

OXIDATION BEHAVIOUR OF CoCrAlYTaCSi+Cr₃C₂ HVOF-SPRAYED COATING ON
T22 STEEL

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Abstract

The operating conditions in power plants boilers are conducive to fire side corrosion in the furnace wall and in the super heater and reheater areas and these effects cause tube wall thinning and premature failure. In coal fired boiler, corrosion occurs in several fashion due to combustion products which change their state of matter and become salts at high temperature. The materials used in the boiler tube are fabricated from low alloy carbon steels with chromium and molybdenum as the primary alloy addition. Although chromium imparts oxidation resistance by forming passive oxide layer on the alloy surface, it's concentration in the boiler tube is not sufficient to form a protective external scale. Present materials being capable of resisting oxidation environments are highly alloyed and thus expensive. In search for cost effective solution for oxidation, various coating like thermal sprayed coatings have become more attractive. The high velocity oxy- fuel (HVOF) process belong to the family of thermal spray process and as grown into a well-accepted industrial technology. This process has been shown to produce coating with better density, coating cohesive and bond strength than other thermal spray process.

HVOF spraying has been carried out using HIPOJET 2700 equipment, using super charging jet generated by combustion of liquid petroleum gas and oxygen mixture. The feed stock powder namely CoCrAlYTaCSi-Cr₃C₂ has been HVOF sprayed on boiler tube steels. The microstructure, physical and mechanical properties of coatings has been studied and characterized. Further, behaviour of the coated materials at high temperature is significant. Thermocyclic oxidation studies in the oxidation environment at 700°C for 50 cycles is carried out. It is seen from the results that the cumulative weight gain for the HVOF coated steel is significantly lower than that of uncoated steel subjected to oxidation.

Keywords: online shopping, convenience, web site quality, awareness

Introduction

A single material will not possess different properties to meet demand of today's industry, hence a composite system of base material providing necessary mechanical strength is resorted to. The decaying of metals on the grounds of the chemical reaction in the presence of the immediate environment called corrosion is encountered.

Oxidation is the accelerated oxidation when the surfaces covered with a thin film of few contaminants are exposed to elevated temperature conditions. This form of oxidation is commonly seen in gas turbines, boilers, internal combustion engines etc. To minimize such oxidation, coating materials have been developed and different coating techniques have also been investigated. In this investigation, an attempt has been made to study the microstructure, physical properties, and mechanical properties of the high velocity oxy fuel sprayed on boiler tube steels.

Review of Literature

The total economic loss from all types of corrosion in India is approximately \$6500 USD [1]. Hot corrosion, which occurs as a result of elevated temperatures, results in rapid oxidation. It is caused by the formation [2]. The sulphur content of the gases reacting with the metal's surface caused fire side corrosion. The coal also contains vanadium, which when burned produces V₂O₅. This reacts again with sodium sulfate to generate vanadates, which are very corrosive at high temperatures [3]. The presence of sulphur in low-quality coal causes SO₂ to be produced during combustion, which then oxidizes to produce sulfur trioxide, which reacts with water vapor [4]. According to a research by Shih et al., corrosion appears at high rates when metal and nonmetal are restricted by a thin layer

of watery salt at a high temperature in a gas environment. Such corrosion is referred to as hot corrosion. The failure of the machine component is brought on by the atmosphere's acidic nature, which can produce terrible conditions with gaseous oxygen, carbon, and sulfur [5]. Chatha et al. [6–7] computed the oxidation and erosion performance of 75Cr₃C₂-25NiCr and Ni-20Cr alloy coating on substrate T91 at 900°C for 1500-hour intervals, and found that Ni-20Cr coated steel produced superior results. Due to the presence of Cr₂O₃ in the top oxide scale, it happened. Sidhu et al. [8–10] formulated Ni and Co on boiler steel tube with thermal spray coating method. When satellite-6 coating was put to the substrate GrA1, the researchers noticed the maximum oxidation and erosion resistance.

