

High-Temperature Corrosion of T92 Steel in N₂/H₂O/H₂S-Mixed Gas

Yuke Shi, Min Jung Kim, Soon Yong Park, M. Ali Abro,
Poonam Yadav, and Dong Bok Lee[†]

School of Advanced Materials Science & Engineering, Sungkyunkwan University, Suwon 16419, Korea

(Received May 31, 2016; Revised June 23, 2016; Accepted June 23, 2016)

The ASTM T92 steel was corroded at 600 °C and 800 °C at 1 atm of N₂/3.1%H₂O/2.42%H₂S-mixed gas. The formed scales were thick and fragile. They consisted primarily of the outer FeS scale and the inner (FeS, FeCr₂S₄)-mixed scale containing a small amount of the Cr₂O₃ scale. This indicated that corrosion occurred mainly via sulfidation rather than oxidation due to the H₂S gas. Since FeS was present throughout the whole scale, T92 steel was non-protective, displaying high corrosion rates.

Keywords : Fe-Cr alloys, corrosion, sulfidation, H₂S

1. Introduction

Fossil-fired power plants require materials with improved strength, and resistance to creep and corrosion at high temperatures. This led to the development of the ASTM T92 steel (Fe-9Cr-1.8W-0.5Mo-0.45Mn-0.2V-0.06Si-0.05Nb-0.03B-0.07C in wt.%)¹. For commercial applications, it is important to study the high-temperature corrosion behavior of T92 steel in N₂/H₂O/H₂S-mixed gas, because water vapor and H₂S gas are frequently entrapped in the processing gas. Water vapor and H₂S gas significantly accelerate the corrosive attack by forming oxides and sulfides having little protectiveness^{2,3}. Traditionally, materials designed for use at high temperatures have been developed primarily for their mechanical properties, but there is now a growing realization that corrosion also limits its lifetime, either directly through metal wastage or indirectly through raising temperatures locally due to the low thermal conductivity of the scale^{4,5}. The fundamental knowledge on high-temperatures corrosion of steels in H₂O/H₂S-mixed gas is therefore of great importance. The H₂S gas dissociates into sulfur and hydrogen, and reacts with metal according to the reaction; H₂S+M → MS+H₂. Water vapor dissociates into oxygen and hydrogen. Hydrogen atoms from H₂S and water vapor ingress into the steels interstitially, form hydrogen clusters, and cause hydrogen embrittlement, accelerating the corrosion rates significantly. In this study, the ASTM T92 steel was corroded at 600 and 800 °C in N₂/H₂O/H₂S-mixed gas in

order to understand its corrosion behavior.

2. Experimental

The T92 steel plate was cut into a size of 2 x 10 x 15 mm³, ground up to a 1000-grit finish with SiC paper, ultrasonically cleaned in acetone, and corroded at 600 and 800 °C for 20 h inside the quartz reaction tube at the hot zone of the Kanthal furnace. The N₂/2.5%H₂S-mixed gas was blown through the water bath kept at 25 °C, and the resultant H₂O-containing N₂/H₂S-mixed gas was further blown into the reaction tube. The corrosion test gas consisted of 0.9448 atm of N₂, 0.031 atm of H₂O, and 0.0242 atm of H₂S. The total gas pressure was 1 atm. The starting N₂ gas was 99.999 % pure, and H₂S gas was 99.5 % pure. The corrosion tested samples were characterized by the scanning electron microscope (SEM), and the X-ray diffractometer (XRD) with Cu-Kα radiation.

3. Results and discussion

In this study, T92 steel always corroded to bi-layered scales. Fig. 1 shows the XRD patterns of T92 steel corroded at 600 °C for 20 h. The outer scale consisted primarily of FeS (Fig. 1(a)). After removing the outer scale, the inner scale was X-rayed, as shown in Fig. 1(b). This shows that the inner scale consisted primarily of FeS (JCPDS No. 80-1026) and FeCr₂S₄ (JCPDS No. 76-1797). After removing most of the scale, the scale retained at the interface of the inner scale and the matrix was X-rayed, as shown in Fig. 1(c). This shows strong α-Fe matrix peaks, and weak peaks of FeS and Cr₂O₃ (JCPDS

