Steam Oxidation Resistance of Ni–Cr Thermal Spray Coatings on 9Cr–1Mo Steel. Part 2: 50Ni–50Cr

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The present work is focused on the steam oxidation resistance of 50%Ni–50%Cr metallic coatings produced using atmospheric plasma spray (APS) and high velocity oxy fuel (HVOF) spray processes on 9Cr–1Mo type steel substrate. Thickness of the coatings obtained in the HVOF and APS processes were about 60 and 40 μm respectively. The steam oxidation resistance of the coatings was evaluated at four different temperatures viz., 600, 650, 700 and 750°C. The results showed that the thick and denser HVOF coating yielded a better steam oxidation resistance than the thin and porous APS coatings. At prolonged aging (1 000 h), the HVOF coating showed the best protection in all tested steam temperatures. APS coating performed satisfactorily well till the 100 h of test duration. But, it started the scale initiation at the coating interface and incorporation of scales occurred at 1 000 h of steam oxidation test. The reason for the protective-ness by HVOF coating and failure of APS coatings at prolonged aging are discussed in detail.

KEY WORDS: steam oxidation; Cr–Mo steel; Ni–Cr coating; 50Ni–50Cr; high velocity oxy fuel (HVOF) spray; atmospheric plasma spray (APS).

1. Introduction

Thermal spray coatings received a widespread attention in recent years as a major industrial process technology. For majority of thermal spray applications, requirements are either wear resistance or corrosion resistance.1,2) The process is well exploited for wear resistance applications than for corrosion resistance.3–5) The reason for their limited use in aqueous corrosion in ambient temperatures is the availability of low cost process such as organic coatings, electroplating and anodizing. At high temperatures, the conventional organic coatings and the other electrochemical process have the limitation for their usage. This necessitated the use of thermal spray at high temperature applications.

In the recent past, thermal spray technology is extensively being used in the area of high temperature applications. In particular, thermal barrier coatings for aerospace and gas turbine components are extensively studied using thermal spray technology on the USC boilers components. The presently used structural material, modified 9Cr–1Mo steel provides satisfactory performance till 550°C steam temperature operating condition. Increasing the steam temperature to 650°C is the goal for fossil power plants in Japan and our institute has undertaken the STX 21 project to develop the material, which can withstand at 650°C. This indicated that the 9Cr–1Mo steel is severely affected by the steam oxidation at and above 600°C. To overcome the creep problem, new alloys developments are under progress. Addition of W, Si, B, N and V in the Cr–Mo type steels showed a marked improvement in their creep resistance.9,10,12) Thermal spray process can be considered to overcome the steam oxidation of USC boiler components since it can offer a thick film and flexibility to deal with onsite modifications. Few earlier attempts were made on the thermal spray coating for fossil power plants. Aguero et al.13) attempted thermal spray coatings of FeAl, FeCrAl and NiAl powders on 9Cr–1Mo type steel to improve the steam oxidation resistance for USC boiler applications. In that, FeCrAl and NiAl showed the promising results. Also, thermal spray was attempted for the super heater/re-heater components where the material severely suffers from fireside corrosion. The powder used for the study is Fe–Si intermetallics with the undercoat of NiCr alloy.14)

In our previous study,11) we attempted 80Ni–20Cr HVOF and APS coatings on 9Cr–1Mo steel substrate. The HVOF spray coatings yielded a good protection till 650°C and moderate protection at 700 and 750°C. The inferior performance at higher temperatures caused by Fe diffused from
the substrate to the coating. Similarly, Ni diffused from the coating to the substrate. Increase in the temperature accelerated the diffusion. However, Cr did not participate in the diffusion process in either side except their enrichment at the surface as oxide. This oxide is attributed for the protection against the scale growth. In the present investigation, 50Ni–50Cr coatings have been undertaken to evaluate their steam oxidation resistance due to the beneficial effect of higher Cr content.

2. Materials and Method

The 9Cr–1Mo type ferritic steel (ASME T91) was used as a substrate specimen with following dimensions. 1 cm² area with 4 mm thick specimens coated with 50Ni–50Cr powder (Manufacturer: Praxair). Chemical composition of the substrate and powder are represented in Table 1. Thermal spray coatings were carried out using HVOF spray and APS processes to compare the performance of these two processes. The process parameters used for respective coatings are given in Tables 2 and 3.

