

High-Temperature Corrosion Observed in Austenitic Coils and Tubes in a Direct Reduction Process

B. Campillo, C. Gonzalez, G. Hernandez-Duque, and J.A. Juarez-Islas

(Submitted 13 October 1998; in revised form 18 October 1999)

The subject of this study is related to the performance of austenitic steel coils and tubes, in a range of temperatures between 425 and 870 °C for the transport of reducing gas, in an installation involving the direct reduction of iron-ore by reforming natural gas. Evidence is presented that metal dusting is not the only unique high-temperature corrosion mechanism that caused catastrophic failures of austenitic 304 (UNS S304 00) coils and HK-40 (UNS J94204) tubes. Sensitization as well as stress corrosion cracking occurred in 304 stainless steel coils and metal dusting took place in HK-40 tubes, a high resistance alloy. The role of continuous injection of H₂S into the process is suggested to avoid the high resistance metal dusting corrosion mechanism found in this kind of installation.

Keywords austenitic steel, coils, corrosion, direct reduction, high temperature

1. Introduction

The direct reduction process involves the continuous reduction of high-grade iron ore by a modified natural gas called "reforming gas." The initial natural gas, mostly methane, CH₄, first flows through desulfurizing drums and then through preheater coils called "reformer stacks." Steam is then mixed with the preheated natural gas, and the mixture passes through hot, catalyst-filled tubes within reformer furnaces, taking place at about 870 °C.^[1] The mixture of gases that emerges is called "reformed gas" with a composition averaging about (in vol.%) 60.08 H₂, 12.42 CO₂, 20.97 CO, 5.30 unconverted methane, 1.19 N₂, and 0.04 H₂O.

It has been pointed out^[2] that when iron-, nickel-, and cobalt-base alloys are in contact with reducing and carbon-containing atmospheres, such as those mentioned above, they can suffer significant attack by carburizing components of the environments, leading to catastrophic carburization such as metal dusting, especially in atmospheres of high carbon activities and at intermediate temperatures between 450 and 800 °C. The result is the disintegration of the alloy into a dust, consisting of particles of carbon, carbides, metal, and oxides,^[3] which are blown off in erosive gas streams leaving behind pits or general abrasion. Metal dusting has been simulated for low and high alloy steels^[4,5] for carbon activities $a_c \geq 1$ in flowing CO-H₂-H₂O, and its proposed mechanism^[6,7] relates the decomposition of cementite for alloy steels. However, Grabke et al.^[2,3] found no M₃C formation in highly alloyed austenitic steels and have proposed a mechanism for high alloy steels that involves supersaturation with carbon followed by graphitization and mechanical breakdown of the resulting products.

B. Campillo, Centro de Ciencias Fisicas-UNAM and Depto. de Metalurgia, Fac. de Quimica-UNAM; **C. Gonzales**, Depto. de Metalurgia, Fac. de Quimica-UNAM; **G. Hernandez-Duque**, Univ. del Mayab, Merida, Yucatan; and **J. A. Juarez-Islas**, Depto. de Materiales Metalicos y Ceramicos, IIM-UNAM.

The carburized layer at the surface subsequently develops into typical metal dusting debris. It has been pointed out^[8] that in a direct reduction plant, the reduction gas is supplied from reformers to the reactor and must be heated to a reaction temperature of about 980 °C.

Protection against metal dusting (for any kind of Fe-base alloys) is possible in two ways: (1) formation of a protective chromium oxide layer, but only on high alloy steels; and (2) the presence of H₂S in the atmosphere, which leads to coverage of the metal surface with adsorbed S_{ad} from the equilibrium of



The former expression is said^[3,4] to be the most effective since sulfur adsorption immediately converts any free metal surface and blocks the steps that are necessary for the start of metal dusting. Thus, the presence of a sufficient concentration of H₂S in the atmosphere can provide a reliable protection against metal dusting, but the H₂S must always be present.

The purposes of this paper are as follows: (a) to present the results of catastrophic failures that occurred in austenitic 304 (UNS S30400) and HK-40 (UNS J94204) coils, transporting reducing gases in the direct reduction process at the Ispat plant in Mexico, in the range of temperatures between 425 to 850 °C; and (b) to present evidence that a continuous injection of H₂S into the process is not the full solution to the problem of high-temperature corrosion mechanisms.

