

High-Temperature Degradation and Protection of Ferritic and Austenitic Steels in Steam Generators

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The useful life of superheaters and reheaters of power stations which use heavy fuel oil is shortened and their continuous service is inhibited by corrosion (fireside) and creep-type problems. The increase of corrosion attack on boilers is caused by the presence of fuel ash deposits containing mainly vanadium, sodium, and sulfur which form low-melting-point compounds. The tubes are exposed to the action of high stresses and high temperatures, producing the so-called "creep damage." In this work, two kinds of results are reported: lab and field studies using a 2.25Cr-1Mo steel. The laboratory work was in turn divided into two parts. In the first, the steel was exposed to the action of natural ash deposits in oxidant atmospheres at 600 °C for 24 h. In the second part, tensile specimens were creep tested in Na₂SO₄, V₂O₅, and their mixture over a temperature range of 580 to 620 °C. In the field work, components of a power station were coated with different types of nickel- and iron-base coatings containing chromium, Fe-Cr, and Fe-Si using the powder flame spraying technique. After testing, the coated tubes were analyzed using electron microscopy. The results showed that all the coating systems had good corrosion resistance, especially those containing silicon or chromium.

Keywords corrosion by deposits, creep resistance, metallic coatings, power plant, reheater

1. Introduction

It is well known that changes in fuel oil properties may produce an undesirable effect on the high-temperature behavior of steam-generator components. Heavy fuel oils rich in asphaltenes (18%), vanadium (300 ppm), sulfur (4.42%), and sodium (150 ppm) will very likely fill an increasing proportion of the oil market in the near future. In fact, most of the oil-fired power plants in Mexico already use heavy oils, as do such plants in other countries (Ref 1-3).

Fireside corrosion can be significant in oil-fired boilers when low-grade fuels with high concentrations of vanadium, sulfur, and sodium are used for firing. During combustion, vapors of vanadium pentoxide (V₂O₅) and alkali metal sulfates are formed. These vapors, combined with other ash constituents, then deposit onto cooler component surfaces. Vanadium pentoxide and alkali metal sulfates in the ash deposits react to form low-melting-point salts that, in turn, form low-melting-point eutectics that flux the protective oxide scale from the metal surface and expose bare metal. This results in accelerated corrosion attack.

High-temperature corrosion of superheaters and, especially, reheaters is strongly dependent on metal temperature. It could be said that the composition, temperature, and velocity of the flue gas play a less important role in material deterioration.

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Work done in the past (Ref 4-8) has shown that for most commercially available steels, metal temperatures above 600 °C produce very rapid corrosion. Moreover, above this temperature, the rate of corrosion increases exponentially with temperature and catastrophic corrosion may occur. Impurities in the fuel such as vanadium, sulfur, and sodium are mainly responsible for the ash corrosion of tubes in oil-fired boilers, and the greatest corrosion is always experienced when an corresponding to a sodium vanadyl vanadate (Na₂OV₂O₄·5V₂O₅) is present.

For most alloys, it is highly desirable that the metal temperature in the combustion environment remain below 590 °C, so that the effects of corrosion become almost negligible, even in the case of burning a very aggressive fuel oil. The materials used to fabricate heat exchangers usually develop a protective layer formed by chromium oxide, aluminum oxide, and silicon oxide. These layers are often cracked, are faulted, or fail by spalling. The slag components rich in vanadium, sodium, and sulfur usually form complex compounds with low melting temperatures that are deleterious to the oxide protective layers or to the metal surface. Normally the protective layers regenerate during service, but if the alloy is depleted in chromium, aluminum, or silicon, the corrosion activity is enhanced (Ref 5, 9, 10).

From the materials standpoint, the problem of degradation of high-temperature boiler components by vanadium, sodium, and sulfur remains unsolved. The first part of this work investigated the effects of synthetic and natural slags on the corrosion and creep resistance of a 2.25Cr-1Mo steel. The second part explored the use of chromium-, aluminum-, and silicon-base coatings to protect a 2.25Cr-1Mo tube of a high-temperature reheater.

