

# Blistering Behavior during Oxide Scale Formation on Steel Surface

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Blistering occurs when oxide scale is swollen during oxidation. Blistered scale causes surface defect problems when it is rolled. Present study investigated the nucleation and growth behavior of blistering when steel is oxidized at high temperature. The following conclusions are drawn. Blistering phenomenon has the nucleation and growth process. At the nucleation stage scale is delaminated at the scale/metal interface. The gas compositions inside blisters at this stage are CO, CO<sub>2</sub>, and N<sub>2</sub>. The steel surface inside blisters is oxidized while the stage changes from nucleation to growth. At the growth stage, the separated steel surface from the scale is not oxidized.

KEY WORDS: blister; scale; carbon; carbon-monoxide; carbon-dioxide; carbon enrichment.

## 1. Introduction

Blistering occurs when oxide scale is swollen during oxidation. Blistered scale causes surface defect problems when it is rolled. It is important to understand the mechanism of blistering and control the blister formation in order to prevent surface defects. Mainly two mechanisms have been already reported. One is that blistering is caused by stress generated during scale formation.<sup>1-4)</sup> The other is gas release at the scale/steel interface.<sup>1,2,5,6)</sup> Griffiths<sup>1)</sup> described experimental results of blistering tests conducted in various atmospheric conditions. Blistering is suppressed in pure oxygen atmosphere or moist atmosphere conditions. Matsuno<sup>3)</sup> investigated the effects of temperature and observed that severe blistering occurs in temperatures between 950 and 1 000°C. He also estimated that stress caused by scale formation induced blister generation. Kizu *et al.*<sup>4)</sup> investigated the effect of an alloying element on blistering initiation time and this analysis revealed that texture of the scale has effects on the blistering phenomenon. Conversely, in steels containing higher carbon content blistering occur easily.<sup>6)</sup> These results led the mechanism of blister inflation from gas generations such as carbon-monoxide (CO) and carbon-dioxide (CO<sub>2</sub>) at the scale/steel interface.<sup>2)</sup> Chen *et al.*<sup>7)</sup> investigated short-time oxidation in air at 850–1 180°C and discovered that blisters form at the edge area of samples with smooth surface scale.

However, research so far has not investigated the nucleation and growth mechanism in detail. Therefore, in the present study focus was placed upon the nucleation and growth process of blistering in order to understand the mechanism of blister formation.

## 2. Experimental

Steel with the chemical composition shown in **Table 1** was used for the experiments. Specimens were cut to a rectangular shape 30 mm×30 mm×4 mm in size. Oxidation was performed in an infrared furnace. The samples were firstly heated up to the oxidation temperature in nitrogen (N<sub>2</sub>) atmosphere and kept for 1 hour at the same temperature. Oxidation was started by changing the flowing gas from nitrogen to oxidizing gas, which are shown in **Table 2**. The gas flow rate was set at 10 L/min. The oxidizing conditions of temperatures and oxidizing atmospheres are shown in **Table 2**. Specimens were subjected to oxidation test under A to E condition. After the oxidation the samples were cooled down in nitrogen atmosphere except for condition E. The purpose of condition E is to measure gas composition inside blisters. The sample in condition E was cooled down in helium gas in order to prevent the entry of N<sub>2</sub> gas inside the blisters. The surface of the samples was observed and

**Table 1.** Chemical compositions of the sample [mass%].

C	Si	Mn	P	S	Al
0.16	0.071	0.7	0.008	0.008	0.018

**Table 2.** Experimental conditions.

No.	Temperature	Oxidizing atmosphere and oxidation time
A	950°C	Air×120 s
B	1 000°C	Air×120 s
C	950°C	Air×12 s
D	950°C	(21%O <sub>2</sub> +31%H <sub>2</sub> O+48%N <sub>2</sub> )×120 s
E	1 000°C	(1%O <sub>2</sub> +31%H <sub>2</sub> O+68%N <sub>2</sub> )×5 min→Air×17 s

recorded by a camcorder.

The surface appearances after the oxidation were observed. The oxide scale and the blisters formed in condition A were analyzed using an optical microscope, scanning electron microscope (SEM), and glow discharge optical emission spectroscopy (GD-OES).

The gas compositions inside blisters in condition E were measured. The surface of the sample was coated with epoxy resin. After solidifying, the coated surface was drilled in a vacuum chamber. During drilling gases inside the blisters were released. The mass-to-charge ratios of the released gases were analyzed by mass spectrometry.<sup>8)</sup>

### 3. Results

#### 3.1. Condition A

The surface appearance after the 950°C oxidation in condition A is shown in Fig. 1. Blistering initiates at 14 seconds after the oxidation starts (Fig. 1(a)). Blisters start to inflate and adjacent blisters coalesce at 19 seconds (Fig. 1(b)). In contrast, some blisters remain small in size (Fig. 1(c)). The blister growth almost stops at 29 seconds (Fig. 1(d)).

