

High-temperature Corrosion of T22 Steel in N₂/H₂S-mixed Gas

Min Jung Kim, Dong Bok Lee*

School of Advanced Materials Science and Engineering, Sungkyunkwan University, Suwon 16419, South Korea.

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Abstract

ASTM T22 steel (Fe-2.25Cr-1Mo in wt.%) was corroded at 600 and 700 °C for 5-70 h under an atmospheric pressure that consisted of N₂-(0.5, 2.5)%H₂S-mixed gas. T22 steel corroded rapidly, forming outer FeS scales and inner (FeS, FeCr₂O₄)-mixed scale. The formation of the outer FeS scale facilitated the oxidation of Cr to FeCr₂O₄ in the inner scales. Since the nonprotective FeS scale was present over the whole scale, T22 steel displayed poor corrosion resistance.

Keywords: Fe-Cr-Mo alloy, T22 steel, corrosion, H₂S gas, Sulfidation

1. Introduction

The integrated gasification combined cycle (IGCC) power plants are operating in U.S., Japan, Germany, and Netherlands. It is a new technology that turns coal into synthesis gas (syngas) and produces the electricity. It promises low emissions and improved efficiency compared to conventional coal-fired power plants that produce the electricity directly by burning coals [1]. However, one of the main problems in IGCC is the corrosion occurring by the syngas in a gasification unit, because the syngas consisted primarily of the extremely corrosive H₂S gas. This limits the operating temperature and the process efficiency of the IGCC power plants. It is noted that the H₂S gas has been a major concern in oil refinery plants, high-temperature gas turbines, and petrochemical units. H₂S gas dissociates into sulfur and hydrogen ions, and reacts with the steel according to the reaction; H₂S+Fe → FeS+H₂ [2-4]. Generally, most sulphides are highly nonstoichiometric, and ionic diffusion in the scales is hence quite fast [5,6]. Sulfidation is therefore a quite serious problem. Hydrogen also significantly decreases the corrosion resistance and mechanical properties of the steel [7-10].

In this study, T22 steel was corroded at 600 and 700 °C for up to 70 h in N₂-(0.5, 2.5)%H₂S-mixed gas in order to understand its corrosion behavior in the H₂S-mixed gas. This is important in IGCC power plants, oil refinery plants, high-temperature gas turbines, and petrochemical units. Although the oxidation behavior of T22 steel was extensively studied [11-12], little is reported about the high-temperature corrosion behavior of T22 steel in H₂S-mixed gas. The purpose of this study is to investigate the corrosion behavior of T22 steel in N₂/H₂S-mixed gas.

2. Method

T22 steel plate with a nominal composition of Fe-2.25Cr-1.0Mo-0.45Mn-0.3Si-0.12C in wt% were cut into a size of 2x10x15 mm³, ground up to a 1000-grit finish with SiC paper, ultrasonically cleaned in acetone, corroded, and inspected to examine its corrosion behavior. Each sample was

suspended by a Pt wire in a quartz reaction tube positioned vertically inside the hot zone of the vertical electrical furnace, and corroded at 600 and 700 °C for up to 70 h in N₂-(0.5, 2.5)%H₂S-mixed gas maintained at 1 atm. The employed N₂ gas was 99.999% pure, and H₂S gas was 99.5% pure. The corroded samples were characterized by a scanning electron microscope (SEM; Jeol JEM-2100F operated at 200 keV), an X-ray diffractometer (XRD) with Cu-K α radiation operating at 40 kV and 300 mA in $\theta/2\theta$ configuration, and an electron probe microanalyzer (EPMA).

3. Results and Discussion

The corrosion kinetics of T22 steel in N₂-(0.5, 2.5)%H₂S gas are depicted in Fig. 1. Weight gains were the sum of weight gain due to scaling and weight loss due to scale spallation. They increased with an increase in the temperature and the H₂S concentration. The fastest corrosion rate was observed in the sample corroded at 700 °C in N₂-2.5%H₂S-mixed gas. The almost linear, large weight gains depicted in Fig. 1 indicate vastly fast corrosion kinetics for all the samples. It is noted that local cracking, partial spallation and void formation in the formed scales were unavoidable for all the samples, including at 600 °C in N₂-2.5%H₂S-mixed gas for 70 h. Such scale failure became more serious as corrosion progressed. Although T22 steel displayed reasonable oxidation resistance in the oxidizing atmospheres, it was non-protective in the harsh H₂S-mixed corrosion environment.

