

# Blistering Behavior during Oxide Scale Formation on Steel Surface

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## Abstract

*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.*

## 1. Introduction

Oxide scale forming on steel surfaces during hot rolling often detaches from the base metal and swells; this is called blistering. It has been known that surface defects arise when steel is rolled with blisters on the surface, and therefore, to prevent surface defects, it is important to understand the formation mechanisms of blisters. Principally, two types of mechanisms have been reported regarding the formation of blisters: the growth stress due to scale formation<sup>1-4)</sup> and gas generation from steel at the interface with scale.<sup>1,2,5,6)</sup> Griffiths<sup>1)</sup> conducted tests in different atmospheric conditions and demonstrated that blisters formed less in an atmosphere of pure oxygen or with high humidity. Matsuno<sup>3)</sup> investigated the effects of temperature on blister initiation formation, demonstrated that blisters were most likely to form in the temperature range from 950 to 1000°C, and presumed that the cause of blister formation was the growth stress of scale. Kizu et al.<sup>4)</sup> studied the effects of alloy elements on the blistering time, analyzed the texture of scale during its growth, and reported that the main cause of blistering was the growth stress of scale.

On the other hand, blisters are more likely to appear when carbon concentration in steel is high,<sup>6)</sup> which indicates that blisters are caused by CO or CO<sub>2</sub> gas arising from decarburization of steel beneath the scale. Chen et al.<sup>7)</sup> examined steel oxidation in a short period in the temperature range of 850 to 1180°C and made it clear that blisters originate from test piece edge regions where the surface is smooth. Although there have been many reports on the formation behavior of scale blisters, only a few of them deal with the nucle-

ation and growth of blisters in detail. In light of this and to clarify the cause of scale blisters, the present paper investigates the processes of their nucleation and growth.

## 2. Experimental

Specimen sheets, 30×30×4 mm<sup>3</sup> in size, of steel having the chemical composition given in **Table 1** were prepared, and the surfaces were ground. They were then heated to predetermined temperatures in an infrared furnace under the conditions given in **Table 2**. In all the experiments, the specimens were heated to the respective oxidizing temperatures in a nitrogen atmosphere, held there for 1 h,

**Table 1** Chemical composition of specimens (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	Atmosphere and time of oxidation
A	950 °C	Air × 120 s
B	1000 °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	1000 °C	(1%O <sub>2</sub> +31%H <sub>2</sub> O+68%N <sub>2</sub> ) × 30 s → Air × 17 s

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and then the atmosphere in the furnace was replaced with different oxidizing atmospheres to oxidize the specimens; the atmospheric gases were supplied into the furnace at a rate of 10 NL/min. After oxidation, the sheets were cooled in a nitrogen atmosphere, except in condition E where the gas composition inside the blisters was analyzed and the cooling was done in an atmosphere of He. The test pieces were continuously observed by a camcorder during the oxidation to record the formation and growth of scale blisters.

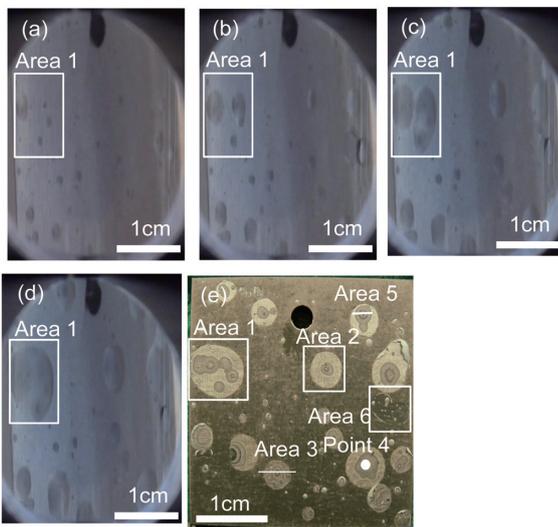
The surface appearances of the samples after the oxidations were observed. In addition, the blisters of condition A were observed at sections using an optical and a scanning electron microscope (SEM). Furthermore, to analyze the chemical composition of the scale, the element depth profiles were measured by glow discharge optical emission spectroscopy (GD-OES).

In condition E, where the gas composition inside the blisters was measured, the scale surfaces were coated with an epoxy resin for vacuum use after cooling. After the resin solidified, the blisters were drilled in a vacuum chamber and the mass-to-charge ratio (mass number, in short) of the gas released was analyzed using a mass spectrometer.<sup>8)</sup>

**3. Results**

**3.1 Condition A**

**Figure 1** shows the change in the appearance of a test piece during oxidation in a normal atmosphere at 950°C (condition A). Blisters begin to show roughly 14 s after the change to the oxidizing atmosphere (Fig. 1 (a)), and then grow gradually at 19 s. Some coalesce together (Fig. 1 (b)) while others show little growth (Fig. 1 (c)), and blister growth mostly comes to a halt at 29 s (Fig. 1 (d)). The appearance of the test piece after cooling and removal of the blistered scale (Fig. 1 (e)) matches with its appearance during the



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

heating. The position where a blister begins to form roughly corresponds to its center after growth. In Fig. 1 (a), five blisters are found to originate in Area 1. These blisters grow and coalesce into one (Fig. 1 (b) to (d)).

