

Correlation Between Molten Vanadium Salts and the Structural Degradation of HK-Type Steel Superheater Tubes

F.C. Nunes, L.H. de Almeida, and A.F. Ribeiro

(Submitted December 5, 2005; in revised form December 20, 2005)

HK steels are among the most used heat-resistant cast stainless steels, being corrosion-resistant and showing good mechanical properties at high service temperatures. These steels are widely used in reformer furnaces and as superheater tubes. During service, combustion gases leaving the burners come in contact with these tubes, resulting in corrosive attack and a large weight loss occurs due to the presence of vanadium, which forms low melting point salts, removing the protective oxide layer. In this work the external surface of a tube with dramatic wall thickness reduction was analyzed using light microscopy, scanning electron microscopy, and transmission electron microscopy. The identification of the phases was achieved by energy dispersive spectroscopy (EDS) analyses. The results showed oxides arising from the external surface. In this oxidized region vanadium compounds inside chromium carbide particles were also observed, due to inward vanadium diffusion during corrosion attack. A chemical reaction was proposed to explain the presence of vanadium in the metal microstructure.

Keywords heat-resistant metals, molten vanadium salts, stainless steels

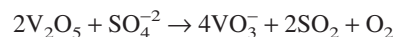
1. Introduction

Stainless steels are used in applications where service under corrosive environment, or under high temperature conditions, is required. The characteristic high chromium content of these alloys provides a protective oxide layer necessary for work in such conditions. Any damage to this layer can cause premature failure of components. Stainless steels can be classified as wrought or cast materials. Among the cast stainless steels, there are corrosion-resistant and heat-resistant types, the latter requiring a higher carbon content, such as in the HK type (Ref 1, 2).

HK cast stainless steel is frequently used in structural stressed parts under temperatures as high as 1150 °C. They present good corrosion resistance to hot gases containing sulfur whether under oxidizing or reducing conditions. Their microstructure consists of an austenitic matrix surrounded by a carbide network in the interdendritic region. During service at elevated temperatures small secondary carbide particles precipitate, thus maintaining good mechanical properties. Due to these characteristics it is a suitable material for the manufacture of radiant tubes in petrochemical furnaces or superheater tubes (Ref 2, 3).

Superheater tubes are used to preheat gases that enter into a petrochemical furnace. Outside these tubes are the fuel burners, which supply heat to the internal gases. During this process the

regions of the tubes closest to the burners come into contact with combustion gases containing vanadium compounds, as a result of the fuel combustion. During combustion solid vanadium pentoxide (V_2O_5) is formed. Ash deposits on the surface of the tubes react with vanadium pentoxide (Ref 4-6). The reaction occurs as follows (Ref 4):



Thus low melting point vanadium salts are formed, fluxing the protective chromium oxide scale and exposing bare metal

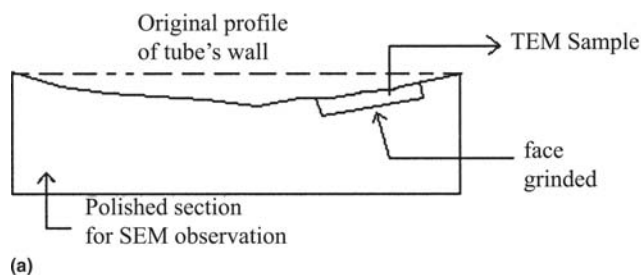


Fig. 1 (a) Schematic drawing showing where the TEM samples were obtained. (b) Visual aspect of the tube's cross section

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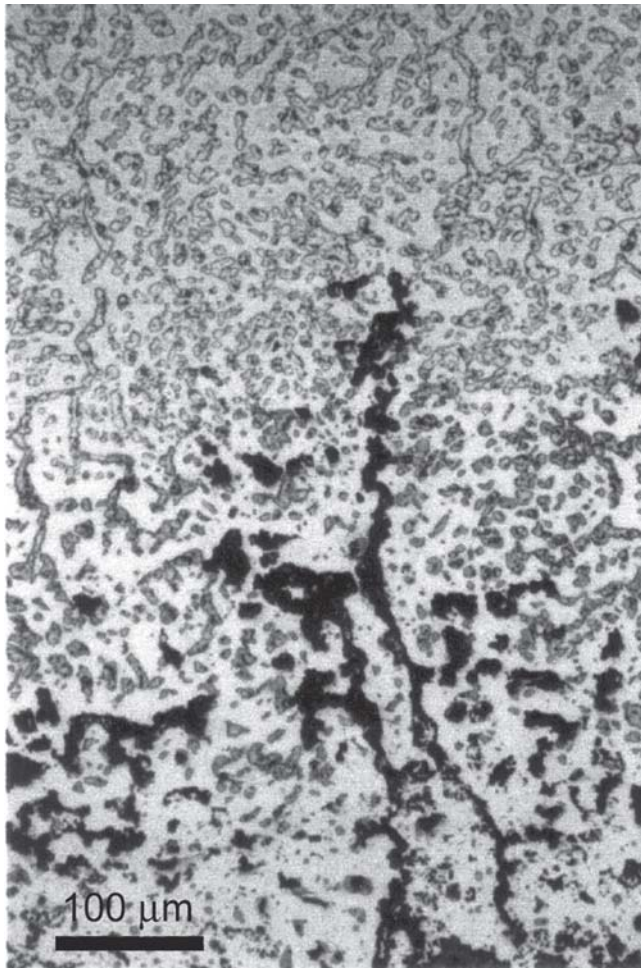