The sample appearance after removal of the swollen oxide scale (Fig. 1(e)) seems to correspond to the results of in-situ observation. The nucleating points of blister are mostly located in the center of the blisters. Five initiating blisters are located in area 1 in Fig. 1(a). The blisters grow and coalesce (Figs. 1(b)–1(d)). Figure 2 shows a magnifying surface image at area 2 in Fig. 1(e). The initiating point is black. The areas where blisters grow look non-oxidized metallic steel surface. This result implies that the blistering process has both the initiating and growing processes. Here,

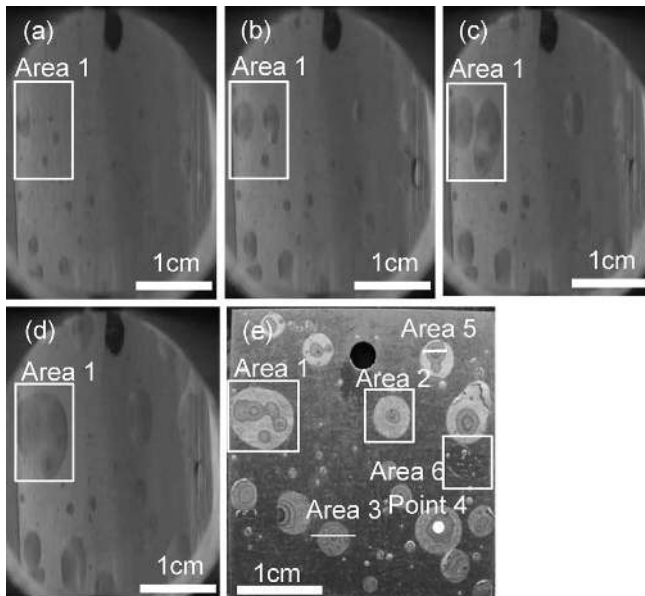


Fig. 1. Surface appearances during and after the oxidation at 950°C in condition A. (a) 14 s. (b) 19 s. (c) 24 s. (d) 29 s. (e) After the oxidation.

the video recording method during in-situ observation is useful for careful observation of the blistering process.

An optical microscope image of the cross section of the blister at area 3 in Fig. 1(e) is shown in Fig. 3. Oxide scale is formed in the center part of the blister at area 3 in Fig. 1(e). The center part of the scale is thicker, and the outskirts become thinner. The non oxidizing steel surface surrounds the oxide scale.

The results of GD-OES measurement in the center of the oxidized scale in the blister at point 4 in Fig. 1(e) are shown in Fig. 4(a), while the result of a normally oxidized scale is shown in Fig. 4(b).

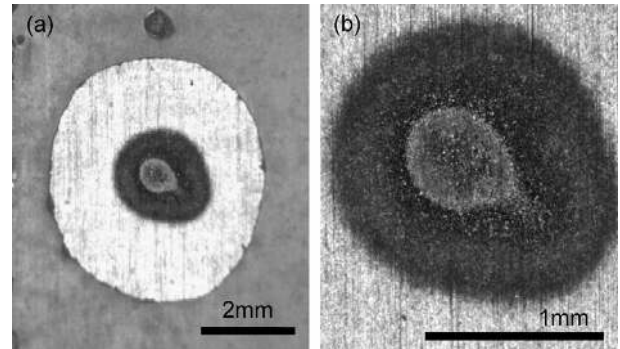


Fig. 2. Magnified blister at area 2 in Fig. 1. (a) Whole blister. (b) Magnified blister center.

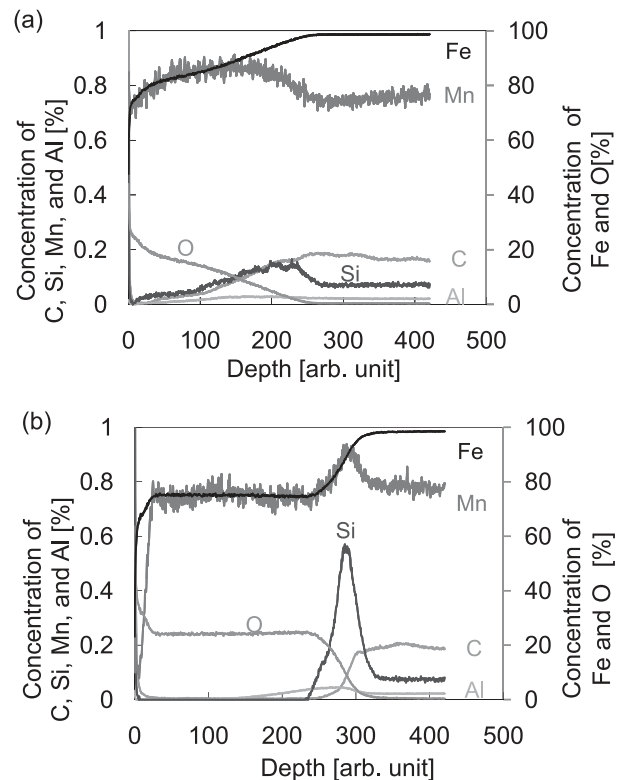


Fig. 4. GD-OES measurements on the sample shown in Fig. 1. (a) At the blister center (point 4 in Fig. 1). (b) At a normal scale area.