[†] Corresponding author: dlee@skku.ac.kr

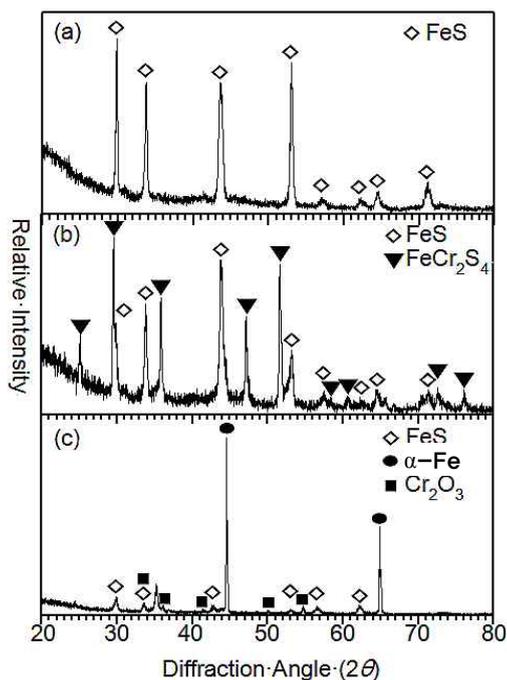
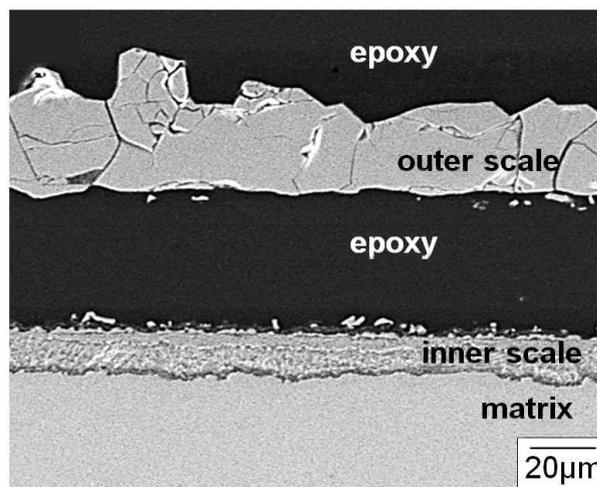


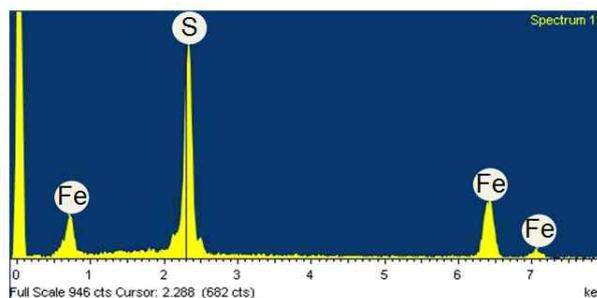
Fig. 1. XRD patterns of scales formed on T92 steel after corrosion at 600 °C for 20 h in $N_2/3.1\%H_2O/2.42\%H_2S$ -mixed gas. (a) outer scale, (b) inner scale, (c) scale/matrix interface.

No. 38-1479). The formation of sulfides decreased the sulfur potential and resultantly increased the oxygen potential underneath so that Cr_2O_3 formed at the interface of the inner scale and the matrix. The highly stoichiometric Cr_2O_3 is protective, the $FeCr_2S_4$ spinel is less protective, and nonstoichiometric $Fe_{1-x}S$ is nonprotective. Since the cation-deficient FeS existed in the whole scale, T92 steel was nonprotective. The $FeCr_2S_4$ spinel enhanced the corrosion resistance to a certain extent by reducing the cross-sectional area for diffusion. The amount of protective Cr_2O_3 in the scale was small. Hence, the corrosion rate of T92 steel was largely determined by the sulfidation rate of Fe to FeS . No corrosion products that were related with minor alloying elements such as W, Mo, and Mn were detected from the XRD analyses, due to their small amount or dissolution in the nonstoichiometric FeS and the less stoichiometric $FeCr_2S_4$ scale.