3. Experimental Procedure

Coils of specimens of 304 stainless steel (UNS S30400) and tubes of HK-40 (UNS J94204) heat-resistant alloy were cut transverse to the origin of failure to observe details of their microstructure. The specimens were mechanically polished and etched with FeCl₃ + ethanol to reveal their microstructure. The regions of characteristic morphology were observed under an optical microscope Philips PMG3 (Philips Electronic Instruments Corp., Mahwah, NJ). Corrosion products were removed for x-ray diffraction (Siemens D5000, Siemens Electrical Equipment, Toronto) studies using filtered Cu K_α radiation. Mi-

croanalysis of areas of interest were performed by an electron microscope using a spot size of 64 nm in a Jeol 6400 (Japan Electron Optics Ltd., Tokyo) scanning electron microscope (SEM) operated at 20 kV with references of pure elements as standards.

4. Results and Discussion

A schematic diagram of heater 3 in the direct reduction process at Ispat is shown in Fig. 1, where 304 stainless steel (UNS S30400) coils were removed after a catastrophic failure occurred in two different locations: (1) in the second stage of the preheating zone of the reduction gases (CC-104); and (2) in the recollection zone of exhaust gases (CC-105). The same diagram also shows the region (marked with a square in Fig. 1), in which a section of a tube of a heat-resistant alloy of the HK40 type was removed after catastrophic failure.

4.1 Sensitization of 304 SS

Figure 2(a) shows a section of a 304 stainless steel coil, which was located in the middle of the coil (section CC-104 of Fig. 1, $T \approx 650\text{ }^\circ\text{C}$), where a hole bigger than 10 cm in diameter was ob-

served in the upper part of the coil after the catastrophic failure occurred). It is important to mention that holes with diameters smaller than 5 cm were also observed along the total length of the coil, and the holes were always positioned on the top part of the coil. Figure 2(a) shows a transverse section of the coil. On the bottom of the coil, it was observed that its wall thickness was bigger (1 cm) than that of the original centrifugally cast tube (0.5 cm). It can be observed from the bottom to the top of the coil that the wall thickness decreased until failure occurred.

Figure 3 shows a transverse optical photomicrograph of the exploded coil of Fig. 2. The region marked **A** corresponds to the microstructure observed in areas close to the outer diameter of the coil, which basically shows a microstructure of austenitic grains and no sign of any kind of high-temperature corrosion. The region marked **B** shows the microstructure in areas close to the inner diameter of the coil. It can be observed how the high-temperature corrosion phenomenon, known as sensitization, is present; in this phenomenon, the grain boundaries rich in chromium precipitates formed a continuous layer. Figure 4 shows the microstructure observed in the thickest section of the pipe of Fig. 2, which consisted of deposited material from dissolution of the sensitized grains at the top of the coil. The white areas are rich in Fe and Cr and the black areas are rich in Fe and Ni, as detected by SEM microanalysis. By optical observation,