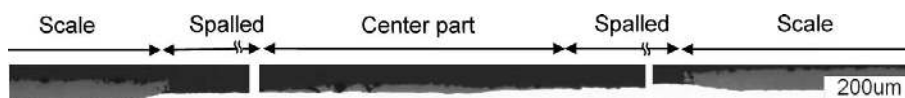


Fig. 3. Optical microscope image at the cross section of the blister at area 3 in Fig. 1.

shown in Fig. 4(b). Element profiles on the scale in the black blister center have broad peak profiles because the scale thickness changes in the measured area. There, manganese (Mn) is located in the scale area and a broad silicon (Si) peak is detected at the scale/metal interface and carbon (C) is detected in the steel (Fig. 4(a)). Compared to the normal scale area, no particular features are obtained.

A SEM image of the black blister center at area 5 in Fig. 1 is shown in Fig. 5. The results of energy dispersive X-ray spectrometry (EDX) at three points in Fig. 5 are presented in Table 3. The scale has uniform structure. Point B in Fig. 5 at the scale/metal interface contains oxygen (O), iron (Fe), and Si. Fayalite (Fe<sub>2</sub>SiO<sub>4</sub>) is considered to form at the interface. This shows that the scale resembles normally oxidized one formed on steel containing silicon.

**3.2. Condition B**

The surface appearance after the oxidation at 1 000°C in condition B is shown in Fig. 6. Blisters start to appear at 17

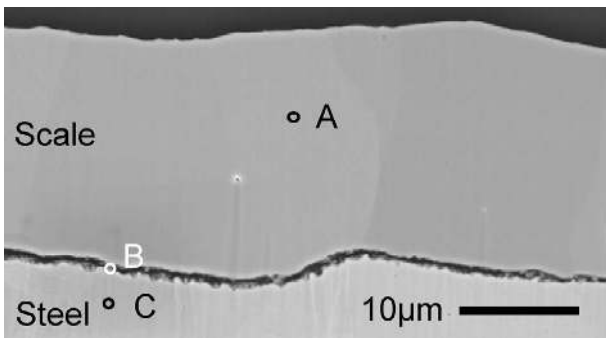


Fig. 5. SEM image of the scale formed at the center of the blister at point 5 in Fig. 1.

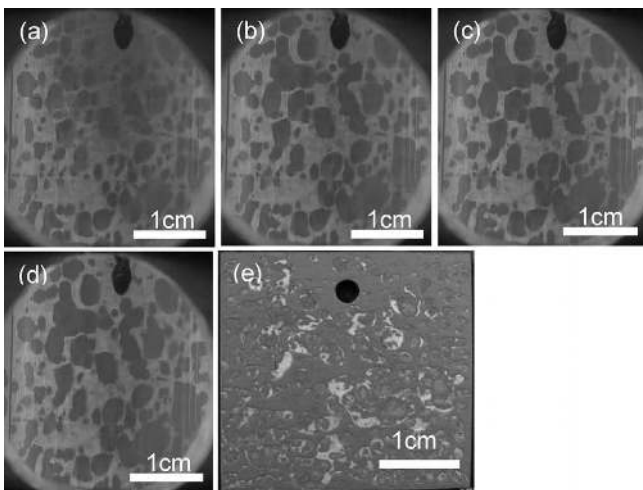


Fig. 6. Surface appearances during and after the oxidation at 1 000°C in condition B. (a) 17 s. (b) 21 s. (c) 25 s. (d) 29 s. (e) After the oxidation.

Table 3. EDX analysis results at the points shown in Fig. 5.

Point	Detected elements
A	O, Fe
B	O, Fe, Si
C	Fe

seconds (Fig. 6(a)). The initiated blister size is larger than that at 950°C (condition A). The blisters grow slightly and some of them coalesce (Figs. 6(b), 6(c)). The blister growth almost stops at 28 seconds (Fig. 6(d)). Comparing the surface during oxidation (Figs. 6(a)–6(d)) to the surface appearance after removal of the swollen scales (Fig. 6(e)), it is recognized that the initiating points of blistering correspond to the black part in the blisters and the surrounding growing area remains not oxidized. This process is similar to that at 950°C (condition A).

**3.3. Condition C**

In order to observe the situation at just after blister nucleation, an oxidation is conducted for 12 seconds. The surface appearance is shown in Fig. 7. The surface after removing the swollen scale looks not oxidized. The blister areas are confirmed to be not oxidized in another cross section observation. This result indicates that scale detaches at the scale/steel interface at the blister nucleation stage and then the steel surface is oxidized inside the blister. After these processes blisters inflate. It is inferred that the mechanism of blister nucleation is different from that of blister growth.

