Formation and Oxidation of Sulfides on Pure Iron and Iron Oxides

Masatoshi Watanabe¹, Minoru Sakuma^{1, *1}, Takeshi Inaba^{1, *2} and Yasutaka Iguchi²

¹Department of Metallurgy, Graduate School of Engineering, Tohoku University, Sendai 980-8579, Japan

²New Industry Creation Hatchery Center, Tohoku University, Sendai 980-8579, Japan

Formation of pyrophoric iron sulfide (PIS) on the inside-walls of molten sulfur, crude oil or asphalt tanks is the problem to be solved to avoid accidental explosions in petroleum industries. In this study, pure Fe, Fe₃O₄ and Fe₂O₃ were sulfidized in Ar-H₂S atmosphere, and the sulfidized products formed were observed and analyzed. Furthermore, sulfidized specimens were oxidized in Ar-O₂ atmosphere to study their oxidizing behavior. Sulfide formed on pure Fe was a dense and uniform film of FeS. On the contrary, sulfide films formed on Fe₃O₄ and Fe₂O₃ were porous FeS₂. Oxidation of FeS₂ formed on iron oxides occurred rapidly, while oxidation rate of FeS formed on iron was much slower. The experimental results suggest that FeS₂ formed on iron oxides may act as a PIS.

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1. Introduction

Steel or iron oxides formed on the inside-walls of molten sulfur, crude oil or asphalt tanks are reacted with hydrogen sulfide, resulting in formation of iron sulfides. Some sort of iron sulfides causes violent exothermic oxidizing reaction when contacted with air. These iron sulfides are called PIS (Pyrophoric Iron Sulfide). Formation of PIS is an awful problem in petroleum industries, because it sometimes causes accidental explosion. Therefore, it is important to know the condition of PIS formation as well as its mechanism.

There are some reports¹⁻⁵⁾ on pyrophoric phenomena of iron sulfides. However, the condition for PIS formation was not clearly known yet. Sulfidation rates of iron were reported by some investigators,⁶⁻¹⁰⁾ but only few reports^{9,10)} explain about sulfidation phenomena in the temperature range below 873 K. McCormick *et al.*¹¹⁾ reports on the sulfidation of wustite at 973 to 1173 K. But wustite can not be formed in molten sulfur tanks, asphalt tanks and so on, because temperature of tanks are lower than the stable limit of wustite.

In this study, pure iron and iron oxides were sulfidized in Ar-H₂S atmosphere. Sulfidized specimens were observed and analyzed by X-ray diffraction, scanning electron microscope (SEM) and electron probe micro analyzer (EPMA). Oxidation of sulfide films formed on specimens were also investigated. Finally, the condition for PIS formation was discussed.

2. Materials and Experimental Procedure

Pure iron plate was used as an initial material. Size of the specimen was 15 mm × 20 mm × 0.5 mm with a small hole for suspending by an alumina hook. Both faces of specimens were polished with emery papers and diamond paste. Sintered tablets of Fe₃O₄ and Fe₂O₃ (φ20 mm × 5 mm) were also used as starting materials. A hole with diameter of 2 mm was made by a supersonic boring machine, and the faces of the specimens were polished with emery papers and diamond paste. Impurity contents in samples were shown in Table 1.

Experimental apparatus used for sulfidation or oxidation experiment consists of mixed gas supplying system, furnace and exhaust gas cleaning system. Schema of apparatus is shown in Fig. 1. Ar, Ar-H₂S mixed gas and Ar-O₂ mixed gas were dehydrated by passing through columns with CaCl and P₂O₅ in gas supplying system. Flow rates of gases were controlled by capillary flow meters. Mixed gas was introduced into a reaction tube via a quartz glass inlet tube. The tip of the inlet tube was placed near the bottom of the reaction tube. The furnace is a vertical type electric resistance heating furnace with silicon carbide heating elements. Furnace body is movable vertically for heating or cooling of the specimens. Sample was suspended by an alumina hook from an electro-balance set up above the top of the furnace, and it was placed in the bottom of the one end closed quartz glass tube. Temperature of the specimen was measured by a Pt/Pt-

Table 1 Impurity contents in materials used.