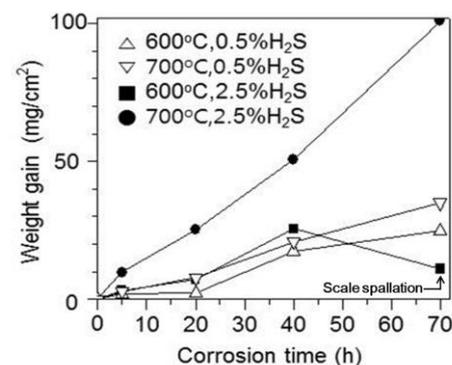


Fig. 1 Weight gains of T22 steel at 600 and 700 °C in N₂-(0.5, 2.5)%H₂S-mixed gas

Fig. 2(a) indicates that T22 steel consisted mainly of α -Fe. The other minor phase, perlite, was not detected Fig. 2(a) due to its small amount. In this study, the corrosion at 600 and 700 °C for 5-70 h in N₂-(0.5, 2.5) %H₂S-mixed gas inevitably led to the formation of the outer FeS scale and the inner (FeS, FeCr₂O₄)-mixed scale. Fig. 2(b) indicates the outer FeS scale that formed after corrosion at 700 °C for 20 h in N₂-2.5%H₂S gas. The outer, non-adherent FeS scale was detached off by slightly hitting the sample, and the inner scale was X-rayed as shown in Fig. 2(c). This revealed the inner (FeS,

FeCr₂O₄)-mixed scale, along with the α-Fe matrix phase. The amount of Cr in T22 steel was not large enough to completely cover the matrix surface with the protective Cr₂O₃ scale. T22 steel reacted with the H₂S gas to form FeS, releasing hydrogen according to the equation; Fe(s) + H₂S (g) → FeS(s) + H₂ (g). Since FeS has a very high concentration of cation vacancies, it grew fast to form the outer scale through the outward diffusion of Fe²⁺ ions [9]. The formation of FeS decreased the sulfur potential, and thereby the oxygen potential underneath, facilitating the formation of the oxides in the inner scale, as shown in Fig. 2(c). The minor alloying elements such as Mo and Mn in T22 steel tended to be expelled from the inner scale, due to their small amount or activity. The distribution of alloying elements depends on the thermodynamic stability of corresponding oxides or sulfides and activity of concerning elements. The impurity oxygen in N₂-(0.5, 2.5) % H₂S-mixed gas reacted with T22 steel according to Eqs. (1) and (2).



Thermodynamically, the oxides are generally more stable than the corresponding sulfides. The spinel is formed by diffusion of Fe²⁺ from FeO to Cr₂O₃ oxides through spinel accompanied by diffusion of hole and evolution of oxygen gas at FeO/spinel interface. The Fe²⁺ reacts with Cr₂O₃ to produce spinel at the spinel/Cr₂O₃ interface, and Cr³⁺ diffuses with hole to the Cr₂O₃/gas interface in order to keep electro-neutrality [13]. The formed FeO and Cr₂O₃ oxides particles, the solid-state reaction occurred to form the more stable FeCr₂O₄ spinel scale, which gradually dispersed in external oxide layer. FeCr₂O₄ spinel reacted with FeO and Cr₂O₃ according to the equation.

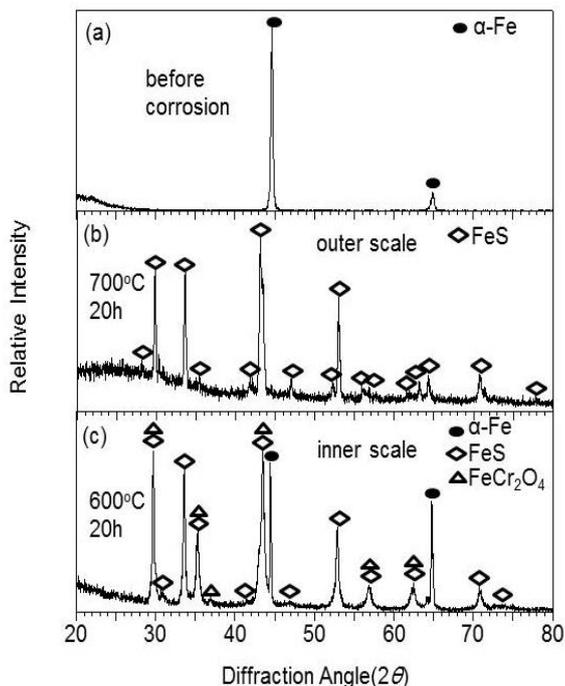
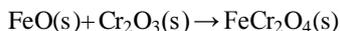