**Figure 2** is a magnified image of Area 2 in Fig. 1 (e). The position where the blister originated is in black, and the area into which it grew and expanded is not oxidized and has a metallic appearance. As seen here, the initial formation of a blister and its growth constitute stages altogether different from each other. It is also clear that direct observation of specimens during heating enables us to understand the nucleation and growth behavior of blistering.

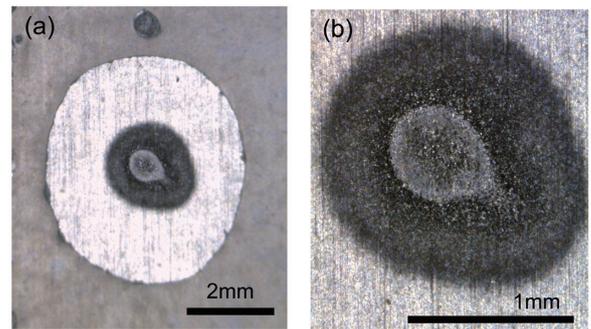
**Figure 3** shows a cross-section image of the initial forming point of the blister in Area 3 in Fig. 1 (e) through an optical microscope. The scale covers the black area at the blister center but not the surrounding area. The scale covering the black area is thick at the center and thinner towards the periphery.

**Figure 4** (a) is an analysis result of the depth profile of the black scale at the blister center by GD-OES, while Fig. 4 (b) is another of a normal part without blisters. In the black area (Fig. 4 (a)), since the scale thickness of analyzed area changed gradually, the elements that were concentrated at the scale/metal interface were detected in a wide range in the depth direction. Mn is found in the black scale layer, Si concentrates at the interface, and C distributes in the base metal. There is no significant difference from the normal portion (Fig. 4 (b)).

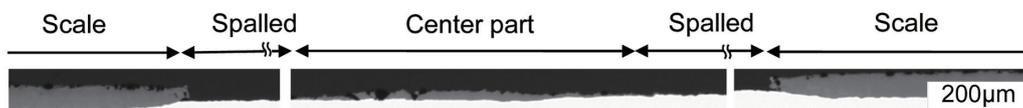
**Figure 5** shows an SEM image of a cross-section of the black scale inside the blister in Area 5 of Fig. 1 (e). No precipitates are found in the scale, the structure of which is homogeneous. Energy dispersive X-ray spectroscopy (EDX) was applied to points A, B and C in Fig. 5, and the results are given in **Table 3**. At the scale/metal interface, O, Fe and Si are detected, which seems to indicate that fayalite (Fe<sub>2</sub>SiO<sub>4</sub>) is precipitated there. The scale inside blisters analyzed here exhibits no structures which would be considered unusual for steel containing Si.

**3.2 Condition B**

**Figure 6** shows the change in the appearance of a test piece during heating in a normal atmosphere at 1000°C (condition B). Blisters begin to form at 17 s after the start of oxidation (part (a)), and



**Fig. 2** Blister in Area 2 of Fig. 1 (a) Whole blister, (b) Center part (magnified)



**Fig. 3** Optical microscope image at cross-section of blister in Area 3 of Fig. 1

their size is larger than that of the blisters that formed at 950°C (condition A). The blisters then grow a little, and some of them coalesce together (Fig. 6(b) and (c)). The blister growth stops after 29 s of oxidation (part (d)). Comparing the blister growth stages (Fig. 6 (a) to (d)) with the surface appearance after the removal of flaked-off scale (Fig. 6(e)), it is noted that the area corresponding to the initial formation of a blister is oxidized to form a black material, and the surrounding area to which the blister expanded has a metallic appearance, which is the same as in the case of heating at 950°C (condition A).