Prior to the coating process, the specimens were sand blasted using alumina powder for better adhesion to the substrate. In both process, totally six passes were adopted including the two pre-heating passes for pre-heating the substrate. Thickness of the coating obtained in the HVOF and APS process are about 60 and 40 μm, respectively. The coated specimens were supplied to XRD and SEM investigations before placing them into the steam oxidation chambers. Steam oxidation tests were carried out at different temperatures viz., 600, 650, 700 and 750°C. The procedure followed for the steam oxidation process was described elsewhere. The sample pieces were taken out in different durations namely 10, 100 and 1 000 h of steam oxidation test. The surfaces of oxidized specimens were supplied to XRD to identify the new phases formed during steam oxidation in comparison with as-coated conditions. SEM and EPMA studies were carried out on the cross sections to reveal their change in morphology and composition of the coating after the steam oxidation.

3. Results and Discussion

3.1. Coating Structure and Morphology

Figure 1 shows the XRD spectra of 50Ni–50Cr powder and their coatings produced by HVOF and APS processes. The powder pattern exhibited three major peaks responsible for Ni (111), (200) and (220) indicated that the powder exists in single Ni (fcc) phase. According to the Ni–Cr phase diagram, 50Ni–50Cr consists of two phases, Ni rich fcc phase and Cr rich bcc phase. The XRD results indicated that the powder and the coatings are in a supersaturated metastable state. In the HVOF coating an identical spectrum as powder without even minor changes. This indicated that the HVOF coating of 50Ni–50Cr retained their phase and composition similar to the powder. However, the peak broadening was noticed for both HVOF and APS coated specimens compared to the XRD pattern for the powder material. This is attributed to the lattice distortion occurred during spray process. In the APS coating, the XRD spectra showed a few extra less intense peaks, which were indexed to NiO and Cr₂O₃. During APS process, the powder has oxidized but the HVOF process did not produce any oxide during the coating process. In our previous studies on 80Ni–20Cr APS coatings, the chromium formed the oxide of Cr₃O₇. Whereas, in the present investigation chromium forms Cr₂O₃ type oxide, a stable oxide form for Cr. This would be attributed to the higher chromium percentage powder (50 mass%) used in the present investigation.

The SEM micrographs of the coatings are represented in
3.2. Steam Oxidation

3.2.1. XRD Studies

The samples obtained from the furnace after 10, 100 and 1000 h of steam oxidation tests were examined by XRD and SEM investigations. Figure 3 shows the XRD pattern for 50Ni–50Cr coated 9Cr–1Mo steel substrate, steam oxidized at 600°C for different durations. HVOF coating of specimen steam oxidized at 600°C/10h specimen showed a few extra peaks, along with their major Ni peaks compared to as-coated specimen (Fig. 1). The single Ni(111) peak observed in the HVOF as-coated specimen turned into triplet in 10 h of oxidation. The extra peaks are indexed to NiO(111) and Cr(110). The other minor peaks present in the spectrum are responsible for Cr$_2$O$_3$, the peaks responsible for NiO shown the higher intensity peaks than Cr$_2$O$_3$ peaks. This indicated that at 600°C of steam oxidation for 10 h duration, NiO is predominates to form on the surface. The fastest growing phase NiO, overgrows on Cr$_2$O$_3$ and layer of NiO developed on the surface. Since NiO is less stable than Cr$_2$O$_3$, it supplies oxygen and its dissociation pressure, which is sufficiently high potential to react with chromium to produce Cr$_2$O$_3$ and results in the complete healing layer. The position of the Cr$_2$O$_3$ layer, whether it is internal or external layer depends on the concentration of chromium in the system. If the system contains about 10% Cr, there is insufficient Cr to form external oxide and it could form only internal oxide. At increased chromium concentration development of external layer of Cr$_2$O$_3$ occurs eventually. For instance, 12% Cr can develop the complete Cr$_2$O$_3$ healing layer when oxidation carried out at air or oxygen atmosphere. In the case of steam oxidation, it requires 25% Cr to form complete healing layer. In the present system, Cr concentration is around 50%, complete external healing layer of Cr$_2$O$_3$ is expected to develop and suppress NiO scale growth. Further increase in the oxidation time from 100 to 1 000 h yielded the increased intensities for Cr$_2$O$_3$ peaks.