**3.4. Condition D**

The surface appearance of the sample in condition D is shown in Fig. 8. The condition is almost the same as condition A, but the oxidizing atmosphere contains water vapor. The surrounding area of the center black scale is oxidized. The blister initiation and growth process is similar to that in condition A.

**3.5. Condition E**

The sample appearance after the oxidation in condition E

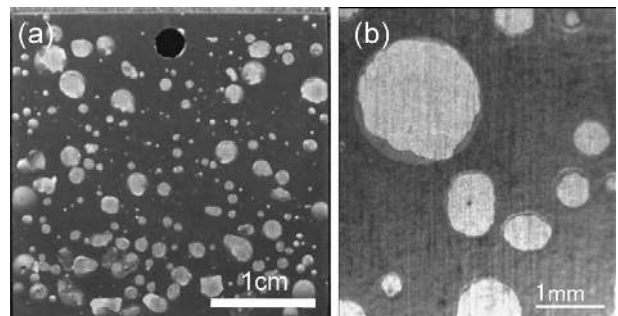


Fig. 7. Surface appearances of the sample oxidized for 12 s at 950°C in condition C. (a) The whole surface area. (b) A magnified image.

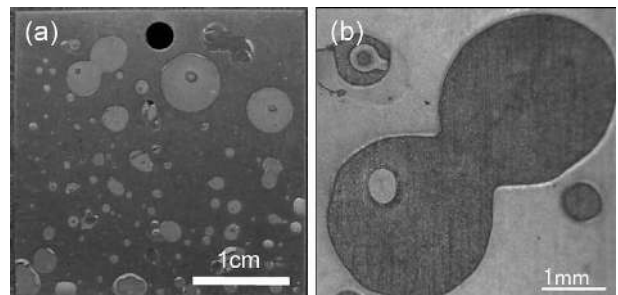
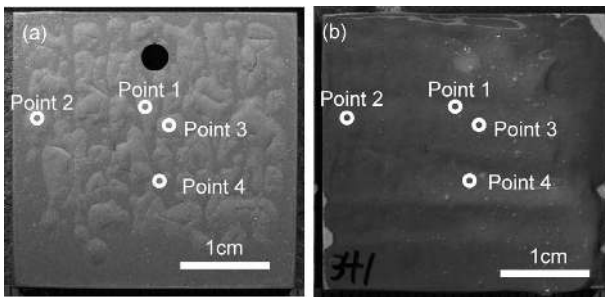


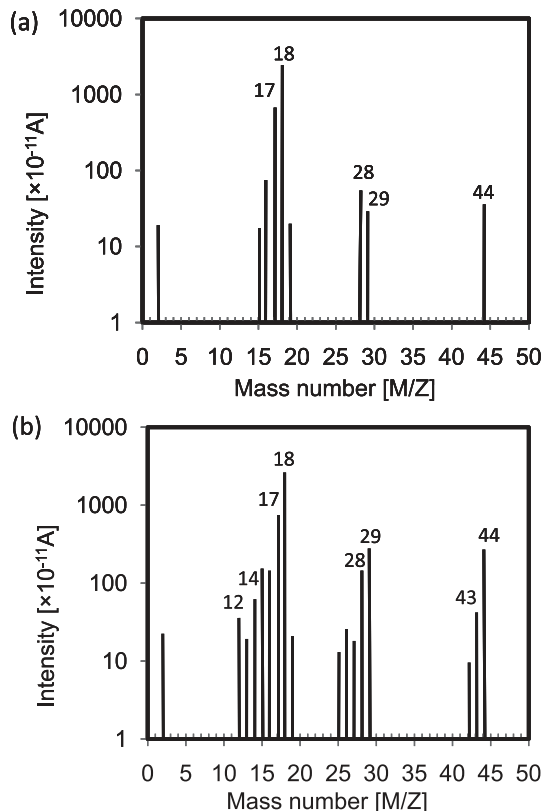
Fig. 8. Surface appearances of the sample oxidized for 120 s at 950°C in the atmosphere with water vapor in condition D. (a) The whole surface area. (b) A magnified image.

and that after coating by epoxy resin are shown in **Fig. 9**. The mass spectrometry measurements of blister internal gas are conducted four times. The four drilled points are shown in the figure. Meaningful data are obtained by the measurements performed at point 2 and point 3 in Fig. 9. The mass-to-charge ratio (mass number) 32 is detected at the other two points. This means that air is entering into the blisters.

The measured spectra at point 2 are shown in **Fig. 10**. The measured spectra were compared to the background spectra. Here, the background are the mass spectra measured just before the gas releases during drilling at the same position. Compared to the background (Fig. 10(a)), meaningful mass numbers at the gas release peak are 12, 14, 15, 18, 28, 29, 43, and 44. The signal of mass number 18 is gradually increased during drilling. This signal is considered to correspond to water released from epoxy resin. Significant spectrum of mass 28 is detected (Fig. 10(b)). This implies the



**Fig. 9.** Surface appearances with gas analysis points of the sample in condition F. (a) After the oxidation. (b) After the resin coating.