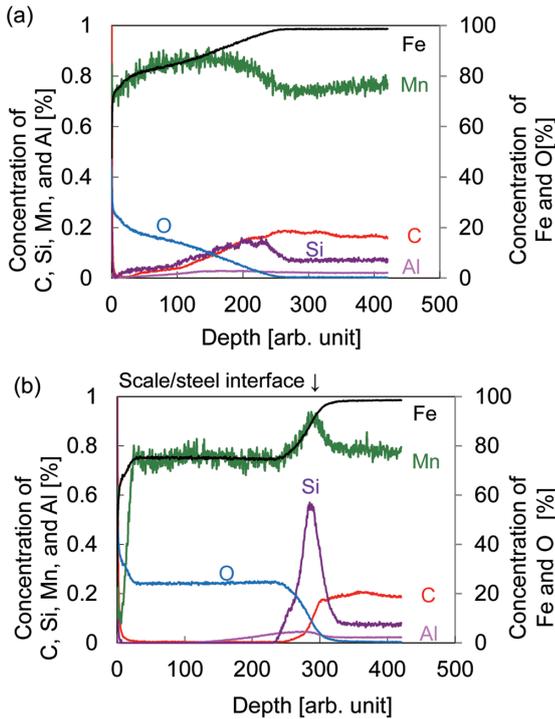


Fig. 4 GD-OES measurements (in depth direction) at Point 4 of Fig. 1 (e) (a) Blister center, (b) Normal scale

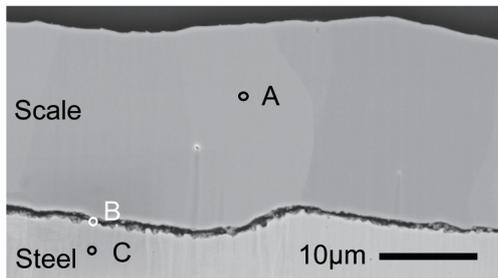


Fig. 5 SEM image of scale cross-section formed at center of blister in Area 5 of Fig. 1

Table 3 EDX results at points in Fig. 5

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

### 3.3 Condition C

Figure 7 shows photographs of the appearance of a test piece heated in a normal atmosphere at 950°C for 12 s only (condition C) for the purpose of observing the state of blisters soon after their initial formation. The area from which a piece of blistered scale was removed has a metallic appearance, and no scale is found beneath the blistered scale; this is confirmed also through cross-section observation. This result indicates that blisters form and grow in the following manner: when a blister initially forms, scale is delaminated at the scale/metal interface, then the steel is oxidized at the detached-off surface, and, while scale continues to detach off the steel as the blister grows, the steel is not oxidized. This seems to lead to an assumption that the initial formation of a blister and its growth advance by two different mechanisms.

### 3.4 Condition D

Figure 8 shows the appearance of a specimen sheet after heating at 950°C in an artificial atmosphere containing water vapor and 21% oxygen (condition D); the heating condition is the same as that of condition A except for the added water vapor. The processes of blister formation and growth are similar to those under condition A except that, when a blistered scale was removed, the area around the center is also found to be oxidized.

### 3.5 Condition E

Figure 9 shows a photo of a specimen surface in an initial stage of blister formation after oxidation for only 17 s (condition E), and

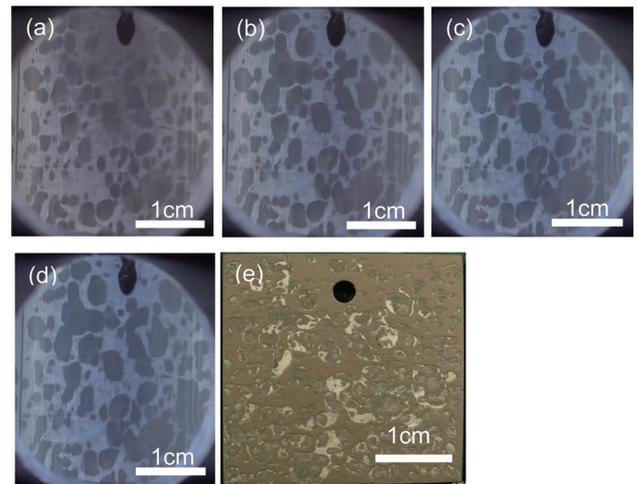


Fig. 6 Surface appearances during and after oxidation at 1000°C under condition B (a) 17s, (b) 21s, (c) 25s, (d) 29s, (e) After oxidation

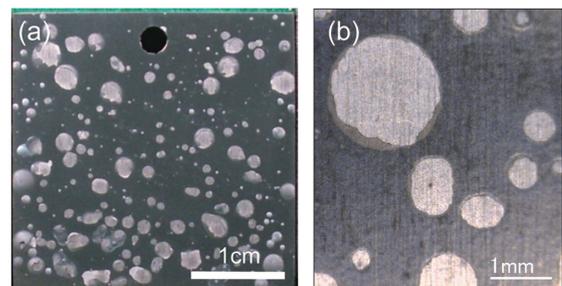


Fig. 7 Specimen oxidized for 12s at 950°C under condition C (a) Whole surface, (b) Partial magnification