Sample	Impurity contents (mass ppm)										
	Al	C	Cr	Cu	Mg	Mn	N	Na	Ni	O	Si
Fe	—	10	3	5	—	2	<10	—	3	176	<20
Fe ₃ O ₄	10	—	30	—	—	10	—	20	10	—	10
Fe ₂ O ₃	—	—	10	—	2	—	—	20	—	—	20

*1 Graduate Student, Tohoku University.

*2 Graduate Student, Tohoku University. Present address: Kobe Steel Ltd., Kakogawa 675-0137, Japan.

Fig. 1 Schematic diagram of experimental apparatus for sulfidation and oxidation.

Table 2 Phases in sulfidized specimens detected by XRD.

Initial material	Sulfidizing temperature, <i>T</i> /K	H ₂ S Contents in Ar-H ₂ S (%)	Detected phases
Fe	573	1	FeS, α-Fe
Fe	673	1	FeS, α-Fe
Fe	773	1	FeS, α-Fe
Fe	573	10	FeS, α-Fe
Fe	673	10	FeS, α-Fe
Fe	773	10	FeS, α-Fe
Fe ₃ O ₄	573	1	FeS ₂ [*] , α-Fe, Fe ₃ O ₄
Fe ₃ O ₄	673	1	FeS ₂ , α-Fe, Fe ₃ O ₄
Fe ₃ O ₄	773	1	FeS ₂ , α-Fe, Fe ₃ O ₄
Fe ₃ O ₄	573	10	FeS ₂ [*] , α-Fe, Fe ₃ O ₄
Fe ₃ O ₄	673	10	FeS ₂ , α-Fe, Fe ₃ O ₄
Fe ₃ O ₄	773	10	FeS ₂ , α-Fe, Fe ₃ O ₄
Fe ₂ O ₃	573	1	FeS ₂ [*] , α-Fe, Fe ₃ O ₄ [*] , Fe ₂ O ₃
Fe ₂ O ₃	673	1	FeS ₂ , α-Fe, Fe ₃ O ₄ , Fe ₂ O ₃
Fe ₂ O ₃	773	1	FeS ₂ , α-Fe, Fe ₃ O ₄ , Fe ₂ O ₃
Fe ₂ O ₃	573	10	FeS ₂ [*] , α-Fe, Fe ₃ O ₄ [*] , Fe ₂ O ₃
Fe ₂ O ₃	673	10	FeS ₂ , α-Fe, Fe ₃ O ₄ , Fe ₂ O ₃
Fe ₂ O ₃	773	10	FeS ₂ , α-Fe, Fe ₃ O ₄ , Fe ₂ O ₃

*XRD peak was weak.

Fig. 2 Potential diagram of the Fe-S-O system at 673 K calculated from thermo chemical data.¹²⁾

Fig. 3 Scanning electron micrographs of surface of pure Fe sulfidized in Ar-1%H₂S for 28.8 ks at 573 to 773 K.

Rh13% thermocouple placed near the specimen in the quartz glass tube. Exhaust gas was passed through the FeCl₃ water solution and NaOH water solution for removing hydrogen sulfide.

After the specimen was placed into the reaction tube, argon gas was flushed into the reaction tube for 1.8 ks to purge the air. Then, the pre-heated furnace body was raised, and the

Fig. 4 Cross sectional analysis of Fe sulfidized in Ar-10% H_2S for 28.8 ks at 773 K by EPMA.

specimen was heated. Flushing of argon gas was continued, until the temperature of specimen reached to the stable state. After the temperature became stable at the specified temperature, Ar-1% H_2S or Ar-10% H_2S mixed gas was introduced into the quartz glass tube. The flow rate of argon gas or mixed gases was $2.5 \times 10^{-6} \text{ m}^3/\text{s}$. The range of sulfidation temperature was from 573 to 773 K, and maximum sulfidation time period was 28.8 ks. When sulfidation was completed, Ar- H_2S mixed gas was altered to Ar gas and the furnace body was pulled down to cool the specimen. The observation and analysis of the surface films formed by sulfidation were performed by X-ray diffraction, SEM and EPMA.

