

High-Temperature Corrosion of Weldment of Fe-2%Mn-0.5%Si Steel in N₂/H₂O/H₂S-Mixed Gas

Sang Hwan Bak, Min Jung Kim, Dong Bok Lee

Abstract—Fe-2%Mn-0.5%Si-0.2C steel was welded and corroded at 600, 700 and 800°C for 20 h in 1 atm of N₂/H₂S/H₂O-mixed gas in order to characterize the high-temperature corrosion behavior of the welded joint. Corrosion proceeded fast and almost linearly. It increased with an increase in the corrosion temperature. H₂S formed FeS owing to sulfur released from H₂S. The scales were fragile and nonadherent.

Keywords—Fe-Mn-Si Steel, Corrosion, Welding, Sulfidation, H₂S Gas.

I. INTRODUCTION

In the area of heavy construction, welding processes are vital in the production and maintenance of pipelines and power plants. The fusion welding process generates formidable residual stress and metallurgical change, which increase the crack driving force and reduce the resistance to the brittle fracture as well as the environmental fracture [1]. Fe-2%Mn-0.5%Si-0.2%C (wt.%) steel pipe, which is used in petrochemical and heavy chemical plants, also suffer serious welding problems. Thus, the investigation of corrosion behavior of weldment of Fe-2%Mn-0.5%Si-0.2%C steel is very important. In this study, the weldment of Fe-2%Mn-0.5%Si steel was corroded at 600, 700 and 800°C for 20 h in 1 atm of N₂/H₂O/H₂S-mixed gas, and its corrosion characteristics were investigated.

II. EXPERIMENTAL PROCEDURE

An eleven-pass welded Fe-2%Mn-0.5%Si-0.2C steel pipe was tested in this study. The mechanical property and welding condition are listed in Tables I and II, respectively. The cross-section and the multi-pass welded pipe are shown in Figs. 1 and 2, respectively. The groove for welding was machined in a V-type. The thickness was 17.5 mm and the inner diameter of the pipe was 272 mm. The first and second passes were welded by gas tungsten arc welding (GTAW) and the other nine passes were welded by shielded metal arc welding (SMAW).

After being cut into sizes of 10×5×5 mm³, the weldment was ground to a 1000 grit finish with SiC paper, ultrasonically cleaned in acetone and ethyl alcohol, and corroded at 600, 700 and 800°C for 20 h inside the hot zone of an electrical furnace under the mixed gas of (20cc/min of N₂, 20cc/min of H₂S, and 25°C H₂O), which was achieved by bubbling the N₂ gas through

the water bath kept at 25°C, while flowing the H₂S gas into the hot zone. The total gas pressure was kept at 1 atm. The employed N₂ gas was 99.999% pure, and H₂S gas was 99.5% pure. Following corrosion, the specimens were investigated by optical microscopy (OM), scanning electron microscopy (SEM), energy-dispersive X-ray spectrometry (EDS) and X-ray diffraction (XRD) analyses.

TABLE I
MECHANICAL PROPERTY OF STEEL WELDMENT

	Yield strength (MPa)	Tensile strength (MPa)
Base	430	486
Weld	380	502

TABLE II
MULTI-PASS WELDING CONDITION

Welding Type	Current (A)	Voltage (V)	Speed (cm/min)	Polarity
GTAW*	118	14~24	8.5	DCSP
SMAW*	116-135	25	6.8~11.5	AC

GTAW*: Gas Tungsten Arc Welding,
SMAW*: Shielded Metal Arc Welding.

