

## High temperature Oxidation and hot corrosion behaviors of uncoated and detonation gun sprayed $\text{Cr}_3\text{C}_2$ -25NiCr coating on SA516 boiler steel at 800°C

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### Abstract

In the present investigation  $\text{Cr}_3\text{C}_2$ -25NiCr powder was deposited on boiler steel SA 516 (Grade 70) by detonation gun process. The oxidation & hot corrosion performance of coated as well as bare boiler steel were studied in air and aggressive environment of  $\text{Na}_2\text{SO}_4$ -50% NaCl under cyclic conditions at an elevated temperature of 800°C. The kinetics of the corrosion was examined by the weight change measurements made after each cycle for a total period of 50 cycles. Each cycle consisted of 60 minutes heating in a silicon wire tube furnace followed by 20 minutes cooling in ambient air. The thermo-gravimetric technique was used to establish oxidation kinetics and Scanning Electron Microscopy /Energy Dispersive Spectrometry (SEM/EDS) techniques were used to analyze the corrosion products. Both the uncoated boiler steels suffered intensive spallation in the form of removal of their oxide scales, which may be attributed to the formation of unproductive  $\text{Fe}_2\text{O}_3$  dominated oxide scales.  $\text{Cr}_3\text{C}_2$ -25NiCr coated boiler steel consists of granules structure, which appear to be interconnected to each other at most of the places and forms oxide of chromium, which has found to be good corrosion resistance on both environments.

**Keywords:** Detonation-Gun, Elevated temperature, SA-516 (grade-70),  $\text{Cr}_3\text{C}_2$ -25NiCr coating, SEM/EDS morphology

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### 1. INTRODUCTION

The ongoing development in the material are intended for the elevated temperatures applications in order to facilitate to check on the degradation under the increased operational temperature of boiler tube, development and cooling schemes will lead to increased operation temperatures of gas turbines, boilers, and industrial waste incinerators. The combination of such high temperatures with contaminants of environment and low-grade fuels, such as sodium, sulfur, vanadium, and chlorine, require special attentions to the phenomenon of hot corrosion, which is one of the main failure modes of hot section components in gas turbines. Superalloys have been developed for high temperature applications, but they are not able to fulfill both the high-temperature strength and the high-temperature corrosion resistance simultaneously, so protective coatings on alloys are used to counter the effect of corrosion [1]. Oxidation is main mode of degradation of metals which affect the electric power generation units, especially in boilers, operating at elevated temperatures 600 °C to 1100°C [2]. In modern power generating units requires materials capable of withstanding high temperature, mechanical load and chemical degradation [3]. Only composite materials are capable of full fill such requirements, the base material provides mechanical strength, creep resistance and coating provides to increase the limit of working temperature and performance capability by allowing the mechanical properties of substrate material at oxidizing environment [4]. Detonation gun spraying is the most efficient technology, which is capable of obtaining high velocity of gas and metal particles tends to many times higher than speed of sound. This technique provides the possibility of producing high hardness coatings with significant adherence strength. This process has been widely used in different fields, such as petroleum, aviation, metallurgy and industries [5- 6]. Detonation gun (D-gun), which is

capable of obtaining high velocity of gas and particles approaching 4-5 times the speed of sound. This coating provides the excellent hardness and sufficient strength [7-8]. The D-gun method offers highest velocity (600-1200 m/s) for sprayed powders that are not obtained by plasma (400 m/s) and high velocity oxy-fuel (500 m/s) [9]. The main objective of this work is to investigate the high temperature oxidation and hot corrosion behavior of Detonation gun sprayed  $\text{Cr}_3\text{C}_2$ -25NiCr coatings in presence of air and salt at 800°C temperature. The experiments were conducted for 50 cycles, each cycle heating the sample one hour and followed by cooling 20 minutes under cyclic process.

## 2. Experimental

### 2.1 Material and coating formulation

**Table-1**

Chemical composition (wt %)	C	Mn	P	S	Si	Fe
SA516 (Grade 70)	027	0.85-1.2	0.035 max	0.035 max	0.13-0.45	Balance

ASTM-SA516 (Grade 70) boiler steel has been chosen as substrate materials as they are used in the boiler and gas turbine component because of their high strength and creep resistance at high temperatures. Specimen each measuring 20 mmx15 mmx5 mm approximately were cut, polished by using emery papers of 220,400,600 grit sizes and subsequently grit-blasted with the alumina particles of grit size 40 after that deposition of the  $\text{Cr}_3\text{C}_2$ -25NiCr coating was done by detonation gun spraying technique. The nominal chemical composition as shown in table1.