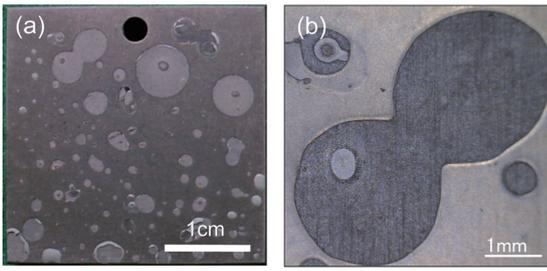


Fig. 8 Specimen oxidized for 120s at 950°C under condition D (with water vapor)  
(a) Whole surface, (b) Partial magnification

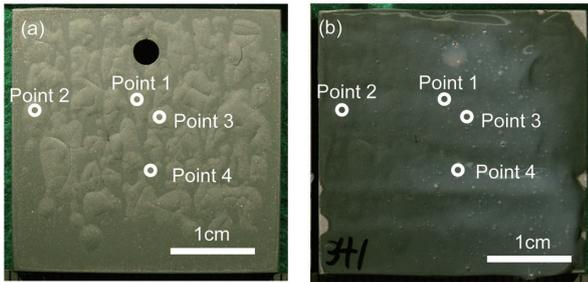


Fig. 9 Specimen oxidized under condition E for gas analysis  
(a) After oxidation, (b) After resin coating

another of the same after coating with resin. The gas composition was analyzed at four points on the blisters, and significant gasses were obtained at points 2 and 3; at the other two points, the gases contained a substance with a mass number of 32, presumably oxygen, by roughly 10%, and it was suspected that the outside atmosphere had entered inside them.

Figure 10 shows the results of the mass spectrometry of gas inside the blister at point 2, obtained by drilling. Fig. 10(a) shows the background just before the blister gas was released, and Fig. 10(b) shows the measured spectra at the time of gas release by drilling. It can be seen from Fig. 10(a) and (b) that the significant mass numbers detected during the gas release are 12, 14, 15, 18, 28, 29, 43, and 44. The intensity of mass number 18 increased as the drill went deeper; it was most probably water from the resin. Mass number 28 was present in high abundance; it was presumed to be due to the presence of either CO or N<sub>2</sub>. The presence of mass numbers 12 and 14, which correspond to the atomic masses of carbon and nitrogen, respectively, in significant intensities gives further evidence for the presence of CO and N<sub>2</sub>. Mass number 44 is presumably due to CO<sub>2</sub>. Mass numbers 15, 29, and 43, however, are not attributable to any of the gas components involved in the test, and they are probably due to some hydrocarbon gases originating from the resin.

Figure 11 shows the results of mass spectrometry at point 3: background (Fig. 11(a)) and during gas release (Fig. 11(b)). In comparison with the background, the significant mass numbers detected during the gas release are 12, 14, 15, 18, 28, 29, 43, and 44, which are the same as those found at point 2.

Figure 12 shows the change in the detection intensities of mass numbers 12, 14, 18, 28 and 44, which correspond to substances presumably related to blister formation. At point 2 of Fig. 9 the intensities of mass numbers 12, 14, 28, and 44 increased when the gas was released, while 18 remained virtually unchanged from the background (see Fig. 12(a)). This is also true at point 3 (see Fig. 12(b)).

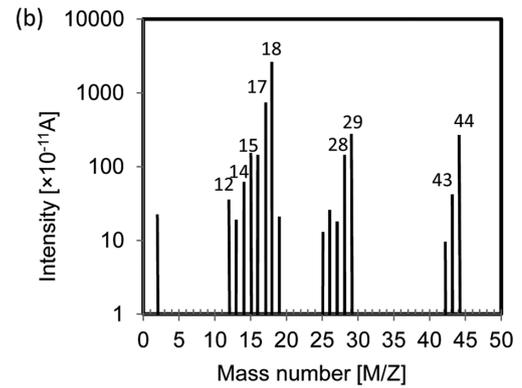
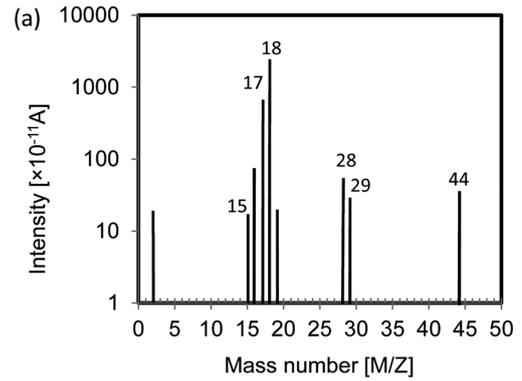


Fig. 10 Gas analysis results at Point 2 in Fig.9 by mass spectroscopy  
(a) Background, (b) At gas release