The APS coatings showed a similar trend to that of HVOF coatings expect the pattern for 1 000 h. In that condition, the XRD pattern showed a few extra peaks, which are indexed to Fe$_2$O$_3$. This indicated that the 50Ni–50Cr coating is not protective at 600°C. The HVOF coatings did not show any Fe$_2$O$_3$ peak till 1 000 h of tested conditions. The occurrence of Fe$_2$O$_3$ peaks in APS coatings is attributed to the more porous coating structure than HVOF coatings. The steam can penetrate into the pores and reacted with the substrate surface resulting in the scale growth.

Figure 4 shows the XRD spectra for HVOF and APS 50Ni–50Cr coated 9Cr–1Mo steel substrate steam oxidized at 750°C for different duration. The HVOF coatings steam oxidized at 10 h showed the major peaks for Ni along with oxide than Cr$_2$O$_3$. It was reported that in the initial stages of oxidation of Ni–Cr system, nuclei of all stable oxide phases, NiO and Cr$_2$O$_3$ form on the surface. The fastest growing phase NiO, overgrows on Cr$_2$O$_3$ and layer of NiO developed on the surface. Since NiO is less stable than Cr$_2$O$_3$, it supplies oxygen and its dissociation pressure, which is sufficiently high potential to react with chromium to produce Cr$_2$O$_3$ and results in the complete healing layer.
the minor peaks for Cr$_2$O$_3$, NiO and Cr. Unlike 600°C, the NiO peak is almost suppressed at 10 hours. This indicated that at 750°C, Cr$_2$O$_3$ predominately formed than the NiO. Also, the coating retains its Ni phase with small amount of Cr(bcc) phase. With further increase in durations to 100 and 1 000 h, the spectra were identical except the increased intensities for Cr$_2$O$_3$ peaks. On the other hand, in APS coatings, Fe$_2$O$_3$ peaks were found in the specimens oxidized for 100 and 1 000 h duration, indicating their inferior protective against the scale growth.

The peak intensity ratio of Ni(111) base peak/Fe$_2$O$_3$ peak were calculated from the XRD pattern for every tested condition. This will give a direct understanding of the protectiveness of the coating against steam oxidation at these temperatures. The values are obtained for both APS and HVOF coated specimens oxidized at four different temperatures. The ratio values plotted with their steam oxidation durations are shown in Fig. 5. In the APS coating, the 600°C tested condition showed very little increase in the ratio values in 100 h and it reached the steady state at 1 000 h. Increasing the temperature from 600 to 650°C showed the identical values till 100 h and little increase was noticed at 1 000 h. The specimens tested at 700 and 750°C showed a gradual but marginal increase in their ratio values with increase in the test duration and temperature. Nevertheless, the ratio value obtained for all the 50Ni–50Cr APS coated specimens are well below the ratio value obtained for 80Ni–20Cr APS coated specimens. This suggests that the increased chromium content in the coating showed the better performance against scale growth.

From the HVOF coatings, all the four tested temperatures showed the zero in their ratio values till the 1 000 h of tested condition. It means, the Fe$_2$O$_3$ peak was absent till 1 000 h of steam oxidation. This indicated that the HVOF coating exhibits an excellent protection against the steam oxidation at this temperature range. Also, HVOF coatings showed its better performance than APS coatings. This is attributed to the dense and less porous nature of the HVOF coating. The HVOF coatings of 80Ni–20Cr specimens showed the presence of Fe$_2$O$_3$ at 700 and 750°C. Though, the scale initiation did not occur at the coating/substrate interface, the diffusion of Fe from the substrate to the coating surface was responsible for the formation of Fe$_2$O$_3$. Absence of Fe$_2$O$_3$ in the present investigation may arise from the lower diffusion rate of Fe in the 50Ni–50Cr system. SEM and EPMA studies are carried out to find out the possible mechanism of this phenomenon.

3.2.2. SEM Studies

Figure 6 shows the backscattered electron (BSE) image cross sections of 50Ni–50Cr coated specimens steam oxidized for 10 h. The HVOF coating at both 600 and 750°C shows its protectiveness. Also, absence of scale at the substrate/coating interface was noticed. In the APS coatings, the coating was intact in both 600 and 750°C specimens. Though, there is no indication for scale initiation at the interface, the coating near the interface showed a slight contrast changes. This might arise from the diffusion of the elements. In APS coatings, traces of scale growth at the coating/substrate interface were noticed for 600°C specimen. The specimens steam oxidized at 750°C, the scale growth occurred at the interface and these grown scales incorporated into the coating. Initiation of scale growth occurred during 10 h, which turned to be
much larger in the prolonged time of 100 h. The scale growth occurred through pores and attained to the surface. However, it has to be noted that there was no exfoliation in the coating even after 100 h despite their low coating thickness. The scale growth occurred only through the pores present in the coating.