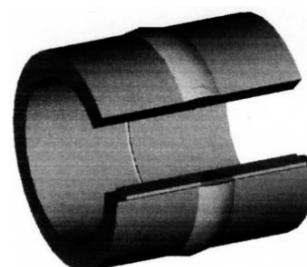


Fig. 1 Cross-section of the steel weld

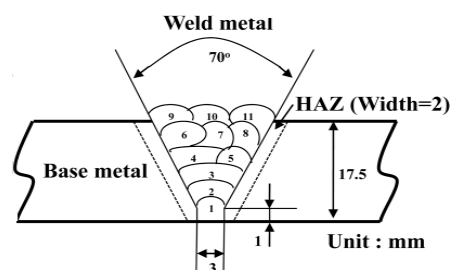


Fig. 2 Multi-pass welded steel pipe

III. RESULTS AND DISCUSSION

The sulfidation behavior of the weldment of the steel in H₂S/H₂O/N₂ atmosphere was examined. Weight gains measured after sulfidation at 600-800°C for 20 h are displayed in Fig. 3. Large weight gains were recorded, indicating vastly fast sulfidation kinetics. The scale failure became more serious

S. H. Bak and M. J. Kim are with School of Advanced Materials Science and Engineering, Sungkyunkwan University, Suwon 16419, South Korea (e-mail: sanghwan.bak@hanmail.net, abc1219@skku.edu).

D. B. Lee is with School of Advanced Materials Science and Engineering, Sungkyunkwan University, Suwon 16419, South Korea (corresponding author, e-mail: dlee@skku.ac.kr).

as sulfidation progressed. The sulfidation appeared to follow the linear rate law, implying negligible protection owing to the formation of the FeS scale. Mn and Si could not protect the weldment from serious sulfidation due to their small amount or dissolution in FeS. An increment in the temperature from 600 to 700°C led to the increment of weight gains by about 5 mg/cm². When the temperature increased from 700 to 800°C, weight gain increased by about 2.5 times. However, it is noted that there was uncertainty in weight gains measured, because scales formed in H₂S-containing atmosphere were usually very thick and highly susceptible to spallation during corrosion and subsequent cooling stage. Nevertheless, it was evident that H₂O and H₂S gas increased the corrosion rate. Water vapor transports through voids cavities and cracks in the scale as H₂ (g) and H₂O (g), and as H atom by dissolving in the lattice, affecting the point defect concentration [2].

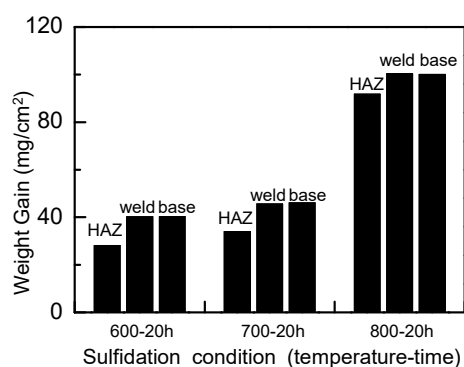
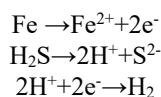


Fig. 3 Sulfidation kinetics of base, weld, and HAZ of Fe-2%Mn-0.5%Si-0.2%C steel after corrosion at 600, 700 and 800°C for 20 h in H₂S/H₂O/N₂ gas

Fig. 4 shows the XRD patterns of Fe-2%Mn-0.5%Si-0.2% steel after corrosion at 700°C for 20 h in H₂S/H₂O/N₂ gas. All the scales consisted primarily of FeS. H₂S 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 Fe²⁺ ions [3].

Fig. 5 shows the SEM cross sectional image and EDS line profiles of the base metal of Fe-2%Mn-0.5%Si-0.2% after corrosion at 700°C for 20 h in H₂S/H₂O/N₂ gas. The outer thick FeS scale detached off, and the inner fragile FeS scale split into a few layers. The scale was ~400 μm thick, implying poor sulfidation resistance. The outer FeS layer had a columnar structure, and the inner FeS layer consisted of fine grains. The inner FeS dissociates according to the reaction: $\text{FeS} = \text{Fe}^{2+} + 1/2\text{S}_2 + 2\text{e}^-$ [4]. This delivers sulfur gas for the inward growth of the innermost layer, whereas the released Fe²⁺ ions and electrons diffuse to the outer surface to form FeS. In the FeS scale, Mn was rather uniformly distributed, while Si was segregated in the inner scale, because Si ions were relatively

immobile owing to the high bonding energy of Si⁴⁺-O²⁻ (465 kJ/mol) [5].