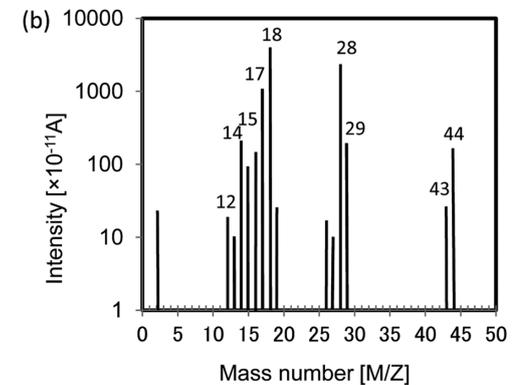
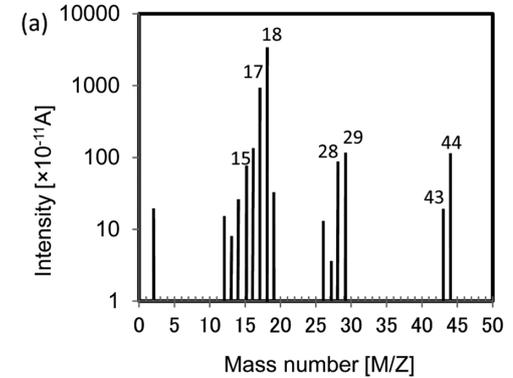


Fig. 11 Gas analysis results at Point 3 in Fig.9 by mass spectroscopy  
(a) Background, (b) At gas release

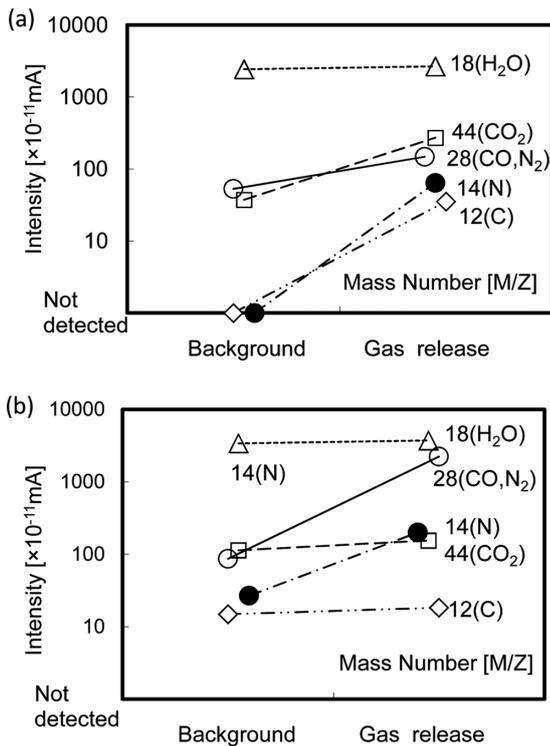


Fig. 12 Comparison of gas spectroscopy between background and gas release  
(a) Point 2 in Fig. 9, (b) Point 3 in Fig. 9

This indicates that there is CO, CO<sub>2</sub>, and N<sub>2</sub> inside scale blisters at the initial stage of their formation.

#### 4. Discussion

Figure 13 schematically illustrates the stages of scale blister growth understood from the test results of conditions A and C, where the specimens were heated in a normal atmosphere at 950°C. Rolls<sup>2)</sup> reported that scale blistering goes through stages of nucleation, coalescence, shrinkage, and collapse. These stages are discussed below based on the test results in Section 3.

##### 4.1 Nucleation

The nucleation of blisters begins within a short period after the start of oxidation. It has been confirmed through the present test that CO, CO<sub>2</sub> and N<sub>2</sub> are inside the blisters at this initial stage (see Fig. 12). Blistering is presumed to result from the growth stress due to scale formation,<sup>1-4)</sup> and gas emission from the base metal.<sup>1, 2, 5, 6)</sup> This indicates that gas emission is involved in blistering, but further investigation is necessary to verify it.

As far as has been observed at steel surfaces before oxidation, there is nothing specific to the position of blister nucleation. Ikeda<sup>6)</sup> pointed out that non-metallic inclusions of alumina were involved at the initial point of blister formation. Despite the elementary distribution analysis by GD-OES at positions beneath blisters where they initially formed (see Fig. 4), and the structure observation there through an SEM (see Fig. 5 and Table 3) in the present study, no such peculiar structure which could possibly lead to blister formation has been found. On the other hand, Melfo has reported that it is possible to observe phase transformation during oxidation by in-situ observation under surface magnification.<sup>9)</sup> Such a method will be effective at examining the points of nucleation of blisters.

