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Degradation Behavior of Ni_3Al Plasma-Sprayed Boiler Tube Steels in an Energy Generation System

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Boiler steels, namely, low-C steel, ASTM-SA210-Grade A1 (GrA1), 1Cr-0.5Mo steel, ASTM-SA213-T-11 (T11) and 2.25Cr-1Mo steel, ASTM-SA213-T-22 (T22) were plasma sprayed with Ni_3Al. The alloy powder was prepared by mixing Ni and Al in the stoichiometric ratio of 3 to 1. The Ni-22Cr-10Al-1Y alloy powder was used as a bond coat, with a 150 µm thick layer sprayed onto the surface before applying the 200 µm coating of Ni_3Al. Exposure studies have been performed in the platen superheater zone of a coal-fired boiler at around 755 °C for 10 cycles, each of 100 h duration. The protection to the base steel was minimal for the three steels. Scale spallation and the formation of a porous and nonadherent NiO scale were probably the main reasons for the lack of protection. In the case of T22-coated steel, cracks in the coatings have been observed after the first 100 h exposure cycle.

Keywords coal-fired boilers, erosion, hot corrosion, Ni_3Al, plasma spray

1. Introduction

Nickel aluminide protective coatings are of relatively recent origin (Ref 1). It has been claimed that nickel aluminides possess high-temperature mechanical strength as well as oxidation resistance (Ref 2, 3). Studies on the oxidation behavior of Ni_3Al date back to 1974. In the last decade, research on nickel aluminides has been conducted more intensely because Ni_3Al-base alloys have been found to be promising structural materials for use in high-temperature applications (Ref 4).

Erosion affects numerous industries, including those dealing with power generation, mining, and the pneumatic transportation of solids. The marine, oil-and-gas, chemical, and power-generation industries have corrosion and oxidation problems, and, to a lesser extent, erosion concerns. However, the worst-case scenarios normally occur where there is a combination of both erosion and high-temperature oxidation such as that found in gas turbine engines and fluidized bed combustors. There are occasions when oxidation can reduce the degree of material loss by such wear processes through the formation of a stable protective oxide layer (Ref 5).

When considering coal-gasification processes, hot corrosion is expected to be a problem because the gas environment generally contains S with low-oxygen content and substantial amounts of salts. At present, methods to minimize the extent of hot corrosion have been identified; however, considerable research is needed to quantitatively evaluate these methods under conditions of interest in coal gasification (Ref 6).

Metallic components in coal-gasification pilot plants are exposed to severe corrosive atmospheres and high temperatures. The corrosive nature of the gaseous environments (i.e., environments containing O, S, and C) may cause rapid material degradation and result in the premature failure of components (Ref 7, 8).

Metallic coatings sprayed on superheater tubes have reduced erosion and corrosion in selected cases (Ref 9). Protective coatings are being used on structural alloys in energy conversion and utilization systems to protect their surfaces from oxidation and erosion (Ref 10-12). An Ni_3Al coating on steel has been reported to improve the oxidation and corrosion resistance as well as the elevated-temperature erosion resistance (Ref 2, 13).

Plasma spray is widely used to apply coatings, including intermetallic, ceramic, and composite coatings, to protect substrates against wear, corrosion, and high temperatures (Ref 14-16). Deposition efficiency for plasma-spray coatings is closely related to the melting point of the spayed powders (Ref 17), and high deposition efficiency is very important in lowering the coating cost (Ref 18). Plasma-spray processing of coatings is also a simple process from a practical point of view (Ref 19).

An attempt has been made to apply Ni_3Al coatings by plasma spraying elemental powders onto the surface of the substrate steels by mixing Ni and Al in a 3-to-1 ratio. The degradation behavior of the coatings has been studied at 755 °C in a platen superheater of a coal-fired power plant. X-ray diffractometry (XRD), scanning electron microscopy (SEM), energy-dispersive x-ray (EDAX) analysis, and electron probe microanalysis (EPMA) techniques were used to analyze the scale formed on the exposed samples.

