

## Study of cyclic high temperature Oxidation behaviour of bare and Ni-Cr coating over low alloy steel

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### Abstract

Oxidation behaviour of low carbon and low alloyed steels at different Ni-Cr coatings thickness are studied, and also resistance offered by different coating thickness is also investigated. Hardness of low alloy steel was found to be increased from 202 to 342 VHN after the application of coatings. Parabolic rate constant ( $K_p$ ) for high temperature oxidation of bare, 200-250 $\mu\text{m}$ , and 250-300 $\mu\text{m}$  thick Ni-Cr coated low alloy steel were calculated to be 787.192, 0.235608, and 0.501787 ( $\times 10^{-10} \text{g}^2 \text{cm}^{-4} \text{s}^{-1}$ ) respectively.

**Keywords: Oxidation; high temperature; thermal spray coatings; D-gun spray.**

### 1. Introduction

Oxidation is the reaction between metal and air or oxygen in dry medium. Virtually every metals and alloys react with air, and rate of oxidation increases with increase in temperature [1]. Thus, in engineering applications oxidation resistance at elevated temperature must be taken into consideration in gas turbine, rocket engines, furnaces, petro-chemical systems etc. It is difficult to evaluate economical losses caused due to oxidation. Some of them are plant downtime, loss of product, loss of efficiency, contamination, overdesign etc. These issues can be resolved by taking number of preventive measures such as controlling process parameters, fuel selection, design aspects, chemical additive, use of inhibitors etc. One of the economical, efficient and reliable ways to control the oxidation problem is the application of a thin layer coating of oxidation resistant material over the components exposed to oxidising environment. Coatings with good thermal conductivity may enhance the service life of the components without affecting the thermal efficiency of the system. Thermal spraying coating technique can provide protection to the underlying substrate by producing a protective oxide layer at elevated temperatures. Detonation-gun (D-gun) technique is one of the efficient thermal spraying techniques that provide hard, wear resistant and dense micro-structured coatings and is considered as best thermal spraying technique in terms of coating density and porosity. Hence, D-gun spray coating is used to deposit coatings on heat facing components of the large units. Coating enhances the life-time of the material up to 10 times of coatings cost. The composition and structure of the coatings depend on exposed environments [2]. Ni-Cr coatings have high temperature oxidation resistance properties in oxidising environment [3]. During the service life of components, applied coatings are expected to form slow growing protective oxides on the exposed surface. These protective oxides should not allow the corrosive species to diffuse into the coating and to reach the substrate material, which results in the failure of the system [4]. Cyclic oxidation of Ti3Al-based alloy (Ti-24Al-11Nb) with a thin 80Ni-20Cr (at.%) protective coating were carried out at 600°C and 900°C in air. Ni-Cr layer formed protective oxide scale and prevented Ti diffusion into substrate material, resulted improved oxidation resistance. Cr has higher affinity to oxygen as

compared to Ni and formed more stable Cr<sub>2</sub>O<sub>3</sub>. Also, oxidation rate was found to be faster at 900°C as compared to that of at 600°C [5].

Oxidation behaviour of bare and cold sprayed Ni-Cr coated (Ni-20Cr, Ni-50Cr) SAE 213-T22 boiler steel were studied at 900°C and observed intense spalling and peeling off its oxide scale in bare specimen, due to the formation of un-protective (Fe<sub>2</sub>O<sub>3</sub>) oxide scale. Coated steel showed better oxidation resistance as compared to the uncoated steel. Author also observed that Ni-50Cr coated steel showed better oxidation resistance as compared to Ni-20Cr coated steel. This oxidation resistance was due to the formation of spinels and oxides of nickel and chromium [6].

Rajput et al. studied the hot deformation behaviour of low carbon and low alloyed steel and determine the safe workability region [7-9]. There are scarce of literature that reported the cyclic high temperature oxidation behaviour of D-gun sprayed Ni-Cr coated low carbon and low alloyed steels (boiler and tube materials). Also the study of resistance offered by different coating thicknesses (200-250 µm and 250-300 µm) of D-gun sprayed Ni-Cr coating were lacking. Hence, there is need to investigate the oxidation behaviour of low carbon and low alloyed steels in a comprehensive manner. In this work, oxidation behaviour of low carbon and low alloyed steels at different Ni-Cr coatings thickness are studied at 750°C, and also investigate the resistance offered by different coating thickness.