Fig. 2 Structural degradation along external surface as evidenced by the presence of dark oxide particles

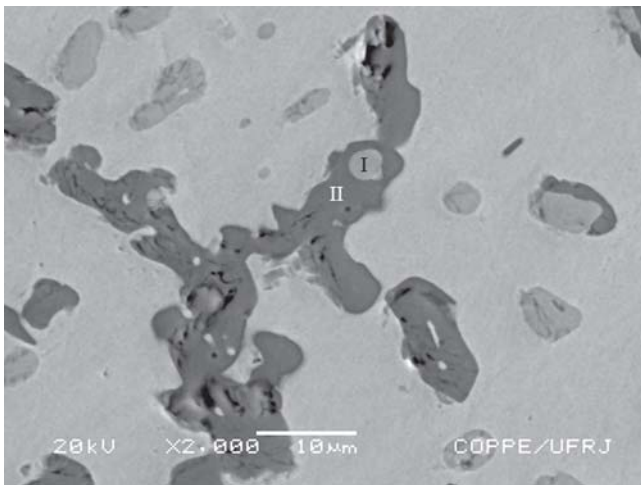


Fig. 3 SEM micrograph presenting chromium carbide particles (identified as II) next to vanadium-bearing particles (identified as I)

to corrosive attack. This corrosive attack occurs very quickly because service temperature exceeds 900 °C (Ref 4, 5, 7-9).

The objective of this work is to contribute to an understanding of the effects that cause the dissolution of the chromium

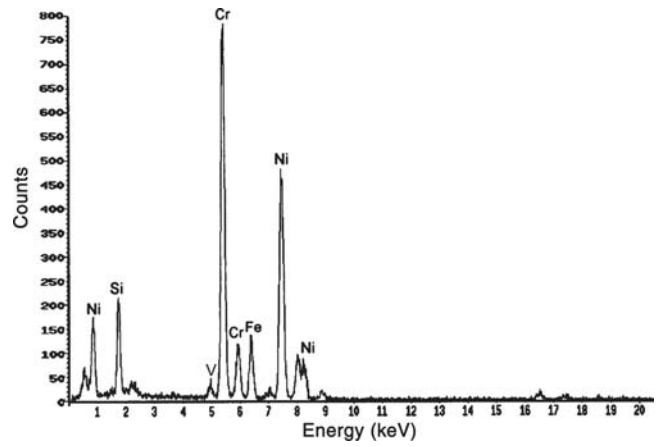


Fig. 4 EDS spectrum of the vanadium-bearing particles

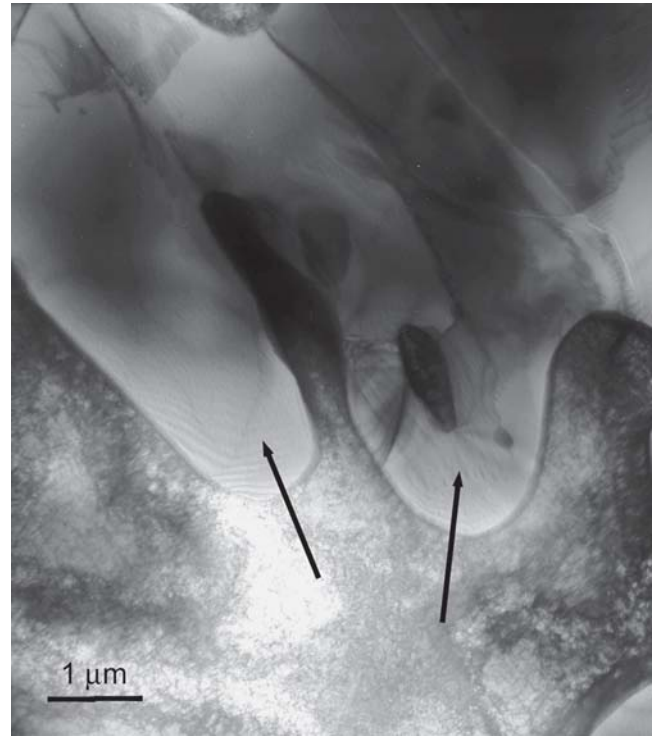


Fig. 5 Rounded chromium carbide particles in the austenitic matrix (shown by the arrows)