Experimental section

Substrate Material

The substrate boiler tube steels for the study were procured from M/S Mishra Dhatu Nigam Limited (MIDHANI). The chrome moly steel (designated as ASTM-SA213-T22) which is being used as material for water wall, super heater and reheater tubes in coal fired thermal power plants in northern part of India has been used as a substrate material in the present study. The nominal composition of the boiler tube steels is given in Table 1.

Table No.1: Chemical composition (Wt. %) of substrate alloy T22.

Alloy Grade (ASTM code)	Chemical Composition (wt. %)							
	Fe	Su	Cr	Ph	Mo	Mn	Si	C
SA213-T22	Bal.	0.025	2.55	0.025	1.10	0.52	0.50	0.14

Coating material

Two types of commercially available feedstock materials have been used in the powder form. This has been used to as a spray coating material on three different types of substrate materials using High velocity oxy fuel coatings (HVOF). The details of the chemical composition and particle size of powder is reported in Table 2.

Table No.2: Chemical composition and particle size of coating powder.

Coating powder	Chemical Composition (Wt. %)	Particle size
CoCrAlYTaNCSi+Cr ₃ C ₂	70%CoCrAlYTaNCSi + 30%Cr ₃ C ₂	15 - 45 μm

Results and Discussion

Thermogravimetric studies

The macrographs of the uncoated T22 steel subjected to cyclic oxidation in air for 50 cycles are shown in Fig 1. The uncoated alloys developed a dark grey colored oxide scale.

The plots of cumulative weight gain (mg/cm²) as a function of time expressed in number of cycles are shown in Fig 2. The weight gain for the T22 steel at the end of 50 cycles are found to be 16.89mg/cm² respectively. Clearly, the T22 steel showed a weight gain during the cyclic oxidation studies. Further, the weight gain square (mg²/cm⁴) data has been plotted as a function of time, as shown in Fig 3, to establish law governing the oxidation. This plot shows the observable deviation from the parabolic rate law for the T22 steel, which indicate that the oxide films were poorly protective at 700°C. The parabolic rate constant k_p was calculated by a linear least-square algorithm function in the form of $(\Delta W/A)^2 = k_p t$, where $\Delta W/A$ is the weight gain per unit area, and t is the oxidation time in seconds. The k_p for the T22 steel are $16.92 \times 10^{-10} \text{ g}^2 \text{ cm}^{-4} \text{ s}^{-1}$ respectively.



Figure 1: Macrographs of uncoated bare boiler T22 steel subjected to cyclic oxidation in air for 50 cycles at 700°C

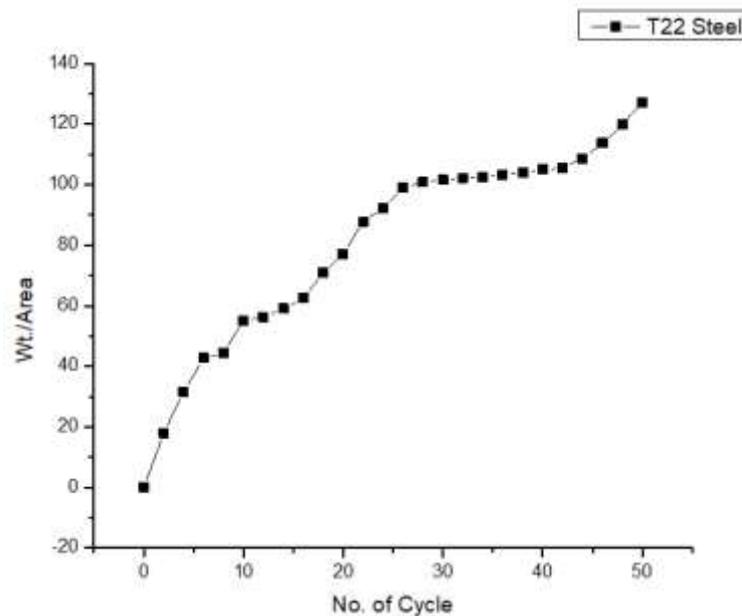


Figure 2: Weight gain vs. number of cycles plot for uncoated T22 steel subjected to cyclic oxidation for 50 cycles in air at 700°C