**Fig. 10.** The results of gas analysis at point 2 in Fig. 9 by mass spectrometry method. (a) At the background. (b) At the peak.

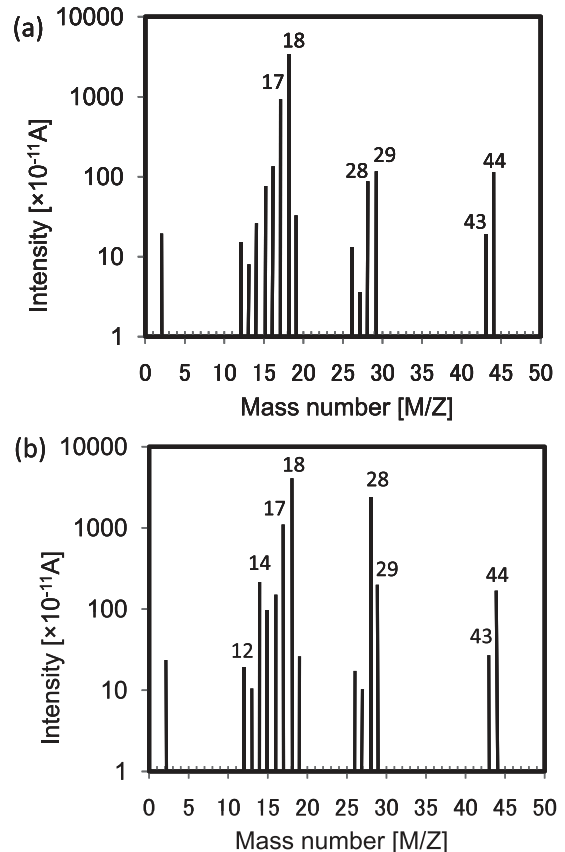
existence of CO and nitrogen ( $N_2$ ). The fragments of these gases are 12 (C) and 14 (N). These mass numbers of 12 and 14 are also increased compared to that of the background. Mass number 44, which means  $CO_2$ , is also detected. There are no proper gases that correspond to the mass numbers of 15, 29, and 49. So these might be hydrocarbon gases released from epoxy resin. This mass spectrometry measurement implies that CO gas,  $CO_2$  gas, and  $N_2$  gas exist inside the blister.

The measured spectra at point 3 are shown in **Fig. 11**. The spectra of mass numbers 12, 14, 15, 18, 28, 29, 43, and 44 increase compared to those of the background, where are similar to the results at point 2.

The peak intensities of mass number 12, 14, 18, 28, and 44, which are thought to be related to blistering behavior, are shown in **Fig. 12**. At point 2 in Fig. 9 the peaks of mass number 12, 14, 28, and 44 increase compared to that at the background (Fig. 12(a)). The peak of mass number 18 remains in same level as that at the background. The result at point 3 (Fig. 12(b)) is similar as that at point 2. These results indicate that inside blisters CO,  $CO_2$ , and  $N_2$  gases are contained.

#### 4. Discussion

The schematic illustration of the blister growth process observed in the experiment at  $950^\circ C$  in condition A and C is shown in **Fig. 13**. Rolls<sup>2)</sup> reported blistering phenomenon has the stages of nucleation, growth, coalescence, shrinkage,



**Fig. 11.** The results of gas analysis at point 3 in Fig. 9 by mass spectrometry method. (a) At the background. (b) At the peak.

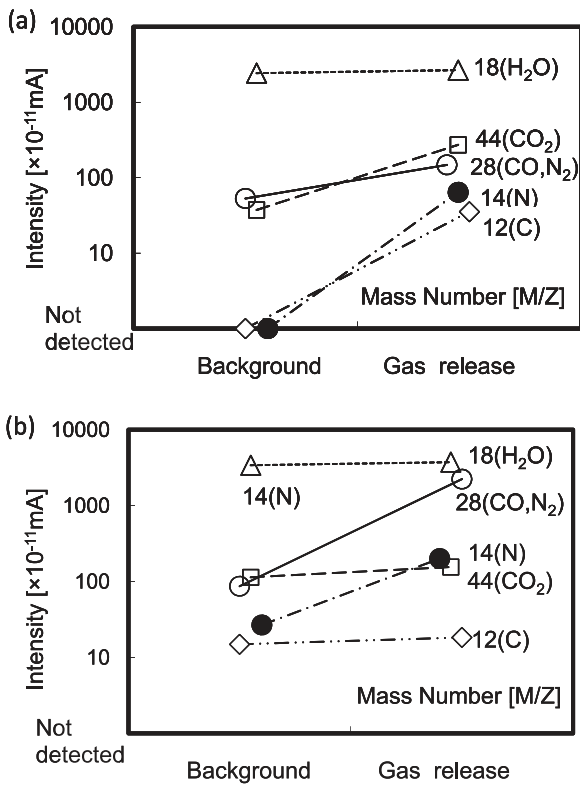


Fig. 12. Comparison of the peak and the background in the gas spectroscopy measurements. (a) At point 2 in Fig. 9. (b) At point 3 in Fig. 9.