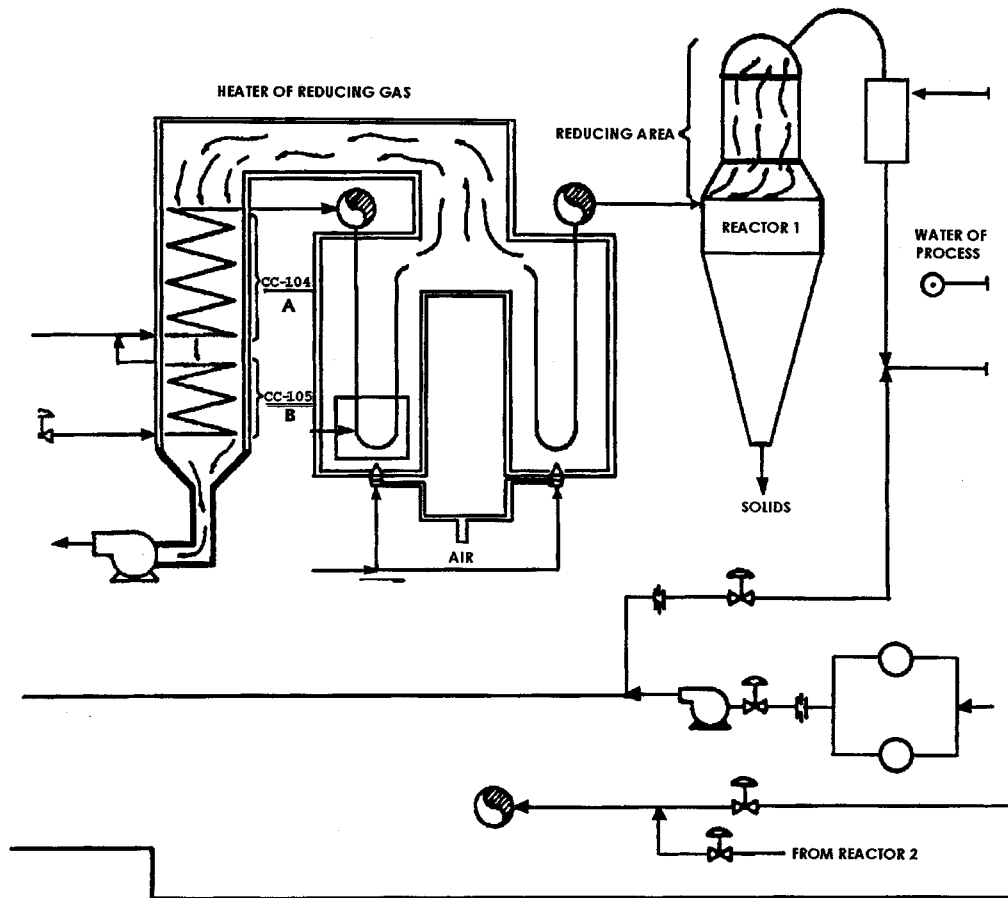
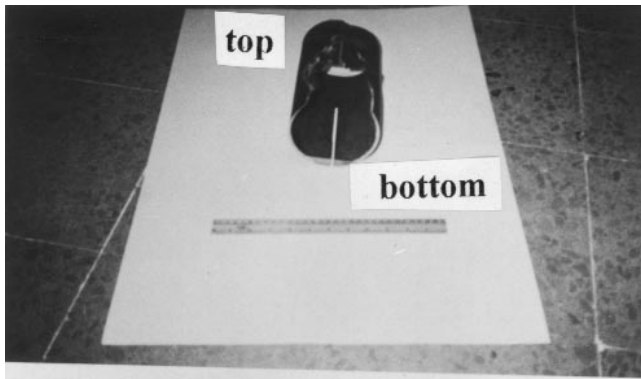
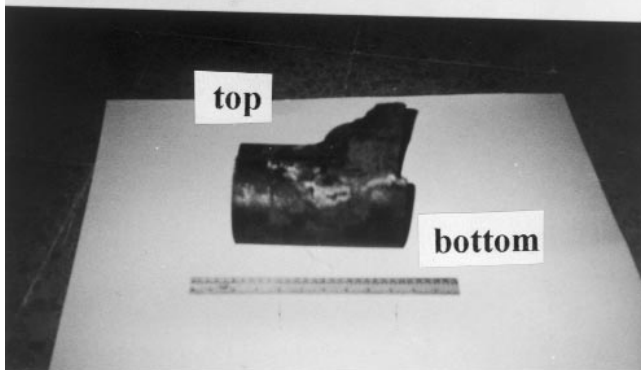


Fig. 1 A section of a diagram of heater 3 of the direct reduction process from which coils (section CC-104 **A** and CC-105 **B**) and tubes were removed after catastrophic failures occurred



2a



2b

Fig. 2 (a) Transverse section of a 304 SS coil located in section CC-104 A, removed after a catastrophic failure. (b) Longitudinal section of a 304 SS coil located in section CC-104 A, removed after a catastrophic failure. The length of the ruler is 30 cm.

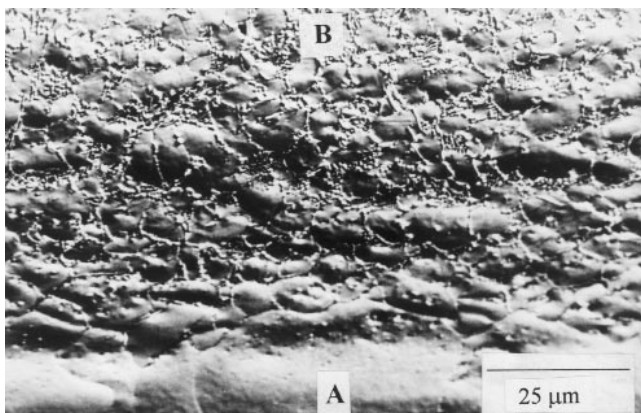


Fig. 3 Optical micrograph of the exploded coil of Fig. 2. The section marked A corresponds to areas that do not show evidence of sensitization (close to the outer diameter). The section marked B shows evidence of sensitization (close to the inner diameter of the coil). 1000X

it can be stated that this morphology was due to the slow dissolution of grains located in the upper section of the coil. This dissolution of the sensitized grains (which explains the observation of a very thin wall on the top of the coil and a very thick section