Fig. 2 XRD patterns of T22 steel. (a) Before corrosion, (b) The outer scale, and (c) The inner scale that formed after corrosion at 700 °C for 20 h in N₂-2.5% H₂S gas

The morphology of surface scales that formed on T22 steel after corrosion in N₂-0.5% H₂S gas is shown in Fig. 3. From the early corrosion stage at 600 °C, FeS platelets progressively protruded through the ensuing outward diffusion of Fe²⁺ ions over the smooth underlying scale (Figs. 3(a) and (b)). They spalled off easily due to their fast growth rate and incorporation of hydrogen released from the H₂S gas. The formed scales were quite fragile so that cracks were seen in Fig. 3(a). At 700 °C, the FeS platelets grew to coarse, protruded FeS grains, as shown in Fig. 3(c). As corrosion progressed, FeS grains grew bigger, leading to the generation of cracks in the surface FeS scale (Fig. 3(d)). The EDS analysis indicated that the outer scale and the inner scale consisted primarily of FeS (Figs. 3(e) and (f)), respectively.

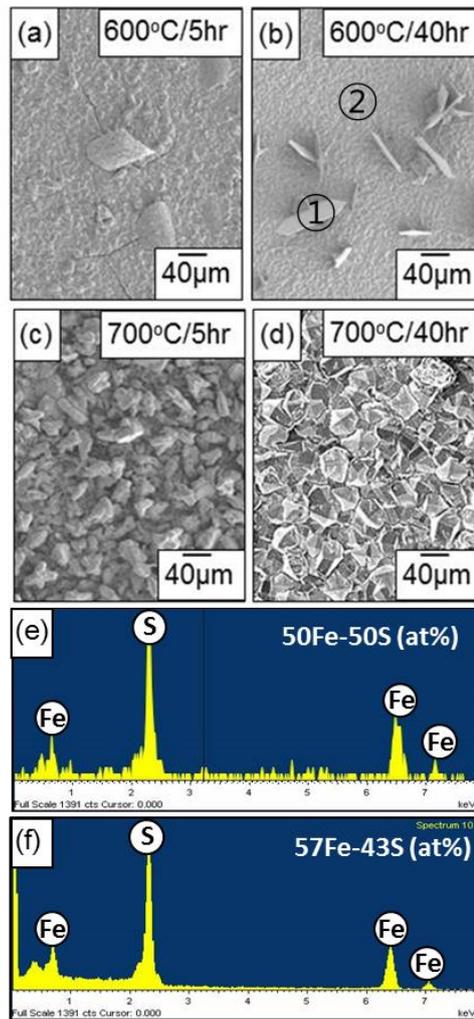


Fig. 3 SEM top view of the scales that formed on T22 steel after corrosion in N₂-0.5% H₂S gas. (a) at 600 °C for 5 h, (b) at 600 °C for 40 h, (c) at 700 °C for 5 h, (d) at 700 °C for 40 h, (e) EDS spectrum of spot ①, (f) EDS spectrum of spot ②

The morphology of surface scales that formed on T22 steel after corrosion in N₂-2.5% H₂S gas is shown in Fig. 4. From the early corrosion stage at 600 °C, coarse, faceted FeS grains covered the whole surface (Fig. 4(a)). They continuously grew bigger as the corrosion progressed (Figs. 4(b)-(d)). In Fig. 4(d), cracks propagated inter- and trans-granularly. With the increase of concentration of the H₂S gas from 0.5 to 2.5 %, the grains at the surface of the scale became much coarser as shown in Figs. 3 and 4, indicating that the H₂S gas accelerated corrosion.