2. Experimental Procedure

2.1 Laboratory Tests

Specimens of SA213 grade T22 (2.25Cr-1Mo) steel were tested. For comparison, SA213 austenitic grades TP 304H

(UNS S30409), TP321H (UNS S32109), and TP347H (UNS S34709) were also tested. Their chemical compositions are given in Table 1. Samples of dimensions 10 by 5 by 3 mm were polished with 600-grade emery paper and degreased with acetone. They were coated with actual ash collected from the superheater of a power plant and were placed in a thermobalance apparatus. The slag compounds identified by x-ray diffraction showed the presence of V_2O_5 , $Na_2OV_2O_4 \cdot 5V_2O_5$, and NaV_6O_{15} . After coating, the specimens were passed through a simulated flue gas (oxygen and 0.25 v/o SO_2 + 3.6 v/o O_2 , balance N_2) containing a Fe_2O_3 catalyst in an attempt to convert SO_2 to SO_3 . The tests lasted 24 h at a temperature of 600 °C.

For the creep experiments, flat tensile specimens measuring 30.00 mm in the gage length and 2.00 by 3.00 mm in the reduced cross section were used in an 8:1 lever-type machine. The gage length was covered with 5 kg/m² of either Na_2SO_4 , V_2O_5 , or the eutectic mixture 80% V_2O_5 + 20% Na_2SO_4 over a temperature range of 640 to 680 °C. After testing, the corrosion products were analyzed using x-ray diffraction techniques, and the failed specimens were mounted in bakelite to be inspected using optical and electron microscopy.

2.2 Field Studies

Some corrosion rate measurements were taken in a high-temperature reheater using the ultrasonic wall thickness readings after a year interval. The tube temperatures were taken with a technique described elsewhere (Ref 11).

To test the protective coatings, a tube from a high-temperature reheater was chosen. Before applying the coatings, the tube was sandblasted and covered with a Ni-20Cr coating. On

top of this, an outer layer was applied. Two different systems were used as an outer layer: 60Ni-20Cr + 40% Si, and chromium-rich alloy. The coatings were applied using the powder flame spraying technique. The reheater operated for 2 years, after which the tube was removed to be inspected using optical and electron microscopy.

3. Results and Discussion

Figures 1 and 2 show the weight gain data for the different materials evaluated in the thermobalance test. It is evident that the corrosiveness of the deposits varied with the atmosphere. The TP347H austenitic stainless steel had the best performance, as expected, and the T22 ferritic steel had the worst. These figures are representative of the weight gain behavior of the ferritic and austenitic alloys (T22, TP304H, TP321H, and TP347H). It is evident that the wastage rate and the corrosiveness of the deposits varied with the atmosphere. The ashes behaved differently in air than in the SO_2 + O_2 atmosphere. TP347H had the best performance and T22 had the worst at 600 °C.

Figure 3 shows a similar trend in the ranking of the steels when they were tested in the reheater of an oil-fired power station. In this case corrosion rate is plotted as a function of the tube temperature, because the lower chromium content in the T22 ferritic steel produces a lower corrosion resistance and a capacity to absorb more sulfur compounds than $Na_2OV_2O_4 \cdot 5V_2O_5$.