### 2.2 Development of coating

A commercially available  $\text{Cr}_3\text{C}_2$ -25NiCr powders having particles size 30-60  $\mu\text{m}$  size (M/S H.C. Stars Company, Germany) were deposited on substrate by Detonation gun method at XVX Powder M Surface Engineering Pvt.Ltd, Noida (India). All the process parameters were kept constant throughout the coating process.

**Table.2.** Thermal spray parameter used for detonation gun coating

Oxygen Flow rate	2800 SLPH
$\text{C}_2\text{H}_2$	600 SPLH
$\text{N}_2$	2400 SPLH
Spray distance	165 mm
Frequency of slots	3

SPLH: standard Liters per Hour

### 2.3. Characterization of as-sprayed Coating

The  $\text{Cr}_3\text{C}_2$ -25NiCr coating has been characterized with the help FESEM and EDS analysis. This microscopy was used to measure the porosity of sprayed coating. Scanning Electron Microscopy (SEM 430 model LEICA electron optix unit, England) was used to characterize the surface morphology of the as sprayed  $\text{Cr}_3\text{C}_2$ -25NiCr coating and Energy Dispersive Spectroscopy (EDS) was used to characterize the formation of oxide scales at particular surface area of the sample.

## 2.4 High Temperature Oxidation Experiment

The studies were conducted at 800°C using silicon wire tube furnace having PID temperature controller. The samples were polished, which will provide uniformity of reaction while oxidation process occurs. Then dimensions measured by digital vernier calipers to calculate surface area which required for plotting of graph of weight gain per unit area verses number of cycle. Finally specimens were cleaned i.e. degreased by ethanol and kept in alumina boat. This alumina boat prior to performing of experiment was kept in silicon wire tube furnace for 5 hours at 250°C and then kept in furnace at 800°C for two hours so that moisture is totally removed from boat. After that the sample was kept in boat and weight was taken initially and then placed in the furnace. Oxidation and hot corrosion behaviors of bare and coated steel SA516 has been investigated in oxidizing and salty environments under cyclic conditions at 800°C for 50 cycles. Each cycle specimen heating one hour at 800°C in silicon wire tube furnace followed by 20 minutes cooling at room temperature and their weight were taken by electronic balance (Make Contech, India) having sensitivity of 0.001 gms. Spalled scale was also taken into consideration which used to fall into the boat i.e. the weight was taken along with the boat.

## 3. Result and Discussion

**3.1 Weight Change Analysis-** Fig.1(a) shows that weight gain of both uncoated and coated samples in presence of air (25.5mg/cm<sup>2</sup>,15.2mg/cm<sup>2</sup>) and weight gain of both uncoated and coated in presence of salty atmosphere Na<sub>2</sub>SO<sub>4</sub>-50% NaCl (32.85mg/cm<sup>2</sup>,20.5mg/cm<sup>2</sup>).

Fig.1(b) shows the square graph of weight gain/area against number of cycle which denotes the parabolic rate of reaction(K<sub>p</sub>).The values of K<sub>p</sub> are based upon the parabolic rate equation for high temperature oxidation process given by-

$y^2 = (K_p \times t) + \text{constant}$ , where y is the weight change per unit surface area,t is the time ,and K<sub>p</sub> is the parabolic growth rate constant. The value of K<sub>p</sub> for uncoated and coated in presence of air are  $5.1 \times 10^{-10} \text{ g}^2\text{cm}^{-4} \text{ s}^{-1}$ ,  $3.8 \times 10^{-10} \text{ g}^2\text{cm}^{-4} \text{ s}^{-1}$  and the value of K<sub>p</sub> for both uncoated and coated samples in presence of salty atmosphere are  $5.5 \times 10^{-10} \text{ g}^2\text{cm}^{-4} \text{ s}^{-1}$ ,  $4.41 \times 10^{-10} \text{ g}^2\text{cm}^{-4} \text{ s}^{-1}$ .