oxide scale, through the characterization of the surface microstructure of HK superheater tubes corroded due to the presence of vanadium using light microscopy, scanning electron microscopy (SEM), and transmission electron microscopy (TEM) imaging, and energy dispersive spectroscopy (EDS).

2. Experimental

The material used in the superheater tubes studied in this work was a HK-40 heat-resistant cast stainless steel of which the nominal composition was: 0.2-0.6% C; 24.0-28.0% Cr; 18.0-22.0% Ni; 2.0% Si max; 2.0% Mn max; Fe-balance.

To obtain a suitable sample the tube was cut, and a section was ground and polished. Figure 1(a) shows the area of the

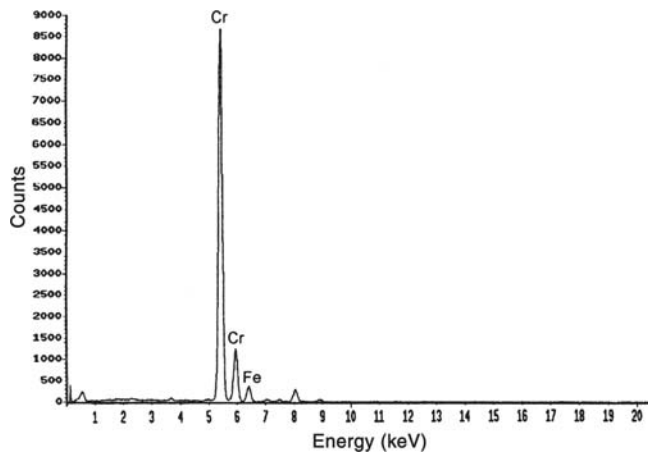


Fig. 6 EDS analysis of the chromium carbide particles

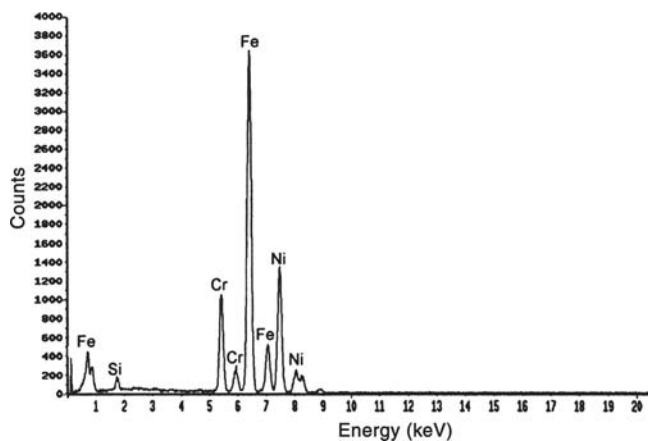


Fig. 7 EDS analysis of the matrix presenting strong peaks of Cr and Ni (main alloying elements, as expected)

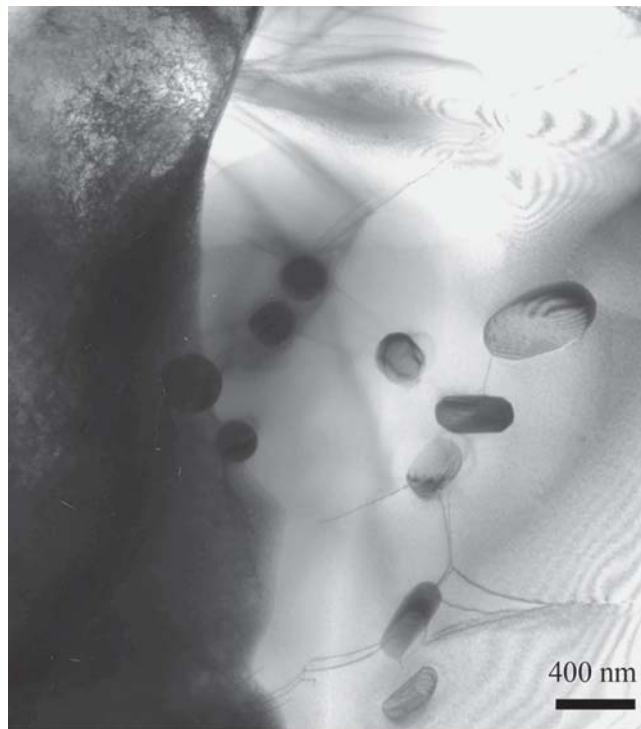
tube from which TEM specimens were obtained, while Fig. 1(b) presents an actual photograph of the tube's cross section.