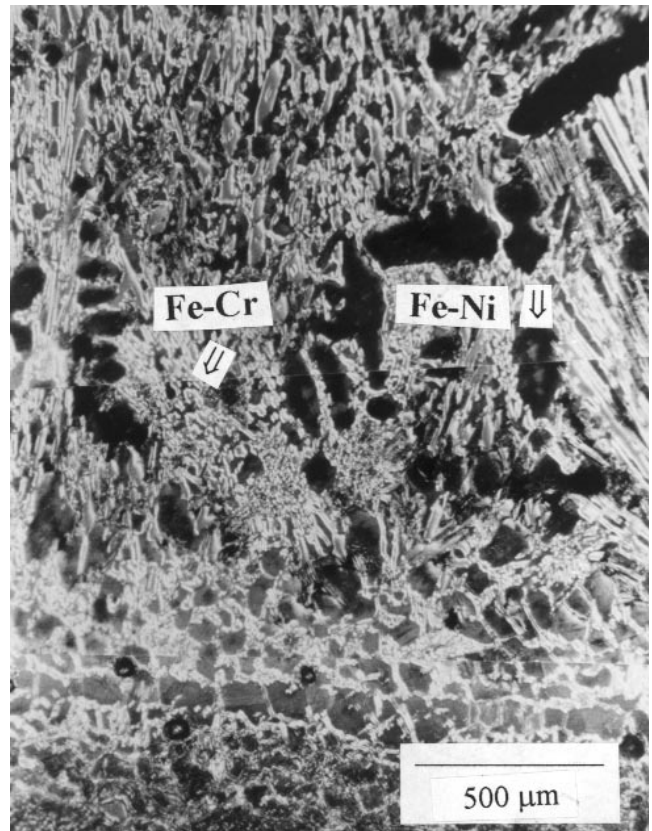


Fig. 4 Microstructure observed in the thickest section of the coil, where material was deposited from the upper part of the coil. The deposit region is denoted Fe-Ni and Fe-Cr. 50X

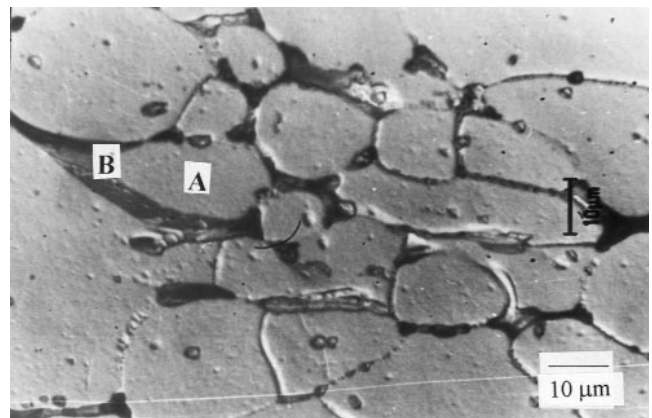


Fig. 5 Microstructure of a 304 SS coil, where depletion of chromium was detected at the grain boundaries. In point A, 18wt% Cr was detected, and in point B, 15wt% Cr was found.

on the bottom) results in a thick section at the lowest part of the coil, as the dissolved grains are deposited (by gravity) to the bottom of the coil.

Microanalysis of the sensitized austenitic grains shows a depletion of chromium. For instance, at point A of Fig. 5, the amount of Cr decreased from 18 to about 15 wt.% close to the grain boundary (point B). Figures 6(a) and (b) show the map-

ping and line scans of elements, respectively. It can be observed that Cr is concentrated at grain boundaries and in regions where slip bands are present. Experimental evidence of this phenomenon is shown in Fig. 6(c), where it can be observed that in intergranular spacing, there is a detachment of particles in which an void of about 10 to 20 μm is present, causing the intergranular corrosion of stainless steels as a result of the precipitation of carbides of the type Cr_{23}C_6 (as identified by mapping and line scans) in the intergranular region and a corresponding depletion in the chromium content.