2. Experimental Details

2.1 Development of Coatings

Three types of boiler steels, low-C steel, ASTM-SA210-Grade A1 (GrA1), 1Cr-0.5Mo steel, ASTM-SA213-T-11 (T11) and 2.25Cr-1Mo steel, ASTM-SA213-T-22 (T22) were used as substrates. The steel samples were cut to 2 × 1.5 × 0.5 cm rectangular specimens. The specimens were polished and then

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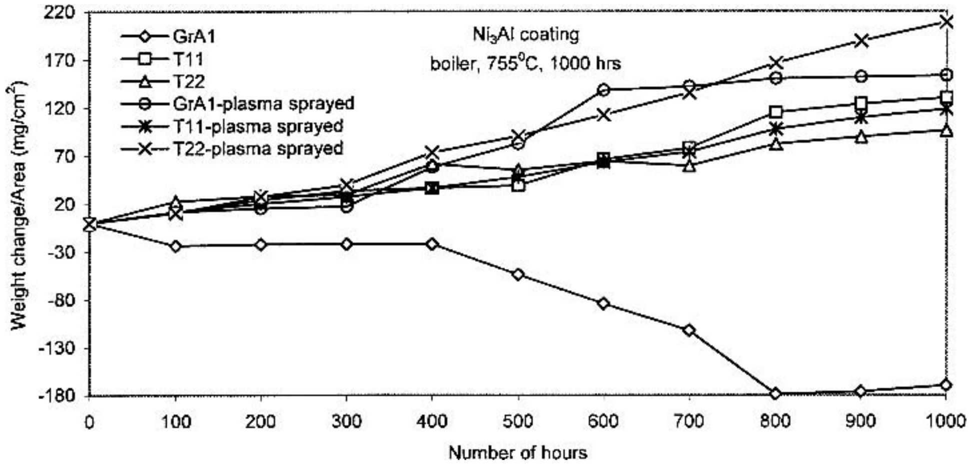

Fig. 1 Weight change plot for uncoated and Ni_3Al-coated steels with bond coat exposed to the platen superheater of the coal-fired boiler for 1000 h at 755 °C

Table 1 Chemical analysis of ash and flue gases inside the boiler

Ash		Flue gases(a)	
Constituent	Wt.% age	Constituent	Value relative to flue gases
Silica	54.70	…	…
Fe_2O_3	5.18	SO_x	236 mg/m^3
Al_2O_3-Fe_2O_3/Al_2O_3	29.56	NO_x	1004 μg/m^3
Calcium oxide	1.48	CO_2	12%
Magnesium oxide	1.45	O_2	7%
SO_3	0.23	40% excess air was supplied to the boiler for the combustion of coal	
Na_2O	0.34		
K_2O	1.35	…	…
Ignition loss	4.31	…	…

(a) Volumetric flow, 231 m^3/s

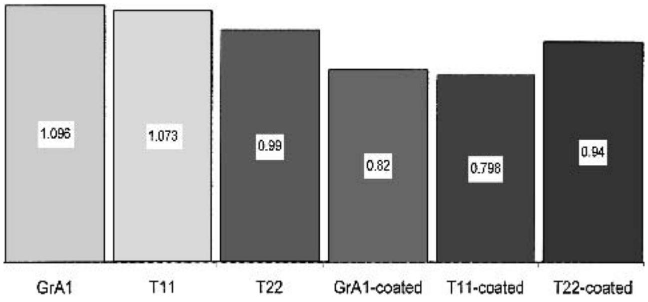

Fig. 2 Bar chart indicating the thickness lost in millimeters by the uncoated and Ni_3Al-coated steels with bond coat after 1000 h of exposure to the coal-fired boiler at 755 °C

Table 2 Metal thickness lost and *E-C rates for original and Ni_3Al-coated steels after exposure to a coal-fired boiler

Type of steel	Metal thickness lost, mm			Degradation rate, mpy		
	GrA1	T11	T22	GrA1	T11	T22
Uncoated	1.096	1.073	0.99	378.190	370.170	333.530
Ni_3Al-coated	0.82	0.798	0.940	282.803	275.319	324.189

* Erosion-corrosion rates in mils per year (mpy)

grit blasted with Al_2O_3 particles (60 grit) before applying the plasma spray coating. Nickel, with a minimum assay of 99.5% and a size equivalent to 200 mesh, and fine Al powder with a minimum assay of 99.7% were mixed in a 3-to-1 ratio in a laboratory ball mill for 8 h.