## 2. Experimental procedure

Low alloyed was procured in the form of rectangular sheet. Chemical compositions of substrate materials was determined using Spark spectroscopy and represented in Table 1, respectively.

**Table 1. Chemical composition of low alloy steel.**

ELEMENTS	C	Mn	Si	Ti	P	Ni	Cr	Al	Fe
Wt. %	0.084	1.12	0.211	0.014	0.023	0.031	0.038	0.037	Bal.

Specimens were cut in the dimensions of 15 x 15 x 5mm, followed by polishing using 320, 600, 1000, 1200 and 1500 grit size polishing papers. Before application of coatings, the specimens were degreased with the help of acetone. D-gun spray technique was used to deposit the Ni-Cr coating over the specimens. Coatings were deposited on the specimens in the thickness ranging of 200-250 µm and 250-300 µm on the six faces of the low alloy specimens at SVX Powder M Surface Pvt. Ltd., Greater Noida. Mechanical interlocking is the main mechanism of thermal spray coating adhesion/adherence.

High temperature oxidation study of bare and Ni-Cr coated low alloy specimens were conducted in a laboratory muffle furnace at a temperature of 750±10°C for 50 cycles with holding time 1 h. Specimens were kept in alumina boats during the experiments. The boats used for the study were preheated at a constant temperature of 1000°C for 10 h, with the assumption that the weight of the boat would remain constant during the course of high temperature study. Specimens were weighing after each cycle with the help of electronics weighing machine (DAB 220). Hardness were performed on bare and Ni-Cr coated specimens at 5 kg load and with dwell time 10 s with the help of Vickers hardness testing machine (VM-50). Scanning electron microscope (Carl Zeiss EVO 50) was used to study images, EDS and elemental mapping of the specimens.

## 3. Results and discussion

### 3.1. Low alloyed steel

Splat-like layered morphologies was present in the coatings due to the deposition and re-solidification of molten or semi molten powder particles. There were no indications of micro cracks in the microstructures. The dark spots in

the coating/coating substrate interface were mostly inclusions (Fig. 1). The circular jet-black dark dots were expected to be porosity. Some micro-pores were present and randomly distributed in the coatings. Further all the coatings irrespective of coating powder composition were found to be free from any visible surface cracks. The coatings in general had smooth surfaces. Energy dispersive x-ray spectroscopy (EDS) and elemental mapping of as-sprayed 250-300  $\mu\text{m}$  thick N-iCr coated low alloy steel specimen is shown in the fig. 1. Value of average hardness of bare low alloyed steel specimen was 202 VHN. Hardness increased rapidly with application of coatings from 202 VHN to 342 VHN.

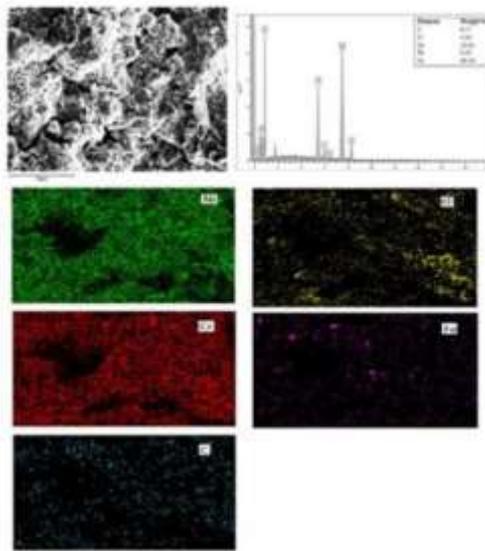


Figure 1. EDS (area analysis) and elemental mapping of as sprayed 250-300  $\mu\text{m}$  thick NiCr coating on low alloy steel.

