

Oxidation resistance of uncoated & detonation -gun sprayed WC-12Co and Ni-20Cr coatings on T-22 boiler steel at 900°C

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Abstract. Oxidation is the major degradation problem in aircraft, marine, coal fired boilers, factories, and sand-bar gas turbines. It is due to the usage of variety of fuels coupled with elevated working temperatures, which dominances to the degradation in all the applications. In the present investigation oxidation behavior of uncoated and detonation Gun sprayed WC-12Co and Ni-20Cr coatings on T-22 boiler steel has been investigated at 900°C in Silicon wire tube furnace for total duration of 50 cycles under cyclic condition, each cycle consisted of keeping the samples for 60 minutes at 900°C temperature followed by 20 minutes cooling at room temperature. Oxidation kinetics of uncoated and coated sample has been established with the help of weight gain measurements. The exposed samples were characterized by scanning electron microscopy/energy dispersive spectroscopy (SEM&EDS).The Ni-20Cr coating, with morphological observations was found to be more protective than uncoated and WC-12Co coated on T-22 boiler steel.

1. Introduction

Oxidation is the most important reaction at elevated temperature of metals which takes place when they are heated in presence of highly oxidizing environment. An oxidation reaction leads off with absorption of oxygen molecules from the ambience, nucleation of oxides, and formation of a thin coating of oxide, followed by its growth to a thicker scale [1].The initial degradation is at the gas/material interface and will proceed until the source material is consumed. Metal oxidation is governed by the Gibbs free energy change associated with the formation of a metal [2].The use of thermo gravimetric analysis and prolonged exposure in air, a Single-crystal Ni-base superalloy was investigated at different temperature range and find that weight gain of specimens was to be lower at higher temperature and higher at lower temperature[3].The coating can be defined as a layer of material established naturally or organized way of deposited on the surface of an object made of another material, with the aim of obtaining required anti-corrosive properties [4].Coating is a



techniques by which enlarge the operational limits of materials at higher temperature such that improve their performance capabilities. Preventive coatings also being used on structural alloys in energy transformation and energy utilization systems to protect surfaces from degradation[5-8]. Plasma sprayed coating is a cost-effective technique which has been used for many industrial application problems [9-10]. Detonation-gun (D-gun) spray technology has develop high standard coatings because of low thermal energy and high kinetic energy associated in the process[11]. D-gun spraying quality significantly change by changing the spraying parameter like volume of flue gas, distance and frequency of spraying[12]. In high temperature oxidation of superalloys, formation of protective oxide scale such as NiO, Cr₂O₃ and Fe₂O₃ is responsible for resistance against oxidation[13]. D-Gun spraying techniques can reach maximum temperature up to 3850°C, and accelerated particles speed from 600 m/s to 1200 m/s while plasma spraying speed up to 400 m/s and HVOF spraying maximum speed up to 500 m/s[14]. As a results, the D-Gun atomizer coating produces a compact microstructure. The focus of the paper are to explore the oxidation resistance of D-Gun deposited WC-12Co & Ni-20Cr coatings on T22 Boiler steel at 900°C heating and cooling is followed by 20 minutes for 50 cycles .

2. Experimental Procedure

2.1 Substrate Material

Boiler steel T-22, recently employed in a thermal power plant was selected as a substrate material. The nominal chemical composition C-0.08-0.12%, Mn-0.3-0.6%, Si-0.01-0.5%, S-0.01%, P-0.02%, Cr-8-9.5%, V-0.18-0.25%, Ni-0.4%, Nb-0.06-0.1%, N-0.03-0.07%, Al-0.04% and remains Fe, has been used as substrate material in the current experimental study. The specimens each measuring 20 mm X 15mm X 5mm, and were cut from the boiler sheet T-22. The specimen were polished up to 220 grit SiC paper finish and then were grit blasted with alumina powder (Al₂O₃) before deposition of coating.