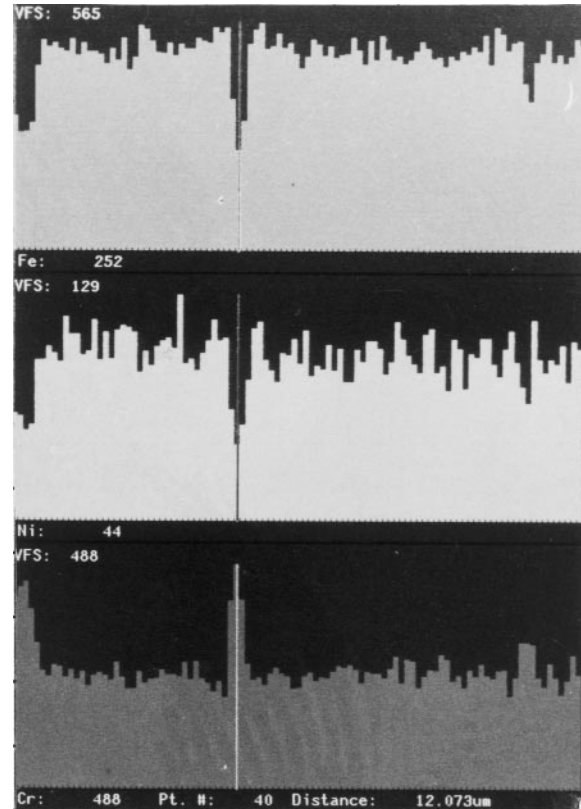
As these precipitates form, local depletion of both Cr and C occurs in the parts of the grain close to the boundary, as shown in Fig. 5. In this specific case, the sensitized process occurs when the 304 stainless steel coils are heated to a temperature close to 650 $^{\circ}\text{C}$, the operating temperature of the second stage of the preheating zone of reduction gases in heater 3. When the heater is occasionally shut down for maintenance, the 304 stainless steel coils are cooled slowly over a period of 48 h from 650 $^{\circ}\text{C}$ to room temperature. It is important to mention that this sensitization phenomenon has only been observed in coils located in the second stage of the preheating zone (CC-104) at a temperature close to 650 $^{\circ}\text{C}$. However, despite the presence of traces of sulfur, no other kind of corrosion mechanism was detected.

4.2 Sulfur Stress Corrosion Cracking

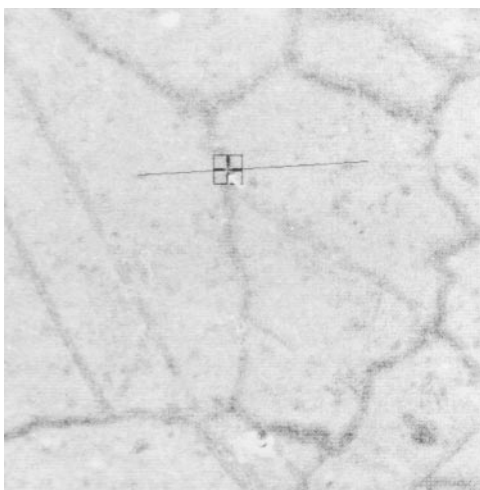
Figure 7(a) shows a series of elongated rhombohedral cracks located on the inside wall of the coil of section CC-105A. Figure 7(b) shows a transverse section of the cracks, which are stress corrosion cracks that run along the grain boundaries. Figure 7(c) shows another area of the grains affected by stress corrosion cracking. Figure 8 shows an x-ray diffraction pattern of the corrosion products removed from the inside wall of the corroded coil. The identified species were Fe_3O_4 and FeS , as a corrosion product is due to some sulfur

being present in the reducing gases, which suggests that the corrosion process of stress corrosion cracking is accelerated by the presence of this element.

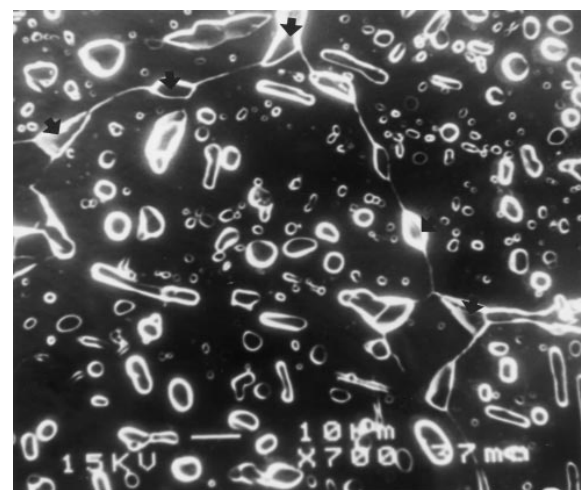
With respect to the process of sulfur stress corrosion cracking, it has been reported:^[4,8] that sulfur can transport across con-



(b)



(a)



(c)

Fig. 6 (a) SEM mapping of chromium in a 304 SS coil. (b) SEM line scan analysis of Cr, Fe, and Ni. (c) Microstructure of a 304 SS coil, where there is detachment of particles in which voids are present (arrow shows the position where particles were detached leaving voids).