For some specimens, Ar-1% O_2 mixed gas was introduced into the reaction tube after sulfidation in Ar-10% H_2S for 28.8 ks at 773 K, and sulfide films formed on specimens were oxidized for 180 s ~ 14.4 ks. Oxidized samples were also observed and analyzed by XRD, optical microscope, SEM and EPMA.

3. Results and Discussion

3.1 The phases formed by sulfidation

Phases detected by XRD in pure iron, Fe_3O_4 and Fe_2O_3 sulfidized at various temperatures were summarized together with the sulfidation conditions in Table 2. No effect of the sulfidation temperature and H_2S content in Ar- H_2S gas on the formed phases was observed. In the case of sulfidation of pure iron, detected phases were α -Fe and FeS. Accordingly,

product of sulfidation of pure iron was FeS. On the other hand, product of sulfidation of Fe_3O_4 or Fe_2O_3 was FeS_2 .

As shown in Fig. 2, the stable sulfide phase is FeS_2 at the sulfur potential of Ar- H_2S gas mixture in the temperature range and H_2S partial pressures in this study. Sulfur potential of gas mixture is determined by equilibrium of reaction (1).

Initial component of gas mixture is Ar and H_2S , and ratio of amount of H_2 and S_2 formed by reaction (1) is 2 : 1, therefore following correlation is assumed to calculate the sulfur potential of gas mixture.

$$P_{\text{H}_2} = 2P_{\text{S}_2} \quad (2)$$

It is also shown in Fig. 2 that Fe_3O_4 or Fe_2O_3 coexists with FeS_2 in equilibrium state, but iron does not coexist with FeS_2 and neighboring sulfide phase of iron is FeS. Accordingly, FeS is formed on surface of pure iron. A possible explanation of reason why FeS formed on pure iron does not sulfidized to FeS_2 is that hydrogen formed by reaction (3) will decline the sulfur potential at the surface of specimen.

α -Fe was also found in sulfidized Fe_3O_4 . Similarly, α -Fe and Fe_3O_4 were also found in sulfidized Fe_2O_3 . These results indicate that reduction of oxides was occurred simultaneously during sulfidation of iron oxides.

(a) 773K

(b) 673K

(c) 573K

Fig. 5 Scanning electron micrographs of surface of sulfidized Fe_3O_4 in $\text{Ar}-10\%\text{H}_2\text{S}$ for 28.8 ks at 573 to 773 K.

3.2 Microscopic observation of sulfidized specimens

SEM photographs of the surface of pure iron sulfidized at 573 to 773 K are shown in Fig. 3. As shown in these pictures, surfaces of the specimens were covered with crystal grains of sulfide. Larger grains were observed on the specimens sulfidized at higher temperature. Results of cross sectional

analysis of sulfidized iron specimen by EPMA are shown in Fig. 4. As shown in these pictures, the sulfide film is single phase, which is confirmed to be FeS by XRD analysis. The FeS film is uniform and dense, but many pores are observed on the interface of iron substrate and FeS film.

SEM photographs of the surface of Fe_3O_4 sulfidized at 573 to 773 K are shown in Fig. 5. Crystal grains of formed FeS_2 were observed on Fe_3O_4 substrate. Sulfide grains with the larger size were observed in specimens sulfidized at higher temperature. Figure 6 shows the results of the EPMA analysis on the cross section of sulfidized Fe_3O_4 . As shown in this picture, the sulfidized layer of the specimen is porous. And the concentration of the oxygen and sulfur changed gradually in the sulfidized layer. Accordingly, the sulfides were supposed to be formed at pore or grain boundary, and oxide phase and sulfide phase are mixed in this layer.

SEM photographs of the surface of Fe_2O_3 sulfidized at 573 to 773 K are shown in Fig. 7. It is observed that small crystal grains of FeS_2 were formed on the oxide grains. The size of sulfide particle is smaller than that of particles observed in Fe_3O_4 . Results of EPMA analysis on the cross section of sulfidized Fe_2O_3 are shown in Fig. 8. As seen in back scattered electron (BSE) image, the most of the surface layer (left hand side of the picture) and the substrate layer are porous, but dense layer existed in the subsurface. Iron content in this dense layer is higher than surrounding area as seen in iron content profile shown in Fig. 8. This layer is considered to be Fe_3O_4 from this results and XRD analysis.