Fig. 6 shows the SEM cross sectional image and EDS line profiles of the weld metal of Fe-2%Mn-0.5%Si-0.2% after corrosion at 700°C for 20 h in H₂S/H₂O/N₂ gas. Cracks developed at the bottom of the nonadherent scale, the main cause of which was attributed to the stress developed in the thick oxide scale. Again, Si was segregated in the inner scale, although Mn was distributed rather uniformly throughout the whole scale.

Fig. 7 shows the SEM cross sectional image and EDS line profiles of the heat affect zone (HAZ) of Fe-2%Mn-0.5%Si-0.2% after corrosion at 700°C for 20 h in H₂S/H₂O/N₂ gas. The scale morphology and elemental distribution were similar with those shown in Figs. 5 and 6, because the principal sulfidation mode was the same in H₂S/H₂O/N₂ atmosphere.

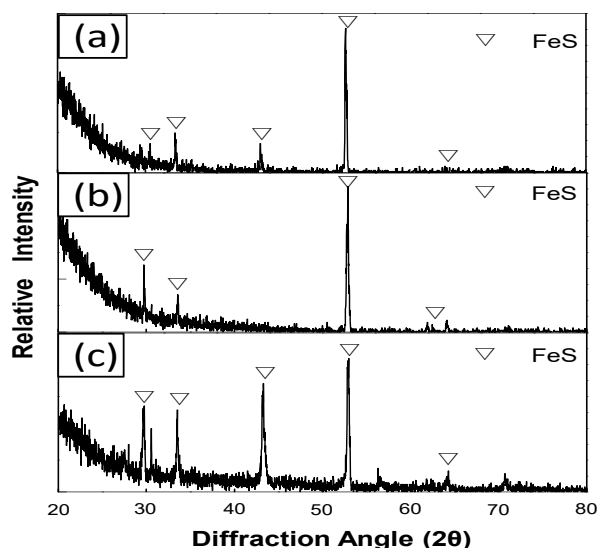


Fig. 4 XRD pattern of Fe-2%Mn-0.5%Si-0.2%C after corrosion at 700°C for 20h in H₂S/H₂O/N₂ gas. (a) base, (b) weld, (c) HAZ

Fig. 8 shows the SEM cross sectional image of Fe-2%Mn-0.5%Si-0.2%C after corrosion at 800°C for 20 h in H₂S/H₂O/N₂ gas. The scale thickness increased with an increase in the temperature. Especially, the scale thickness of the base metal increased more rapidly than those of the welding and heat affect zone (HAZ). The outer FeS grains kept growing outwardly, as Fe continuously diffused out from the matrix via the pre-formed FeS grains. The outer scale was thicker than the inner scale. The outer fast-growing FeS grains were susceptible to cracking, and detached off from the inner mixed scale, owing to the large compressive stress developed. The scales were quite thick, brittle, cracked and detached easily. Mn and Si were incorporated in the FeS scale. The outer scales were formed by the outward transport of predominantly Fe and a small amount of Mn and Si, whereas the inner scales were formed by the inward diffusion of predominantly sulfur along cracks and interconnected pores that developed particularly around the interface of the outer and inner scale.

Fig. 9 shows the oxidation kinetics of the steel in air at 700 and 800°C for 20 h. Compared with sulfidation, the oxidation weight gains were much smaller. The base metal was the least

oxidation resistant. The weld metal was more oxidation resistant. HAZ was the most oxidation resistant, indicating that welding can change the oxidation resistance.