2.2 Coating Formulation

The WC-12Co and Ni-20Cr were coated on sample T-22 boiler steel using by the commercially available detonation gun spray process. The WC-12Co and Ni-20Cr powder with its particle size 5–25 µm was used to coat the steel T22 by detonation gun spray technique. D-Gun was used to apply WC-12Co and Ni-20Cr coating on the steel T22 substrates at SVX Powder M Surface Engineering Pvt.Ltd, Greater Noida (India). All the process parameters were kept constant throughout coating process. The process parameters are given in Table.1

Table .1 Parameter used in detonation gun spray coating

1.Parameter	WC-12 Co- Ni-20 Cr
2.Pressure of working gases	MPa
2.1 Oxygen	0.2
2.2 Acetylene	0.14
2.3 Nitrogen	0.4
2.4 Air	0.4
3.Consumption of working gases per shot	m ³
3.1 Oxygen	27.10 ⁻⁵
3.2 Acetylene	23.10 ⁻⁵
3.3 Nitrogen	5.10 ⁻⁴
3.4 Air	5.10 ⁻⁴
4.Consumption of powder per shot	0.05-0.02 shot
5.Water consumption rate	15-25litter/minute
6.Firing rate	1-10

7.Diameter of acceleration portion of barrel or coating coverage	0.022m
8.Coating thickness per shot	5-25micro meter
9.Coating capacity at the rate of 7 micro/shot	0.75m ² /h
10.System control	Manual semi /auto
11.Over all dimensions	Meter
11.1 Gun	1.80 x 1.1
11.2 Control console	102x0.5x1.5
12.Power supply for main	
12.1 Frequency	50-60Hz
12.2 Voltage	430V
12.3Power	450VA
13.Sound pressure level	150Db
14.Relative humidity of ambient	50%

2.3 High Temperature Oxidation Experiments

The experiment was conducted at 900°C by using silicon wire tube furnace which consists of PID temperature controller. The substrate material T22 was subjected to polishing which will provide homogenous reaction while oxidation process occurs. The dimension was measured by digital venire callipers to calculate dimensions of the sample. Finally specimens were finished i.e. cleaned by ethanol and kept in alumina boat. The WC-12Co and Ni-20Cr coatings on T22 boiler steel were dried at 250°C for 2 hrs and 30 min's in tube to remove the moisture and then weighed, after this process the sample T-22 were ready for experiment. A cyclic study of 50 cycles was performed, one hour heating and cooling is followed by 20 minutes at ambient temperature in each cycle at 900°C. The temperature of experiment necessitated to be kept high at 900°C with respect to the earlier studies reported [15]. Sample of T-22 bare steel were kept in alumina boat and then inserted in silicon wire tube furnace. These samples were required to be kept in furnace at a temperature of 900°C followed by cooling down for 20 minutes at room temperature. Thereafter weight was recorded by electronic balance (Make Contech, India) having sensitivity of 0.001 gms. Spelled scale was also taken into consideration which used to fall into the boat i.e. the weight was taken along with the boat and this cycle repeated in 50 cycles in similar manner.

3. Results and Discussion

3.1 Weight Change Analysis- Weight change/area verses number of cycles plots for uncoated and WC-12CO & Ni-20Cr coated T22 boiler steel oxidized at 900°C in air up to 50 cycles have been shown in fig.1. The weight change data is usually used to establish the kinetics of the oxidation process. A higher weight gain represents higher rate of oxidation. Therefore, the oxidation rate of uncoated and coating of WC-12CO & Ni-20Cr can be compared with the help of weight change data. Uncoated and coated boiler steel shows weight gain from first six cycles are approximately same. The boiler steel material shows 108.48mg/cm², 29.92mg², 4.32mg/cm² are the average weight changes per unit area of uncoated, coated WC-12CO & Ni-20Cr coating materials. Ni-20Cr shows no weight change as compared to the uncoated and WC-12CO coating. WC-12CO coating had converted in to α -CO, so that coating is fully lost its efficiency and afterward oxidation would almost matches the direct oxidation of the substrate alloy material [2], but Ni-20Cr coated T22 boiler steel material when come in contact with the surrounding air, it forms Cr₂O₃ oxide scale which protects the material from the oxidation [16]. Initial weight gain may be attributed to lower oxidation rate of the coated specimen due to air which is entrapped during D-gun deposition and sheltered in the pores, since the cooling of

the coating was rapid i.e. there is shortage of time for the residual air to react with the surrounding coated alloy.