Ni-Cr coated specimens showed minor weight gain up to 50<sup>th</sup> cycle, whereas high weight gains were observed in case of bare low alloy steel starting from 1<sup>st</sup> cycle and continued till 50<sup>th</sup> cycle. During oxidation of bare low alloy steel, scale formation was noticed at the end of 1<sup>st</sup> cycle and swelling of the scale was observed at the end of 13<sup>th</sup> cycle. Oxidized bare low alloy steel had irregular scales with cracks at the edges. The fragile scale formed over the surface of the bare steel that could not sustained, and started peeling off from the surface. Minor spalling of scale started at the end of 27<sup>th</sup> cycle for bare specimens. However, the scale formation continued till 50<sup>th</sup> cycle. Also some metallic sound was observed during cooling. Coated low alloy steel showed a continuous and defect free interfacial contact with the substrate steel. The colour of oxide formed just after 1<sup>st</sup> cycle over the bare and coated low alloy steel specimens was dark gray which remained till the completion of 50<sup>th</sup> cycle.

Fig. 2 shows the surface morphology (EDS and elemental mapping) of the bare and D-gun sprayed Ni-Cr coated low alloy steel specimens of different coating thickness after 50 cycles at  $750\pm 10^\circ\text{C}$ . Elemental mapping analysis of oxidized bare specimen shows scale rich in Fe and O as shown in fig. 2(a). This indicates the formation of iron oxides ( $\text{Fe}/\text{FeO}/\text{Fe}_3\text{O}_4/\text{Fe}_2\text{O}_3$ ). Small content of Fe was observed at the top layer of the coated specimen probably due to diffusion as shown in fig. 2(b) and 2(c). Scale formed over the bare specimen after 50 cycles was amorphous in appearance, and composed of peeled off particles. EDS results of coated specimens reported large amount of Cr and O and marginal amount of Ni at the points of analysis. This represents that the exposed areas of the scale seemed to be adherent in the case of coated specimens. Thus, the coated specimens were good oxidation resistance as no scaling was observed till the completion of 50<sup>th</sup> cycle, while the bare specimens were totally consumed.

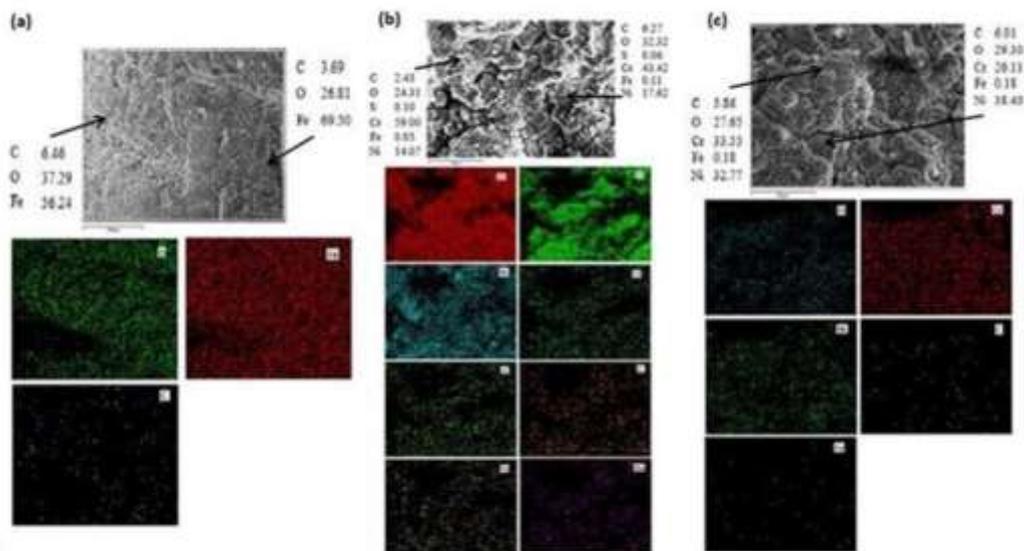


Figure 2.EDS spectrum and elemental mapping of (a) bare, (b) 200-250 μm, and (c) 250-300 μm, thick NiCr coated low alloy steel after high temperature oxidation of 50 cycles.