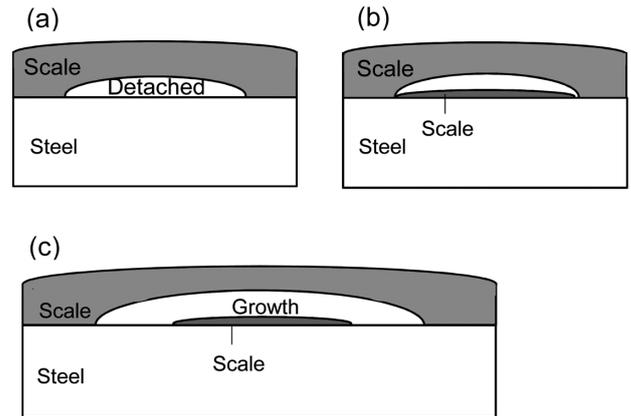


Fig. 13 Schematic illustration of blister nucleation and growth  
(a) Nucleation, (b) Oxidation inside blister, (c) Growth

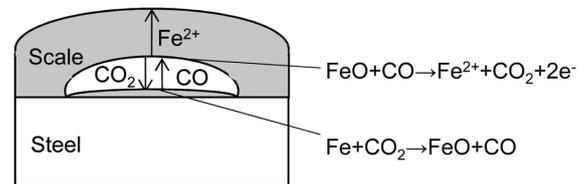


Fig. 14 Dissociative process within blister  
Process of steel surface oxidation inside blister by this process

At the transition from blister nucleation to growth, the base metal surface is oxidized beneath the blistered scale (see Fig. 13 (c)); this oxidation reaction advances within a few seconds. Since steel is not oxidized at the nucleation stage (see Fig. 7), it is unlikely that an oxidizing gas from the atmosphere enters the insides of blisters. The oxygen partial pressure inside the blisters is the value that equilibrates between wustite and iron. Supposing that there is oxygen gas inside the blister, its partial pressure is presumed to be  $2 \times 10^{-17}$  atm, approximately; such a low partial pressure of oxygen cannot account for steel oxidation within a short period.<sup>10)</sup>

It is therefore necessary to assume that there is an oxidation mechanism such as a dissociative process<sup>10, 11)</sup> whereby detached scale oxidizes steel through the blister inside gas. Figure 14 illustrates such a dissociative process. When scale is separated from the base metal and there is a gaseous mixture of CO-CO<sub>2</sub> or H<sub>2</sub>-H<sub>2</sub>O in the void in between, the scale releases oxygen which oxidizes CO into CO<sub>2</sub>, and this CO<sub>2</sub> is then capable of oxidizing the base metal. As CO and CO<sub>2</sub> have been found by the gas analysis after the blister nucleation stage, it is reasonable to assume that a dissociative process by these gases is involved in the oxidation of the base metal beneath the blistered scale.

The scale on the base metal surface inside a blister gradually becomes thinner when moving from the center towards the periphery (see Fig. 3). While the steel surface in a blister is oxidized at an early stage of blistering through the mentioned dissociative process involving CO-CO<sub>2</sub>, the oxidation does not advance further during the following blister growth. This makes it necessary to assume a mechanism whereby CO and CO<sub>2</sub> gradually disappear from inside the blister.

It is entirely conceivable that gas inside the blister escapes through the blistered scale. This assumption is viable if the crust is permeable to gas, but if so, the atmosphere can also get into the in-

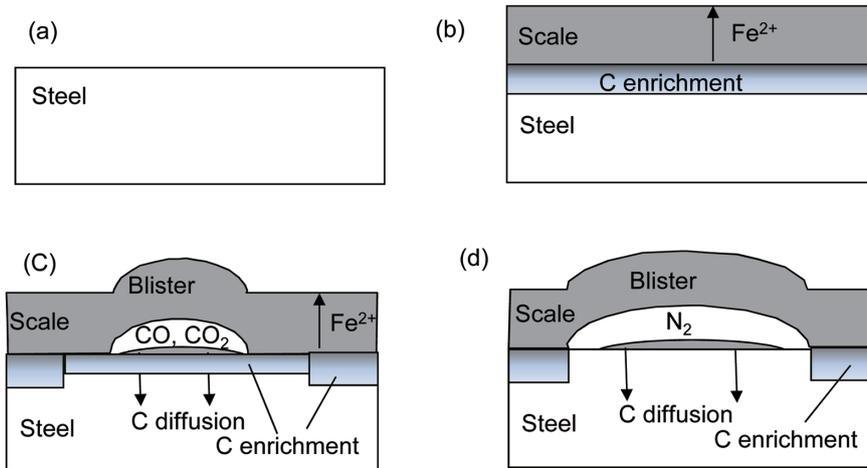


Fig. 15 Assumed mechanism of blister nucleation

(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

side, which is contradictory to the test result that the steel is not oxidized in the insner peripheral area.

