Development of Cold Spray Nanostructured Ni-20Cr Coatings for High Temperature Applications

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ABSTRACT

In the current investigation the high temperature oxidation behavior of bare and cold-spray nanocrystalline coated T22 and SA 516 boiler steels was studied under cyclic conditions at 900°C for 50 cycles. The kinetics of oxidation was established using weight change measurements for the bare and the coated boiler steels. Different characterization techniques such as X-ray Diffraction (XRD), Scanning Electron Microscopy/Energy Dispersive Spectroscopy (SEM/EDS) and X-ray mapping techniques were used to analyse the oxidation products. In terms of weight gain reduction, the coating was successful in reducing the weight gain of SA 516 and T22 steel by 94% and 67% respectively and thus offered good oxidation resistance to base steels. This may be attributed to its relatively denser structure, lower porosity and lower oxide content. Moreover, the developed nano-structured Ni-20Cr powder coating was found to perform better than their counterpart micron-sized Ni-20Cr powder coatings in terms of hardness and oxidation resistance.

Keywords: High temperature oxidation, oxide scale, cold-spraying, boiler steels, coatings.

1. INTRODUCTION

Materials degradation imposes a cost penalty on all engineering systems. Erosion and corrosion creates huge economic loss of the machinery used in the high-temperature applications, this loss alone in India is accounted to US$ 6500 million annually [1]. The high performance machinery/materials, subject to harsh temperature environments such as in boilers, steam turbines, gas turbines, require surface protection to avoid premature failure. The thermal degradation of materials due to oxidation and corrosion is a serious issue in many high-temperature applications [2]. Amongst the various alternatives, such as electroplating technique, chemical vapor deposition (CVD) and physical vapor deposition (PVD), the thermal spraying has gained wider popularity due to their capability to coat almost any material on almost any substrate [3-6]. Further, the thermal spray coatings can induce desired surface properties without affecting the metallurgical properties of the substrate material, without any significant damage to environment [7-10]. Since the temperature involved in other thermal spray coating techniques is high so there are chances of oxidation of feedstock powder during coating. Keeping view of this aspect a new thermal spray process called, cold-spray (CS) process, was developed by A. Papyrin and colleagues [11-13]. CS is a promising thermal spray process to deposit nano-structured coatings, and coatings having microstructures similar to original feedstock powder for several applications such as corrosion and wear protection.

In the recent past, fine-grained nanostructured coatings deposited, have received a considerable attention, due to their superior properties in comparison to conventional coatings [14-16]. Nano-structured coating materials synthesized by ball milling route exhibits good material properties [17-18]. Ni-Cr alloys possess several attractive properties, which include wear, erosion and corrosion resistance, and good thermal conductivity. Due to these properties, Ni-Cr coatings are frequently considered to control the problem of erosion-corrosion of power plant boilers [19]. The nanostructured coatings found to exhibit high corrosion resistance because of the fact of less porosity, enhanced grain boundary diffusion in nanostructured coating promoted the formation of denser Cr_2O_3 scale.

This work aims to study the high-temperature oxidation behavior of cold-spray nano-structured Ni-20Cr coating on T22 and SA 516 steel. The outcome of the study shall be useful to explore the possible use of the developed coating for boiler tubes protection under actual boiler conditions.

2. EXPERIMENTAL DETAILS

Substrate materials and coating powder

The substrate steels used in the present study were SAE213-T22 (T22) and SA 516-Grade 70 steels. Test specimens of 20 mm × 15 mm × 5 mm dimensions were cut from boiler steels and polished with SiC papers down to 220 grit. The polished specimens were then grit blasted using Al_2O_3 (grit 60) powder.

The nanocrystalline Ni-20Cr powder was used to coat T22 and SA 516 steel specimens. The powder was synthesized by blending three types of powders in a planetary ball mill. One of the powders was a commercially available Ni-powder (Loba Chemie, India) having 99.9% purity and 74 μm particle size, whereas the other powder constitutes of pre-synthesized Ni nano-particles (ball-milled) having an average particle of 67 nm. The third starting powder comprised pre-synthesized Cr nano-particles (ball-milled) with an average particle size of 60 nm. These three materials are designated as P1, P2 and P3 respectively for easy identification. These three powders were mixed so as to achieve a composition (wt%) of 64%P1-16%P2-20%P3.