The coating was applied at Anod Plasma Spray (Kanpur, India) using a 40 kW plasma-spray apparatus. Argon was used as a powder-carrying and shielding gas, and all process parameters, including the spray distance, were maintained at a constant throughout the coating process. Ni-22Cr-10Al-1Y powder was used as a bond coat to form a 150 μm thick layer prior to the final application of the Ni_3Al. After the application of the bond coat, the Ni_3Al coating was applied (approximately 200 μm thick). Details regarding the development of the coatings have been reported elsewhere (Ref 20).

2.2 Industrial Environment Description

Erosion-corrosion studies have been performed in the middle zone of a platen superheater in a stage-III boiler (Guru Nanak Dev Thermal Plant, Bathinda, Punjab, India). A stainless steel wire was passed through a predrilled 1 mm diameter hole in the rectangular exposure samples, which were then inserted through the soot blower dummy points at a height 31.5 m from the base of boiler. The average temperature and volumetric flow of the flue gas in this region of the boiler were 755 ± 10 °C and 231 m^3/s, respectively. The chemical analysis of the flue gas and ash present inside the boiler is given in Table 1.

Exposure studies were performed for 1000 h in 10 cycles, where each cycle consisted of a 100 h exposure to the environment followed by a 1 h interval during which the samples cooled to ambient conditions. At the end of each cycle, the samples were visually examined for any change in, for example, color or luster, and were measured for mass change. At the end of the cyclic study, the samples were analyzed using XRD analysis, SEM/EDAX analysis, and EPMA.

The extent of degradation was monitored by measuring the thickness of the unreacted samples, because simultaneous spalling and ash deposition make mass change measurements irrelevant. Measurements of thickness loss have further been

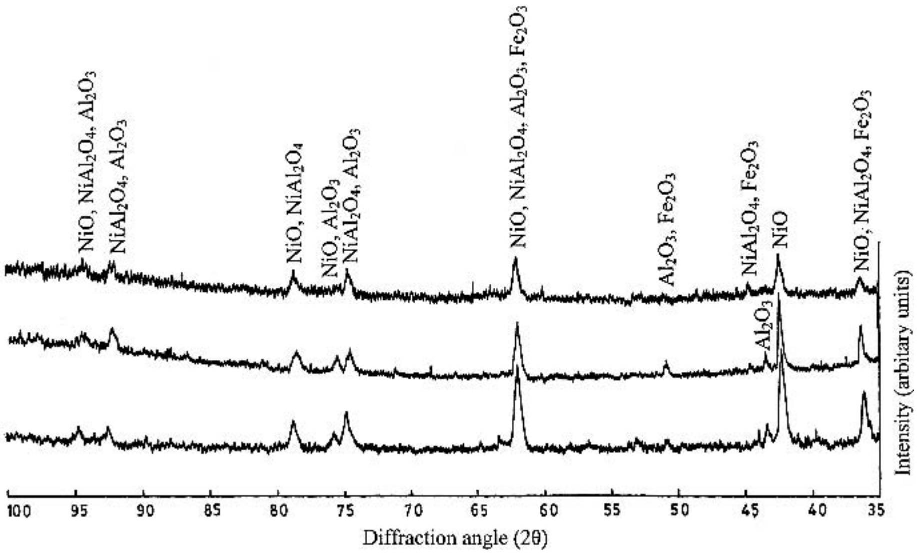

Fig. 3 X-ray diffraction profiles for Ni$_3$Al-coated steels with the bond coat exposed to the platen superheater of the coal-fired boiler for 1000 h at 755 °C

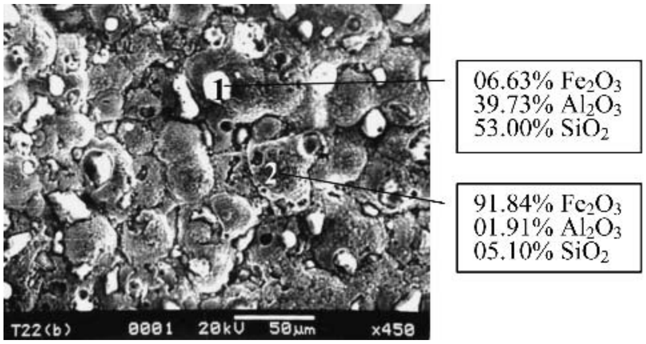

Fig. 4 Surface scale morphology and EDAX analysis for T22 boiler steel exposed to the platen superheater of the coal-fired boiler for 1000 h at 755 °C (magnification 450×)

monitored to predict the erosion-corrosion rates in mils per year.