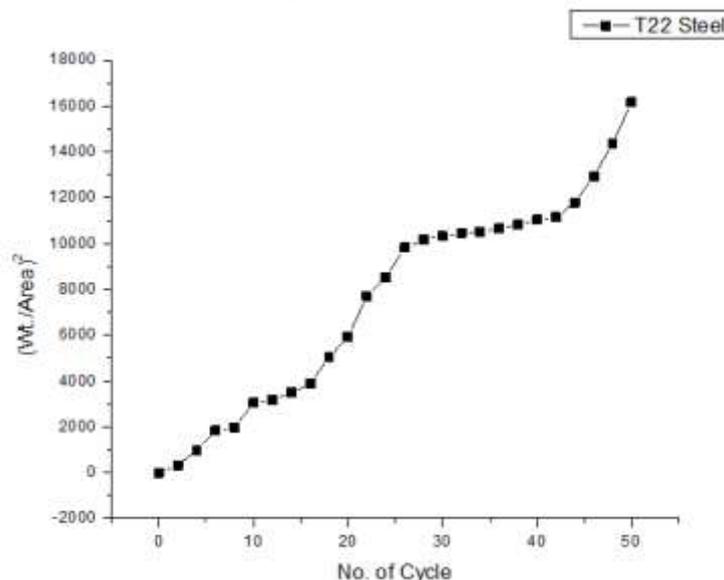


Figure 3: (Weight gain/area)² vs. number of cycles plot for uncoated T22 steel subjected to cyclic oxidation for 50 cycles in air at 700°C

The X-ray diffraction pattern for the steels, after exposure to air at 700°C for 50 cycles is compiled in Fig 4. As obvious from the composition, all the steels show Fe₂O₃ as the major peak. The T22 steel showed minor peaks of Cr₂O₃, MoO, FeCr₂O₄ and SiO₂

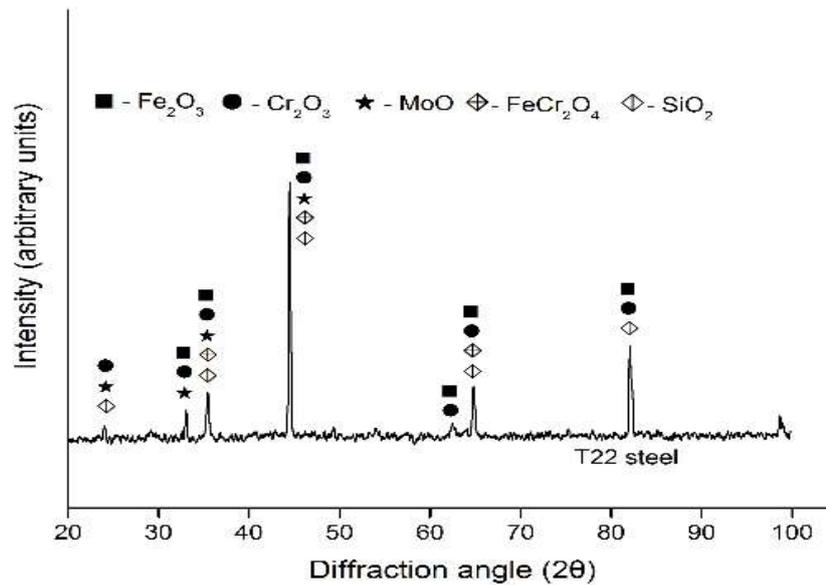


Figure 4: X-ray diffraction patterns for the uncoated T22 steel subjected to cyclic oxidation for 50 cycles in air at 700 °C

SEM/EDX analysis

The SEM micrograph showing the scale morphology along with the EDAX analysis is shown in Fig 5. The T22 steel consists of iron oxide as the main constituent in the oxide scale. The surface scale formed on the T22 steel shows cracks.