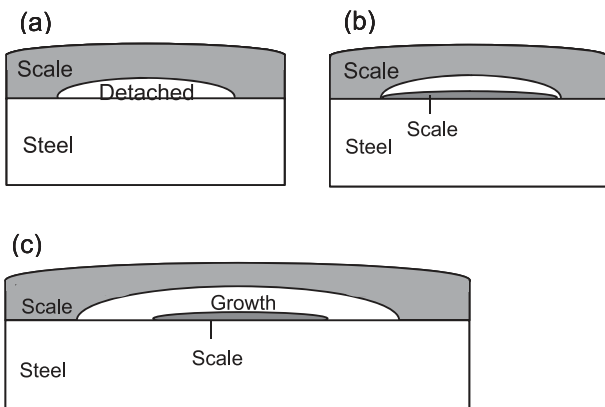


Fig. 13. Schematic illustration of nucleation and growth process of blistering. (a) Blister nucleation. (b) Oxidation inside blister. (c) Blister growth.

and collapse. We discuss these processes based on our new findings.

#### 4.1. Nucleation

Blistering initiates for a short time (Fig. 1). At this stage the gases inside the blister are CO, CO<sub>2</sub> and N<sub>2</sub> (Fig. 12). It is reported that blistering is caused by the stress generated during scale formation<sup>1-4)</sup> and also gas release at the scale/steel interface.<sup>1,2,5,6)</sup> The experimental result of blister internal gas measurement supports the latter idea. However, further research is necessary to draw concrete conclusions.

Ikeda<sup>6)</sup> pointed out that alumina inclusion in the steel is the blister nucleation site. However, the GD-OES measurement in the present work (Fig. 4) and the cross section anal-

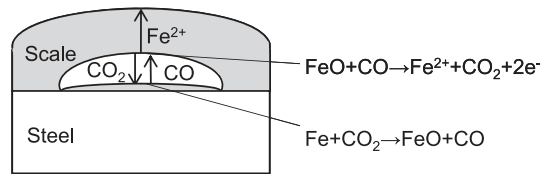


Fig. 14. Dissociative process within voids. Separated scale oxidized steel surface by this process.

ysis (Fig. 5 and Table 3) yield no such features. The in-situ surface observation study in this work also yields no information concerning the blister nucleation point. There are no particular features at the points on the surfaces before or during the oxidations. A magnified in-situ surface observation technique<sup>9)</sup> can observe the oxide nucleation process when surface phase is changing. Such magnified observation may be useful for obtaining any information concerning the blister nucleation site.

Steel surfaces inside the initiated blisters are oxidized during the change from the nucleation stage to the growth stage (Fig. 13(c)). The oxidation occurs only for several seconds. It is unlikely that the oxidizing atmosphere enters into the blister because the steel surface is not oxidized at the nucleation stage. The oxygen partial pressure inside the blister is the value that equilibrates between iron (Fe) and wustite (FeO). The partial pressure of oxygen (O<sub>2</sub>) is estimated to be  $2 \times 10^{-17}$  atm. at 950°C. If the internal oxidizing gas is O<sub>2</sub>, the oxygen partial pressure is too low to oxidize for such a short time.<sup>10)</sup>

Another oxidation mechanism is necessary such as the dissociative process.<sup>10,11)</sup> That process explains that detached oxide scale oxidizes the separated metal surface (Fig. 14). When H<sub>2</sub>-H<sub>2</sub>O are contained in a space such as void located inside a scale, hydrogen (H<sub>2</sub>) is oxidized to water (H<sub>2</sub>O) at the bottom surface of the detached scale and the water reaches the metal surface and oxidizes the metal surface. The water is reduced to hydrogen there. This process also works in the CO-CO<sub>2</sub> system.<sup>11)</sup> Gas measurement inside the blisters detects both CO and CO<sub>2</sub>. It is estimated that a similar process occurs in the oxidation inside the blisters.

Here, the oxidation inside the blister occurs for several seconds because the steel surface is not oxidized at the next growth stage. It is necessary that oxidation lasts only for a short time. That means the oxidizing gases of CO and CO<sub>2</sub> disappear or are gradually consumed. One possibility for this is that gases inside the blisters permeate through scale. This means that scale has gas permeability. It also means the oxidizing atmosphere can enter the blisters. This is inconsistent with the result that the steel surface is not oxidized at the stage of nucleation and at the growth stage.