3. Experimental Results

The Ni$_3$Al coatings have been characterized previous to exposure studies, and the results have been published (Ref 21). The coatings provided good protection to the base steels when tested in air and molten salt environments at 900 °C (Ref 20).

3.1 Mass Change and Thickness Measurements

The mass change per unit area for Ni$_3$Al-coated steels, plotted as a function of time in hours, is shown in Fig. 1. After 1000 h of exposure to the boiler environment, among the coated steels the mass gain was observed to be higher for Ni$_3$Al-coated T22 steel. The metal thickness loss after exposure for Ni$_3$Al-coated GrA1, T11, and T22 steels was 0.82, 0.08, and 0.94 mm, respectively (see Fig. 2). The total thickness lost due to exposure, and the erosion-corrosion rates in mils per year for bare and Ni$_3$Al-coated steels, are given in Table 2.

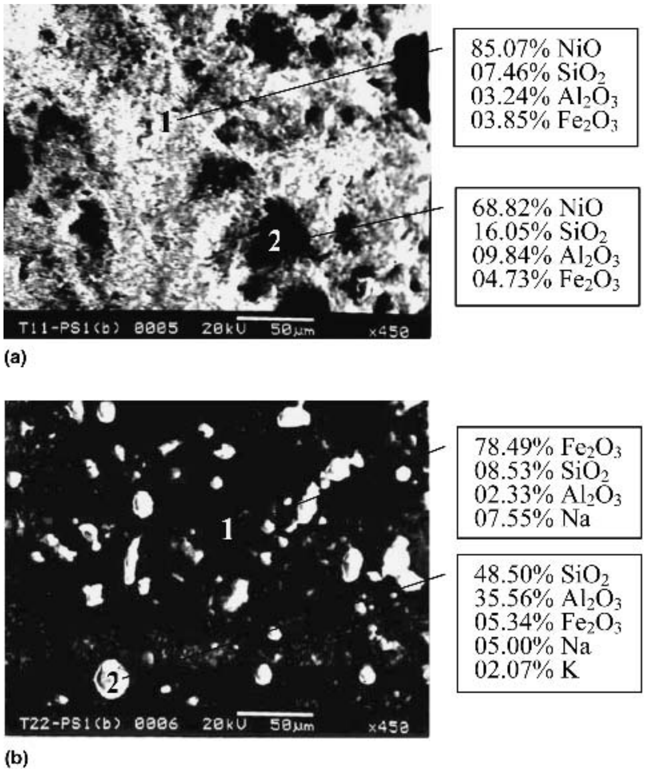

Fig. 5 Surface scale morphology and EDAX analysis for Ni$_3$Al-coated steels with bond coat exposed to the platen superheater of the coal-fired boiler for 1000 h at 755 °C: (a) T11 steel (magnification 450×); and (b) T22 steel (magnification 450×)

3.2 X-Ray Diffractometry Analysis

The XRD profiles for Ni$_3$Al-coated GrA1, T11, and T22 steels after 1000 h of exposure in the coal-fired boiler at 755 °C are shown in Fig. 3. The three coated steels developed identical phases. X-ray diffractometry analysis has shown the formation of nickel oxide (NiO), aluminum oxide (Al$_2$O$_3$), and iron oxide (Fe$_2$O$_3$), along with spinels of Ni and Al.