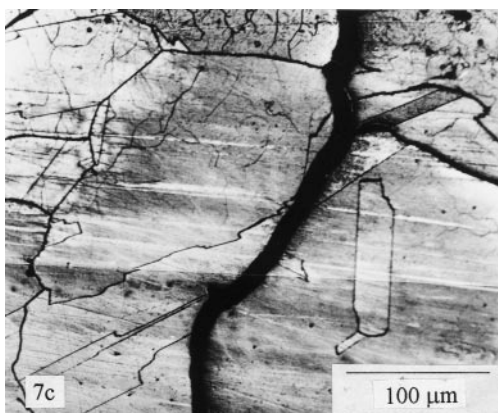
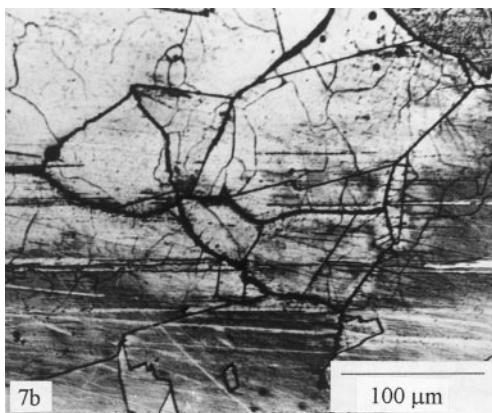


Fig. 7 (a) Elongated rhombohedral cracks are observed in the inside wall of the coil located in section CC-105 (section B, Fig. 1). (b) and (c) The microstructure observed in transverse sections of the rhombohedral cracks. Both at 500X

tinuous protective scales of chromium sesquioxide under certain conditions, resulting in a discrete presence of sulfide precipitates immediately beneath the protective oxide scales. In our case, FeS can be detected by x-ray diffraction, which allows the presence of the assumption that this sulfide is the product of an accelerated attack caused by a rich amount of sulfur present in the gas (about 4 to 7 ppm of S).

4.3 Metal Dusting of HK-40

Finally, a tube was located in the region of high temperature marked by a square in Fig. 1, which showed a composition of 1.35–0.42% C, 1.45–1.55% Mn, 1.42–1.53% Si, 24–27% Cr, 33–36% Ni, Fe balance. Alloys of this composition are fully austenitic and exhibit high strength at elevated temperatures. They can withstand considerable temperature cycling and severe thermal gradients and are well suited for many reducing, as well as oxidizing, environments. These heat-resistant steel castings are extensively used for applications involving service temperatures in excess of 650 °C. Strength at these elevated temperatures is only one criteria by which these materials are selected, because the applications also involve aggressive environments to which the steel must be resistant. The atmospheres most commonly encountered are air and flue gases; such atmospheres may be either oxidizing or reducing and may be sulfidizing or carburizing if sulfur or carbon is present. As shown in Fig. 9, the phenomenon of metal dusting occurred in this alloy.

According to Grabke,^[8] the presence of an adequate concentration of H₂S in the reducing atmosphere can be a reliable method to protect against metal dusting for any kind of Fe-base alloys.

For the radiation zone (region marked B in Fig. 2), steels of higher alloy content are used, which can form a protective layer of chromium oxide, *i.e.*, steels with 25% Cr-20% Ni or 25% Cr-35% Ni. However, when H₂S is not present, such steels are susceptible to metal dusting, depending on the alloy composition. The metal dusting phenomenon is initiated as a defect caused by creep, fatigue, erosion, *etc.*, giving place to pitting or the formation of holes. The combined action of a protective layer of oxide and sulfur provides reliable protection to the material in the radiation zone. As was mentioned,^[2] the resulting atmosphere from the reduction gas is highly reducing. The activity of carbon can be calculated from it, because at relatively low temperatures (<900 °C) and at high flows of gas ($P \approx 4 \text{ kg cm}^{-2}$), the formation and reaction of CO₂ and CH₄ are negligible. Therefore, the carbon activity can be calculated according to

