Role of Coating in Improving High Temperature Oxidation of Steel

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Abstract:- Oxidation is the major degradation mechanism of failure for various components operating at high temperature. Protective coatings are used to improve the oxidation resistance of such component. In the present investigation, Al_2O_3 and Ni-20Cr coatings have been deposited on SAE431 boiler steel by Detonation Gun Spraying Method. The oxidation performance of Al_2O_3 and Ni-20Cr coated as well as uncoated SAE-431 steel has been evaluated in air under cyclic conditions at an elevated temperatures of $800^{\circ}C$. Al_2O_3 coating on SAE431 boiler steel has shown approximately 26% improvement in the oxidation resistance of SAE431 steel whereas Ni-20Cr coating on SAE431 boiler steel has indicated about 21% improvement in the oxidation resistance as compared to the uncoated SAE431 boiler steel.

Keywords:- high temperature oxidation, boiler steel, detonation gun spray, Al₂O₃ coating, Ni-20Cr coating

I. INTRODUCTION

High temperature oxidation is the main failure modes of components in the hot sections of gas turbines, boilers, industrial waste incinerators, metallurgical furnaces, etc. [2]. Oxidation occurs when metals or alloys are heated in oxidizing environments, such as combustions atmosphere with excess of air or oxygen [3]. The stainless steels used for the tubes face the acute problem of degradation by high-temperature oxidation [1]. Susceptibility of particular metal surface to oxidation is dependent upon the free energy of formation of its metallic oxide [4]. Surface oxidation of metals is difficult to suppress at high temperature since oxide formation is thermodynamically favourable for most metals even in the presence of extremely small amount of oxygen [4,5]. Oxidation rates can be reduced through the formation of protective oxide layers from the selective oxidisation of alloying elements thereby suppressing the oxide formation of the other elements which have less affinity for the oxygen. In the initial stages of high temperature oxidation exposed metal atoms on the surface compete in oxide formation until the most thermodynamically stable oxide dominates [6].

Coatings are used in a wide range of applications including automotive systems, boiler components, power generation equipments, chemical process equipments, aircraft engines, etc. Thermal spraying is an effective and low cost method to apply thick coatings to improve the surface properties of the component [7][8]. Among the commercially available thermal spray coating techniques, detonation-gun spray is used to get hard, dense and wear resistant coatings [9][10].

Bala et al [11] investigated the oxidation behaviour of cold-sprayed Ni-20Cr and Ni-50Cr coatings on SAE213-T22 boiler steel at 900°C in air under cyclic heating and cooling conditions for 50 cycles. They established the kinetics of oxidation of coated and bare boiler steel with the help of weight change measurements. They observed that all the coated and bare steels obeyed parabolic rate law of oxidation. The uncoated steel suffered corrosion in the form of intense spalling and peeling of its oxide scale, which was perhaps due to the formation of unprotective Fe_2O_3 oxide scale. According to them both the coatings showed better resistance to the air oxidation as compared to the uncoated steel. Kaushal et al [12] used detonation gunspray technique to deposit Ni-20Cr coating on a commonly used boiler steel ASTM A213 TP347H. They subjected the specimens with and without coating to cyclic oxidation at an elevated temperature of 700°C in actual boiler environment to ascertain the usefulness of the coating. They observed that overall mass loss of ASTM A213 TP347H was reduced by 83% and thickness loss by 53% after the application of the coating. According to their investigation the detonation gun-sprayed Ni-20Cr coating was found suitable to impart erosion resistance to the given steel in the actual boiler environment. Badaruddin et al [13] investigated the oxidation characteristic of 1.10Cr-0.25Mo steel and the aluminized steel at 850°C for 49 h. The authors obtained significant improvement in the high-temperature oxidation resistance in case of aluminide coating due to the Al₂O₃ scale formation.

The present investigation is aimed to evaluate the oxidation performance of Al₂O₃ and Ni-20Cr coatings deposited by detonation gun spraying method on SAE431 boiler steel. The oxidation study is carried out in air under cyclic conditions at an elevated temperature of 800°C.

II. **EXPERIMENTAL PROCEDURE**

2.1 Development of coating

SAE 431 boiler steel which is commonly used as a boiler tube material is selected as the test material for the present investigation. The chemical composition of the material is given in Table 1. Specimens with dimensions of approximately 20 mm ×15 mm× 5mm were polished with SiC papers down to 180 grit size. Detonation gun spray coatings were deposited at SVX Powder M Surface Engineering (Pvt.) Limited, Greater Noida. The commercially available Ni-20Cr and Al₂O₃ powders were used as coating materials. Fig. 1 show the morphologies of Al₂O₃ and Ni-20Cr powder particles obtained using scanning electron microscopy (SEM). The powder particles sizes are found varying between 5µm to 22 µm for Al₂O₃ whereas particles sizes are found varying from 20µm to 45 µm for Ni-20Cr. The shapes of Al₂O₃ powders are angular whereas the shape of Ni-20Cr powder particles are spherical as can be seen from Fig.1 (a) and (b). The various parameters used during spraying are given in Tables 2 and 3.