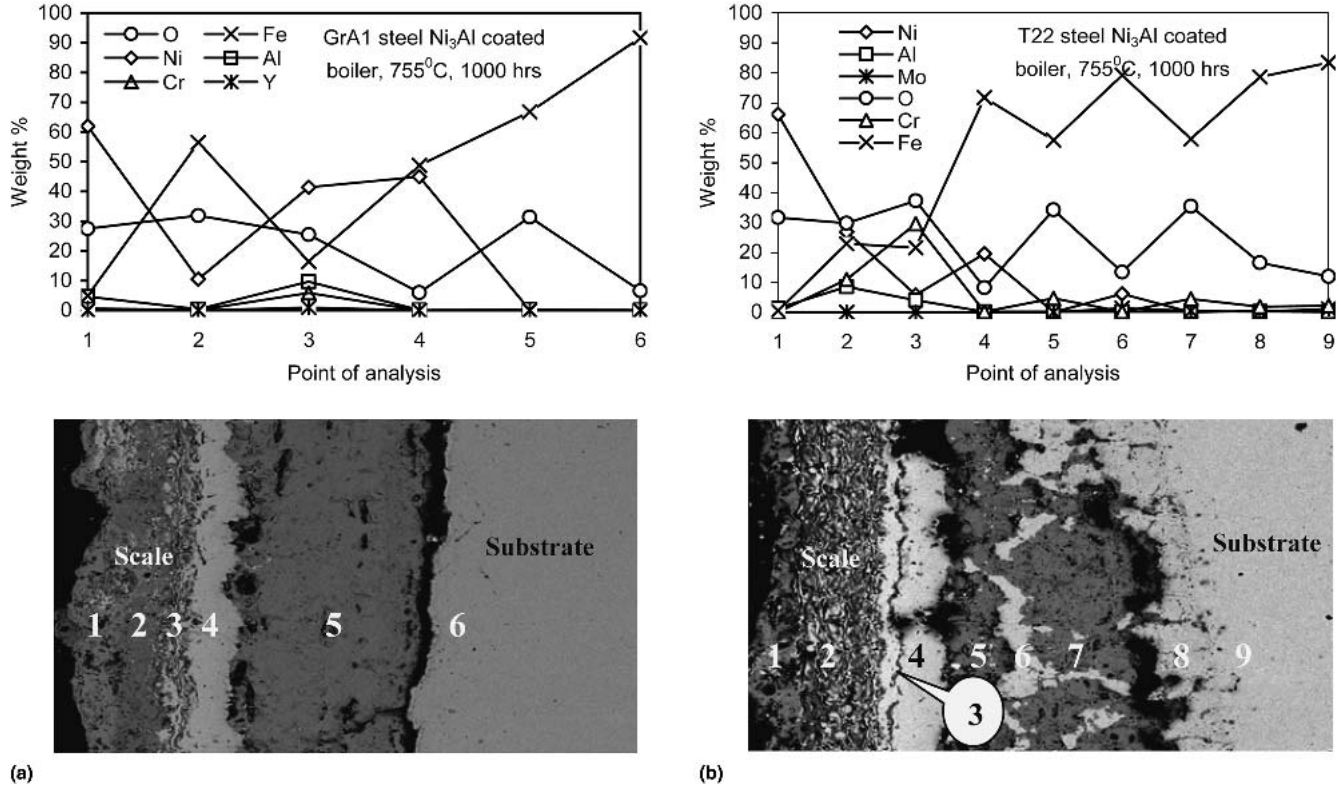

Fig. 6 Oxide scale morphology and elemental composition variation across the cross section of Ni_3Al coating with bond coat exposed to the platen superheater of the coal-fired boiler for 1000 h at 755 °C having substrate steels as (a) GrA1 (magnification 100×); and (b) T22 (magnification 130×)

3.3 Scanning Electron Microscopy/Energy-Dispersive X-Ray Analysis

3.3.1 Surface Morphology. The SEM micrographs (Fig. 4) for bare T22 steel after exposure to the boiler environment indicate a continuous granular scale consisting mainly of Fe_2O_3 (89.8%), with small amounts of SiO_2 (5%) and Al_2O_3 (2%). Ash particles can be seen embedded in the scale (white-colored nodules). These particles have a composition of 39% Al_2O_3 and 53% SiO_2 plus other minor constituents.

The SEM/EDAX analysis of the exposed Ni_3Al-coated T11 steel indicates that the top surface consists mainly of NiO (85%). There are spalled areas (Fig. 5a) having NiO with higher amounts of SiO_2. The scale of coated T22 steel after exposure contains mainly Fe_2O_3 with small amounts of Na. The white particles that are seen to be embedded in the scale (Fig. 5b) appear to be ash particles consisting of Al_2O_3 and SiO_2 (from EDAX analysis of one of these particles).