Figure 4 shows the effect of applied stress on rupture life with 500 mg/cm² coating of the different synthetic deposits for

Table 1 Chemical compositions (wt%) of the steels tested in the corrosion rate tests

Steel	C	Si	Mn	P	S	Ni	Cr	Mo	Ti	Cb + Ta	Fe
T22	0.09	0.31	0.49	0.015	0.010	...	2.19	0.91	bal
TP304H	0.08	0.50	1.73	0.026	0.003	10.13	18.47	bal
TP321H	0.08	0.64	1.53	0.023	0.002	10.48	17.28	...	0.46	...	bal
TP347H	0.08	0.49	1.50	0.024	0.004	12.30	18.45	0-72	bal

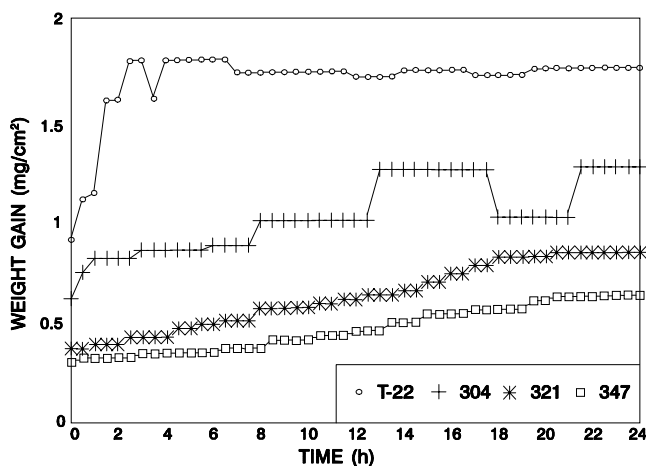


Fig. 1 Weight gain of ferritic and austenitic materials in oxygen at 600 °C for 24 h

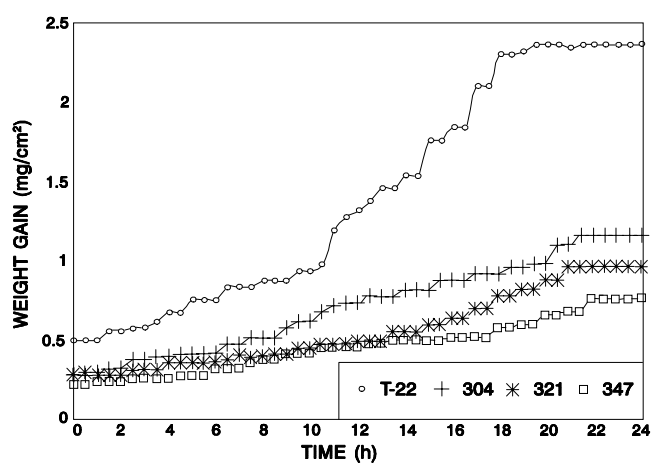


Fig. 2 Weight gain of ferritic and austenitic materials in SO_2 + O_2 atmospheres at 600 °C for 24 h

the T22 steel. For comparison, the results in air are also shown. For all cases, the rupture times in Na_2SO_4 were virtually the same as those obtained in air. This is due to the fact that the melting point of this compound is much higher than the testing temperature (884°C), so the deposit is not melted and it cannot diffuse into the metal. The shortest times to rupture were obtained in the 20% $\text{Na}_2\text{SO}_4 + 80\% \text{V}_2\text{O}_5$ mixture.

The fractured specimens always showed intergranular cracks and presented severe corrosion in the reduced cross-sectional area, more severe than the specimens tested in the other deposits. The compounds identified by x-ray diffraction in this case included FeCr_2O_4 , FeS , FeV_2O_4 , Fe_2O_3 , Cr_3S_4 , V_2O_5 , FeVO_4 , FeO , and Cr_2O_3 . Ahila (Ref 12) has shown that ternary systems such as $\text{V}_2\text{O}_5\text{-NiO-Cr}_2\text{O}_3$ and $\text{Fe}_2\text{O}_3\text{-V}_2\text{O}_5\text{-Cr}_2\text{O}_3$ can be in a liquid state at temperatures as low as 550 and 480°C . Under some circumstances, nonprotective oxides can form due to the formation of eutectics such as these. The degradation of the coated specimens with vanadium-containing deposits is attributed to the fluxing of the protective scales by the salt deposits, which are liquid at the test temperatures, and to easier crack nucleation in the presence of a liquid deposit at the grain boundaries. An additional effect is the loss in the load-bearing cross-sectional area due to the action of the corrosive species present. These three factors are responsible for the degradation of the mechanical properties of the steel.

