Effect of Nitrogen on Blister Growth Process during High Temperature Oxidation of Steel

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Blistering occurs when oxide scale swells during oxidation at high temperatures. Blistered scale causes surface defects when rolled. The present study investigated the effect of nitrogen on blister growth when steel is oxidized at high temperatures, and drew the following conclusions. Atmospheric conditions before oxidation affect blister growth. Blisters nucleate but do not grow, when a steel sample is held in Ar gas or in vacuum before oxidation. Blisters inflate when a steel sample is held in N2 gas before oxidation. The gas inside the grown blisters is mainly N2 gas. The steel surface is nitrided in N2 gas at high temperatures. It is deduced that the steel surface is nitrided before oxidation, and the nitrogen component causes blister growth upon its release as N2 gas at the scale/steel interface.

KEY WORDS: blister; nitrogen; growth; nitriding; gas generation; scale; oxidation.

1. Introduction

When steel is oxidized, the oxide scale happens to swell at high temperatures. This is known as blistering phenomenon. These blisters cause surface defects on the steel during the hot-rolling process. It is important to understand the mechanism of blistering in order to prevent such surface defects. Mainly two mechanisms have been proposed for blister formation. One is the gas generation under the oxide scale.1,2) The other is compressive stress initiation during the oxide scale formation.3–5) The blistering phenomenon has several stages of nucleation, growth, coalescence, shrinkage, and collapse.6,7) For the point of blister prevention, most research work is associated with nucleation conditions and mechanism.2,4,5) However, this is not enough to understand whole blistering mechanisms. For example, little work has been done concerning effects of gas compositions on the blistering behavior. Griffith presented several results.3) Oxidation in pure oxygen does not cause blistering. He also reveals that blistering occurs in the atmosphere with nitrogen concentration exceeded 30%. In this work effect of nitrogen gas before oxidation on the blister growth process is focused to be investigated in detail.

2. Experimental

Steel with the chemical composition shown in Table 1 was used for the experiments. Specimens were cut into rectangular shapes with dimensions 30×30×4 [mm].

Two types of oxidation experiments were performed. One is that samples were oxidized during cooling in the air. An electric furnace was used for the experiments. The samples were heated to 1100°C in non-oxidizing atmosphere and held for 3600 seconds at the temperature. Oxidations were started when the samples were taken out from the furnace. The non-oxidizing conditions were nitrogen (N2), argon (Ar), and vacuum.

The other type of experiment is that the samples were oxidized in isothermal conditions. The samples were first heated up to the oxidation temperature in a non-oxidizing atmosphere for 3600 seconds at the same temperature. The non-oxidizing gases were either nitrogen (N2) or argon (Ar). Oxidation was initiated by changing the flow-though gas from the non-oxidizing gas to air. These experimental conditions are indicated in Table 2. The surface of the samples was observed and recorded using a camcorder during oxidation. The surface appearance after oxidation was also observed.

The purpose of Condition F is to measure the gas composition within the blisters after the blister growth. The oxidation time was 41 seconds. The sample was cooled in helium gas in order to prevent the entry of nitrogen gas into the blisters. The surface of the sample was coated with an epoxy

| Table 1. Chemical compositions of the sample [mass%]. |
|---------|-----------|----|-----|-----|----|-----|
| C       | Si        | Mn | P   | S   | Al | N   |
| 0.16    | 0.071     | 0.7 | 0.008 | 0.008 | 0.018 | 0.0032 |

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After solidifying, the coated surface was drilled in a vacuum chamber. Upon drilling, the gases inside the blisters were released. The mass-to-charge ratios (mass numbers) of the released gases were analyzed by mass spectrometry. The measured spectra were compared to the background spectra. Here, the background is the mass spectra at the same position measured just before the gas is released by drilling.