(a)

(b)

Fig1: SEM micrographs of coating Powder (a) Al₂O₃ powder (b) Ni- 20Cr powder

Table 1 Chemical Composition (wt.%) of Boiler steel SAE-431.								
Material	С	Mn	Si	S	Р	Cr	Ni	Fe
SAE-431	0.04-0.1	2.0	0.75	0.03(max)	0.04(max)	17-20	9-13	Bal

	O ₂ (SLPH)	C ₂ H ₂ (SLPH)	N ₂ (SLPH)	Dist.
Al ₂ O ₃	4800	1920	720	200mm
Ni-Cr	2800	2240	720	165mm

SLPH:- Standard Liters Per Hour

Working Gases	Oxygen, Acetylene, Nitrogen, and Air	
Pressure of working gases	MPa	
Oxygen	0.2	
Acetylene	0.14	
Nitrogen	0.4	
Air	0.4	
Consumption of Powder per shot	0.05-0.02 g/shot	
Water consumption rate	15-25 liters/minute	
Firing rate	1-10Hz	
Coating thickness per shot	5-25µm	
Coating capacity at the rate of 7 µm/shot	$0.75 \text{ m}^2/\text{h}$	
System control	Manual/Semi auto	
Power supply from main		
Frequency	50-60Hz	
Voltage	430V	
Power	450VA	

Table 3: Specification of Detonation Spray Coating System

2.2 High temperature oxidation test

The cyclic oxidation studies of the coated and uncoated steel were conducted in a kanthol wire tube furnace at an elevated temperature at 800°C. The physical dimensions of the specimens were recorded carefully with a vernier calliper to evaluate their surface areas. The specimens were washed properly with acetone and dried in hot air to remove any dirt and moisture over them. During the experimentation, each prepared specimen was kept in an alumina boat and the weight of the boat and specimen was measured. The alumina boats used for the study were preheated at a constant temperature of 900°C for 6 h, with the assumption that their weight would remain constant during the high temperature cyclic oxidation study. Then the boat containing the specimen was inserted into the hot zone of the furnace set at a temperature of 800°C. The holding time in the furnace was 1 h in still air at an isothermal temperature of 800°C, followed by 20 min cooling at ambient temperature, after which the weight of the boat along with the specimen was measured and this constitute one cycle of the oxidation study. Visual observations were also made after the end of each cycle to record any change in colour, lustre and appearance.

III. RESULTS AND DISCUSSIONS

3.1 Characterization of the as sprayed coating

The surface morphology of as-sprayed Detonation Gun Sprayed Ni-20Cr coating on SAE431 boiler steel is shown in Fig. 3(a). The microstructure consists of irregular sized particles, most of the splats have deformed significantly due to the excessive deformation of the powder particles during impact on the substrate/coated layer. Some voids are also visible in the SEM image of the surface. Fig. 3(b) shows the SEM micrograph of as-sprayed Al₂O₃ coating on SAE431 boiler steel. The deposition of coating seems to be uneven and some can also be seen in the microstructure.



Fig. 3 SEM micrographs of as-sprayed (a) Ni-20Cr coating on SAE431 boiler (b) Al₂O₃ coating on SAE431 boiler steel

3.2 High – Temperature Oxidation Study

The oxidation behaviour of uncoated, Al_2O_3 coated and Ni-20Cr coated specimens was investigated at 800^{0} C.Weight gain data is obtained by dividing the weight gain after each cycle to the surface area of respective sample. Weight gain per unit surface area with number of cycles has been plotted for each uncoated and coated samples. Each samples were examined for change of colour during oxidation test.



Fig 4 Macrograph of the boiler steel samples subjected to cyclic oxidation in air at 800°C after 50 cycle

(a) uncoated SAE431 boiler steel (b) Al₂O₃ coated boiler steel (c) Ni-20Cr coated boiler steel

The macrographs of the bare, as well as, Al_2O_3 and Ni–20Cr coated boiler steel samples subjected to the cyclic oxidation in air at 800°C after 50 cycles are shown in Fig.4 (a), (b) and (c), respectively. During the oxidation studies the boiler steel underwent intense spalling, as well as, sputtering. At the end of 35th cycle some material removal in the powder form was observed in Fig4(a). During initial 5 cycle shows grey colour appeared on the surface of Al_2O_3 coated and after that gradually convert in blackish grey colour in Fig4(b). A corresponding macrograph of Ni–20Cr coated SAE 431 boiler steel has been depicted in Fig4(c) The initial colour of the sample was silver grey which changed to grey after first cycle. Some dark black lines were formed on the edges ,in all samples ,some spallation was observed ,the colour further changed to greenish with the progress of the experiment.