Figure 8 depicts the BSE image cross sections of the 50Ni–50Cr coated specimens steam oxidized for 1 000 h. The APS coating oxidized at 750°C showed the scale incorporation in the coating and as well as at the surface, whereas at 600°C the scales were present only at the coating/substrate interface. From the HVOF coatings, the BSE images showed a compact coating layer present on the substrate with neither scales nor delamination. There is no sign of scale initiation at the coating/substrate interface. This substantiated the results obtained from the XRD studies. At 600°C, the contrast changes near the interface at both coating and substrate was observed. This might arise from the diffusion of the elements. On the contrary, at 750°C, there was no such contrast difference at the interface but the whole coating showed uniform black spots. The EPMA studies have been undertaken to map the elements of the HVOF spray coated specimen to find out the diffusion and distribution of the elements in the coating structure.

3.2.3. EPMA Studies

Figure 9 shows the EPMA elemental mapping for the 750°C/1 000 h HVOF specimen. The elemental mapping for C showed high intensity layer at and above the interface. The Cr elemental map also exhibits the high intense dots at the interface. The above results suggest that the chromium carbide formation at the interface occurred in the HVOF coated specimen steam oxidized for 750°C/1 000 h specimen. The carbon present in the substrate material diffused
to the coating and lead to the chromium carbide. Chromium has high affinity towards carbon and formation of carbides is well documented. Formation of chromium carbides in the Fe–Cr and Ni–Cr systems leads to the adjacent chromium depleted zones results in the corrosion and oxidation attack\(^\text{16,17}\). However in the present system, chromium carbide formation occurred only near the coating/surface interface and not on the top surface of the coating. This avoided the depletion of chromium at the top coating surface and the Cr present in the top layers will be exploited to form protective chromium oxide layer. Additionally, Cr did not diffuse into the substrate, which is evident from the Cr map in the substrate zone, where, Cr concentration is almost same thought the scanned area over the substrate. This may be attributed to the formation of chromium carbide.

The elemental mapping for Fe shows that a small amount of outward diffusion occurred from the substrate to the coating. But, the Fe is absent in the position where C is enriched. The diffusion seems to have proceeded for less than 10 \(\mu\)m from the interface. Similarly, the Ni elemental map showed that the Ni present in the coating diffused to the substrate 9Cr–1Mo steel. The depth of the Ni diffusion is also very small (less than 10 \(\mu\)m) and scattered. In our earlier studies\(^\text{11}\) 80Ni–20Cr coated specimen steam oxidized under the same condition (750°C/1 000 h) showed a very high diffusion rate for both Fe and Ni. The diffusion of Fe almost reached the coating surface (\(~50 \mu\)m). In this investigation the diffusion rate is very slow. This may be attributed to the following reasons: Fe has the faster diffusion rate in the Ni system.\(^\text{18}\) The rate of Fe diffusion in Ni is two fold higher than the Fe diffusion in Cr (Diffusion coefficient for Fe in Cr is 0.47 whereas Fe in Ni is 1.0 cm\(^2\)/s).
Moreover, the formation of chromium carbide may hinder the further diffusion of Fe into the coating. This is evident from the absence of Fe in the chromium carbide formed zone near the interface.

Chromium is enriched at the top surface layers. The O mapping also showed the high intensities at this region arise from the formation of chromium oxide film at the surface of the coating. The oxidation resistance of Ni–Cr coating is solely based on the formation of Cr₂O₃. The mechanism of Cr₂O₃ formation in Ni–Cr system is discussed in the previous XRD chapter and elsewhere.¹¹) The depletion of Cr was observed beneath the oxide layer and above the carbide layer. This is attributed to the diffusion of chromium for the respective compound formations. In the O elemental map, the higher concentration was noticed at the interface. These islands do not match with the major elements like Fe, Cr and Ni. These islands were identified as aluminum oxides possibly due to the incorporation of alumina powder during polishing. This additionally confirms that the HVOF coatings do not initiate the scales at the interface till 1 000 h of steam oxidation.