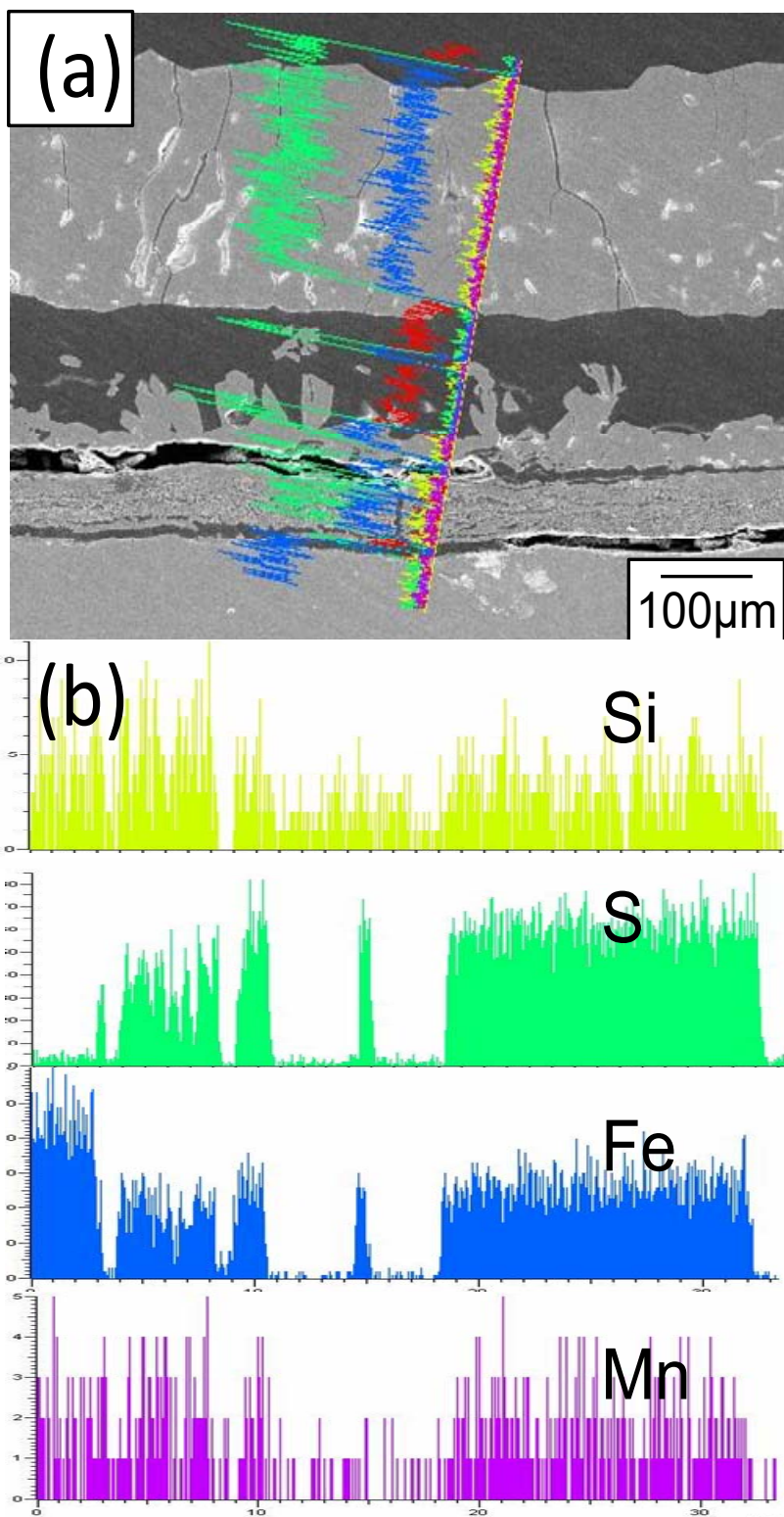


Fig. 5 Base metal of Fe-2%Mn-0.5%Si-0.2%C steel after corrosion at 700°C for 20 h in H₂S/H₂O/N₂ gas. (a) SEM cross sectional image, (b) EDS line profiles