Fig 5 Weight change /area Vs. number of cycles plot for the uncoated , Al₂O₃ coated & Ni-20Cr coated SAE- 431 Boiler Steel subjected to cyclic oxidation in air at 800⁰C for 50 cycle.

The weight change for the bare and coated steel subjected to cyclic oxidation for 50 cycle in air at 800°C as shown in Fig5. It is evident from the plot that the uncoated steel has shown higher oxidation rate in comparison with its coated counterparts, The overall weight gain of SAE431 boiler steel is found to be 2.923977 mg/cm^2 at 800° C and where as Al₂O₃ & Ni-20Cr coated boiler steel it is found to be 2.30263 mg/cm^2 and 2.412281 mg/cm^2 respectively. From the graph it is seen that as the temperature increases oxidation rate increases approximately parabolically.

The (weight gain/unit area)² versus no of cycle plot as shown in Fig6 indicates that all the samples during oxidation process has nearly followed the parabolic rate law. The value of parabolic rate constant (K_p) have been calculated for all the investigated samples ,which are based on the parabolic rate equation for the high temperature oxidation process [14,15] given by

 $x^2 = K_P t + C$

where x is the weight change per unit surface area, t the time and K_P is the parabolic-growth rate constant. The parabolic rate constants K_p (×10⁻¹² g² cm⁻⁴ s⁻¹) for the Al₂O₃, Ni-20Cr coated SAE-431 in oxidation process are shown in Table 4. There is a visible deviation from the parabolic rate law in case of SAE-431 steel in to linear law . The Detonation gun sprayed Al₂O₃ & Ni-20Cr coated SAE-431 specimens have nearly follow the parabolic behavior up to 50 cycles at800°C. Lower the value of Kp , higher will be the oxidation resistance. The Kp value of Al₂O₃ & Ni-20Cr coated SAE-431 are found to be similar.



Fig6 (Weight gain/area)² VS number of cycles plot for the uncoated and Al₂O₃ & Ni-20Cr coated boiler steel SAE-431 subjected to cyclic oxidation for 50 cycles in air at 800°C

Table4 Parabolic rate constant, Kp values of SAE-431 and Detonation Gun sprayed Al2O3 & Ni-20Crcoated SAE-431 after oxidation at 800°C

Substrate	K_P Values (× 10 ⁻¹² g ² cm ⁻⁴ s ⁻¹)		
SAE-431 at 800°C	1.94		
Al ₂ O ₃ coated SAE-431 at 800°C	1.11		
Ni-20Cr coated SAE-431 at 800°C	1.11		



Fig7 Surface SEM micrographs of the samples after oxidation in air at 800°C for 50 cycles. (a)Ni-20Cr coated SAE431 boiler steel (b) Al_2O_3 coated SAE431 boiler steel (c) SAE431 boiler steel

V. CONCLUSIONS

In the present investigation, oxidation tests of boiler steel SAE-431 has been carried out at the temperatures of 800^{0} C. Further to improve the oxidation resistance of SAE-431 steel, Detonation Gun sprayed Al₂O₃ & Ni-20Cr coatings have been deposited and investigated. Following conclusions are drawn from the present investigation.

- Al₂O₃ & Ni-20Cr coating has been successfully deposited on the Boiler steel SAE-431by Detonation Gun Spraying method.
- The bare steel underwent spalling, sputtering, and peeling-up of its oxide scale, and the weight gain was higher during the cyclic oxidation studies in the air at 800°C.
- The weight gain per unit surface area graph of SAE431 Boiler Steel is found to be 2.923977 mg/cm² at 800^{0} C and for Al₂O₃ & Ni-20Cr coated boiler steel it is found to be 2.30263 mg/cm² and 2.412281 mg/cm² respectively.
- The oxidation processes for the detonation spray Ni-20Cr and Al_2O_3 coating followed the parabolic rate law of oxidation.
- Al₂O₃ coating has shown approximately 26% improvement in the oxidation resistance to SAE-431 steel. Whereas approximately 21% improvement in the oxidation resistance by Ni-20Cr coating on SAE-431 steel has been observed.
- Detonation sprayed Ni-20Cr & Al₂O₃ coating is found useful in imparting high temperature oxidation resistance to the boiler steel under investigation.

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