The parameters used in ball milling were ball-to-powder (B:P) weight ratio of 10:1, running time (min) to pause time (min) ratio as 30:10, at 300 rpm with process control agent as Toluene. These parameters were selected after a comprehensive literature review and extensive experimentation [20-24]. The average particle size of Ni-20Cr alloy powder obtained after 20 hours of milling was confirmed by particle size analyser (Microtrac Bluewave) and found to be 11 μm. The average crystallite size of powder was calculated by Scherrer's formula using highest intensity peak and was found to be 10 nm, which was further confirmed by transmission electron microscope (TEM) (TECNAI G20) and found to be 10 nm.
Deposition of coating

The cold spaying (CS) process was used to deposit nanocrystalline Ni-20Cr powder on substrate steels at International Advanced Research Centre for Powder Metallurgy and New Materials (ARCI), Hyderabad, India. This cold-spray system uses a De Laval nozzle with a rectangular exit was used for deposition of the coating. The details about the nozzle geometry and the coating parameters were reported elsewhere [25].
Microstructural characterization of as-sprayed coatings and high temperature oxidation studies in air

Details regarding the characterization of as-sprayed coatings and high temperature oxidation studies in air have already been reported elsewhere [26]. After the exposure for 50 cycles, the oxidized samples were characterized by using XRD and SEM/EDS for the surface as well as cross-sectional analysis as per the standard metallurgical procedure.

3. RESULTS AND DISCUSSION

XRD analysis of as-sprayed coatings

The XRD analysis reveals the presence of Ni as the primary phase in both the coated steels. The grain size of the coating on T22 steel and SA 516 steel was found to be 36 nm and 31 nm respectively. The grain size of the coating was calculated from the width of high intensity peak of Ni. Porosity and surface morphology of as-sprayed coatings

The SEM micrographs of as-sprayed Ni-20Cr coating on T22 and SA 516 steels, along with EDS elemental composition (%) at selected points are shown in Fig. 1a and 1b respectively. A SEM micrograph of as-sprayed Ni-20Cr coating on T22 steel, along with EDS elemental composition (%) at selected points is shown in Fig. 1. The coating, in general is found to have a dense rock-like morphology. It is perceptible that this type of microstructure is a result of appropriate coalescence of nano-sized powder particles. The coalescence is so strong that individual powder particles have lost their identity to get packed properly to give rocky appearance. Some micro-voids are also present in the coating microstructure, which may give rise to porosity. The average apparent porosity of the coating was found to be 1.47 %. The element composition taken at selected points resembles with the composition of feed stock powder. Only a marginal amount of O (7 wt.%) is found at point 3. Similarly The SEM micrograph of Ni-20Cr coated SA 516 steel shown in Fig. 1b reveals a microstructure consists of irregular sized particles. Some of the typical dark regions are expected to be porosity. The particles seem to be deformed due to high impaction energy which is a characteristic of cold spray process. The elementary composition taken at the points 4 and 5 resemble the composition of the feedstock powder. Small amount of O (3 wt.%, 7 wt.%) is also found at point 2 and 3. This shows that the coating does not have oxides in its composition, as has also been supported by XRD analysis.