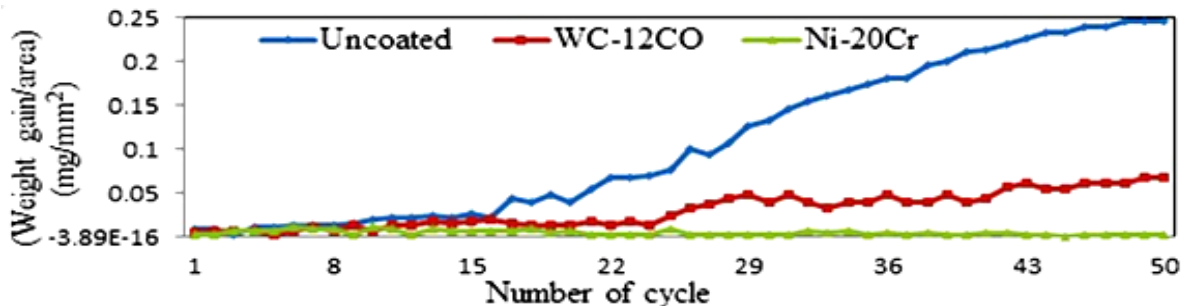


Figure.1.Weight gain /Area versus number of cycles plot for WC-12CO and Ni-20Cr coated and uncoated boiler steel subjected to air at 900°C for 50 cycles.

3.2 Oxidation kinetics

The oxidation kinetics may be defined by examining by growth-time constant k_p value, which was found by the following rate equation: $[(\Delta W/A)]^2/t = K_p$, where $(\Delta W/A)$ = change in weight gain per unit surface area, K_p = oxidation rate constant, t = exposure time. The square of weight gain data were plotted against the number of cycles as shown in fig.2, both of the coating followed the law of oxidation for the entire 50 cycles of study, as can be inferred from the plots. The parabolic rate constant of uncoated material was found to be much larger as compared to the both coated materials. Ni-20Cr coating shows stronger oxidation resistance as compared to uncoated material as well as WC-12Co coated material.

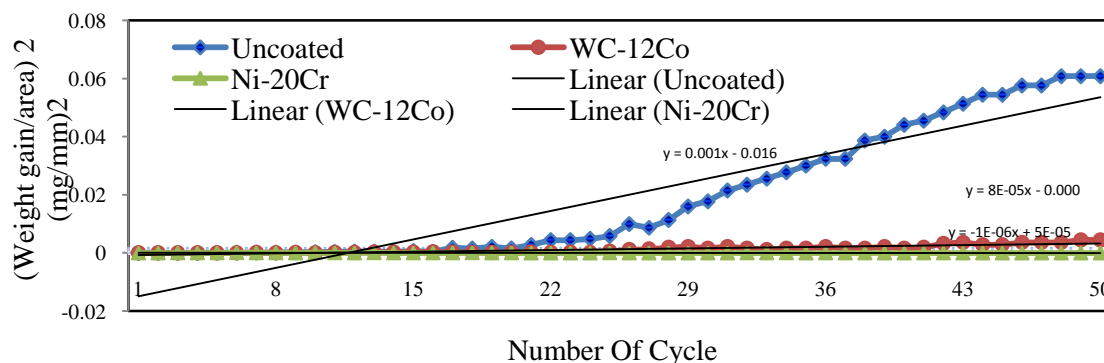
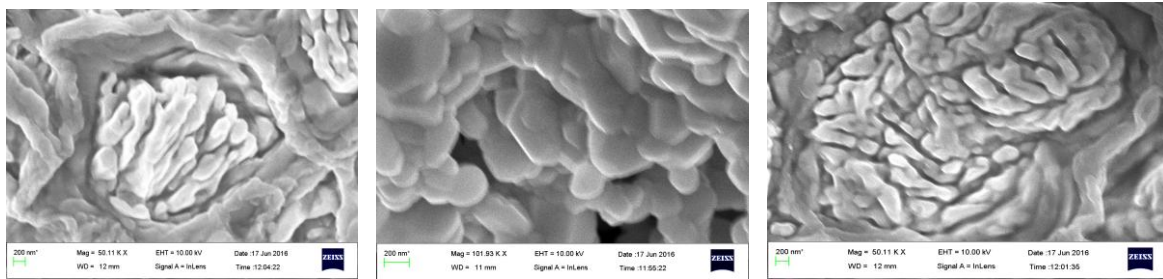