3.3.2 Cross-Sectional Analysis. Oxygen seems to have penetrated through the coating into the substrate in the case of Ni_3Al-coated GrA1 and T22 steels (Fig. 6). The outermost layer of scale for both steels is rich in NiO. The layer just below this one contains more iron oxide in the case of the coated GrA1 steel, whereas EDAX analysis at point 3 in Fig. 6(a) for coated GrA1 steel, and at point 2 in Fig. 6(b) for coated T22 steel, shows the oxides to be identical in terms of the composition of the bond coat, with oxides of Ni, Al, and Cr along with diffusion of Fe into the bond coat. A continuous thin layer containing mainly Cr and O is present in the oxidized steel just below the bond coat in the case of Ni_3Al-coated T22 steel.

3.4 Electron Probe Microanalysis

Electron probe microanalysis of the exposed cross-section of Ni_3Al-coated GrA1 steel indicated the formation of an Ni-rich and Al-rich layer in the top region of the scale, which contained small pockets of Cr and a small percentage of Fe (Fig. 7). A subscale containing a higher concentration of Ni, depleted of Al and Cr, is present just above the oxidized bond coat. In this area, Fe coexists with Ni. The middle region of the Ni-rich and Fe-rich layer contains small nodules of Al. A thin, irregular, Cr-rich layer has formed at the scale-substrate interface. Cr, Al, Ni, and Fe are present in the bond coat. Y is also present in a small concentration.

Compositional images and elemental distributions (Fig. 8) for Ni_3Al-coated T11 steel indicate the formation of a scale below the coating. The top scale contains Ni, Al, Cr, and Fe. Nickel coexists with Fe in the subscale. The inner scale mainly contains Fe with small amounts of Cr. Chromium in the inner scale is also present in high concentrations in the form of streaks, which is an indication of internal oxidation. Yttrium is also present in minor concentrations only in the top-most scale.

4. Discussion

A fragile scale with a tendency to spall has been observed on all noncoated steels. However, noncoated GrA1 steel showed severe spalling, as can be seen from the mass gain plots (Fig. 1). Because this steel exhibited mass loss instead of mass gain, severe spalling is suspected. Identical results have also