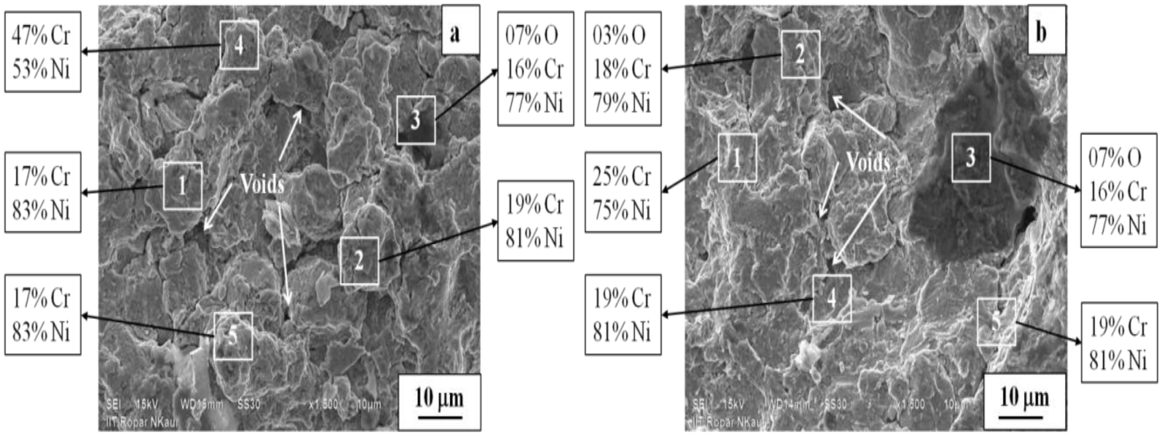


Fig. 1 Surface morphology and SEM/EDS analysis of cold-sprayed Ni-20Cr coating on (a) T22 (b) SA 516 boiler steels Cross-sectional analysis of as-sprayed coatings

The average coating thickness as measured from cross-sectional image (not shown here) was 225 μm. The coating also has some micro-voids at the coating-steel interface, as well as, throughout its microstructure. The average coating thickness of Ni-20Cr coating on SA 516 steel is 250 μm.

Cyclic oxidation studies
Weight change data

Weight change (mg/cm^2) versus number of cycles plots are shown in Fig. 2. The overall weight gain for the bare T22 and SA 516 steels was found to be 193.6 mg/cm^2 and 230.5 mg/cm^2 respectively. Therefore in terms of weight gain, T22 steel showed a relatively higher air oxidation resistance in comparison with SA 516 steel. In case of Ni-20Cr coated steels, the weight gain reduced to 63.15 mg/cm^2 and 14.5 mg/cm^2 respectively for T22 and SA 516 steels. In terms of weight gain, the cold-sprayed Ni-20Cr coating was found to reduce the weight gain of T22 by 67 % and of SA 516 steel by 94 % respectively, which is significant contribution with regard to controlling the oxidation of the substrate steels. Furthermore the plots between (weight change/area)^2 versus number of cycles have been shown in Fig. 3, which reveal that the bare, as well as, the coated steel samples, by and large, show conformance with the parabolic rate law of oxidation, especially the coated steels, for which deviations are very meager. This indicates that the coatings have shown tendency to act as diffusion barrier to the oxidizing species. The parabolic rate constant (K_p) was calculated by a linear least-square algorithm to a function in the form of $(x)^2 = K_p t$, where, 'x' is the weight gain per unit surface area (mg/cm^2) and 't' indicates the number of cycles representing the time of exposure. The parabolic rate constants for the bare and coated boiler steels calculated based on 50 cycles' exposure data are shown in Table. 1. These values clearly indicate that the coating is very successful in reducing the oxidation rate of the steels.

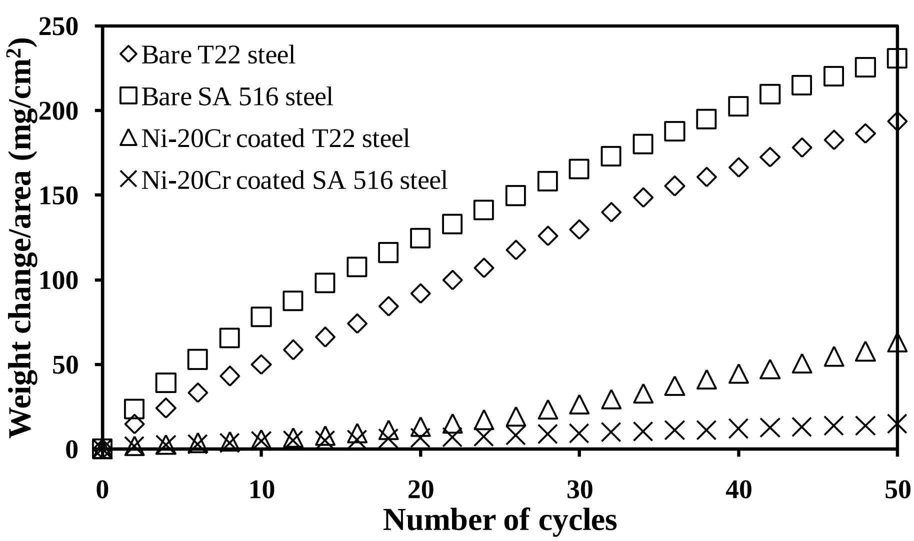


Fig. 2 Weight change per unit area vs. number of cycles plots for bare and cold-spray Ni-20Cr coated T22 and SA 516 boiler steels subjected to cyclic oxidation in air at 900°C for 50 cycles.