Another explanation is that CO and CO<sub>2</sub> gradually disappear from the inside of the blister over time (see Fig. 15). There is a report to the effect that when scale is permeable to CO, the steel surface is decarburized during its oxidation.<sup>12)</sup> As stated above, however, scale is considered to be only slightly permeable to gas at the initial stages of blister formation. It has been known that in such a case C is enriched in steel near the scale/metal interface, as illustrated in Fig. 15 (b).<sup>12, 13)</sup> In this situation, the activity of C in steel near the interface increases, the reactions of Equations (1) and (2) below advance towards the right-hand side at the interface, and the partial pressures of CO and CO<sub>2</sub> there increase. Supposing that CO and CO<sub>2</sub> are the cause of blister formation, a blister is considered to form when their pressures surpass the critical pressure to separate scale from the metal (see Fig. 15 (c)).

Since steel oxidation stops at the part where scale is detached from the metal, forming a blister, C does not enrich there any longer, and rather the C that has concentrated there begins to diffuse to deeper regions of steel (see Fig. 15 (c)), which gradually lowers the activity of C in the region beneath the blister. As a consequence, the reactions of Equations (1) and (2) begin to reverse (go towards the left-hand side), and the steel is oxidized. Nitrogen, which is not involved in these reactions, is presumed to remain in the blister; this accounts for the steel not being oxidized during the blister growth (see Fig. 15 (d)).



#### 4.2 Conditions for nucleation

Next, let us study the condition for the nucleation owing to which a blister initially forms in consideration of the adhesive force, the deformability of scale, and the gas pressure at the scale/metal interface.

First, the adhesive force of scale at high temperature is estimated. The authors conducted a series of test to measure the load for separating scale from the metal. The measurement method described below is identical to that of Kushida et al.<sup>14)</sup> two specimen rods, 10 mm in diameter each, were placed one over the other at a vertical distance of 10 mm; the specimen sets were heated in a nitrogen atmosphere to the oxidizing temperature; then air was introduced to

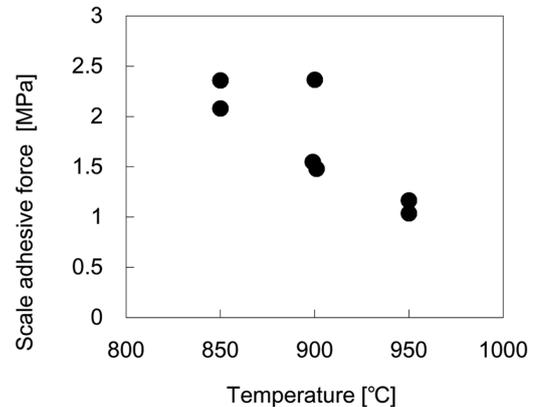


Fig. 16 Measured scale adhesive force

the test chamber to oxidize them; the upper rod was lowered and pressed to the other at a certain pressure for a certain period; after the scale layers were attached to each other firmly, the chamber atmosphere was switched to nitrogen, the specimen sets were pulled apart, and the change in the tensile force was measured. The test was regarded valid only when the scale was completely detached at the scale/metal interface, and the maximum load during the separation was defined as the scale adhesive force.

Figure 16 shows the results of the measurement. Blisters formed at 1000°C or above, and therefore the measurement was impossible. The graph shows that the adhesive force of scale tends to decrease as the heating temperature becomes higher; similar results have been reported by Krzyzanowski et al.<sup>15)</sup> The readings of the adhesive force ranged from 1 to 2 MPa, which were considerably lower than those reported by Kushida et al.<sup>14)</sup>

Next, the deformability of scale is examined. The main component of scale that forms on hot steel surfaces is FeO. There have been several reports on its yield strength.<sup>16-18)</sup> According to the study of Hidaka et al.,<sup>18)</sup> the yield strength is in the range of 1 to 4 MPa in a temperature range of 900 to 1000°C. Figure 17 shows the yield strength; the graph also shows measurement results of scale adhesive force, which is smaller than its yield stress. This indicates that blister formation depends on the adhesive force of scale.

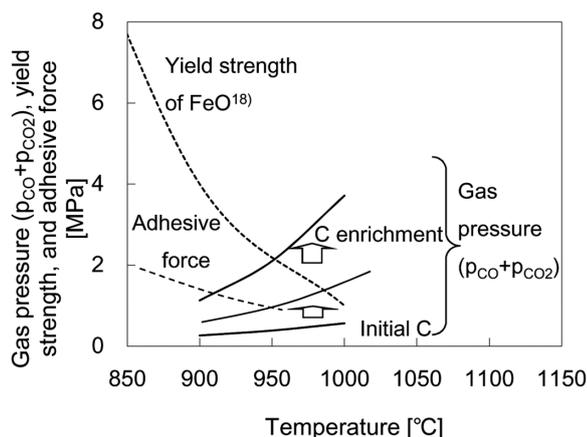


Fig. 17 Gas pressure of CO and CO<sub>2</sub> equilibrated carbon in  $\gamma$ -steel at the scale/steel interface including yield strength of FeO and scale adhesive force

