by in-situ development of a stable and slowly growing protective oxide scale such as $Cr_2O_3$ or $Al_2O_3$ on the external surface of alloy. Oxidation resistance of the alloy depends on the characteristics of the oxide layers, such as the growth rate and composition, which is better if the growth rate of the oxide is slower [4]. Protective coatings are normally produced by high-velocity oxy-fuel (HVOF) thermal spray process and chemical vapour deposition (CVD) process. Presence of varying amounts of rapidly solidified splats, oxide inclusions, porosity, high density locations, and residual stresses make these coating microstructures complex [5]. A strong need exists to develop reliable, durable coatings to enhance the long-term performance of USC boilers. The development of nanocrystalline coatings in recent years offers many advantages over conventional coatings currently used in the power plant industry. Nanocrystalline coatings deposited under optimized processing conditions can show noteworthy resistance to corrosion and oxidation. Gao et al [6] evaluated the behaviour of nanocrystalline Fe-Ni-Cr-Al alloy coatings on 310 stainless steel targets for oxidation at $950^o$–$1050^o$ C using the unbalanced magnetron sputter deposition technique [6]. Short term, 50 to 200 hour tests conducted on Fe-Ni-Cr-Al, Ni-Cr-Al [7-13], demonstrated the formation of a continuous layer of alumina $Al_2O_3$, which is required for oxidation and corrosion resistance. This oxide scale showed good scale spalling resistance during cyclic oxidation. Cheruvu et al [14] established that the oxidation service life of the nanocrystalline Ni-20Cr-4Al coating was limited to few thousand hours. Govindaraju *et al* [15] determined the influence of aluminium content on the long-term cyclic oxidation and corrosion behaviour of nanocrystalline coatings of Fe-18Cr-8Ni-xAl (where x = 0, 4, 10%) on 304L stainless steels produced by the plasma-enhanced magnetron sputtering process. In the present study Fe-18Cr-8Ni-5Al coating was deposited on SS304L steel by magnetron sputtering technique. The cyclic oxidation behaviour of the uncoated and coated steel has been studied.

## II. EXPERIMENTAL DETAILS

### *A. Samples and Sample Preparation*

The substrate material used in the study was 304L stainless steel whose nominal chemical composition by wt. % is: 0.02C, 1.67 Mn, 0.35Si, 18Cr, 8Ni, 0.19Mo, and 0.23Cu. The steel samples were cut to form approximately 15 x 12 x 4 mm size specimens. All the samples were machined to the final dimensions by water jet machining. Samples were polished to a mirror finish prior to coating process. The samples were coated with nanostructured coatings of Fe-18Cr-8Ni-5Al alloys by the Plasma Enhanced, Magnetron Sputtering (PEMS) process.

### *B. Coating Process*

PEMS process developed by Southwest Research Institute (SWRI) was used for depositing nanostructured coatings. In the PEMS coating process, argon gas had been used to operate the balanced magnetron target at a selected power level to deposit the coatings on the substrate. Filament-generated plasma was produced to provide ion bombardment of the substrate which heated the substrate to the required deposition temperature as well as controlled the coating microstructure. In the coating process, two magnetrons were used; one for Ni-Cr deposition and the other one for the aluminium deposition. Samples were hung on a rotating fixture mounted from the top of the chamber and the filament was placed at the bottom of the chamber. Samples were coated for 6 hours to produce an estimated coating thickness of 25-30 μm.

### *C. Surface Morphology/EDAX Analysis*

The surface morphologies of the coated specimens were studied with the help of a Scanning Electron Microscope (SEM) on JSM-6610LV Scanning Electron Microscope at IITR, Roopnagar, Punjab. The SEM analysis was done with an aim to understand the morphology of the as-sprayed coatings and to identify inclusions and pores in the as-sprayed coatings. The EDAX analysis gives the phases present in the specimen.

### *D.X-ray Diffraction (XRD) Analysis*

The samples were polished down to cloth wheel polishing. X-ray diffraction (XRD) analysis of the coated samples was carried out using Expert Pro PANalytical Company (Netherland) Model Expert pro MPD with CuKα radiation and nickel filter at 20 mA under a voltage of 35 kV at IITR, Roopnagar. The specimens were scanned with a scanning speed of 1Kcps in 2θ range of $10^0$ to $120^0$ and the intensities were recorded at a chart speed of 1cm/min with $2^0$/min as Goniometer speed. The software interfaced with the equipment showed the different phases present in the specimen.