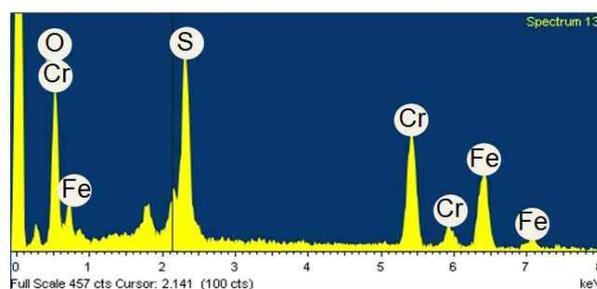
Fig. 2 shows SEM/EDS results of the scale that formed on T92 steel after corrosion at 600 °C for 20 h. The thickness of the outer and inner scale was 40 and 15 μm , respectively (Fig. 2(a)). The outer scale consisted of coarse FeS grains (Figs. 2(a) and (b)). The inner scale consisted of fine grains with a chemical composition of Fe, Cr, S, and oxygen (Figs. 2(a) and 2(c)). Since FeS is the cation-deficient nonstoichiometric compound,⁶⁾ Fe grew through the outward diffusion of Fe^{2+} ions from the matrix across



(a)



(b)



(c)

Fig. 2. T92 steel after corrosion at 600 °C for 20 h in $N_2/3.1\%H_2O/2.42\%H_2S$ -mixed gas. (a) cross-sectional SEM image, (b) EDS spectrum of the outer scale, (c) EDS spectrum of the inner scale.

the pre-formed FeS grains to the outermost surface of the FeS scale. The outer, fast-growing FeS scale was susceptible to cracking, and detached off from the inner (FeS , $FeCr_2S_4$, Cr_2O_3)-mixed scale, not only owing to the excessive, compressive stress developed in the thick scale but also due to the dissolution of hydrogen that released from the H_2S gas. The oxygen source for the formation of the small amount of Cr_2O_3 , as shown in Fig. 1(c), was

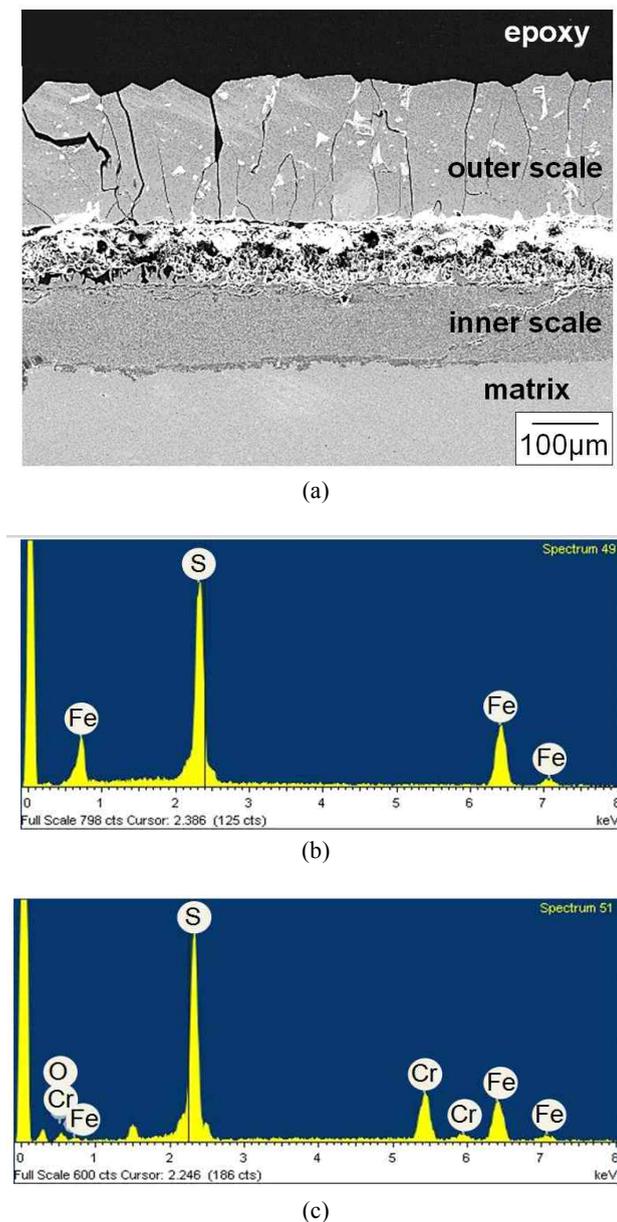


Fig. 3. T92 steel after corrosion at 800 °C for 20 h in N₂/3.1% H₂O/2.42% H₂S-mixed gas. (a) cross-sectional SEM image, (b) EDS spectrum of the outer scale, (c) EDS spectrum of the inner scale.