$$a_c = p_{\text{CO}} \cdot p_{\text{H}_2} \cdot K/p \cdot \text{H}_2\text{O} \quad (\text{Eq 2})$$

where

$$\log K = 7,100 / T + 7.49 \quad (T \text{ in } K) \quad (\text{Eq 3})$$

Table 1 shows the carbon activity calculated from Eqs. 2 and 3, according to the value of the reducing atmosphere used in the direct reduction process and for a temperature range between 500 and 1100 °C. As can be observed from the table, at all temperatures, carbon activity is always >1. As the temperature increases, carbon activity increases, as expected.

Therefore, it can be assumed that at higher temperatures, there is greater susceptibility to metal dusting. However, this phenomenon was observed in tubes exposed from 900 to 1100 °C and was not observed in failed coils at lower activities, where the only process observed was sensitization. This may be due to the presence of sulfur, as it has been pointed out,^[9] that the presence of sulfur in a reducing atmosphere can be useful for protection against metal dusting for any kind of Fe-base alloys, if the optimum content of sulfur is not exceeded.

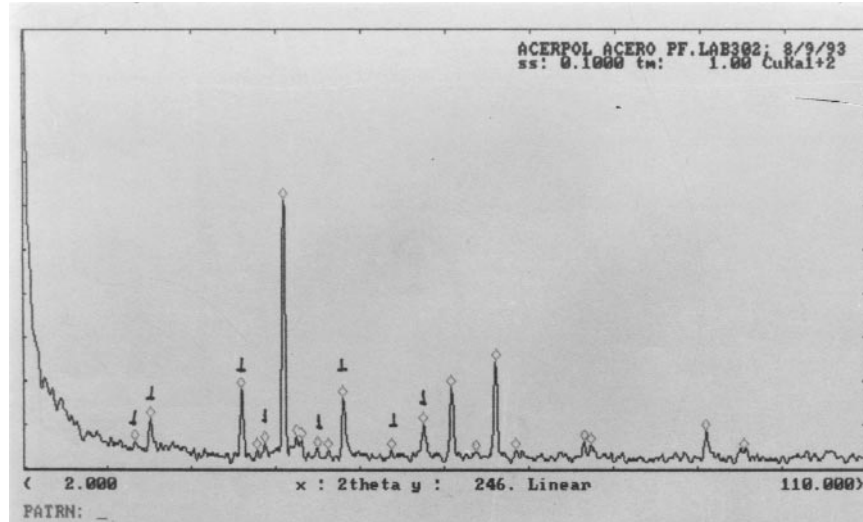


Fig. 8 X-ray diffraction pattern (counts per second; cps vs KeV) of corrosion products removed from the inside wall of a 304 SS coil section CC-105 (section **B**, Fig. 1). Peak notations are 1 = FeS; others are Fe₃O₄.

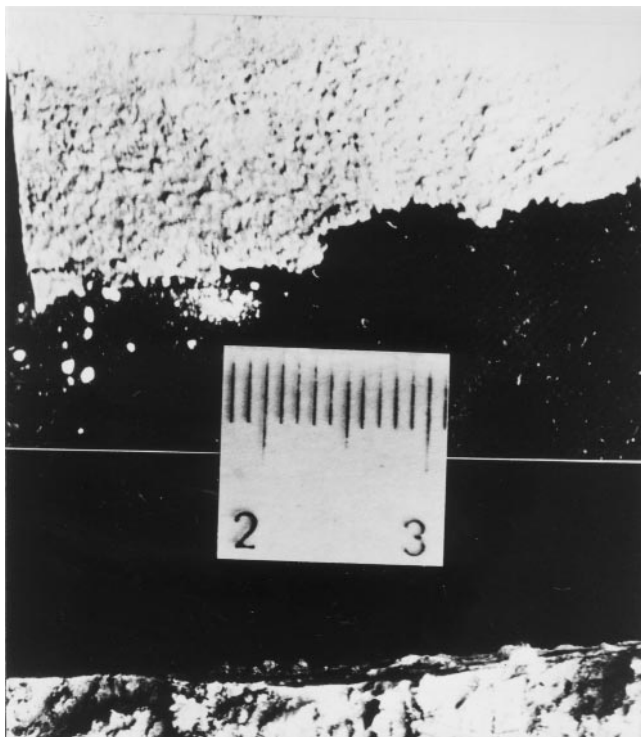


Fig. 9 Metal dusting observed in the inside wall of HK-40 heat-resistant alloy tube. The distance scale is in centimeter units of length.