### *E. High Temperature Oxidation Studies*

The oxidation studies were conducted in a silicon carbide laboratory tube furnace at an elevated temperature of 750ºC. The furnace was calibrated to an accuracy of ±5ºC using a platinum/platinum-13% rhodium thermocouple fitted with a temperature indicator. During the experimentation, each prepared specimen was kept in an alumina boat which was preheated at a constant temperature of 1200ºC for 12 hours and the weight of the boat and specimen was measured. The boat containing the specimen was inserted into the hot zone of the furnace set at a temperature of 750ºC and it was kept in the furnace for 1 hour followed by 20 minutes cooling at ambient temperature, after which the weight of the boat along with the specimen was measured and this constituted one cycle of the oxidation study.

### *F. Cyclic Oxidation Tests*

Cyclic oxidation tests were conducted on coated and uncoated specimens. The coated and uncoated specimens were inserted into a furnace which was maintained at a desired peak temperature of $750^o$ C and held at that temperature for 50 minutes. After soaking the specimens at the temperature of $750\ ^o$ C, the specimens were removed from the furnace for forced air cooling for 20 minutes to room temperature and then reinserted them back into the furnace. The thermal cycling testing was interrupted at predetermined intervals to weigh the specimens.

## III. COATING CHARACTERIZATION SEM/EDAX

### *A. Analysis of As-sprayed Coatings*

The SEM for the PEMS Fe-18Cr-8Ni-5Al coating on SS304L steel has been represented in Fig. 1. As shown in the figure SEM for Fe-18Cr-8Ni-5Al coating represents a massive structure consisting of clusters of small nodules. The surface has a smooth uniform facade. The EDAX analysis of the coating shows that it mainly contains Ni along with significant presence of Cr. No oxygen has been found at points 1 and 2, which indicates the absence of oxides in the coating. This might be due to the reason that coating process had been carried out in a vacuum chamber. The coating at point 1 contains 66% Ni, 27%Cr and 7% Al. At point 2, significant presence of Ni along with Cr can be seen.

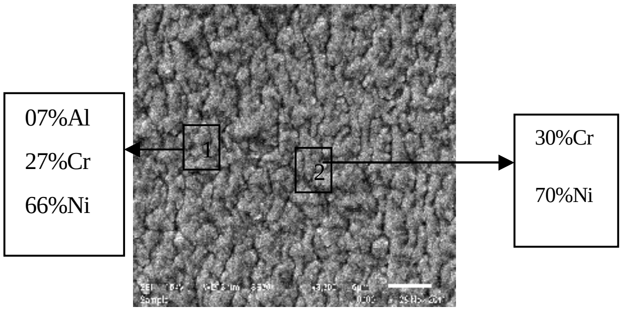


**Fig. 1.** SEM/EDAX analysis for Ni-Cr-5Al coating sprayed by PEMS technique on SS304L steel.

*B. XRD Analysis*
The XRD patterns for the PEMS coated sample with Fe-18Cr-8Ni-5Al coating in as-sprayed condition have been represented in Fig 2. This graph exhibits phases for Al-Cr-Ni.

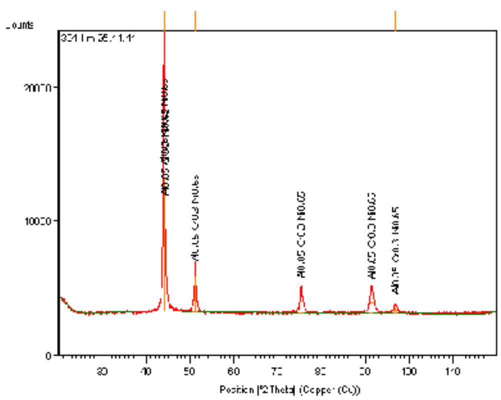

**Fig. 2.** XRD pattern for as-sprayed Ni-Cr-5Al coating.

## IV. CYCLIC OXIDATION TESTS

*A. Visual Examination*

**a. Uncoated Steels**

Macrograph of uncoated SS304L steel after oxidation for 50 cycles at 750°C has been depicted in Fig. 3. The colour of the oxide scale for the steel after the very first cycle of oxidation became greyish. Some portions of specimens were shiny golden greyish in colour. After the completion of 2nd cycle the top surface lost the luster and became grey. After 13th cycle grey colour started changing to brown which after 27th cycle started getting blackish brown. This colour became darker at the end of 39th cycle. After 45 cycles some part of surface became black while rest portion converted to dark grey.