the oxygen impurity in the N₂/H₂O/H₂S-mixed gas. The XRD/SEM/EDS analyses shown in Figs. 1 and 2 indicated that the dominant corrosion reaction was not oxidation but sulfidation. Cracks propagated inter- and trans-granularly (Fig. 2(a)), because the formation of FeS from Fe led to the large volume expansion. The FeS scale was

fragile and nonadherent, because it grew fast and formed Kirkendall voids at the scale-matrix interface through the outward diffusion of Fe²⁺ ions. Cracking and spallation of the scale facilitated the ingress of corrosive gases. Hence, T92 steel suffered serious corrosion.

The scale formed after corrosion at 800 °C for 20 h was analyzed using SEM/EDS, as shown in Fig. 3. The outer scale cracked and detached from the inner scale (Fig. 3(a)). The outer FeS layer had the coarse columnar structure (Fig. 3(b)), and the inner (FeS, FeCr₂S₄, Cr₂O₃)-mixed layer consisted of fine grains (Fig. 3(c)). The outer scale formed mainly by the outward diffusion of Fe²⁺ ions, whereas the inner scale formed by the inward diffusion of sulfur and a small amount of oxygen. The compositional difference between the outer and inner scale would aggravate the stress in the scale, facilitating the crack propagation. The FeCr₂S₄ spinel and a small amount of Cr₂O₃ in the inner scale suppressed the outward diffusion of Fe²⁺ ions to reduce the growth rate of the outer FeS scale, and the inward transport of sulfur by forming the somewhat dense or adherent inner scale. However, T92 corroded fast, forming 210 μm-thick outer scale, and 120 μm-thick inner scale (Fig. 3(a)). The inner FeS scale partially dissociated according to the reaction; FeS=Fe⁺²+1/2S₂+2e.⁷⁾ This delivered the sulfur gas for the inward growth of the inner scale. The released Fe⁺² ions and electrons diffused toward the outer surface to form FeS.

4. Conclusions

T92 steel was corroded at 600 and 800 °C for 20 h in N₂/H₂O/H₂S-mixed gas under total pressure of 1 atm. Sulfidation occurred dominantly. The outer scale consisted primarily of FeS that formed by the outward diffusion of Fe⁺² ions. The inner (FeS, FeCr₂S₄, Cr₂O₃)-mixed scale formed by the inward diffusion of sulfur and a lesser amount of oxygen. The FeCr₂S₄ spinel and Cr₂O₃ could not effectively deter corrosion, because they were intermixed with nonprotective FeS. The outer scale was coarse, the inner scale was fine, and the whole scale was non-adherent, and susceptible to cracking.

Acknowledgments

This work was supported by the Human Resource Development Program (No. 20134030200360) of the Korea Institute of Energy Technology Evaluation and Planning (KETEP) grant funded by the Korea government Ministry of Trade, Industry and Energy.

References

1. S. Mrowec and K. Przybylski, *Oxid. Met.*, **23**, 3 (1985).
2. S. Mrowec, T. Walec and T. Werber, *Oxid. Met.*, **1**, 1 (1969).
3. S. Mrowec and M. Wedrychowska, *Oxid. Met.*, **13**, 6 (1979).
4. H. J. Lee, H. M. Kim and C. H. Jang, *Corros. Sci. Tech.*, **13**, 2 (2014).
5. T. D. Nguyen, J. Zhang and D. J. Young. *Corros. Sci. Tech.*, **14**, 3 (2015).
6. M. Danielewski, S. Mrowec and A. Stołosa, *Oxid. Met.*, **17**, 1 (1982).
7. M. Schulte, A. Rahmel and M. Schutze, *Oxid. Met.*, **49**, 1 (1998).