Cross sections of the coated tubes with the different coating systems are shown in Fig. 5 and 6, together with energy dispersive spectroscopy microanalysis mappings of some elements. Generally speaking, all of the systems showed good adherence to the metal and excellent corrosion resistance. The x-ray mapping of vanadium shows, in all systems, that the external layer of the coating was attacked. The x-ray mapping in the system containing silicon (Fig. 5) shows a strong layering of vanadium-rich over silicon-rich (oxides). The system that did not present any corrosion was the one coated with the chromium-rich alloy, that is, $\text{Ni-20Cr/Ni-20Cr-50FeCr}$, as can be seen in Fig. 6. These are very clear examples of how metallic coatings are an excellent barrier against vanadium compounds in the molten state.

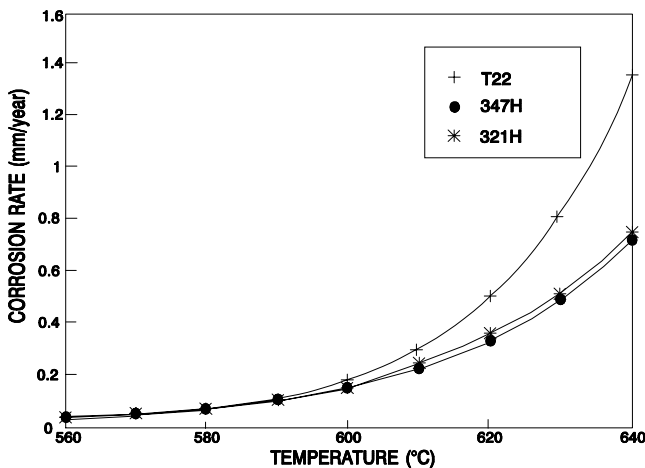
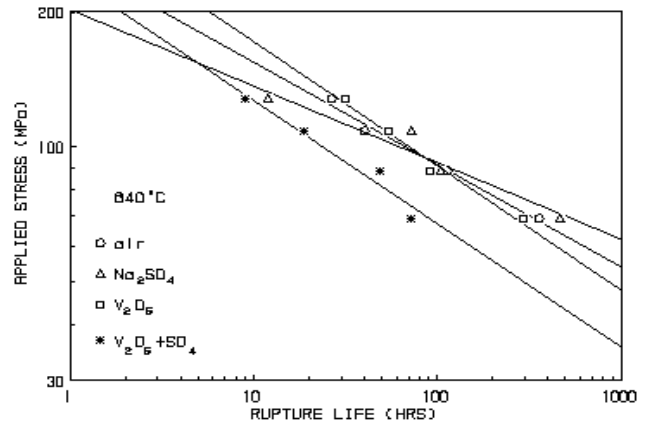
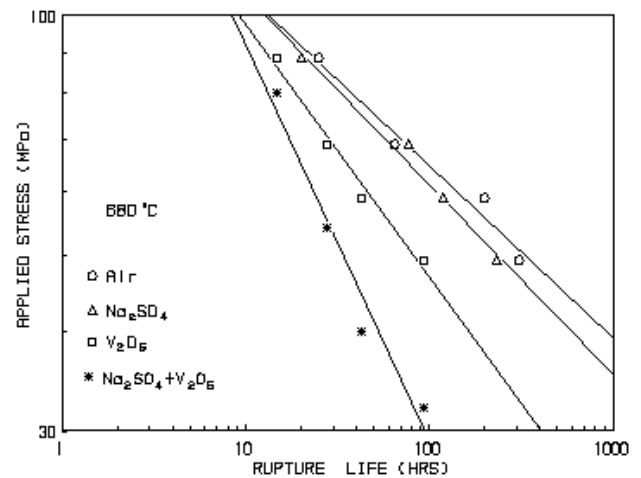