3.3 Reaction of sulfide film formation

The overall reaction processes of sulfidation of pure iron and iron oxides by hydrogen sulfide were considered based the above results, which are expressed by the following equations.

In the case of sulfidation of Fe_2O_3 , following two step reaction seemed to be occurred due to hydrogen formed by reaction (4) or (5).

3.4 Oxidation of sulfide films

Results of cross sectional analysis of oxide film formed in $\text{Ar}-1\%\text{O}_2$ atmosphere at 773 K for 420 s or 14.4 ks on sulfidized layer of iron by EPMA are shown in Fig. 9. Uniform and dense oxide film was observed on the surface layer of specimen. The thickness of the oxide film was approximately $5\text{ }\mu\text{m}$ after oxidized for 14.4 ks, and most of the inner sulfide layer was still existing.

Figures 10 and 11 show the results of cross sectional analysis of surface layer oxidized in $\text{Ar}-1\%\text{O}_2$ atmosphere at 773 K for 180 or 420 s on sulfidized Fe_3O_4 and Fe_2O_3 , respectively. In the case of oxidation of sulfidized layers on Fe_3O_4 and

Fig. 6 Cross sectional analysis of Fe_3O_4 sulfidized in $\text{Ar}-10\%\text{H}_2\text{S}$ for 28.8 ks at 773 K by EPMA.

(a) 773K

(b) 673K

(c) 573K

Fig. 7 Scanning electron micrographs of surface of Fe_2O_3 sulfidized in $\text{Ar}-10\%\text{H}_2\text{S}$ for 28.8 ks.

Fig. 8 Cross sectional analysis of Fe_2O_3 sulfidized in Ar-10% H_2S for 28.8 ks at 773 K by EPMA.

Fig. 9 Cross sectional analysis of oxide film formed in Ar-1% O_2 atmosphere at 773 K for 420 s or 14.4 ks on sulfidized layer of iron by EPMA.

Fig. 10 Cross sectional analysis of surface layer oxidized in Ar-1%O₂ atmosphere at 773 K for 180 s or 420 s on sulfidized Fe₃O₄ by EPMA.

Fig. 11 Cross sectional analysis of surface layer oxidized in Ar-1%O₂ atmosphere at 773 K for 180 s or 420 s on sulfidized Fe₂O₃ by EPMA.

Fe₂O₃, sulfide phase was observed in specimens oxidized for 180 s, but sulfide phase disappeared after oxidized for 420 s. The present results showed that oxidation rate of FeS₂ formed in iron oxides was much faster than that of FeS formed in pure iron. It is also seen from BSE images in Figures 10 and 11 that the surface layer of sulfidized iron oxides became porous during oxidation progress.

Oxidation reactions of iron sulfides can be expressed by the following equations.

Enthalpy of the reactions (7) and (8) were calculated with a thermochemical data book.¹²⁾ Heat of oxidizing reaction of FeS₂ is greater than that of FeS.

From these analysis and the present results of difference of oxidation rate between FeS and FeS₂, it may be concluded that iron oxide formed on inside-wall of tank is sulfidized by H₂S contained in atmosphere in tank, and then exothermic reaction may occur between FeS₂ formed on iron oxide and oxygen contained in leaked air. Walker *et al.*³⁾ reported that the rapid exothermic reaction was observed when FeS₂ contacted with air. Their report is in accord with our conclusion.

4. Conclusions

Sulfidation experiments of pure iron and iron oxides in Ar–H₂S atmosphere were carried out as well as oxidation experiments in Ar–O₂ atmosphere after sulfidation. The following conclusions were obtained.

(1) Sulfide film formed on pure iron was dense and uni-

form FeS. On the other hand, sulfide films formed on Fe₃O₄ or Fe₂O₃ were porous FeS₂.

(2) Oxidation of FeS₂ formed on iron oxides occurred rapidly, while oxidation rate of FeS formed on pure iron was much slower.

(3) FeS₂ formed in iron oxides on inside-wall of tanks might act as PIS.

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