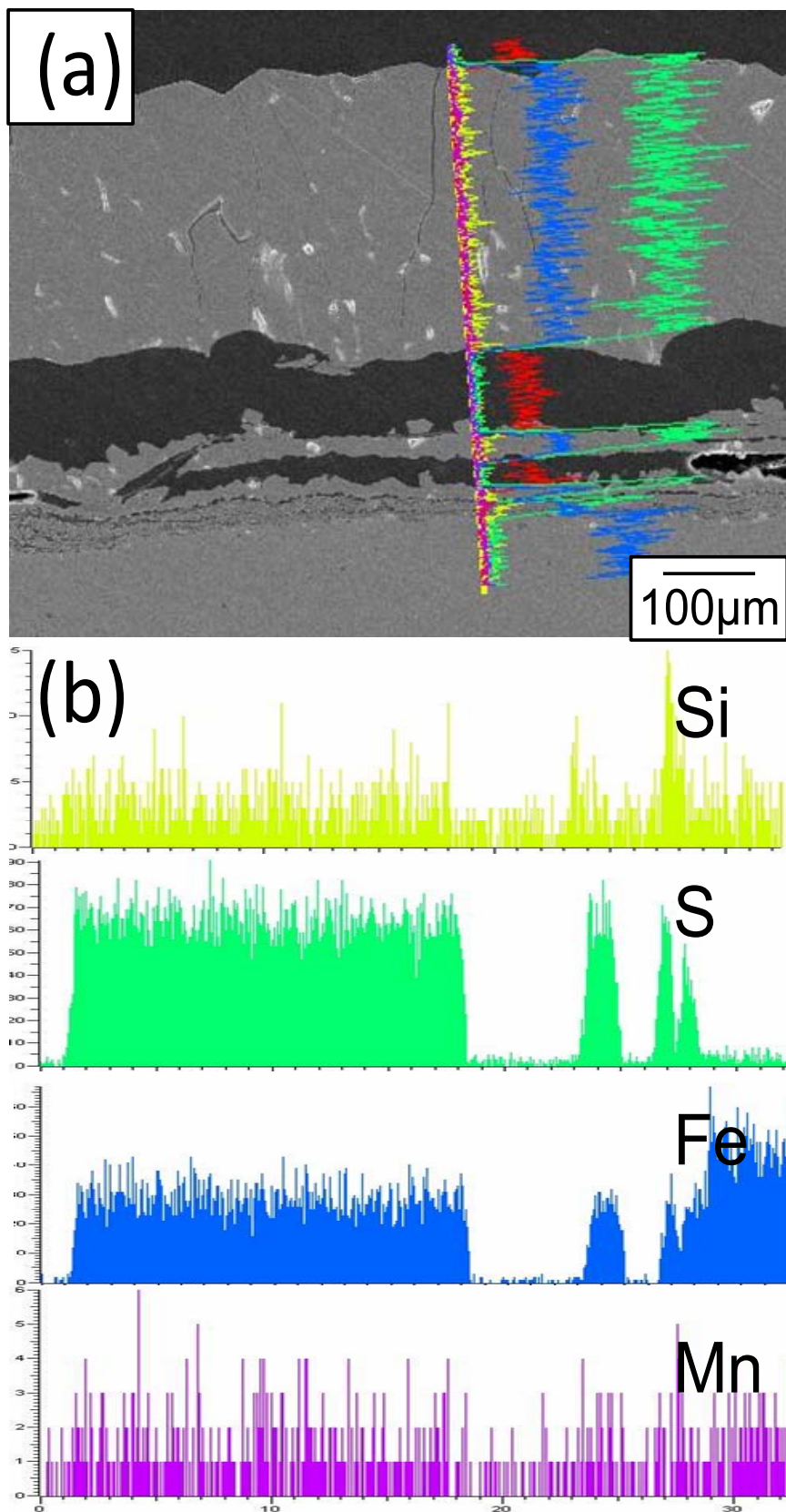


Fig. 6 Weld metal of Fe-2%Mn-0.5%Si-0.2%C steel after corrosion at 700°C for 20 h in H₂S/H₂O/N₂ gas. (a) SEM cross sectional image, (b) EDS line profiles