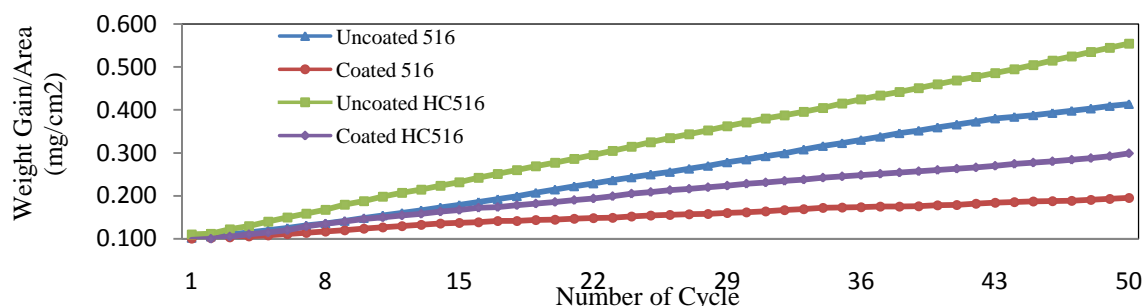


Figure. 1.(a)

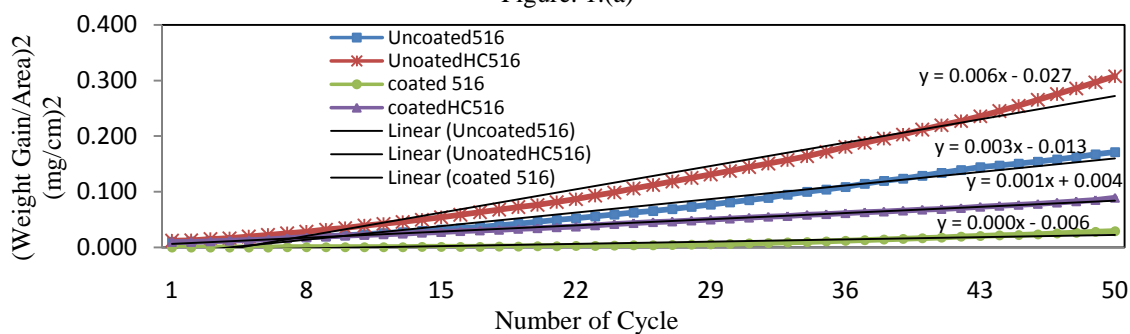


Figure.2 (b).

Fig.1. Shows that weight change/area vs number of cycle in fig1.(a) and fig.2(b) shows  $[\text{weight change/area}]^2$  vs number of cycle, for uncoated and coated with  $\text{Cr}_3\text{C}_2\text{-25NiCr}$  coating at  $800^\circ\text{C}$  for air and salty atmosphere for 50 cycles.

3.2 EDS - The energy dispersive spectrometer analysis fig.3(a), fig.(b),fig.3(c) & fig.3(d) shows peak of Fe,Cr,Ni,Cu,Mn,Zn,Si in both cases of coated and uncoated at  $800^\circ\text{C}$  in presence of air and salt. The uncoated sample in presence of air and salty environment, formation of Fe peaks dominates but in coated samples with  $\text{Cr}_3\text{C}_2\text{-25NiCr}$  sprayed coating by detonation-gun method,Cr,Ni,Mn peaks generated in major scale.