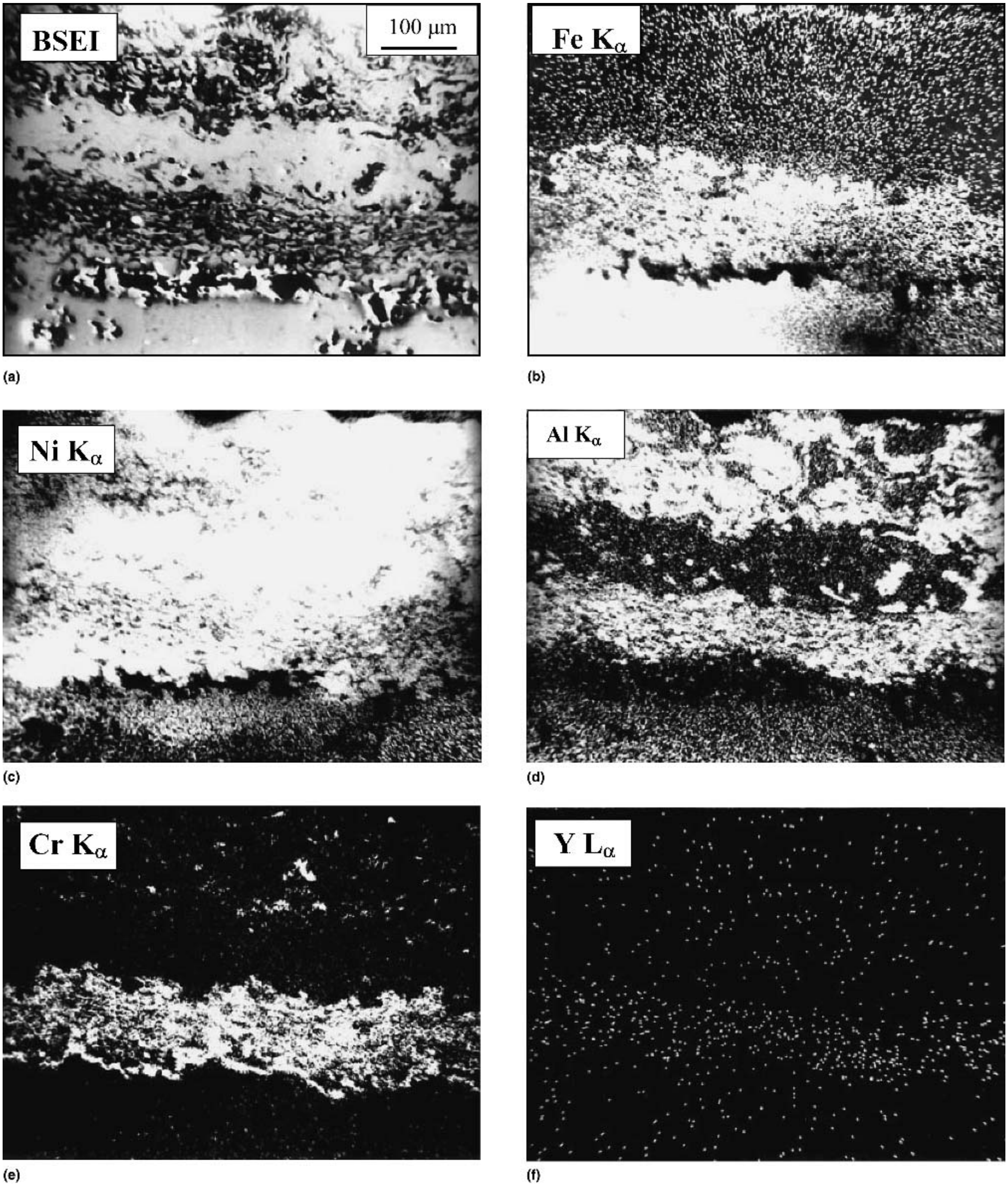

Fig. 7 BSEI and elemental x-ray mapping of the cross section of Ni_3Al-coated GrA1 steel with bond coat exposed to the platen superheater of the coal-fired boiler for 1000 h at 755 °C (magnification 170×)

been reported in the study by Wang (Ref 8), in which severe scaling and spalling was observed for a 2.25Cr-1Mo steel during 1000 h of cyclic exposure at 740 °C in a medium-Btu, coal-fired boiler. Spalling of the scale was estimated to exceed 70%.

From visual observation and mass change, it was immediately apparent that the protection provided by Ni_3Al coating to the steels in this environment was not significant. Even in Ni_3Al-coated T22 steel, in which the scale cracked after the first 100 h cycle, the erosion-corrosion rate was almost equiva-