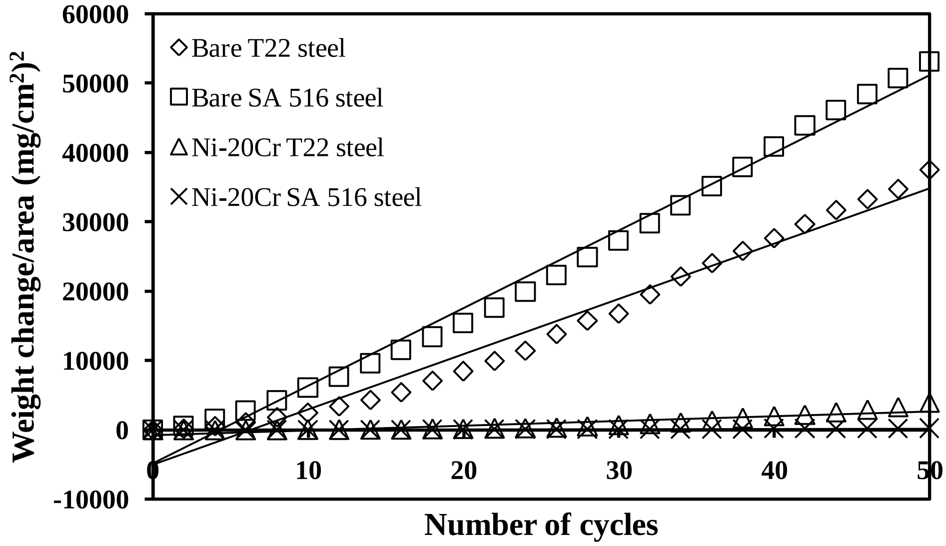


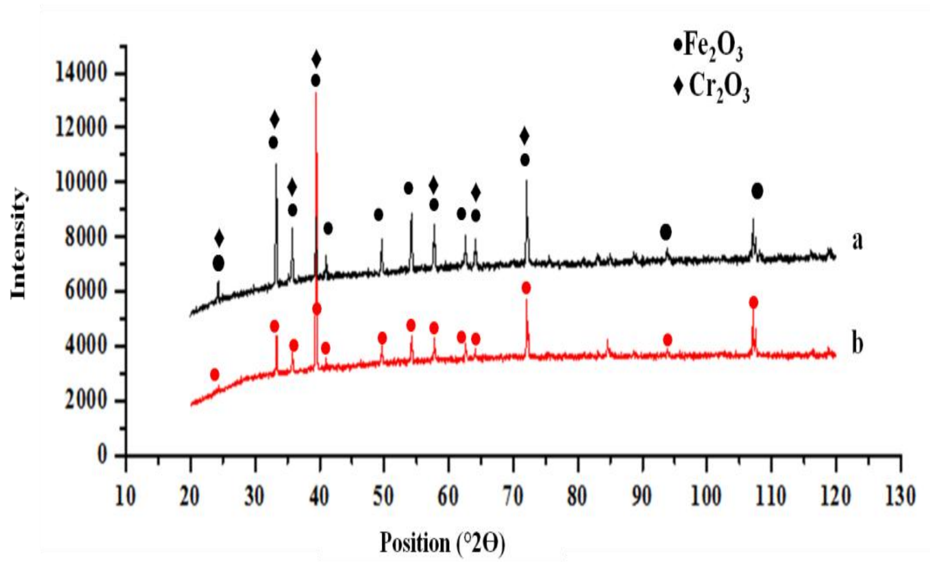
Fig. 3 (Weight gain per unit area)^2 vs. number of cycles plots for bare and cold-spray Ni-20Cr coated T22 and SA 516 boiler steels subjected to cyclic oxidation in air at 900°C for 50 cycles.

