<연구논문>

한국표면공학회지

J. Kor. Inst. Surf. Eng.

Vol. 44, No. 5, 2011.

<http://dx.doi.org/10.5695/JKISE.2011.44.5.201>

Corrosion of Fe-2%Mn-0.5%Si Steels at 600-800°C in N₂/H₂O/H₂S Atmospheres

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(Received September 19, 2011; revised October 26, 2011; accepted October 28, 2011)

Abstract

Fe-2%Mn-0.5%Si alloys were corroded at 600, 700 and 800°C for up to 70 h in 1 atm of N₂ gas, or 1 atm of N₂/H₂O-mixed gases, or 1 atm of N₂/H₂O/H₂S-mixed gases. Oxidation prevailed in N₂ and N₂/H₂O gases, whereas sulfidation dominated in N₂/H₂O/H₂S gases. The oxidation/sulfidation rates increased in the order of N₂ gas, N₂/H₂O gases, and, much more seriously, N₂/H₂O/H₂S gases. The base element of Fe oxidized to Fe₂O₃ and Fe₃O₄ in N₂ and N₂/H₂O gases, whereas it sulfidized to FeS in N₂/H₂O/H₂S gases. The oxides or sulfides of Mn or Si were not detected from the XRD analyses, owing to their small amount or dissolution in FeS. Since FeS was present throughout the whole scale, the alloys were nonprotective in N₂/H₂O/H₂S gases.

Keywords: Fe-Mn alloys, Corrosion, H₂S

1. Introduction

Korea is currently building a 300 MW integrated gasification combined cycle (IGCC) power plant by 2017. U.S., Japan, Germany, and Netherlands are also building and operating IGCC-based coal-fired power plants. IGCC is a technology that turns coal into synthesis gas (syngas). It is the rapidly emerging, advanced power generation system, which promises low emissions and improved efficiency compared to conventional pulverized coal power plants. However, one of the main problems in IGCC is the corrosion occurring by H₂S and H₂O gases within the syngas, which limits operating temperatures and thus the process efficiency. The H₂S gas dissociates into sulfur and hydrogen ions, and reacts with metal according to the reaction; H₂S + M → MS + H₂^{2,3}. Also, water vapor in the syngas reacts with metal to generate hydrogen according to the reaction; H₂O + M → MO + H₂. This can be absorbed by the metal, and dissolved in metal, accelerating the corrosion rates significantly²⁻⁴. Generally, the sulfidation rates are 10~100 times faster

than the oxidation rates because sulfides have much larger defect concentrations, and have lower melting points than the corresponding oxides⁵⁻⁸. Sulfidation is therefore a quite serious problem⁹⁻¹¹.

In this study, the Fe-2Mn-0.5Si alloy (in wt.%) sulfidized between 600 and 800°C for up to 70 hr in N₂/H₂O/H₂S-mixed gases in order to understand its sulfidation behavior in the simulated IGCC gas atmosphere. Mn and Si are added during the steelmaking process mainly to remove oxygen from the melt, and increase strength. Mn is among the most important alloying element for the design of high-strength steels. However, little is reported about the high-temperature sulfidation behavior of Fe-2Mn-0.5Si in H₂O/H₂S-mixed gases. The purpose of this study is to investigate the sulfidation behavior of Fe-2Mn-0.5Si in N₂/H₂O/H₂S-mixed gases for the first time. Furthermore, the obtained results were compared with the oxidation test results of the same alloy in the pure N₂ gas, and N₂/H₂O-mixed gases.