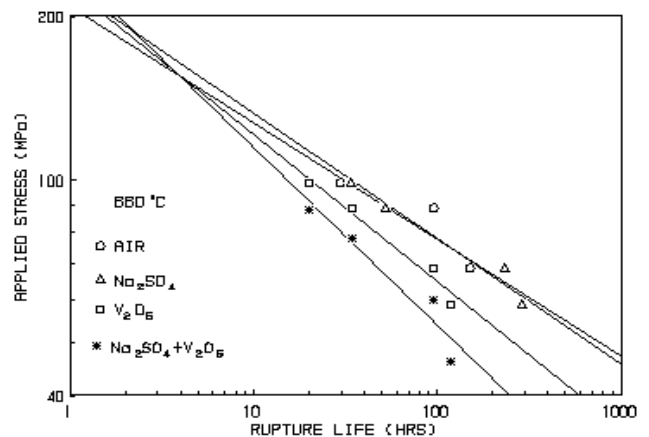
Fig. 3 Corrosion rate for ferritic and austenitic materials in the high-temperature reheater of an oil-fired power plant



(a)



(b)



(c)

Fig. 4 Effect of temperature and applied stress on the rupture times of a T22 steel tested in different environments with 5 kg/m^2 of synthetic deposits

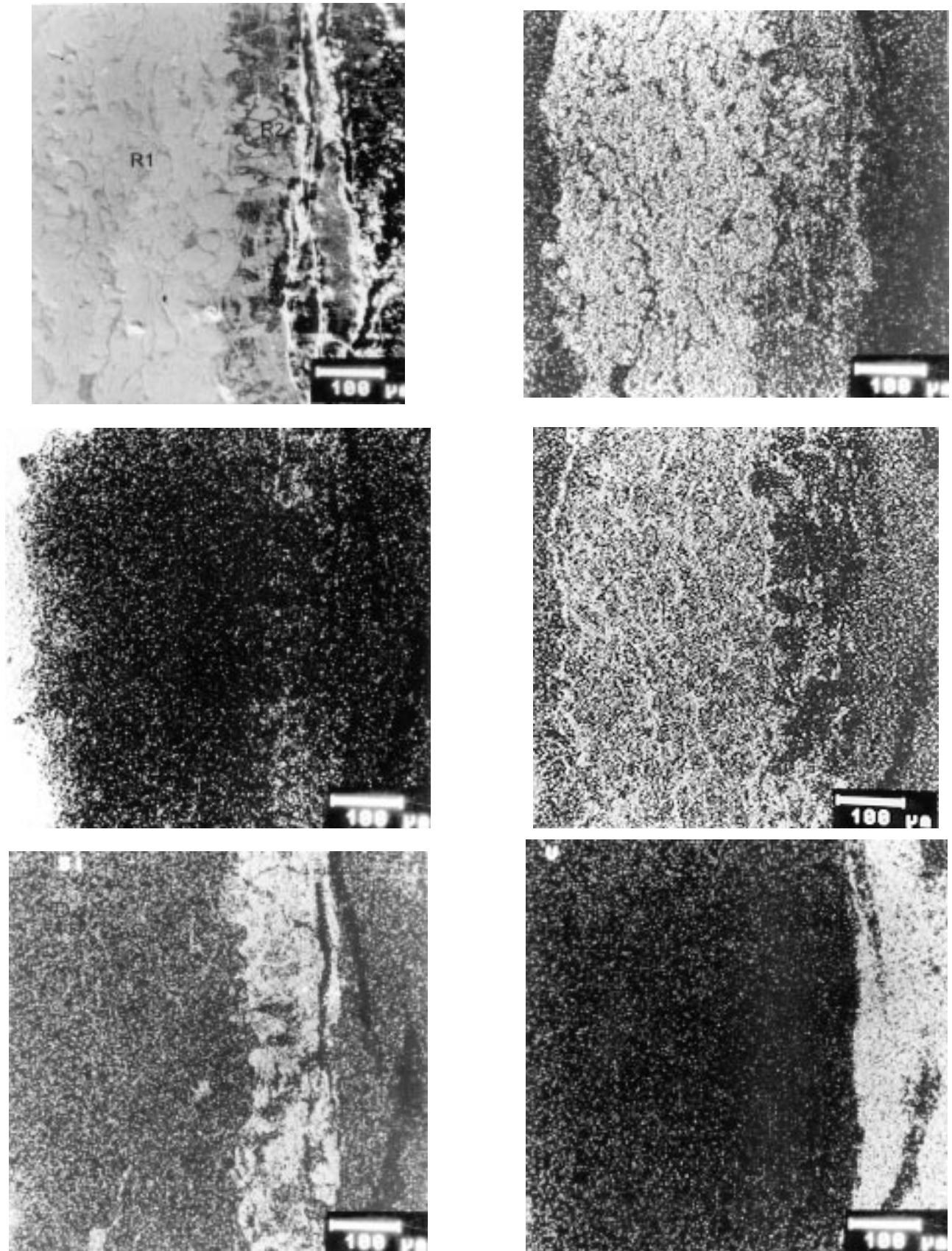


Fig. 5 Cross section of a field-tested reheater tube with the coating system Ni20Cr/Ni20Cr-40FeSi showing x-ray mapping of Ni, Fe, Cr, Si, and V. (M, metal; R1, Ni-20Cr; R2, Ni20Cr-40FeSi).