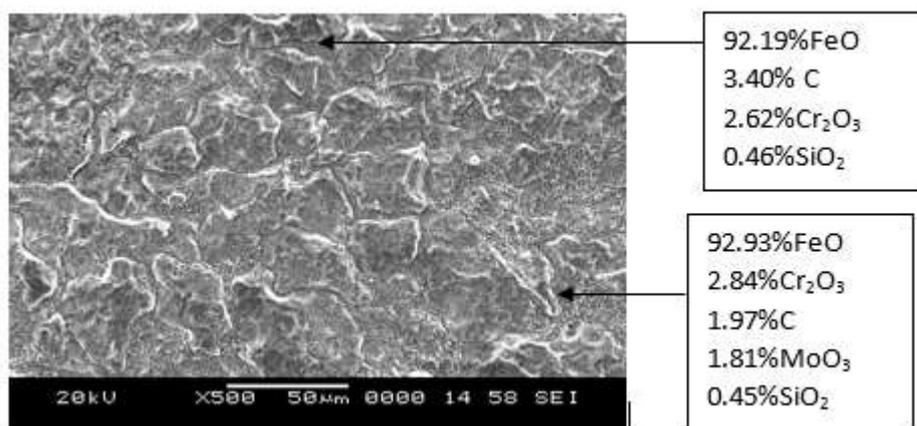


Figure 5: Surface scale morphology and EDAX point analysis for the uncoated T22 steel subjected to cyclic oxidation for 50 cycles in air at 700°C.

Uncoated T22 steel discussion

The XRD results show an outer layer of scale which mainly consists of Fe₂O₃ in T22 steel. The weight gains for T22 steel during oxidation studies are found to be less than.

The scale formed on the T22 steel was found to be fragile and cracked from centre of the sample. It is a well-known fact that the stresses developed due to a higher volume of oxides formed on the metal leads to scale cracking. The attainment of critical stress to cause scale rupture may be related to the critical thickness. The difference in the thermal coefficients of the oxide scale and the metal also contribute to the development of cracks in the scale. These cracks help in the internal oxidation and spalling of the scale.

Oxidation Study of CoCrAlYTaNi+Cr₃C₂ coating

Thermogravimetric studies

Macrograph of the HVOF sprayed CoCrAlYTaNi+Cr₃C₂ coating on T22 steel subjected to cyclic oxidation for 50 cycles at 700°C are shown in Fig 6. The oxide scale formed on the surfaces of the CoCrAlYTaNi+Cr₃C₂ coated steel is found to be compact, adherent and no tendency for spalling. This indicates that the coatings can sustain the thermal shocks owing to heating and cooling (cyclic oxidation), which serves as an index for good adhesion and anti-spallation capability of the coatings. The plots of cumulative weight gain (mg/cm²) as a function of time expressed in number of cycles are shown in Fig 7. The total weight gain value for the coated T22 steel at the end of 50 cycles of oxidation studies are found to be 0.01mg/cm² respectively. Further, the weight gain square (mg²/cm⁴) versus the number of cycles are plotted in Fig 8. The parabolic rate constant k_p was calculated by a linear least-square algorithm function in the form of $(\Delta W/A)^2 = k_p t$, where $\Delta W/A$ is the weight gain per unit area, and t is the oxidation time in seconds. The coated steel show parabolic behaviour and the k_p for the coated T22 steel are found to be $0.0919 \times 10^{-15} \text{g}^2 \text{cm}^{-4} \text{s}^{-1}$ respectively.

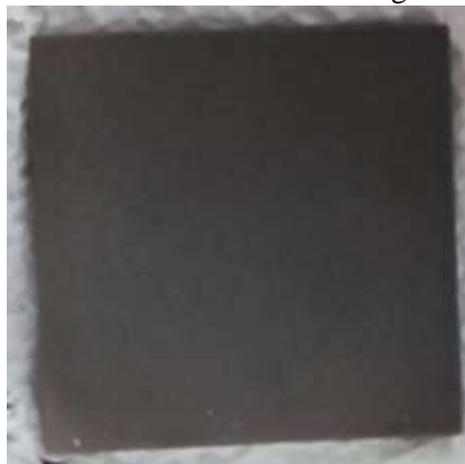


Figure 6: Macrograph of the CoCrAlYTaNi+Cr₃C₂ coating subjected to cyclic oxidation in air for 50 cycles at 700°C for T22 steel.