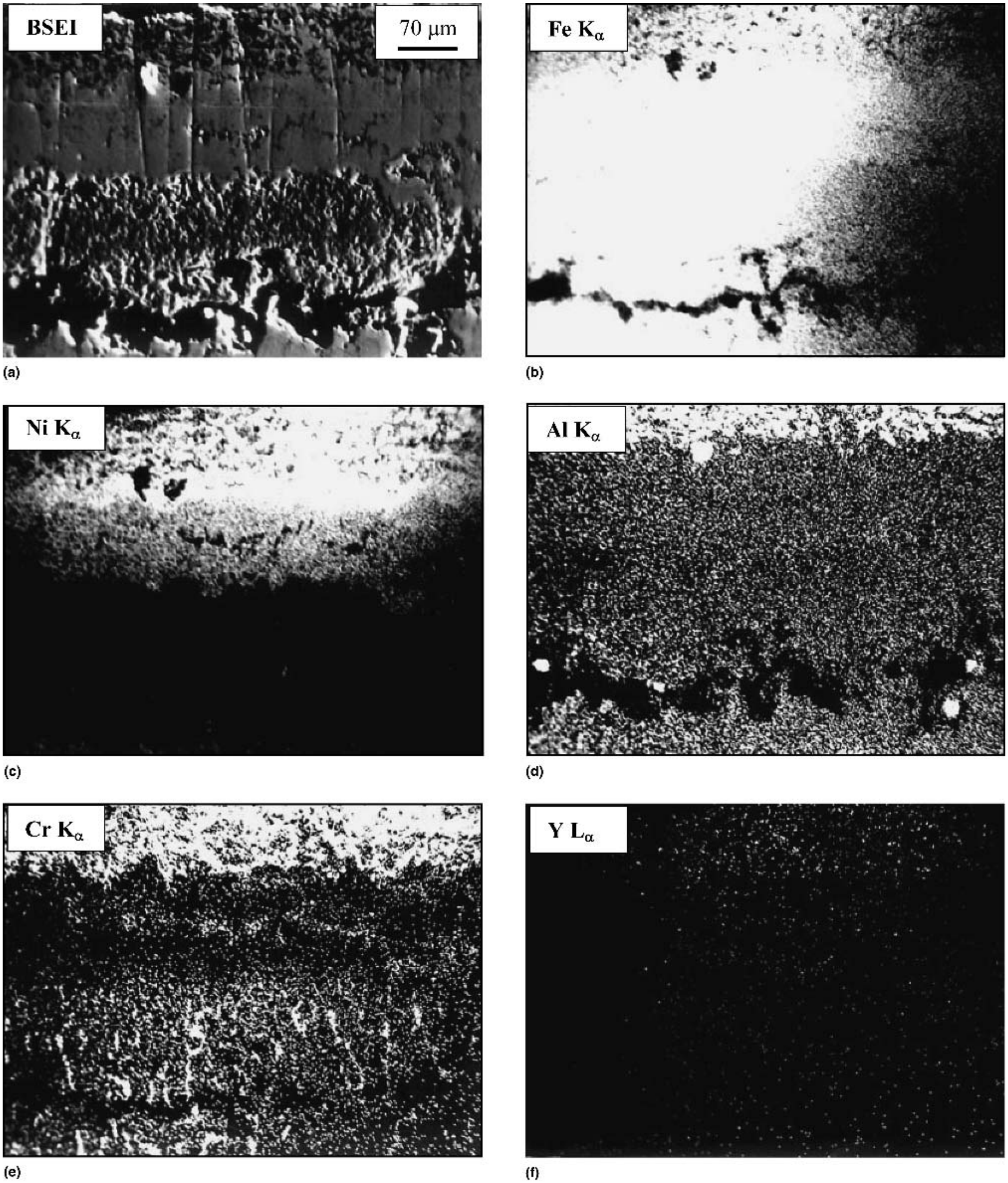

Fig. 8 BSEI and elemental x-ray mapping of the cross section of Ni_3Al-coated T11 steel with bond coat exposed to the platen superheater of the coal-fired boiler for 1000 h at 755 °C (magnification 180×)

lent to that of the uncoated steel. The protection provided to the other two steels by the Ni_3Al coating was also minimal. Poor scale adherence is perhaps the reason for the ineffectiveness of this coating.

The absence of sulfide formation in this environment is further supported by the findings of the study by Crossley et al. (Ref 22), in which the presence of fly ash particles rich in magnetite reduced the concentration of SO_3 in the boiler.

Another reason for spalling may be the formation of an NiO layer. This layer is porous and does not provide effective protection (Ref 23). The spalling tendency of these coatings might be due to their interaction with the fly ash particles, which cause the erosion of this fragile NiO scale. An increase in the NiO fraction in the scale with increased exposure time has been observed by Wu et al. (Ref 23) Niranatlumpong et al. (Ref 11) have also reported an increase in the pore size of the Ni-rich and Cr-rich scales with increased exposure time. This increase in pore size may facilitate O penetration through the coating, resulting in the oxidation of the base metal. In the present investigation, cross-sectional EDAX analyses have confirmed that O has penetrated up to the substrate steels as both of these substrate steels have been corroded in case of the coated T22 and GrA1 steels (Fig. 6). The degradation of substrate steels has also been confirmed by EPMA analysis.

5. Conclusions

Ni_3Al coatings can be successfully applied to boiler tube steels by plasma spray using a bond coat layer made of Ni-22Cr-10Al-1Y.

Noncoated steels, as well as coated steels, have ash particles embedded in the scale after exposure. For the coated steels, O has penetrated the coating up to the base metal. As such, base metal protection is minimal. A loosely adhering, porous scale is the main reason for this lack of protection by the coating.

Minimum protection has been provided to T22 steel, in which cracking of the coating has been observed during the first 100 h of cyclic testing. The formation of a porous NiO layer may also contribute to the poor performance of the coating.

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