Table 1 Calculated values of parabolic rate constant (K_p) for the investigated cases

Description	K_p(x 10^{-10} $g^2/cm^4/s$)
Bare T22 steel	2212
Bare SA 516 steel	3108
Cold-spray Ni-20Cr coated T22 steel	193
Cold-spray Ni-20Cr coated SA 516 steel	11

XRD analysis of air oxidized samples

XRD analysis of the bare and the coated samples subjected to air oxidation at 900°C for 50 cycles is shown in Fig. 4. It is found from Fig. 9a and 9b that the oxide scale of bare T22 steel and bare SA 516 steel contains Fe_2O_3 as the main phase, whereas the analysis of Ni-20Cr coated T22 and SA 516 steel (Fig. 4c and 4d) indicates the presence of NiO and Cr_2O_3 as the main phases. Low oxidation shown by the coating may be due to the formation of these oxides in the scale. These oxides may form quickly due to enhanced grain boundary diffusion in the investigated nanostructured coating [27-28].



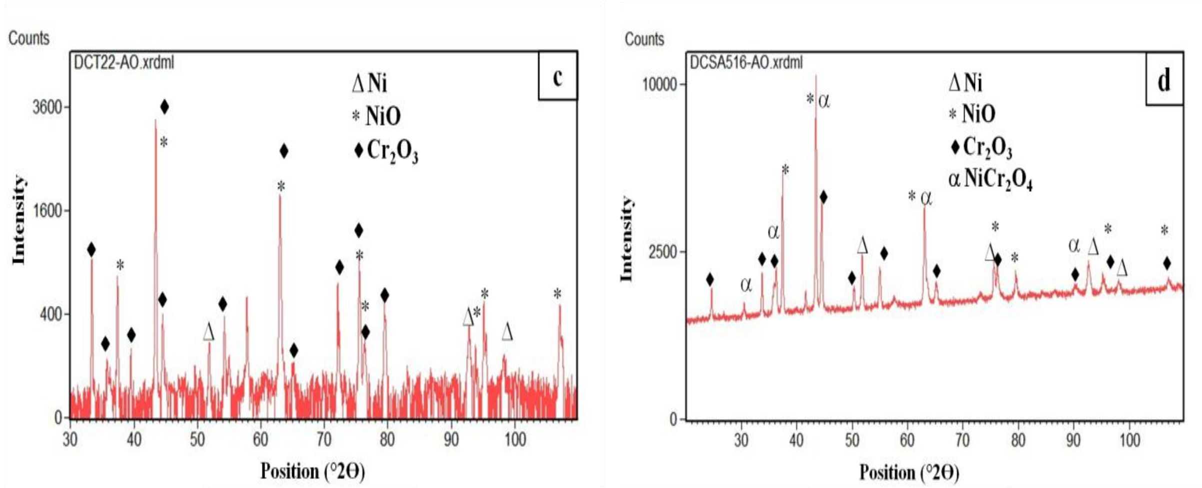


Fig. 4 Xrd Profiles Of Bare And Cold-Spray Coated Steels Subjected To Cyclic Air Oxidation At 900°C For 50 Cycles (A) Bare T22 Steel (B) Bare Sa 516 Steel (C) Ni-20cr Coated T22 Steel (D) Ni-20cr Coated Sa 516 Steel

DISCUSSION

Air-oxidation studies

The bare T22 steel and SA 516 showed extensive spalling of their oxide scales and their weight gain, 193.6 mg/cm^2 and 230.5 mg/cm^2 respectively, was quite high after exposure to air in silicon carbide tube furnace at 900°C for 50 cycles as shown in Fig. 2. A comparison of air-oxidation data of the investigated nanostructured Ni-20Cr coated SA 516 steel shows that the coating has reduced the weight gain (14.5 mg/cm^2) by 68% in comparison to its conventional (micron-sized powder coating) counterpart (45 mg/cm^2) [29], which is substantial.