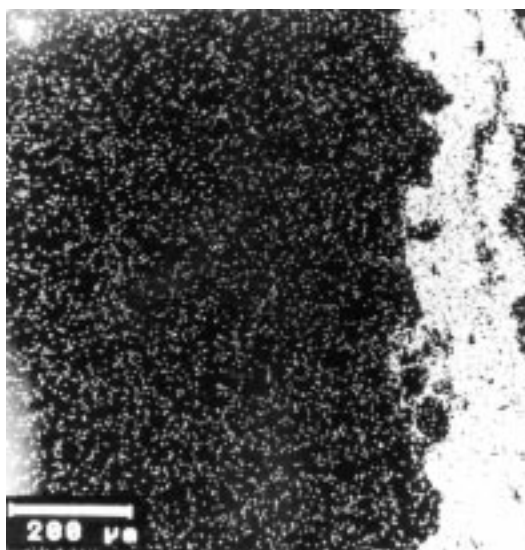
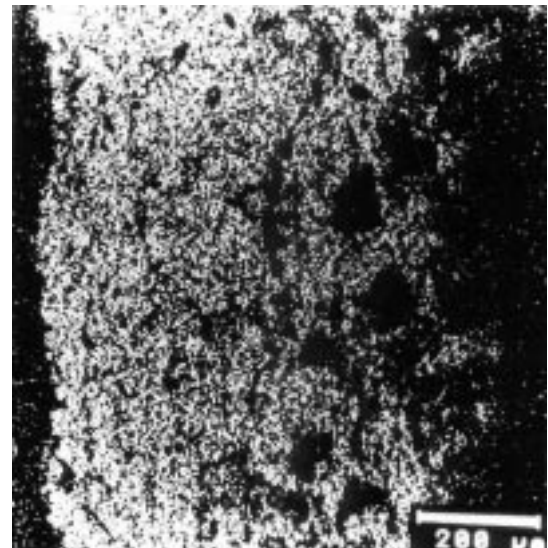
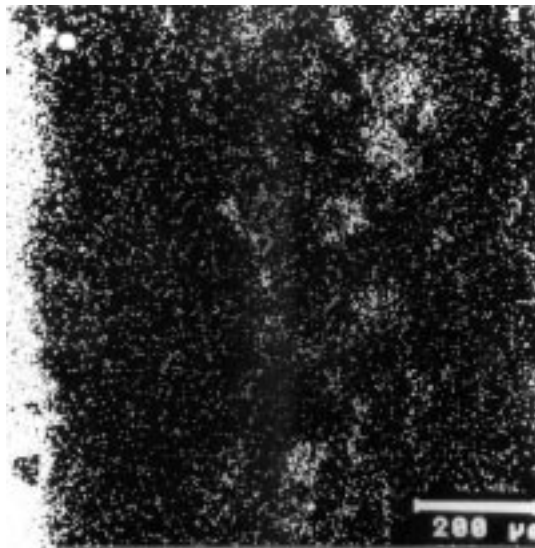
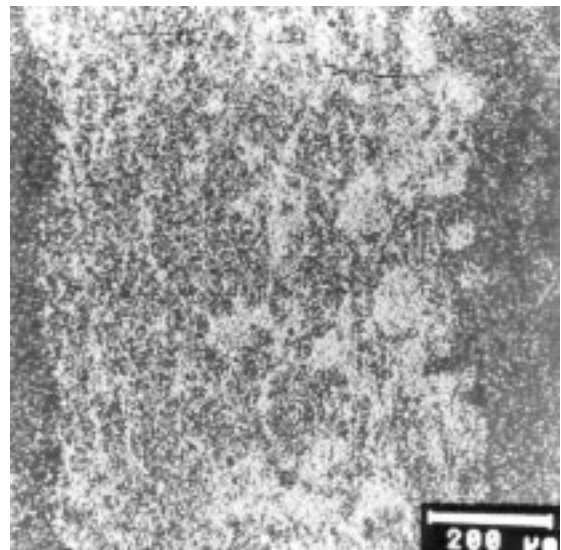
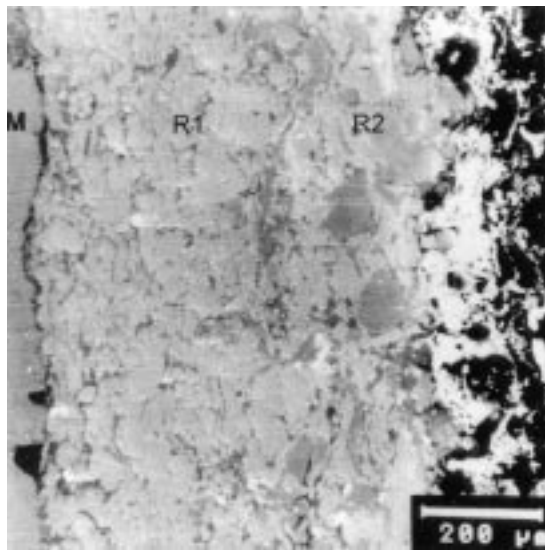


Fig. 6 Cross section of a field-tested reheat tube with the coating system Ni20Cr/Ni20Cr-50FeCr showing x-ray mapping of Ni, Fe, Cr, V, and Al. (M, metal; R1, Ni-20Cr; R2, Ni20Cr-50FeCr).

4. Conclusions

- The weight gain of a 2.25Cr-1Mo (T22) ferritic steel was greater than for 18Cr-8Ni austenitic stainless steels in oxygen and in O₂ + SO₂ atmospheres at 600 °C for 24 h.
- The corrosion rate of a 2.25Cr-1Mo steel in a high-temperature reheater was also higher than that for austenitic stainless steels.
- In units fired by heavy fuel oil the corrosion is high when the metal temperature is about ≥600 °C.
- The rupture times of a creep-tested 2.25Cr-1Mo steel were shorter in vanadium-containing deposits than those tested in air due to the loss in load-bearing cross-sectional area, easier crack nucleation, and the formation of low-melting-temperature compounds from the deposits.
- Metallic coating, an internal Ni-20Cr coating and an external coating of Ni₂₀Cr + either FeSi or FeCr alloys, were found to be excellent barriers against vanadium compounds in the molten state.

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