The EPMA studies were carried out for specimens steam oxidized at 600, 650 and 700°C/1 000 h specimens. This study is to compare the Fe, Cr and Ni line profiles of those specimens along with 750°C/1 000 h specimen and also to understand the effect of diffusion and chromium carbide formation near the interface with respect to steam temperature. Figure 10 depicts the Fe and Ni line profiles for the specimens oxidized for 1 000 h at four different temperatures. For comparison purpose, the line profile for as-coated specimen is also included in the figure. The as-coated specimen showed a sharp concentration changes at the interface with falling to the bottom concentration at the coating region. At 600°C, the profile showed a shoulder towards the coating region indicating that diffusion of Fe took place towards the coating. Further increase in the temperature decelerated the Fe diffusion towards the coating. At 750°C, the Fe diffusion is lowest compared to the other tested conditions. Similar behaviour was noticed for Ni diffusion from the coating to the substrate. At 600°C, the profile showed a shoulder towards the substrate indicated the diffusion of Ni from coating to substrate. Further increase in the temperatures from 600°C to 650, 700 and 750°C, considerable reduction in the Ni diffusion was noticed.

The Cr and C line profiles for the above specimens are represented in Fig. 11. At 600°C, the profile showed the shoulder towards the substrate indicated the diffusion of Cr from coating to substrate. Further increase in the temperature from 600°C, considerable reduction in the diffusion was noticed. On the other hand, Cr enriched at the coating/substrate interface. The C profiles showed significant peaks at the interface for the 650, 700 and 750°C specimens. The intensity of the peak increased with increase in the steam temperature. The peaks coincide with the enrichment of Cr observed in the same segment for the respective specimens. This suggested the formation of chromium carbide at the interface. From the EPMA results it can be summarized that both Cr and Ni can diffuse from the coating to the substrate at 600°C. The formation of chromium carbide at 650°C and above decelerate the diffusion by act as the barrier for further Ni, Cr diffusion to the substrate and similarly, Fe diffusion to the coating. Additionally, the line profiles for Cr and Ni showed the uniform concentrations across the coating layers for the as-coated specimen. Whereas, the steam oxidized specimens showed the scattered lines for both Cr and Ni indicated their non-uniform concentration in the coating layers. This arises from the separations Ni rich fcc phase and Cr rich bcc phase during
steam oxidation tests.

The schematic of the entire above phenomenon occurred in the coating structure before and after steam oxidation tests are represented in Fig. 12. In the as-coated specimens, the coating exists in the single fcc phase with uniform Cr and Ni concentrations. After the steam oxidation this single phase turned into dual phase of Ni rich fcc phase and Cr rich bcc phase. This can be confirmed from the both XRD (Figs. 3 and 4) and EPMA lines profiles for Ni and Cr (Figs. 10 and 11). Also after steam oxidation tests, the Cr diffused near the interface to form chromium carbide and at the coating surface to form Cr2O3 layer. Formation of chromium carbide and chromium oxides leads to the adjacent Cr-depleted zones, i.e. Ni(fcc) rich phase. The inner coating zone remains as the dual phase. The formation of Cr2O3 would prevent the scale growth and the formation of chromium carbide at the interface decelerates the further diffusion of Fe, Ni and Cr.

4. Conclusions

(1) Thermal spray of 50Ni–50Cr powder was carried out on 9Cr–1Mo steel substrate by APS and HVOF processes. HVOF process yielded a denser and less porous coating than the APS coatings.

(2) HVOF coatings showed a better steam oxidation resistance till 1 000 h of test duration in the tested temperature range of 600–750°C. APS coatings survived 100 h in the temperature of 600°C but the scale growth at the interface was noticed for specimen steam oxidized at 750°C in the same test duration. In the APS coating, the scale initiation was found at the interface whereas it was absent in the HVOF coating.

(3) HVOF coating forms a complete chromium oxide-healing layer, which prevents the scale growth. The Fe diffusion to the coating was controlled by chromium carbide formation at the interface.

(4) Ni and Cr diffusion was found from the coating to the substrate in the tested temperature of 600°C. But the diffusion is controlled at higher temperature tested specimens.

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Fig. 12. Schematic representation of the coating structure (a) before and (b) after steam oxidation test.