### 3.1.1. Evaluation of oxidation rate

Fig. 3 shows the graph between cumulative weight gains per unit surface area ( $\text{mg}/\text{cm}^2$ ) vs. number of cycles for the low alloy steel specimens subjected to high temperature oxidation at  $750 \pm 10^\circ\text{C}$ . Graph indicates that Ni-Cr coated low alloy steel specimens attained marginal weight gain till 50<sup>th</sup> cycle, whereas high weight gain was observed bare low alloy steel specimen. Overall weight gain after 50 cycles of high temperature oxidation for the bare, 200-250 μm, and 250-300 μm thick Ni-Cr coated low alloy steel specimens were calculated to be 118.44759, 2.1428, and 3.24849  $\text{mg}/\text{cm}^2$ , respectively. Overall weight gain in 250-300 μm thick Ni-Cr coated was higher as compared to 200-250 μm thick Ni-Cr coated specimens because bond strength decreased with increase in coating thickness results corrosive media penetrates easily in higher thickness. Therefore 200-250 μm thick Ni-Cr coated specimens showed better resistance against high temperature oxidation in comparison to 250-300 μm thick Ni-Cr coated low alloy steel. Further, square of weight gain ( $\text{mg}^2/\text{cm}^4$ ) vs. number of cycles graph was plotted for the low alloy steel specimens as shown in fig. 4. Parabolic rate constant ( $K_p$ ) values were calculated by fitting the plotted curves with the linear regression.

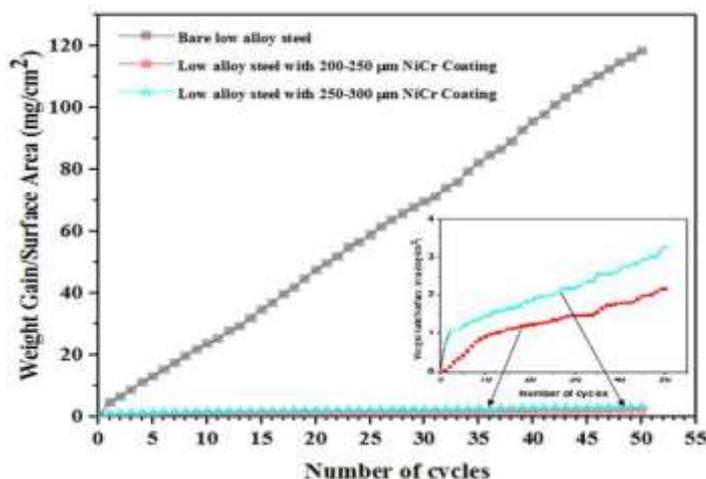


Figure 3. Weight change/surface area ( $\text{mg}/\text{cm}^2$ ) vs number of cycles graph of low alloy steel subjected to high temperature oxidation after 50 cycles.

In 1993, Wanger showed that ideal ionic diffusion-controlled oxidation of pure metals should follow a parabolic oxidation rate law as represented by equation (1) [6].

$$W^2 = k_p t + C \tag{1}$$

where  $W$  is the weight gain per unit area,  $t$  is time,  $k_p$  is the parabolic rate constant, and  $C$  is a constant.

Metals demonstrating a parabolic oxidation rate yield a straight line when the data are plotted as  $W^2$  versus time. It can be concluded from fig. 4 that Ni-Cr coated specimens follow nearly a parabolic rate law. The parabolic rate constants ( $K_p$ ) for bare, 200-250  $\mu\text{m}$ , and 250-300  $\mu\text{m}$  thick Ni-Cr coated low alloy steel specimens are shown in Table 3. Parabolic rate constant of coatings was found to be very small in comparison to that of bare steel specimen, indicating the protective nature of the coatings against high temperature oxidation. Since, lower the value of  $K_p$ , better the oxidation resistance.

Table 3. Parabolic rate constant ( $K_p$ ) of oxidized low alloy steel.

Specimen	$K_p(10^{-10} \text{ g}^2/\text{cm}^4/\text{s})$
Bare low alloy steel	787.192
200-250 $\mu\text{m}$ thick Ni-Cr coated low alloy steel specimens	0.235608
250-300 $\mu\text{m}$ thick Ni-Cr coated low alloy steel specimens	0.501787

The correlation coefficients for bare, 200-250  $\mu\text{m}$ , and 250-300  $\mu\text{m}$  thick Ni-Cr coated low alloy steel specimens were 0.96, 0.98, and 0.98 respectively, as shown in the fig. 4.