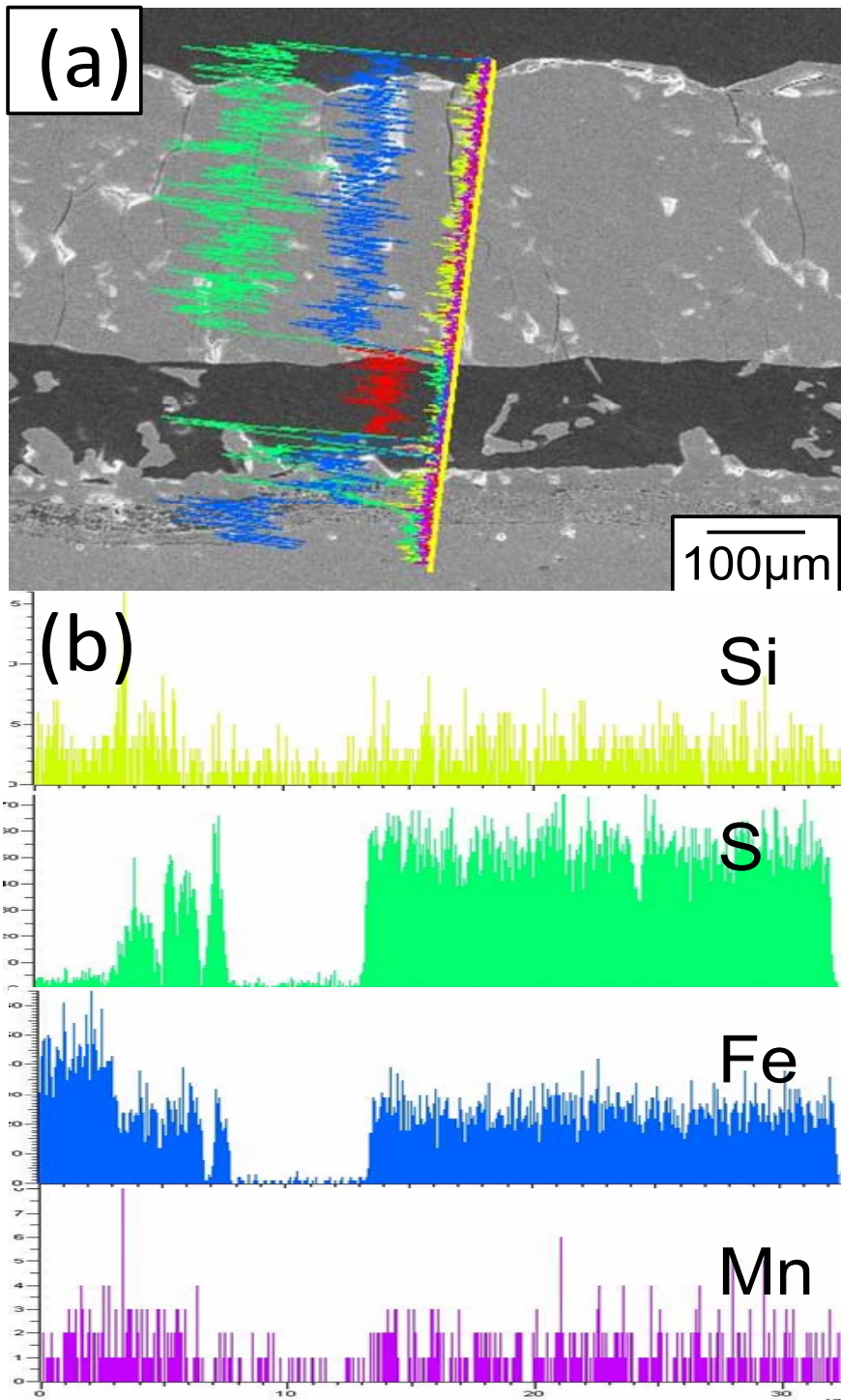


Fig. 7 HAZ metal of Fe-2%Mn-0.5%Si-0.2%C steel after corrosion at 700°C for 20 h in H₂S/H₂O/N₂ gas. (a) SEM cross sectional image, (b) EDS line profiles

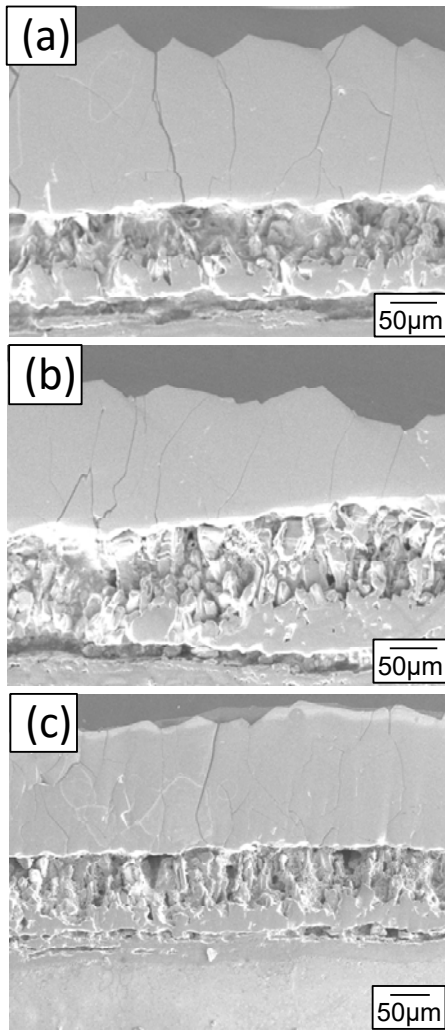


Fig. 8 SEM cross sectional image of Fe-2%Mn-0.5%Si-0.2%C steel after corrosion at 800°C for 20 h in H₂S/H₂O/N₂ gas. (a) base, (b) weld, (c) HAZ

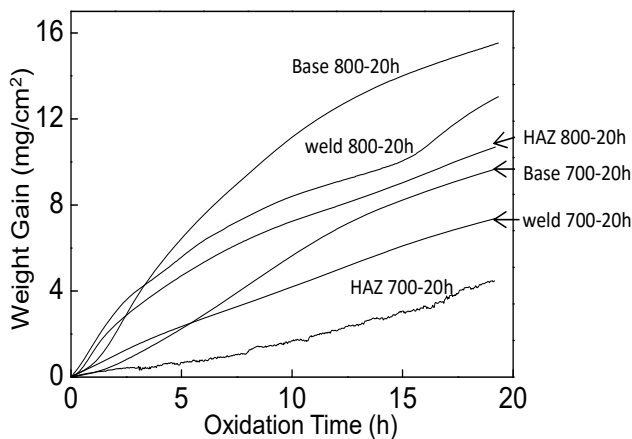


Fig. 9 Oxidation kinetics of base, weld, and HAZ of Fe-2%Mn-0.5%Si-0.2%C steel at 700 and 800°C in air

IV. CONCLUSION

In the high-temperature H₂S/H₂O/N₂ gas, Fe-2%Mn-0.5%Si-0.2%C steel had poor sulfidation resistance. HAZ displayed better sulfidation resistance than base metal and weld metal. FeS was the main scale. The scale was quite thick, cracked and easily detached. Compare with sulfidation, the steel displayed better oxidation resistance. Especially, HAZ displayed the best oxidation resistance.

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