This may be due to the formation of denser oxide scale due to enhanced grain boundary diffusion [30-31]. Further, it is pertinent to note that softer is the steel, harder is the coating produced and hence dense is the scale produced, which may be responsible for reducing the oxidation rate. The hardness of the coating may be attributed to the fact that softer surface may allow striking particles/splats to deform and stick to the surface more effectively, in comparison with, that by the harder surface. But in case of nanostructured Ni-20Cr coated T22 steel the weight gain (63 mg/cm^2) is comparable to its conventional counterpart (40 mg/cm^2) after 50 cycles, the nanocrystallinity of the coating is not useful to enhance the oxidation performance of the coating. However, the coating is expected to perform better in erosion-corrosion environment of boilers (where both erosion and corrosion act simultaneously) due to its significant high hardness. This is anticipated because hardness plays a significant role to the develop erosion resistance. The studies on erosion-corrosion performance in actual boiler conditions are under progress.

However the crack between coating and T22 steel is observed at the interface after exposure, this crack may have risen due to difference in coefficient of thermal expansion of coating (17.3×10^{-6} /°C), oxide scale and the base steel (14×10^{-6} /°C).

The surface XRD analysis indicated the formation of Fe_2O_3 as the main constituent of the top scale in the bare steels after the high-temperature cyclic air oxidation at 900°C. These results were further supported by SEM/EDS analysis. The line scan EDS analysis of the cross-section shows the presence of Fe along with O along the outer layer in case of oxidized T22 and SA 516 steels respectively. Small amount of Cr is also seen along with Fe and O along the outer layer of oxidized T22 steel, this may be due to presence of small amount of Cr in steel. The XRD analysis of cold-spray nanocrystalline Ni-20Cr coated T22 and SA 516 steels after oxidation for 50 cycles, revealed the presence of protective oxides of Ni and Cr in the scale. These results were further supported by surface SEM/EDS and X-sectional line scan analysis. X-ray mappings also support the presence of these elements. The EDS analysis indicates the significant concentration of Ni and O along with small amount of Cr in the oxide scale of coated steels.

The oxide scale showed poor adhesion on bare T22 boiler steel sample, similar behavior was shown on the coated T22 steel at the interface of substrate steel and coating, but no spallation was seen. Similarly, in case of bare SA 516 steel, oxide scale shown cracks parallel to surface of the substrate, but in case of coated SA 516 steel, no spallation was observed and oxide scale was found to be intact. The calculated parabolic rate constants (K_p) followed an order of bare SA 516 steel > bare T22 steel > coated T22 > coated SA 516 as shown in Table 2,which indicates that the coating was successful in reducing the oxidation rate of the steel. Further, it was found that nanostructured Ni-20Cr coating decreased the oxidation rate for T22 steel by 67%, and for SA 516 steel by 94%, which may be attributed to the presence of NiO, $NiCr_2O_4$ and Cr_2O_3 in the oxide scale. The presence of these phases is well supported by surface, as well as, cross-sectional SEM/EDS analysis. The Cr_2O_3 phase is said to be thermodynamical stable phase upto very high-temperatures due to its very high melting point and forms a dense, continuous and adherent layers that inhibits interaction of oxygen with the underlying coating/substrate [32]. Based on the above discussion it may be concluded that the cold-sprayed nano-crystalline Ni-20Cr coating can provide significant high-temperature oxidation resistance.

CONCLUSIONS

1. A pre-synthesized nano-crystalline Ni-20Cr alloy powder was successfully deposited on T22 and SA 516 boiler steels by cold-spray process. The thickness of the coating achieved was 225 µm and 250 µm respectively for T22 and SA 516 steels.
2. The cold-sprayed Ni-20Cr nanostructured coating on T22 steel was helpful in reducing the overall weight gain of bare steel by 67% whereas as a corresponding reduction of 94% was achieved for bare SA 516 steel. The cold-sprayed Ni-20Cr nanostructured coating was found to be very useful in developing high-temperature oxidation resistance in T22 and SA 516 boiler steels.
3. The improvement in high-temperature oxidation resistance of the coating was found to be due to the presence of stable phases Cr_2O_3 and NiO.
4. The investigated coating on SA 516 steel has reduced the weight gain (14.5 mg/cm^2) by 68% in comparison to its conventional (micron-sized powder coating) counterpart (45 mg/cm^2).

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