2. Experimental Details

Steel plates with a composition of Fe-2Mn-0.5Si

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Fig. 1. Corrosion testing apparatus.

were cut into a size of $2 \times 10 \times 15 \text{ mm}^3$, ground up to a 1000-grit finish with SiC paper, ultrasonically cleaned in acetone, and corroded at 600, 700 and 800°C for up to 70 h using an apparatus shown in Fig. 1. Each test coupon was suspended by a Pt wire in a quartz reaction tube within the hot zone of an electrical furnace. Three kinds of atmospheres were employed for corrosion tests. Firstly, 1 atm of N_2 gas. Secondly, a gas mixture of 0.968 atm of N_2 and 0.032 atm of H_2O , which was achieved by bubbling the N_2 gas through the water bath kept at 25°C. Thirdly, a gas mixture of 0.9448 atm of N_2 , 0.031 atm of H_2O and 0.0242 atm of H_2S , which was achieved by bubbling the N_2 gas through the water bath kept at 25°C, while flowing the H_2S gas into the reaction tube. The total pressure of test gases was kept at 1 atm. The employed N_2 gas was 99.999% pure, and H_2S gas was 99.5% pure. The samples were characterized by a scanning electron microscope (SEM), an X-ray diffractometer (XRD) with Cu-K α radiation, and an electron probe microanalyzer (EPMA).

3. Results and Discussion

Fig. 2 shows weight gains that were measured using a microbalance without spontaneously spalled scales. An increase in the temperature from 700 to 800°C led to the increment of weight gains by ~ 2 times in N_2 , $\text{N}_2/\text{H}_2\text{O}$, or $\text{N}_2/\text{H}_2\text{O}/\text{H}_2\text{S}$ gases. Impurities of 3 ppm H_2O and 2 ppm O_2 in the employed N_2 gas oxidized the samples. At 700 and 800°C, the change of gases from N_2 to $\text{N}_2/\text{H}_2\text{O}$ increased the weight gains by 1.1 times, and that from $\text{N}_2/\text{H}_2\text{O}$ to $\text{N}_2/\text{H}_2\text{O}/\text{H}_2\text{S}$ increased the weight gains by 6 times. However, it is noted that there was uncertainty in weight gains measured in $\text{N}_2/$

Fig. 2. Weight gains of Fe-2Mn-0.5Si, which were measured after oxidation/sulfidation at 700 and 800°C for 70 h. N means N_2 , N/H means $\text{N}_2/\text{H}_2\text{O}$, and N/H/S means $\text{N}_2/\text{H}_2\text{O}/\text{H}_2\text{S}$ gases used as oxidation/sulfidation media.

$\text{H}_2\text{O}/\text{H}_2\text{S}$ -mixed gases, because scales formed in H_2S -containing atmosphere were usually thick, and highly susceptible to spallation during corrosion and subsequent cooling stage¹⁻³). Nevertheless, it was evident that H_2O and, much more seriously, H_2S gas increased the corrosion rates. Water vapor transports in the scale as $\text{H}_2(\text{g})$ and $\text{H}_2\text{O}(\text{g})$ within voids, cavities, and cracks, and as H atom by dissolving in the lattice and thereby affecting point defect concentration^{2,3}).

Fig. 3 shows the XRD patterns of the corroded samples. The scales that formed in N_2 and $\text{N}_2/\text{H}_2\text{O}$ atmospheres consisted primarily of Fe_3O_4 as the major phase and Fe_2O_3 as the minor one, as typically shown in Figs. 3(a) and (b). Here, the Fe_2O_3 layer exists on the Fe_3O_4 layer^{1,2}). The scales that formed in $\text{N}_2/\text{H}_2\text{O}/\text{H}_2\text{S}$ atmosphere consisted primarily of FeS , indicating the sulfidizing tendency was stronger than the oxidizing tendency because of H_2S (Figs. 3(c)~(f)). H_2S reacts with Fe according to the following reactions.