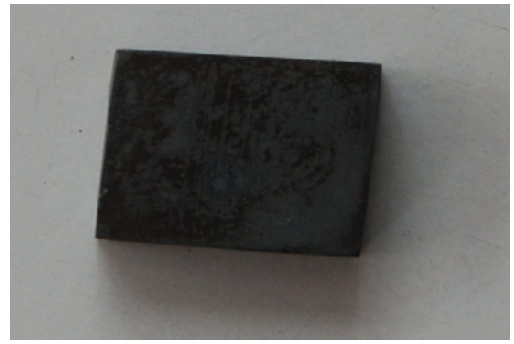

**Fig. 3.** Macrograph of uncoated coated steel subjected to oxidation in air at 750°C.

**b. Fe-18Cr-8Ni-5Al PEMS Coating on SS304L Steel**

A macrograph of PEMS coating of Ni-Cr-5Al on SS304L steel after oxidation for 50 cycles at 750°C has been depicted in Fig. 4. The top surface of the specimen lost luster and surface colour became partially brownish after the very first cycle. After three cycles the partially brownish colour of the surface became darker. This darkness kept on increasing upto the 7th cycle. A red coloured spot appeared on the surface of the specimen at the end of 9th cycle. After 12th cycle the number of spots rose to five of which two were very small. At the end of 15th cycle surface colour started changing to partially bluish gray. After 18th cycle the colour of edges of the sample started changing to brown. At the end of 29th cycle bluish gray colour of the surface started getting light. The coating remained intact by the end of the experimentation.

**Fig. 4**. Macrograph of Fe-18Cr-8Ni-5Al coated steel subjected to oxidation in air at 750°C.

*B. Weight change data*
The weight change plot for the uncoated and coated steel has been shown in Fig. 5. As clear from the plot both the uncoated and coated steels represented weight loss.

Though the initial weight loss of coated steel is higher which may be due to evaporation of volatile oxide scales of Al and Cr but after some cycles weight change became insignificant whereas the uncoated steel showed fluctuations in the weight change. The weight change remained constant after an initial weight loss of Fe-18Cr-8Ni-5Al coated steel.

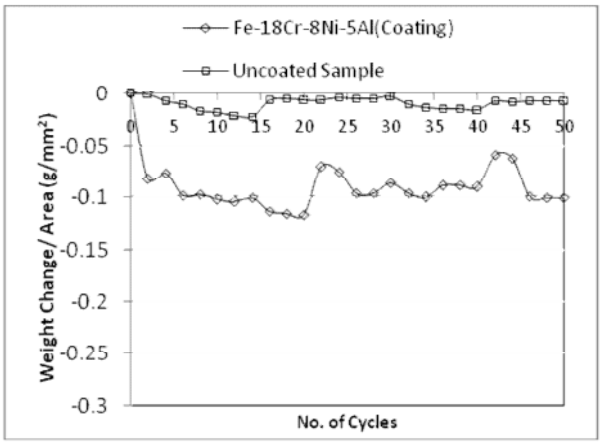


**Fig. 5.** Plot for weight change/area for uncoated and coated steel.

**a. Uncoated Oxidised SS304L Steel**

Fig. 6 represents the SEM for the oxidised uncoated SS304L steel. Analysis for the coating represents an uneven structure. The microstructure consists of two scales the lower scale contains micro particles and the upper surface gives a porous appearance. The EDAX analysis of the coating shows that amount of Ni is 5% at points 1and 2 and is nil at point 3 of investigation. Cr amount varies from 3% to 10% at the points of investigation. O has been found at all the points as major constituent ranging from 22% to 44%, which indicates the oxidation of the steel. C is also present at all the points of consideration in significant amounts. Very small amount of Cu is seen at point 3 along with 5% of Fe from the EDAX analysis.