Figure.2 (Cumulative weight gain/area)² vs number of cycles for uncoated & WC-12CO & Ni-20Cr coated boiler steel subjected to air at 900°C for 50 cycles.

3.3. SEM Analysis

The surface morphology of the samples, substrate material of uncoated T22 shows that scale formation on the surface of the uncoated T22 boiler steel material was like flacks structure which has more porosity for absorption of oxygen. The WC-12CO coated material sample shows iceberg like structure which indicates that the sample coated with WC-12CO is more porous, but Ni-20Cr coated sample shows honeycomb like structure which has sufficient vacant sites for the absorption of oxygen.

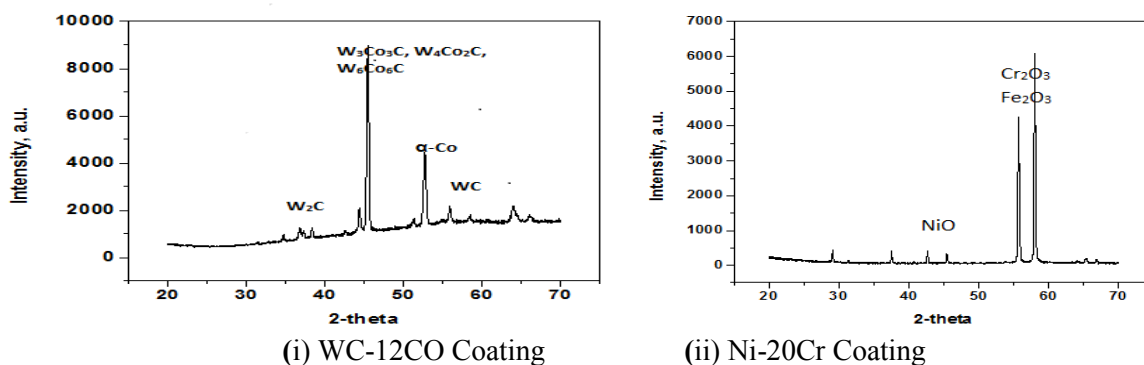


i) Uncoated T22 ii) WC12-CO Coating iii) Ni-20Cr Coating

Figure 3. Surface Scale Morphology of uncoated (i), and D-gun Sprayed WC-12CO (ii) and Ni-20Cr (iii) coatings on T-22 Boiler Steel subjected to Cyclic Oxidation in Air at 900°C for 50 Cycles

3.4. XRD Analysis

The X-Ray Diffraction analysis in fig.4 (a) shows of WC-12CO coating on boiler steel T-22 at 900°C and it is found that carbides of tungsten and cobalt (W_3Co_3C , W_4Co_2C , W_6Co_6C) are mainly formed. In fig.4 (b) shows of Ni-20Cr coating on boiler steel T-22 at 900°C and found that Fe_2O_3 , Cr_2O_3 form a protective oxide at the surface due to which further oxidation is prevented, but minute amount of NiO formed which acts as non-protective oxide.