The net reaction is $\text{Fe} + \text{H}_2\text{S} \rightarrow \text{FeS} + \text{H}_2$. FeS has a very high concentration of cation vacancies so that it grows rapidly by the outward diffusion of Fe^{++} ions⁷). A weak α -Fe matrix peak was detected in Fig. 3(c), because the partial spallation of FeS exposed the underlying matrix. In Fig. 3(d), only FeS was detected, because the X-ray beam could not penetrate the partially spalled FeS scale. In order to examine the inner scale, the outer scale was abraded off, and the inner scale was X-rayed, as shown in Fig. 3(e). Here,

Fig. 3. XRD patterns of scales formed on Fe-2Mn-0.5Si after oxidation/sulfidation. (a) $N_2/800^\circ C/70$ h, (b) $(N_2/H_2O)/800^\circ C/70$ h, (c) $(N_2/H_2O/H_2S)/600^\circ C/40$ h, (d) $(N_2/H_2O/H_2S)/600^\circ C/70$ h -outer scale, (e) $(N_2/H_2O/H_2S)/600^\circ C/70$ h -inner scale, (f) $(N_2/H_2O/H_2S)/800^\circ C/40$ h.

FeS was found together with the α -Fe matrix. Also in Fig. 3(f), only FeS was detected. Hence, it is seen that H_2S always forms FeS. When the samples corroded in N_2 , N_2/H_2O , and $N_2/H_2O/H_2S$ gases, no oxides or sulfides of Mn or Si were detected from the XRD analyses, due to their small amount or dissolution in FeS.

The sample whose XRD pattern is shown in Fig. 3(a) was examined using SEM, as shown in Fig. 4. Fine Fe_2O_3 grains had a slightly rugged surface (Fig. 4(a)). The scale was ~ 150 μm thick, and broken into two parts (Fig. 4(b)). In the scale that consisted primarily of Fe_3O_4 and Fe_2O_3 , Mn was rather

Fig. 4. Fe-2Mn-0.5Si after oxidation at $800^\circ C$ for 70 h in N_2 atmosphere. (a) SEM top view, (b) cross-sectional image, (c) EDS spectrum of the outer scale, (d) EDS spectrum of the inner scale.

uniformly distributed (Figs. 4(c) and (d)). However, Si was segregated in the inner scale, because Si ions were relatively immobile owing to the high bonding energy of $Si^{4+}-O^{2-}$ (465 kJmol^{-1})¹².

The sample whose XRD pattern is shown in Fig. 3(b) was examined using SEM, as shown in Fig. 5. The Fe_2O_3 scale had a rather flat surface (Fig. 5(a)). Its thickness increased to ~ 240 μm (Fig. 5(b)). Cracks developed at the surface and middle of the scale, the main cause of which was attributed to stresses developed in the thick oxide scale. Again, Si was segregated in the inner scale, although Mn was distributed rather uniformly throughout the whole oxide scale (Figs. 5(c), (d)). The scale morphology and elemental distribution of Fig. 5 were similar with those of Fig. 4, because the principal oxidation mode was the same in N_2 and N_2/H_2O atmospheres. The main difference was the acceleration of corrosion rates by H_2O . The compositional difference between the outer and inner oxide layers seemed to aggravate

Fig. 5. Fe-2Mn-0.5Si after oxidation at 800°C for 70 h in N_2/H_2O atmosphere. (a) SEM top view, (b) cross-sectional image, (c) EDS spectrum of the outer scale, (d) EDS spectrum of the inner scale.

stresses in the scale, facilitating the crack propagation in Figs. 4 and 5.

The sulfidation behavior of the samples in $N_2/H_2O/H_2S$ atmosphere was examined in detail, as shown in Figs. 6–9. Weight gains measured after sulfidation at 600, 700 and 800°C for up to 70 h are displayed in Fig. 6. They are the sum of weight gain due to scaling and weight loss due to scale spallation. Large weight gains were recorded in Fig. 6, indicating vastly fast sulfidation kinetics. The scale failure became more serious as sulfidation progressed. Local cracking, partial spallation and void formation in the formed sulfide scales were unavoidable, the extent of which varied for each test run. Hence, weight gains depicted in Fig. 6 should be regarded as approximate values. However, the major trends can be observed in Fig. 6 as follows. The sulfidation appeared to follow the linear rate law, implying negligible protection owing to the formation of FeS. Mn and Si could not protect the alloy from the serious sulfidation, due to their small

Fig. 6. Weight gain versus sulfidation time curves of Fe-2Mn-0.5Si at 600, 700 and 800°C for 70 h in $N_2/H_2O/H_2S$ atmosphere.