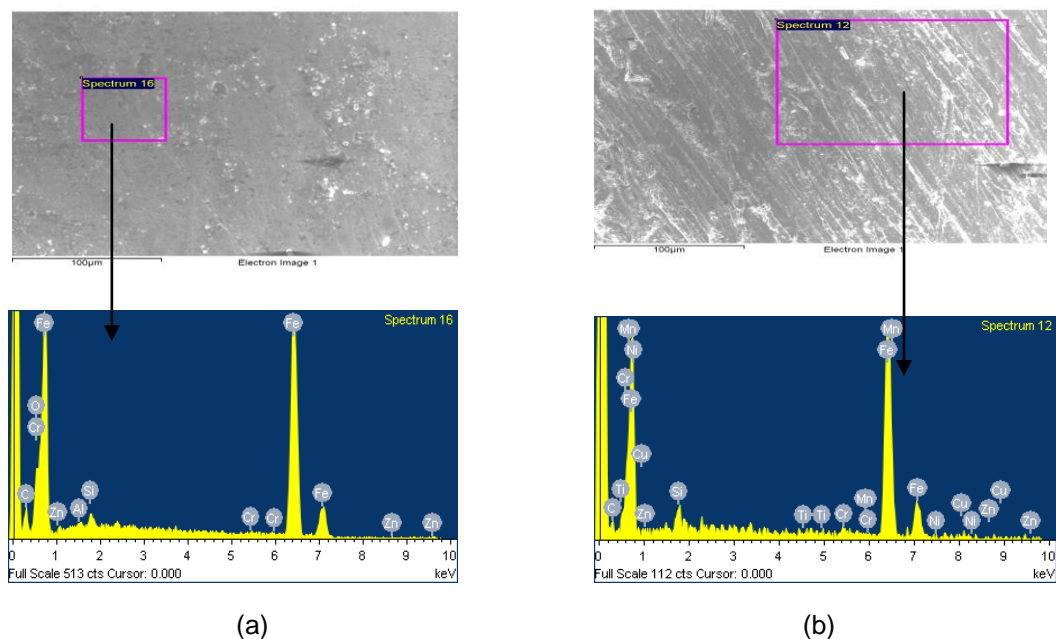


Fig.3 Shows EDS patterns of (a) uncoated (b) coated with  $\text{Cr}_3\text{C}_2\text{-25NiCr}$ , in presence of air on boiler steel SAE-516 at  $800^\circ\text{C}$

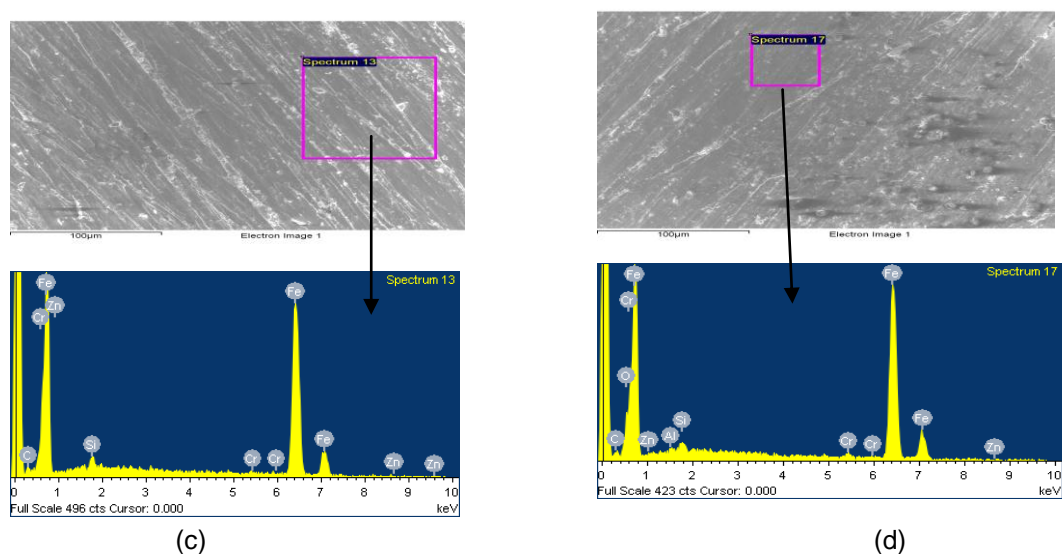


Fig.3 Shows EDS patterns of (c) uncoated (d) coated with  $\text{Cr}_3\text{C}_2\text{-25NiCr}$ , in presence of salty environment ( $\text{Na}_2\text{SO}_4 + 50\%\text{NaCl}$ ), on boiler steel SAE-516 at  $800^\circ\text{C}$