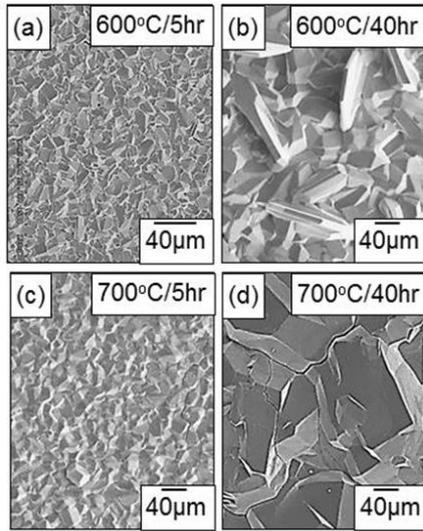


Fig. 4 SEM top view of the scales that formed on T22 steel after corrosion in N_2 -2.5% H_2S gas. (a) at 600 °C for 5 h, (b) at 600 °C for 40 h, (c) at 700 °C for 5 h, (d) at 700 °C for 40 h.

Fig. 5 shows SEM/EDS analytical results of T22 steel after corrosion in N_2 -0.5% H_2S gas at 600 °C for 70 h. The scale consisted of about 120 μm -thick outer scale, and about 70 μm -thick inner scale. The outer scale was detached from the inner scale, and vertical cracks were seen in the inner scale, owing to the large stress arisen by (1) the mismatch in the thermal expansion coefficients among the outer scale, inner scale, and the matrix, (2) the difference in the growth rates of various oxides and sulfides, and (3) the hydrogen dissolution in the scale. The EDS analysis indicated that the outer scale and the inner scale consisted primarily of FeS (Fig. 5(b)), and (FeS, $FeCr_2O_4$) (Fig. 5(c)), respectively. This was consistent of the XRD results depicted in Fig. 2. FeS platelets protruded over the outer FeS scale (Fig. 5(a)).

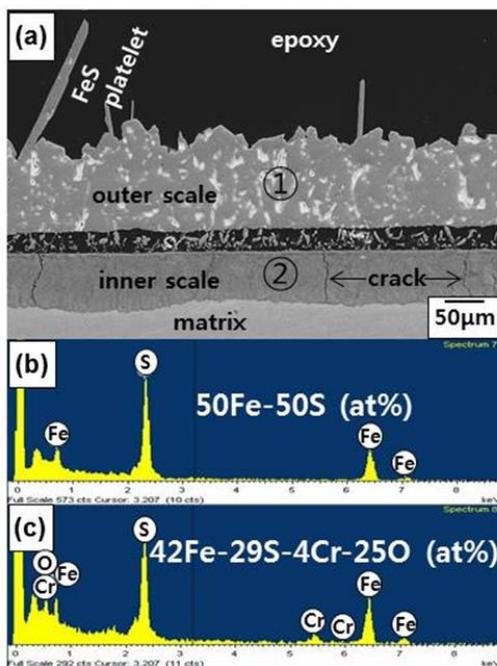


Fig. 5 SEM/EDS analytical results of T22 steel after corrosion in N_2 -0.5% H_2S gas at 600 oC for 70 h. (a) cross-sectional image, (b) EDS spectrum of spot ①, (c) EDS spectrum of spot ②.

4. Conclusions

T22 steel was corroded at 600 and 700 °C for up to 70 h in N_2/H_2S -mixed gas under total pressure of 1 atm. The corrosion occurred almost linearly through the sulfidation, together with oxidation to a less extent. The outer scale consisted primarily of FeS that formed by the outward diffusion of Fe^{2+} ions. The inner (FeS, $FeCr_2O_4$)-mixed scale formed by the inward diffusion of predominantly sulfur and a small amount of oxygen. The outer scale kept growing outwards during corrosion. The formed scales were non-adherent, and susceptible to cracking. Since the nonprotective FeS scale was present over the whole scale, T22 steel displayed poor corrosion resistance in N_2/H_2S -mixed environments at high temperatures. Hence, pack-cementation, hot dipping, plasma evaporation, plating techniques were developed in order to improve its corrosion resistance.

Acknowledgement

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