Fig. 7. Fe-2Mn-0.5Si after sulfidation at 700°C for 20 h in $N_2/H_2O/H_2S$ atmosphere. (a) SEM top view, (b) cross-sectional image.

amount or dissolution in FeS.

The scale that formed after sulfidation at 700°C for 20 h in $N_2/H_2O/H_2S$ atmosphere were analyzed, as shown in Fig. 7. Fig. 7(a) shows outer, coarse, faceted FeS grains. Cracks propagated inter- and trans-granularly, because the formation of FeS from Fe resulted in 261% volume expansion. FeS was fragile, and nonadherent because it grew fast and formed voids at the scale-matrix interface¹³⁾. In Fig. 7(b), the outer thick FeS scale detached off, and the inner fragile FeS scale split into a few layers. The total thickness of the scale was $\sim 270 \mu m$, implying poor sulfidation resistance. The outer FeS layer had either an equiaxed or a columnar structure, and the inner layer consisted of fine grains. The inner FeS dissociates according to the reaction; $FeS = Fe^{2+} + 1/2S_2 + 2e^{-14)}$. This delivers S gas for the inward growth of the innermost layer, and the released iron ions and electrons diffuse to the outer surface to form FeS.

Fig. 8. Fe-2Mn-0.5Si after sulfidation at 700°C for 70 h in $N_2/H_2O/H_2S$ atmosphere. (a) SEM top view, (b) cross-sectional image.

Fig. 9. Fe-2Mn-0.5Si after sulfidation at 800°C for 70 h in $N_2/H_2O/H_2S$ atmosphere. (a) EPMA cross-sectional image, (b) line profiles.

The sample was sulfidized further for 70 h at 700°C, as shown in Fig. 8. The outer FeS grains kept growing into the air, as Fe continuously diffused out

from the matrix via the pre-formed FeS grains to the outermost surface (Fig. 8(a)). Here, excessively coarse FeS grains were protruded into the air. The outer scale was thicker than the inner scale (Fig. 8(b)). The outer, fast-growing FeS grains were susceptible to cracking and detached off from the inner mixed scale, owing to the serious, compressive stress developed. Cracking and spallation of scales facilitated the ingress of corrosive gases, making the sample sulfidize almost linearly, as shown in Fig. 6.

The scale formed after sulfidation at 800°C for 70 h was analyzed using EPMA, as shown in Fig. 9. It was quite thick, brittle, cracked and detached easily (Fig. 9(a)). In Fig. 9(b), Mn, Si, and oxygen were incorporated in the FeS scale. The outer scale formed by the outward transport of predominantly Fe and a small amount of Mn and Si, whereas the inner scale formed by the inward diffusion of predominantly sulfur and a small amount of oxygen along cracks, and interconnected pores that developed particularly around the interface of the outer and inner scale.

4. Conclusions

The Fe-2Mn-0.5Si alloys were oxidized or sulfidized at 600, 700 and 800°C for up to 70 h in N_2 , or N_2/H_2O , or $N_2/H_2O/H_2S$ gases under total pressure of 1 atm. In N_2 or N_2/H_2O gases, Fe_2O_3 and Fe_3O_4 formed. H_2O stimulated the oxidation rates by 1.1 times, and H_2S further accelerated the corrosion rates by 6 times. In $N_2/H_2O/H_2S$ gases, sulfidation occurred almost linearly. The outer scale consisted primarily of FeS that formed by the outward diffusion of iron. The inner scale formed by the inward diffusion of predominantly sulfur and a small amount of oxygen. The outer scale was coarse, the inner scale was fine, and the whole sulfide scale was nonadherent, and susceptible to cracking.

Acknowledgments

This work was supported by New & Renewable Energy R&D program (2009T00100316) under the Ministry of Knowledge Economy, Republic of Korea.

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