In addition, the pressure of gas formation at the scale/metal interface is studied. As Equations (1) and (2) indicate, the partial pressures of CO and CO<sub>2</sub> at the interface are considered to be balanced with the activity of C at the steel surface. As has been stated above, when scale forms, C is enriched at the steel surface and its activity increases, and, as a result, the partial pressures of CO and CO<sub>2</sub> increase. Considering the activity of C in  $\gamma$ -iron,<sup>19)</sup> when scale forms at 950°C and C enriches at the scale/steel interface to approximately 0.5 mass%, the total partial pressure of CO and CO<sub>2</sub> will be 1.5 MPa, equal to the adhesive force of scale. As is seen in Fig. 17, blister nucleation is presumed to take place when the gas pressure at the scale/steel interface increases to be equal to the adhesive force of scale. Here, besides the pressures of CO and CO<sub>2</sub>, it is necessary to take the pressure of nitrogen gas into consideration. In the GD-OES analysis given in Fig. 4, however, no significant C enrichment was observed at the scale/steel interface; this is possibly because C diffused during cooling, and further studies are required regarding the formation of the gases.

#### 4.3 Growth

Blisters grow through gradual swelling. During the process of blister growth, the steel surface inside it is not oxidized, and it remains not oxidized after the blister growth process is finished. From what has been described herein, the gas inside the blister is considered to be N<sub>2</sub>. The growth stress of scale,<sup>1-4)</sup> or other mechanisms such as nitrogen release,<sup>2)</sup> are presumed to act as the driving force for blister growth. The N<sub>2</sub> in the inside of the blister presumably originates from steel nitriding during holding in the nitrogen atmosphere before the oxidation, and is related to blister growth.<sup>20)</sup>

The steel surface inside blisters may be oxidized in growth stages if a dissociative process such as the one mentioned earlier (Fig. 14) is provided, when the oxidizing atmosphere contains water vapor (condition D), and hydrogen can enter inside blisters through the blistered scale.<sup>10,11)</sup> This is considered to be the reason for the steel oxidation during blister growth (Fig. 8).

#### 4.4 Breakage and collapse

Blisters were seen to break and collapse under condition A. This is observed at 18 to 19 s after the start of oxidizing. **Figure 18** shows the steps: the blistered scale on the right-hand side of the view broke (Fig. 18(a)); the blister collapsed rapidly (Fig. 18(b)); soon thereafter, the scale surface near the breakage turned dark (Fig. 18(c)); then gradually returned to the color before breakage (Fig. 18

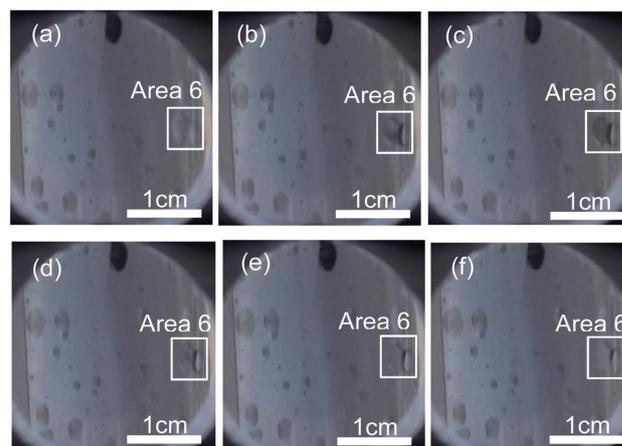


Fig. 18 Blister collapse process in Condition A  
(a) -0.03 s, (b) 0.00 s: blister collapse, (c) +0.03 s, (d) +0.36 s, (e) +0.73 s, (f) +1.00 s

(d), (e) and (f)). This is suspected to result from gas release from inside the blister, as the partial pressure of oxygen is so low inside a blister that wustite and steel exist in an equilibrium, and the scale surface is reduced only temporarily after the gas release.

## 5. Conclusions

The present study focused on the nucleation and growth of blisters that formed when steel is oxidized at high temperatures, and the following conclusions have been obtained:

- 1) Scale blisters follow the steps of nucleation and growth.
- 2) At the initial blister formation, scale detaches from the interface with steel. At this stage, the gas inside the blisters consists of CO, CO<sub>2</sub>, and N<sub>2</sub>.
- 3) The steel surface inside a blister is oxidized during the transition from the nucleation to the growth stage.
- 4) During blister growth, the scale detaches off the interface with the steel, but the steel surface is not oxidized inside the blister.

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