In the same reference,^[9] this optimum amount of sulfur is expressed in terms of the ratio H₂S/H₂ (for carbon activity = 1). For instance, in order to retard the occurrence of metal dusting at temperatures between 850, 900, 1000, and 1100 °C, it is necessary to keep the ratio H₂S/H₂ equal to 1 × 10⁻⁷, 4 × 10⁻⁵, 1.38 × 10⁻⁴, and 2 × 10⁻⁴, respectively. As can be observed from these

Table 1 Data on carbon activity in the temperature range between 773 and 1373 K, for reducing atmospheres consisting of 60.08% H₂, 12.42% CO, 20.97% CO₂, 5.3% CH₄, 1.19% N₂, and 0.04% H₂O

a_c	$K(a)$	$T(K)$
3.7309	0.0200	773
4.30367	02307	873
29.49516	1.5811	973
141.19662	7.5689	1073
517.530033	27.7424	1173
1546.73248	82.9132	1273
3941.208047	211.2700	1373

(a) K is the equilibrium constant from Eq. 3.

values, for each temperature with a fixed value of carbon activity, an optimum value of the ratio H₂S/H₂ is required to ensure that the metal dusting will not occur.

This implies that the use of a continuous injection of H₂S into the reducing atmosphere in the direct reduction process will probably solve the problem of metal dusting in the temperature range between 900 and 1000 °C (*i.e.*, H₂S/H₂ ≈ 10⁻⁴, a_c ≈ 1). It will not solve the problem at lower temperatures, because carbon activities will be higher and different values of the ratio H₂S/H₂ will be needed. It will also not solve the problem of stress corrosion cracking and the sensitization observed in the range of temperatures between 200 to 650 °C.

5. Conclusions

- In accordance with observations on specimens that failed catastrophically, at least three high-temperature phenomena were detected. They are sensitization of 304 at 650 °C, sul-

for stress corrosion cracking of 304 at 500 °C, and metal dusting of HK-40 at 900 °C.

- From thermodynamic and process data, it was determined that the carbon activity increased as the temperature increased. This suggests that a continuous injection of H₂S into the reducing atmosphere of the process will only solve the problem of metal dusting in the high resistant alloy HK-40, which operates at 900 °C, but will not solve the problem of stress corrosion cracking and that of sensitization in 304 stainless steel coils.

Acknowledgments

J. A. Juarez-Islas is grateful to Mr. Caballero and Ing. L. Baños for their technical contribution. Also, we gratefully acknowledge Messrs. A. Gonzalez and O. Flores. This work was supported by DGAPA-UNAM Grant No. IN-101895.

References

1. *The Making, Shaping and Treating of Steel*, 10th ed., U.S. Steel Corporation, Pittsburgh, PA, 1990.
2. H.J. Grabke, R. Krajak, and E. Muller-Lorenz: *Werstoffe Korrosion*, 1993, vol. 44, pp. 89-97.
3. H.J. Grabke, C.B. Bracho-Troconis, and E. Muller-Lorenzo: *Werstoffe Korrosion*, 1994, vol. 45, pp. 215-21.
4. H.J. Grabke, R. Krajak, and J.C. Nava-Paz: *Corr. Sci.*, 35 (5-8), pp. 1141, 1993.
5. J.C. Nava-Paz, and H.J. Grabke: *Oxid. Met.*, 39, (5-6) pp. 437, 1993.
6. R.H. Hochman: *Proc. 4th Int. Congr. on Metal Corrosion*, National Association of Corrosion Engineers, Houston, TX, 1972, pp. 258.
7. R.F. Hochman: *Proc. Symp. of Properties of High Temperature Alloys with Emphasis on Environmental Effects*, Z.A. Foroulis and F.S. Petit, eds., The Electrochemical Society, Pennington, NJ, 1977, p. 715.
8. H.J. Grabke: Max-Planck-Institute fur Wisenforschung GmbH, Dusseldorf, Germany, private communication, Dec. 1994.
9. H.J. Grabke, R. Moller, and K. Schnass: *Werstoffe Korrosion*, 1979, vol. 30, pp. 794-802.