**b. Fe-18Cr-8Ni-5Al PEMS Coating on SS304L Steel**

The SEM for the oxidised PEMS Ni-Cr-5Al coating on SS304L steel has been represented in Fig. 7. As shown in figure the SEM for Ni-Cr-5Al coating represents a massive structure consisting of clusters of particles separated by dark boundary lines. The surface has an uneven appearance. The EDAX analysis of the coating shows that Ni varies from 13% to 19% along the points of investigation.

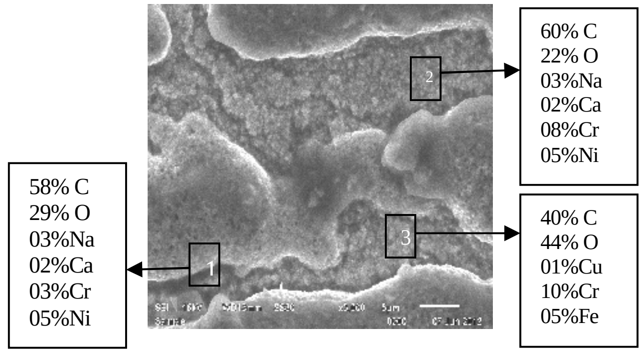


**Fig. 6.** SEM/EDAX analysis for oxidised uncoated SS304L steel.

Cr is also present after oxidation in nominal amounts compared to as sprayed coating. O has been found at point 1, 2 and 3 in significant amounts ranging from 23% to 33%, which indicates the oxidation of the coating. C is also present at all the points of consideration. Very small amounts of Fe are also seen at all the points of interest during SEM analysis. Al is also found at all the points during this microscopic study.

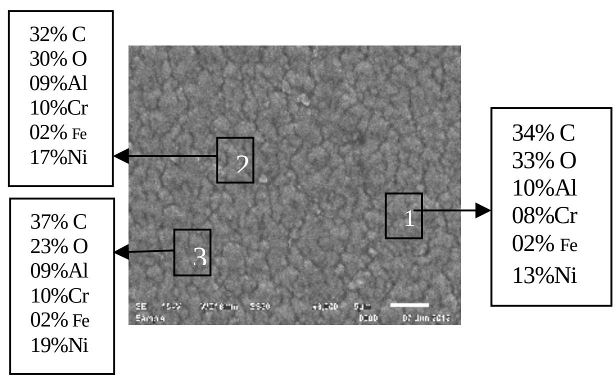


**Fig. 7.** SEM/EDAX analysis for oxidised Ni-Cr-5Al coating sprayed by PEMS technique on SS304L steel.

**V. DISCUSSION**

Nanocrystalline coatings of Fe-18Cr-8Ni-5Al (304 SS) were successfully deposited on 304L substrates using the plasma enhanced magnetron sputtering process. The phases of the coating were detected by the XRD analysis. The SEM/EDAX analysis confirmed the presence of Ni, Cr, and Al in the coating. The weight change analysis represented negligible weight change for the coated steel after an initial weight drop. This represents that the coating would be beneficial for long term usage under cyclic conditions. The enhancement in oxidation resistance of nanocrystalline coatings can be attributed to the short-circuit diffusion of aluminum or chromium through the net work of nanosized grain boundaries. The SEM/EDAX analysis represented presence of $Cr_2O_3$ and $Al_2O_3$ phases on the outer surface of the specimen after exposure to cyclic oxidation of coated steel. Both the oxides are protective in nature against oxidation. These oxides form a protective barrier against the diffusion of oxidising species [16]. This might have lead to better performance of the Fe-18Cr-8Ni-5Al coating under cyclic oxidation conditions.

## VI. CONCLUSIONS

- Nanocrystalline coating of Fe-18Cr-8Ni-5Al (304 SS) was successfully deposited on 304L substrate using the plasma enhanced magnetron sputtering process.
- XRD and SEM/EDAX analysis of the as-sprayed coating confirmed the presence of coating elements in the as-sprayed coating.
- The sputtered coating of Fe-18Cr-8Ni with aluminium showed improved oxide scale spallation resistance compared to uncoated specimen.
- The presence of protective $Cr_2O_3$ and $Al_2O_3$ phases on the outer surface of the coated steel after exposure to cyclic oxidation might have provided better protection to the base steel.

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