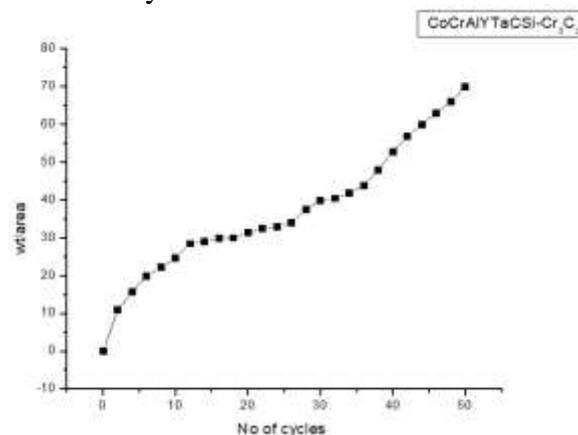


Figure 7: Weight gain vs. number of cycles plot for CoCrAlYTaNi + Cr₃C₂ Coated T22 steel subjected to cyclic Oxidation for 50 cycles in air at 700°C.

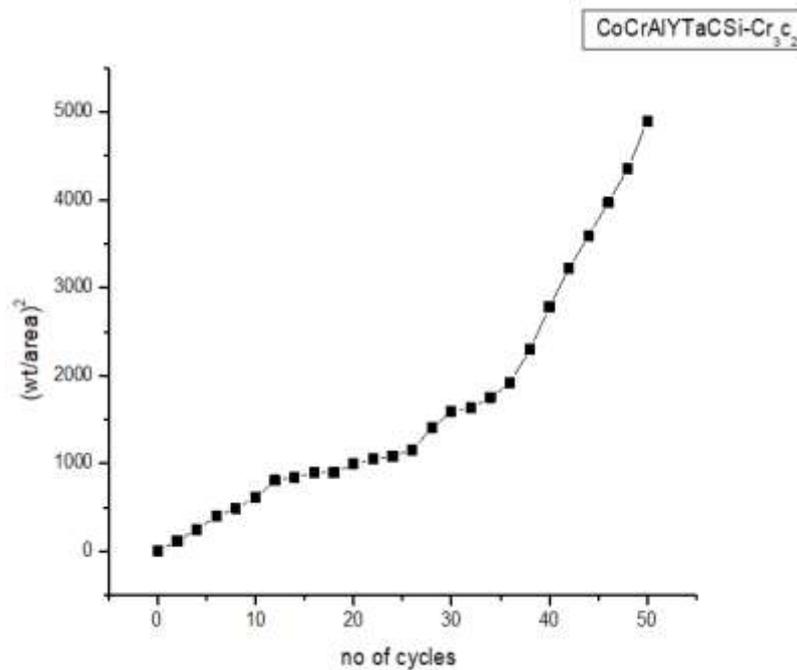


Figure 8: (Weight gain/area)² vs. number of cycles plot for CoCrAlYTaNiSi+Cr₃C₂ coated T22 steel subjected to cyclic oxidation for 50 cycles in air at 700°C.

SEM/EDAX Analysis

The surface morphology (Fig 9) of the oxide scale formed on the surface of CoCrAlYTaNiSi+Cr₃C₂ coated steel is thick, continuous, and non-uniform consisting of voids. Fig.9 shows the surface morphology of oxide scale formed on the oxidised CoCrAlYTaNiSi + Cr₃C₂ coated T22 steel. Oxide scale consists of spherical globules dispersed in the non-uniform matrix. The EDAX analysis on the spherical globules revealed the possibility of formation of oxides and carbides of tantalum and chromium (35.73%Ta, 10.04%Cr, 28.64%C, and 16.46%O) as the main constituent along with YO (8.03%Y) and the EDAX analysis on the matrix showed similar morphology composed of oxides and carbides of tantalum and chromium (37.44%Ta, 17.08%Cr, 21.57%C, and 19%O) as principal phases along with a minor amount of YO (4.87%Y).