TEM specimens were obtained by cutting a small plate very close to the surface, as presented in Fig. 1(a). This small plate was then ground and polished in such a way as to preserve as much as possible the external surface, thus enabling a precise observation of the phases present close to the corroded area. After grinding and polishing, 3 mm discs were cut by electro-erosion, and then prepared in dimple grinder equipment. The finishing was carried out by polishing in an ion milling device.

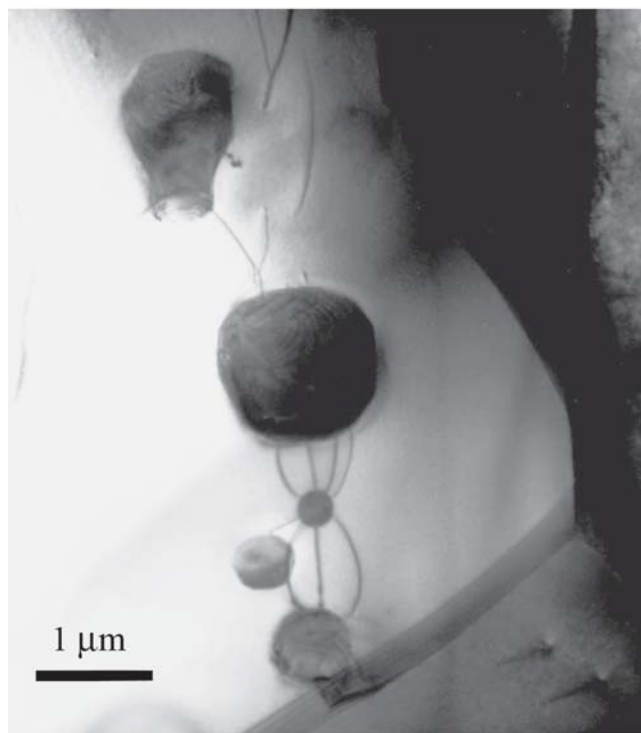
3. Results and Discussion

As shown in Fig. 1(b), the external surface of the tube shows dramatic mass loss due to corrosive attack. The microstructural aspect close to the external surface can be observed in the light microscopy micrograph presented in Fig. 2. As one can observe there is a large number of chromium carbide particles, coarsened due to exposure to high temperatures. The degradation is indicated by the significant amount of dark oxide particles, which are formed due to an inward oxygen flow.

A higher magnification micrograph obtained near the external surface through SEM is presented in Fig. 3, where it is possible to observe chromium carbide particles in detail (iden-



(a)



(b)

Fig. 8 (a) TEM micrograph showing vanadium-bearing particles in detail. (b) TEM micrograph showing vanadium-bearing particles in detail

tified as II), as well as small bright regions (identified as I). SEM EDS analysis (Fig. 4) shows that these bright spots contain vanadium. The vanadium-containing particles are chromium carbides with the M_7C_3 stoichiometry, as opposed to the stoichiometry of the chromium carbides far from the exposed

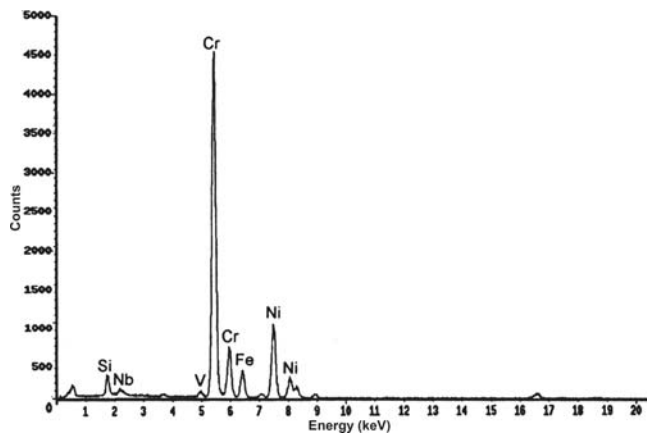


Fig. 9 EDS spectrum presenting a V peak along with strong peaks of Cr, Ni, Nb, and Si

surface ($M_{23}C_6$). This difference in stoichiometry can be ascribed to the carburization process that takes place in the external surface. As observed in Fig. 3, these vanadium-containing particles are associated with chromium carbide particles. Yoon and Jeong (Ref 10) also pointed out the presence of vanadium in the oxidized region of HK-40 steel tubes.