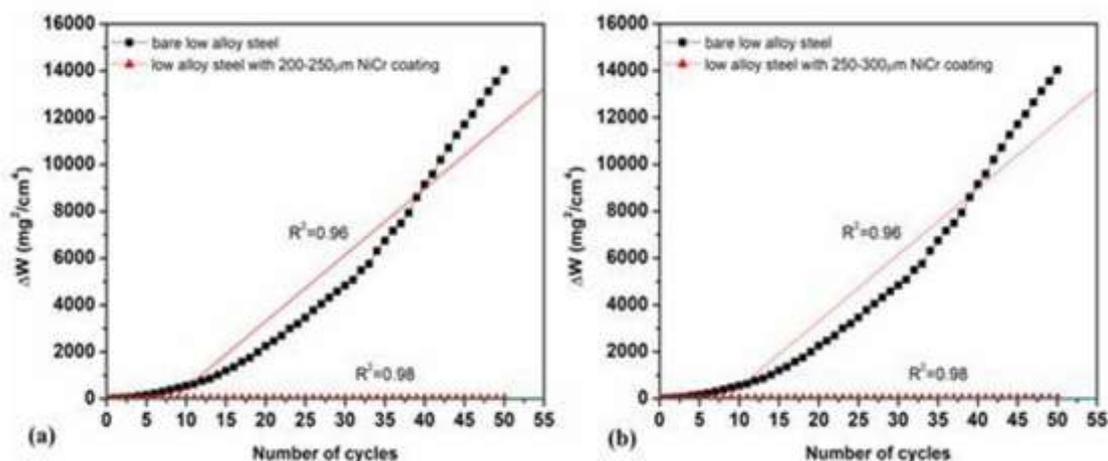


Figure 4. Weight gain square ( $\text{mg}^2/\text{cm}^4$ ) vs number of cycles graph of (a) bare and 200-250  $\mu\text{m}$  thick, and (b) bare and 250-300  $\mu\text{m}$  thick, Ni-Cr coated low alloy steel subjected to high temperature oxidation.

It was observed that coated specimens followed parabolic rate law and show constant weight gain, thereby slowing down the further oxidation process. Initially higher weight gain was observed probably due to accelerated interfacial reaction. This weight gain may be due the oxidation of entrapped air in the coating [3]. Elemental mapping of oxidized mild steel specimen show Fe and O element, that confirms the formation of iron oxides. Presence of Cr and O were confirmed by the needle/platelet type of oxides. Surface morphology of the coated specimen indicates higher amount of Ni, Cr and O which may be attributed to the formation nickel oxide and chromium oxide. Chromia provide resistance against oxidation at elevated temperatures, as it preferentially reacts with  $\text{O}_2$  to form the chromate and stabilizes the melt chemistry [10]. The presence of thick continuous band of protective oxides in the scales of coated

specimens does not allow the oxidizing species and the metallic ions to travel into the substrate and acts as a barrier to diffusion, results prevention of further oxidation processes.

#### 4. Conclusions

1. Hardness of low alloy steel was increased from 202 to 342 VHN after the application of coatings.
2. Parabolic rate constant( $K_p$ ) for high temperature oxidation of bare, 200-250  $\mu\text{m}$ , and 250-300  $\mu\text{m}$  thick Ni-Cr coated low alloy steel were be 787.192, 0.235608, and  $0.501787(\times 10^{-10} \text{g}^2 \text{cm}^{-4} \text{s}^{-1})$  respectively, The parabolic rate constant of coatings was found to be very small as compared to that of bare steel, indicating the protective nature of the coatings against high temperature oxidation.
3. 200-250  $\mu\text{m}$  thick Ni-Cr coated steel showed better resistance against high temperature oxidation as compared to 250-300  $\mu\text{m}$  thick Ni-Cr coated low alloy, because bond strength decreases with increase in coating thickness thereby corrosive media penetrates higher coating thicknesses easily as compared to lower coating thicknesses.

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