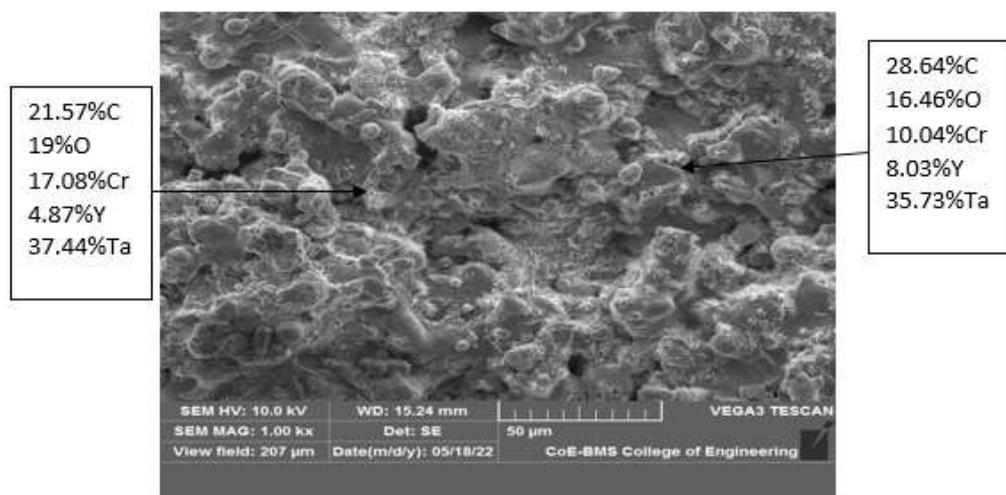


Figure 9: Surface scale morphology and EDAX point analysis for CoCrAlYTaNiSi+Cr₃C₂ coated T22 steel subjected to cyclic oxidation at 700°C

X-ray Diffraction Analysis

X-ray diffraction patterns of the oxide scale formed on the surface of oxidized CoCrAlYTaNi+Cr₃C₂ coated T22 steel after cyclic oxidation in air at 700°C have been compiled in Fig 10. The X-ray diffraction pattern for CoCrAlYTaNi+Cr₃C₂ coated T22 steel shows the phases of Cr₂O₃, Fe₂O₃ along with the formation of intermetallic like MoO, SiO₂, and FeCr₂O₄.

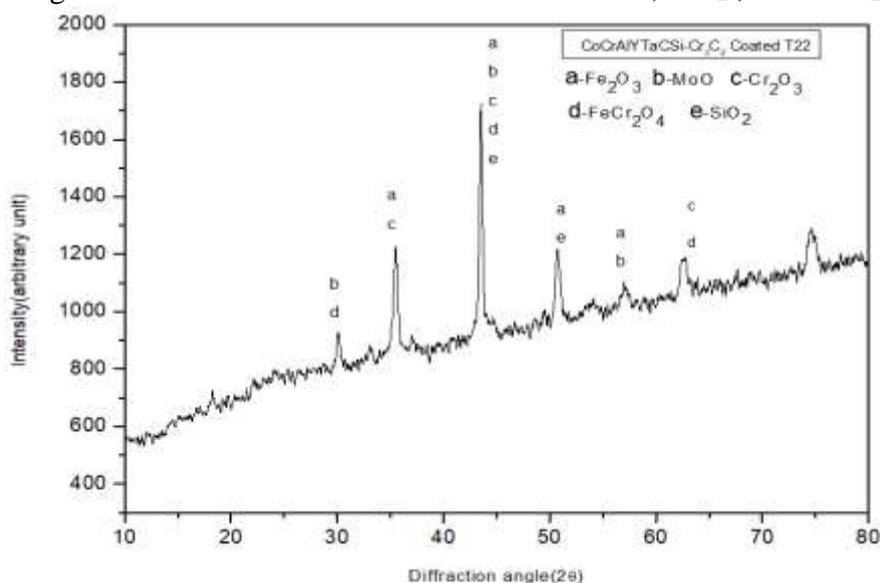


Figure 10: X-ray diffraction patterns for CoCrAlYTaNi+Cr₃C₂ coated T22 steel subjected to cyclic oxidation in air for 50 cycles at 700°C