(i) WC-12CO Coating

(ii) Ni-20Cr Coating

Figure 4. X-ray diffraction patterns for WC-12CO coated (i) & Ni-20Cr coated (b) on boiler steel T-22 at 900 °C by cyclic oxidation for 50 cycles

3.5. EDS analysis of the scales:

The surface morphologies with EDS spectrum for uncoated & coated with WC-12Co, Ni-20Cr coatings on T-22 boiler steel after oxidation at 900°C for 50 cycles are shown in fig.5 (i), (ii),(iii) respectively. The EDS spectrum of the oxidized WC-12Co, Ni-20Cr & coatings & uncoated boiler steels have shown peaks of Fe, W, Co, O, Ni and Cr that indicates the possibility of formation of oxides of Fe, Cr and CO in the scale. Presence of significant quantities of Ni and W are also revealed. In the presence of oxygen, Ni-20Cr coated T22 boiler steel forms Cr_2O_3 and WC-12CO coated T22 boiler steel forms α -CO, which oxides were more protective as compared to uncoated T22 boiler steel materials. These chromium containing oxides are protective as reported by UI Hamid [17] and Sundararajan et.al [18].

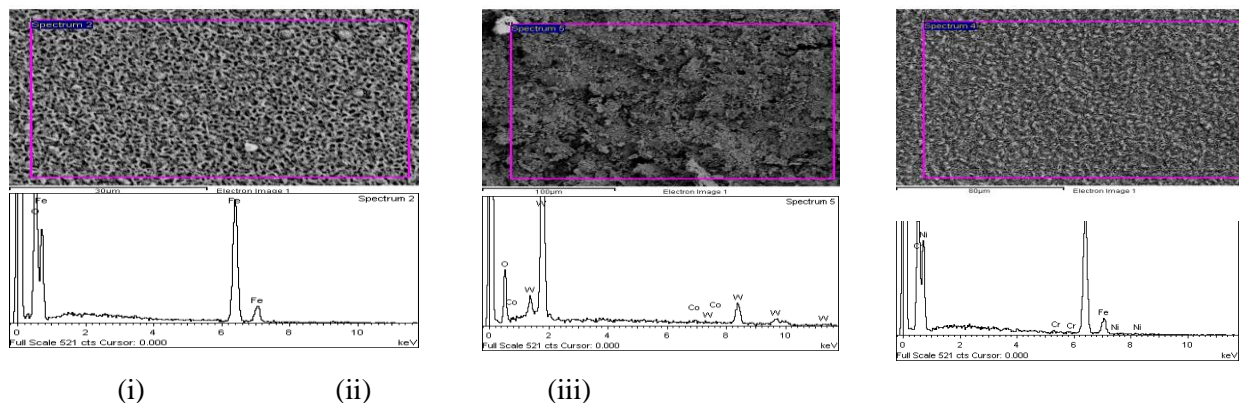


Fig.5. Energy Dispersive X-Ray of uncoated (i), D-gun Sprayed WC-12Co (ii) & Ni-20Cr (iii) coatings on T-22 boiler steel subjected to cyclic oxidation in air at 900°C for 50 cycles

4. Conclusions

Boiler steel T22 was successfully sprayed with two coating materials Ni-20Cr and WC-12Co by using detonation gun method. It was observed that average weight gain values 108.48mg/cm^2 , 29.92mg/cm^2 , 4.32mg/cm^2 and oxidation rate constant K_p 193×10^{-10} , 13×10^{-10} , $2.6 \times 10^{-10} \text{g}^2\text{cm}^{-4}\text{s}^{-1}$ of uncoated, coated WC-12Co & Ni-20Cr coatings respectively, hence Ni-20Cr coating is most resistive coating as compared to the WC-12Co coated and uncoated of boiler steel. X-ray diffraction analysis showed Ni-20Cr coated material has been found more resistive as compared to the WC-12Co coated material, due to the formation of Cr_2O_3 which has been more protective oxide at elevated temperature.

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