A new mechanism is proposed here and schematically shown in Fig. 15. The steel surface under the oxide scale is decarburized if the scale has CO gas permeability.<sup>12)</sup> However, it is supposed that gas permeability of the scale is low as described above. In such case, carbon is enriched at the steel surface (Fig. 15(b)).<sup>12,13)</sup> As scale grows, carbon activity at the surface of the steel increases. The reaction shown in Eqs. (1) and (2) advances and the partial pressure of CO and that of CO<sub>2</sub> are increased. There the ratio of the CO partial pressure to the CO<sub>2</sub> maintains a state that equilibrates

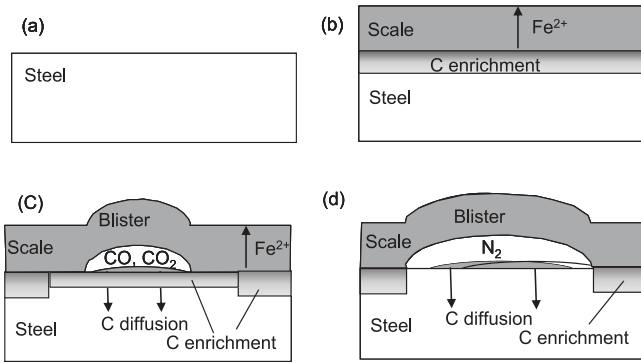
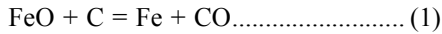


Fig. 15. Assumed mechanism of blister nucleation. (a) Before oxidation. (b) Scale formation and carbon enrichment. (c) Scale separation and steel oxidation under the separated scale. (d) CO and CO<sub>2</sub> gas consumption and blister growth.

between Fe and FeO. The scale starts to separate when the total pressure at the scale/steel interface exceeds the scale adhesion limit (Fig. 15(c)), which is discussed in the next section. The enriched carbon starts to diffuse inside the steel because the scale separation stops the oxidation reaction and the carbon enrichment. It decreases the carbon activity at the steel surface. Reaction (1) and reaction (2) start to go backward. These backward reactions decrease the partial pressure of CO and that of CO<sub>2</sub>. However, N<sub>2</sub> gas does not take part in these processes and remains after this stage. This explains why the steel surface at the next growth stage remains not oxidized (Fig. 15(d)).



**4.2. Nucleation Condition**

Next, we discuss blister nucleation conditions taking into consideration scale adhesion, scale deformation, and gas pressure at scale/metal interface.

Firstly, we estimate scale adhesion at high temperature. Another test to measure scale detaching force was conducted. The procedure followed the method that Kushida *et al.* reported.<sup>14)</sup> Separated two cylindrical specimens with 10 mm diameter are set and oxidized at high temperature. Oxidized samples are contacted to each other and oxide scales are joined at the same temperature. After joining, two samples are separated and the force during detaching was recorded. If oxide scale separated to the one side completely, the maximum force is considered as scale adhesive force at the temperature. Several trials were done and only a few tests were successfully performed at each temperature. The obtained results at temperatures between 850°C and 950°C are shown in Fig. 16. Blisters are formed at the surface of the sample above 1 000°C during oxidation. Consequently no data were obtained above 1 000°C. The scale adhesive force decreases as temperature increases. This is same as the result that Krzyznowski *et al.* reported.<sup>15)</sup> The value is in the range from 1 MPa to 2 MPa. It is worthwhile to note that the values are quite small than those obtained by Kushida *et al.*<sup>14)</sup>

Secondly we consider scale deformation. Main composition of oxide scale formed at high temperature is FeO. Some studies on yield strength of FeO are reported.<sup>16-18)</sup> The val-

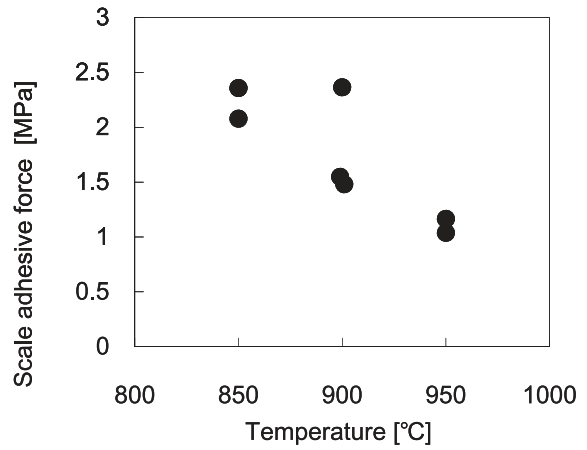


Fig. 16. Measured scale adhesive force.