### 3.3 SEM (Scanning Electron Microscopy)-

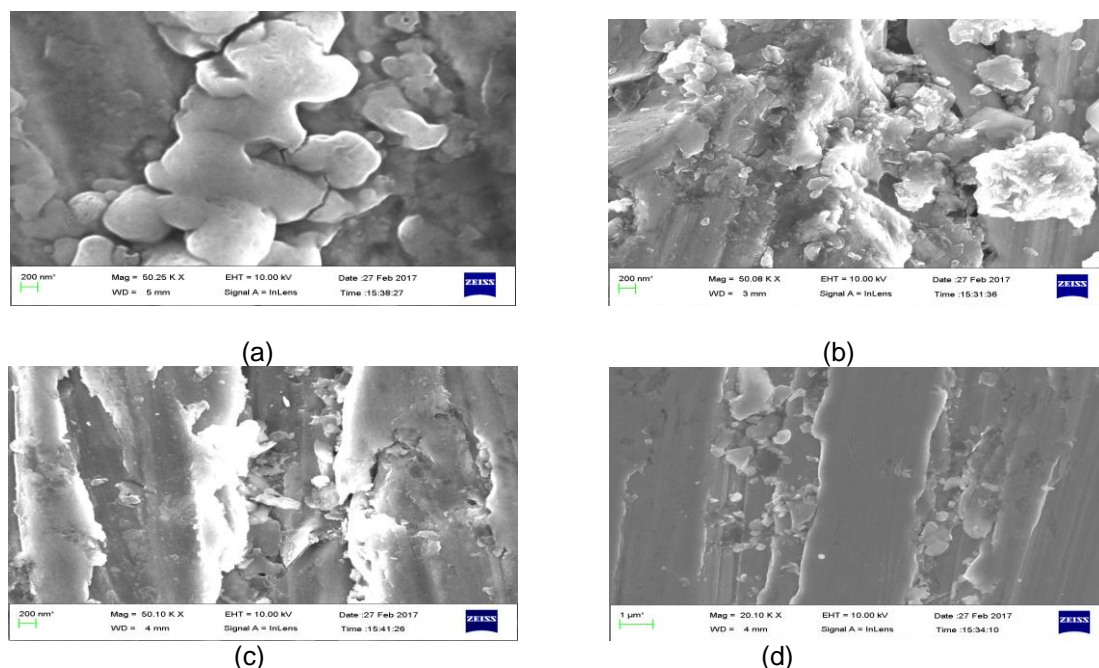


Fig.4. SEM micrographs of (a) SAE-516 uncoated with air (b) SAE-516 coated with air (c) SAE-516 uncoated with salt (d) SAE-516 coated with salt, subjected to  $\text{Na}_2\text{SO}_4$  -50% NaCl at  $800^\circ\text{C}$  for 50 cycles.

FE-SEM analysis of the scale formed after 50 cycles of the oxidation and hot corrosion in air and salt environments at  $800^\circ\text{C}$  on SAE-516 boiler steel. The upper layer has cloudy structure, with irregular sized cloud dispersed in the structure in Fig.4 (a) which has major space for the absorption of oxygen but Fig. 4(b) shows ice-berg structure, which has sufficient space for the absorption of oxygen. In salty atmosphere ( $\text{Na}_2\text{SO}_4$  -50% NaCl), uncoated upper layer has removing chips of metal in bulk space for the absorption of oxygen shows in Fig.4(c), but in coated structure Fig.4(d) consists of granules, which appear to be interconnected to each other at most of the places. There are some places where the black matrix is seen. The scale mainly has Cr and O as its main constituents. The uncoated boiler steel suffers from a catastrophic degradation in the form of intense spalling of scale in both the environments but  $\text{Cr}_3\text{C}_2$ -25NiCr sprayed coating showed good adherence to the boiler steel during the exposure with no tendency for spallation of its oxide reported by M.Kaur et.al [10] & Manpreet Kaur et.al [11].

Based upon the above discussion & results of the present study. It may be concluded that the detonation- gun spray  $\text{Cr}_3\text{C}_2$ -25NiCr coating could be useful to impart high-temperature oxidation and hot corrosion resistance to be given boiler steel.

## 4. Conclusions

1.  $\text{Cr}_3\text{C}_2$ -25NiCr coating could be deposited on SAE-516 boiler steel by D-gun spray technique and The value of  $K_p$  for uncoated and coated in presence of air are  $5.1 \times 10^{-10} \text{ g}^2\text{cm}^{-4} \text{ s}^{-1}$ ,  $3.8 \times 10^{-10} \text{ g}^2\text{cm}^{-4} \text{ s}^{-1}$  and the value of  $K_p$  for both uncoated and coated samples in presence of salty atmosphere are  $5.5 \times 10^{-10} \text{ g}^2\text{cm}^{-4} \text{ s}^{-1}$ ,  $4.41 \times 10^{-10} \text{ g}^2\text{cm}^{-4} \text{ s}^{-1}$ .

2. The  $\text{Cr}_3\text{C}_2$ -25NiCr sprayed coating was found to have ice-berg structure in presence of air and granular structure in presence of salty environment.
3. Uncoated SAE-516 steel suffered from accelerated oxidation and hot corrosion in the form of intense spalling of the scale during the oxidation and hot corrosion studies with a significant overall weight gain. During the exposure to the actual boiler environment at  $800^\circ\text{C} \pm 10^\circ\text{C}$ , the steel suffered from higher weight gain in comparison with its coated counterpart.
4. The Detonation-gun spray  $\text{Cr}_3\text{C}_2$ -25NiCr coating was found to be successful in maintaining its excellent adherence on the boiler steel in both environments. The coated SAE-516 boiler steel showed better oxidation and hot corrosion resistance in comparison with its uncoated counterpart.

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