TEM was used to observe and identify the phases present near the external surface in more detail. Figure 5 shows massive chromium carbide particles in the austenitic matrix (shown by the arrows). The EDS analysis of these particles is presented in Fig. 6. On the other hand, EDS from the matrix (Fig. 7) also displayed strong peaks of iron, chromium, and nickel, as expected.

Figure 8(a) and (b) show in more detail vanadium-rich regions associated with chromium carbide particles. The EDS spectrum shows vanadium peaks along with nickel, niobium, and silicon as well as chromium, as seen in Fig. 9.

In contrast to the results obtained by Goebel et al. (Ref 11), the presence of vanadium-rich particles near the external surface where the corrosive attack has occurred indicates that there was an inward vanadium flow. That means that vanadium diffuses into the material as the corrosive attack takes place. It is believed that due to the high temperature at the surface of the tube, vanadium salts could dissociate, leading to the diffusion of this element, resulting in the formation of small intermetallic particles. It was proposed that the dissociation reaction takes the following form (Ref 12):



This reaction also explains the chromium oxide protective layer destruction, leading to the dramatic material dissolution observed.

Vanadium appears to react with Ni-Nb-Si compounds. These compounds, known as G phase, can be present in cast stainless steels modified by the addition of Nb after exposure at high temperatures over long periods of time. However, niobium can be present in small quantities in nonmodified steels as an impurity originated from the recycling of raw material, which explains the peaks presented in Fig. 9.

Next to these vanadium-containing particles there are accommodation dislocations due to the volume mismatch between the chromium carbide and these particles. These dislo-

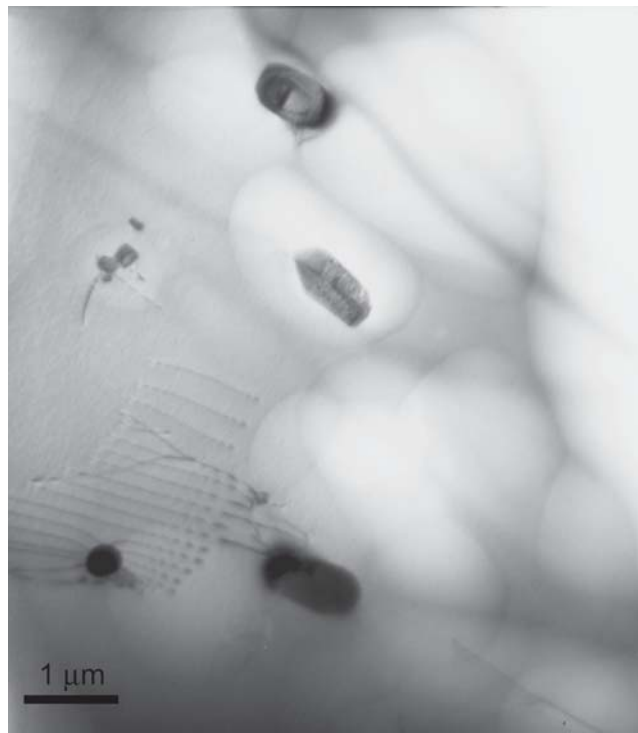


Fig. 10 Accommodation dislocations next to vanadium-bearing particles

cations can be seen in the TEM micrograph presented in Fig. 10 as well as in Fig. 8(b).

4. Conclusions

The presence of vanadium in fuels is highly deleterious to HK tubes because vanadium low melting point salts are formed and flux the protective chromium oxide layer, thus exposing bare metal to corrosive attack. During this process vanadium diffuses into the material forming small vanadium intermetallic compounds with Nb, Ni, and Si, as shown by EDS analysis.

This inward vanadium diffusion is caused by the vanadium salts dissociating due to the high temperature at the tube surface. The proposed reaction described by $6VO_3^- + Cr_2O_3 \rightarrow 2CrO_4^{2-} + 6V^{+4} + 13O^{-2}$ explains the source of atomic vanadium necessary for this process.

This dissociation reaction is also responsible for the protective layer destruction because chromium oxides react with these vanadium molten salts.

Acknowledgments

The authors thank ANP, CNPq, and CTPETRO for financial support and Military Institute of Engineering—Rio de Janeiro (IME) for the TEM/EDS analysis. The authors also thank Tito Silveira Consultoria e Engenharia for supplying the material and the helpful discussion and the engineer Jorge Leandro for help in the experimental work.

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