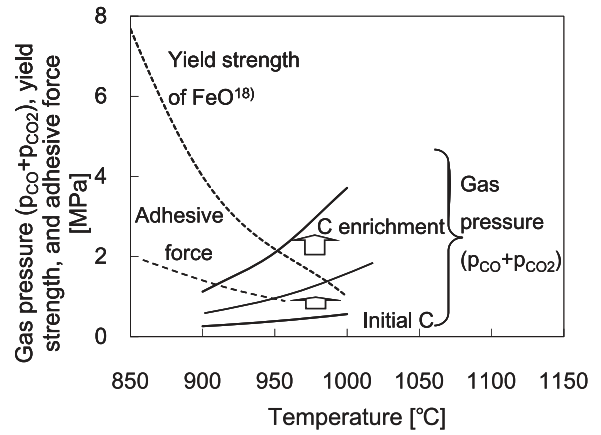


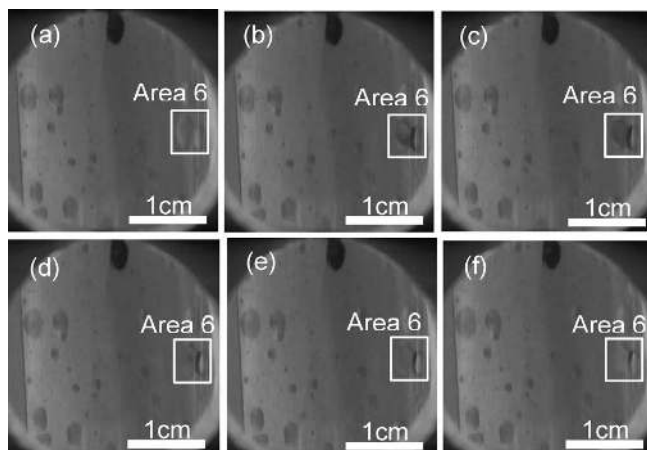
Fig. 17. Gas pressure of CO and CO<sub>2</sub> equilibrated carbon in  $\gamma$ -steel at the steel/scale interface including yield strength of FeO and scale adhesive force.

ues are ranged 4 MPa to 1 MPa between 900°C and 1 000°C by Hidaka *et al.*,<sup>18)</sup> which are shown in Fig. 17. Yield strength decreases as temperature increases. However, the values are higher than the value of scale adhesive force. This suggests that blistering nucleation condition is limited by scale adhesion.

Thirdly we consider gas pressure at scale/metal interface. When oxide scale is formed, CO partial pressure and CO<sub>2</sub> partial pressure at scale/metal interface equilibrated carbon activity in the steel surface in Eqs. (1) and (2) respectively. As discussed above, during scale formation carbon may be enriched at the surface and carbon activity increases. This increases the partial pressure of CO and that of CO<sub>2</sub>. Considering carbon activity in  $\gamma$ -steel,<sup>19)</sup> total pressure of CO and CO<sub>2</sub> can reach the scale adhesive force of 1.5 MPa at 950°C when carbon enriched to about 0.5mass%. Therefore, as schematically shown in Fig. 17, the nucleation condition for blistering is considered to the case where the gas pressure inside blister reaches the scale adhesive force. Another factor such as scale formation stress or N<sub>2</sub> gas pressure in blisters may make blisters deform plastically. However, GD-OES measurement does not indicate such carbon enrichment. Carbon might diffuse during cooling or be located partly in steel. Further research is necessary.

**4.3. Growth**

Blisters gradually inflate at the next growth stage. The



**Fig. 18.** Blister collapse process in condition A. (a) 0.03 s before the collapse. (b) blister collapse. (c) 0.03 s after collapse. (d) 0.36 s after the collapse. (e) 0.73 s after the collapse. (f) 1 s after the collapse.

separated steel surface does not oxidize at this stage, which explains why  $N_2$  gas remains inside the blisters as described above. In this growth process the main driving force of blistering may be scale growth stress<sup>1-4)</sup> or  $N_2$  gas release.<sup>2)</sup> The detailed mechanism of this growth process will be reported in a separate paper.

The steel surface inside the blisters on the sample oxidized in the atmosphere with water vapor of condition D. This is explained by the dissociative process. Hydrogen can migrate through oxide scale and  $H_2$  and  $H_2O$  gases are in the space between the separated scale and steel.<sup>10,11)</sup> The dissociative process oxidized the steel surface in this condition.

#### 4.4. Collapse and Shrinkage

The stages of collapse and shrinkage are observed in the experiment of condition A. These occur between 18 and 19 seconds. The processes are shown in **Fig. 18**. The coalesced blister located on the right side of the sample (area 6 in **Fig. 18**) is ruptured and immediately shrinks (**Fig. 18(b)**). The shrinkage behavior looks elastic deformation. The scale surface color at the ruptured area darkens (**Fig. 18(c)**). The col-

or then begins to lighten (**Figs. 18(d), 18(e), 18(f)**). Based on these findings, it is inferred that the gas with low oxygen partial pressure is released and the gas reduces the scale surface.

#### 5. Conclusion

The preset study investigated the nucleation and growth behavior of blistering when steel is oxidized at high temperature. The following conclusions are drawn.

(1) Blistering phenomenon has the nucleation and growth process.

(2) Scale is detached at the scale/metal interface at the nucleation stage. The gas compositions inside blisters at this stage are  $CO$ ,  $CO_2$ , and  $N_2$ .

(3) The steel surface inside blisters is oxidized while the stage changes from nucleation to growth.

(4) The scale separates at the scale/metal interface and the separated steel surface does not oxidize in the growth stage.

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