CoCrAlYTaNi+Cr₃C₂ coating discussion

Weight gain data for HVOF sprayed coated and bare steels obtained from the oxidation data, the plots clearly indicate that the coated T22 steel follow a parabolic rate law up to 50 cycles, the values of parabolic rate constant K_p was calculated by a linear least-square algorithm function in the form of $(\Delta W/A)^2 = k_p \times t$, where $\Delta W/A$ is the weight gain per unit area, and t is the oxidation time in seconds. The parabolic rate constant (k_p) for the coated steels is lower when compared to the uncoated steels, hence coated steels exhibit lower oxidation rates. Weight gain for the coated T22 steel is less when compared with the uncoated steels, indicating that the coating acts as a diffusion barrier to the oxidizing species in air environment. The overall weight gain after 50 cycles of air oxidation for CoCrAlYTaNi+Cr₃C₂ coated T22 steel are 0.01mg/cm² respectively. The overall weight gain of 16.89 mg/cm² was observed for the T22 steel respectively.

Conclusion

- High velocity oxy-fuel thermal spraying with liquid petroleum gas as the fuel gas has been used successfully used to deposit CoCrAlYTaNi + Cr₃C₂ alloy coatings on boiler tube materials.
- Uncoated specimen suffered a higher oxidation and intense spalling of oxide scale was observed. The main constituent of oxide scale formed on specimen is iron oxide.
- The cumulative weight gain for all the HVOF coated T22 boiler materials are significantly lower than that of uncoated specimen subjected to oxidation in air environment for 50 cycles at 700°C. All the coated specimens exhibit characteristic thick protective oxide scale, composed of oxides and spinel oxide of the active elements of the coating and imparted resistance to the oxidation in the given air environment.
- Based on the Thermogravimetric data, the relative oxidation resistance of the CoCrAlYTaNi + Cr₃C₂ is greater.

References

1. R.A. Rapp, Y.S. Zhang. (1994), "Hot corrosion of materials: fundamental studies", JOM, Vol. 46, No. 12, pp. 47–55.
2. S. Srikanth, B.R. Kumar, S.K. Das, K. Gopalakrishna, K. Nandakumar, P. Vijayan (2003), "Analysis of failures in boiler tubes due to fireside corrosion in a waste heat recovery boiler", Eng. Failure Anal – Granthaalayah, Vol. 10, pp. 59–66.
3. Shih, Y. Zhang, X. Li (1989), "Sub-melting point hot corrosion of alloys and coatings", J. Mater. Sci. Eng, Vol. 120, pp. 277–282.
4. F. Pettit.(2011), "Hot corrosion of metals and alloys", Oxidation Met., Vol. 76, pp. 1–21.
5. R. Viswanathan (1989), "Damage mechanism and life assessment of high-temperature components", , ASM Int., pp. 1–483.
6. S.S. Chatha, H.S. Sidhu, B.S. Sidhu (2016), "Performance of 75Cr₃C₂-25NiCr coating produced by HVOF process in a coal-fired thermal power plant", Adv. Mater. Res, pp. 88–100.
7. S.S. Chatha, H.S. Sidhu, B.S. Sidhu. (2012), "High-temperature behavior of Ni-Cr coated T91 boiler steel in the platen superheated of coal-fired boiler", Thermal Spray Technol, Vol. 22, No. 5, pp. 838–847.
8. B.S. Sidhu, S. Prakash, (2006), "Evaluation of the behavior of shrouded plasma spray coatings in the platen super heater of coal-fired boiler", I Metall. Mater. Trans, Vol. 37, No. A, pp. 1927–1936.
9. B.S. Sidhu, S. Prakash, (2005), "Nickel-chromium plasma spray coatings: a way to enhance degradation resistance of boiler tube steels in boiler environment", Thermal Spray Technol, Vol. 15, No.1, pp. 131–140.
10. B.S. Sidhu, S. Prakash, (2005), "Erosion - corrosion of plasma as sprayed and laser Remelted stellite-6 coating in a coal fired boiler", Wear, Vol.260, No.9-10, pp. 1035–1044.