3. Results

3.1. Condition A to C

The appearances of the specimens after the oxidations are shown in Fig. 1. The sample held in N$_2$ before oxidation has many blisters on the surface (Fig. 1(a)). The samples held in Ar and in vacuum before the oxidations have small number of blisters on the surfaces (Figs. 1(b) and 1(c)). These results imply non-oxidizing atmosphere before oxidation affects blistering behavior.

3.2. Condition D and E

In order to understand the effect of non oxidizing atmosphere, isothermal oxidation tests were conducted. The surface appearance after oxidation at 950°C in Condition D is shown in Fig. 2. The sample was held in N$_2$ atmosphere before the oxidation. Blister nucleates 14 seconds after oxidation starts (Fig. 2(a)). The blisters start to inflate at 18 seconds (Fig. 2(b)). The blister growth almost stops at 28 seconds (Fig. 2(d)). The sample appearance after removal of the swollen oxide scale (Fig. 2(e)) seems to correspond to the results of in-situ observation. The nucleating points of the blisters are mostly located in their centers. Figure 3 shows a magnified surface image at Area 1 in Fig. 2(e).

Table 2. Experimental conditions.

| No. | Temp. | Before oxidation | Oxidation | Cooling |
|-----|-------|------------------|-----------|---------|
| A   | 1 100°C | N$_2$×3 600 s  | Oxidized during cooling in the air |
| B   | 1 100°C | Ar×3 600 s      | Oxidized during cooling in the air |
| C   | 1 100°C | Vacuum×3 600 s  | Oxidized during cooling in the air |
| D   | 950°C  | N$_2$×3 600 s   | Air×120 s N$_2$ |
| E   | 950°C  | Ar×3 600 s      | Air×120 s N$_2$ |
| F   | 1 000°C | N$_2$×3 600 s   | (1%O$_2$+31%H$_2$O+68%.N$_2$)×300 s→Air×41 s He |

There are three nucleating points in Area 1 (Fig. 2(a)). The nucleating points are black where oxide scales have formed (Fig. 3(a)).

The condition E is for the condition to clarify the effect of as non oxidizing condition. The sample was held in Ar atmosphere before the oxidation. The surface appearance of the sample is shown in Fig. 4. Blisters start to initiate after 18 s oxidation (Fig. 4(a)). The blisters do not grow after that. The steel within the blisters is mostly black. It looks that the
blisters remain in the same state as the nucleation stage. Figure 5 is the pictures of the blister in Area 1 shown in Fig. 4(e). Most area within the blister is oxidized. These results indicate that a non-oxidizing atmosphere affects blister growth process.

### 3.3. Condition F

The sample appearance after oxidation in Condition F and that after coating by epoxy resin are shown in Fig. 6. The mass spectrometry measurements of the internal gases in blisters were conducted four times. The four drilled points are shown in the figure. Meaningful data was obtained by the measurements performed at Point 2 in Fig. 6.

The measured spectra at the point are shown in Fig. 7. The results of gas composition analysis at Point 2 in Fig. 6 by mass spectroscopy. (a) The background. (b) The gas release.

|   | H2O | N2  | O2  | Ar | CO2 |
|---|-----|-----|-----|----|-----|
|   | 2.1 | 95.8| 1.5 | 0.6| <0.1 |

**Table 3.** Gas compositions in a grown blister [%].

![Fig. 8. GD-OES measurements at the surface of the samples just after heating in a non-oxidizing atmosphere. (a) Heated in N2; (b) Heated in Ar.](image)

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The measured spectra at the point are shown in Fig. 7. The measured spectra at gas release (Fig. 7(b)) were compared to the background spectra (Fig. 7(a)), revealing meaningful mass numbers at the gas release peak of 14, 28, 29, 32, and 40. The detection of mass number 32 indicates that air intruded into the blister. The detected oxygen (O2) concentration is estimated at only about 1.5%. This means that the measured spectra are significant enough. Mass number 28 has increased compared to the background. Mass number 14, the proportion of N2, also increased, but mass number 12, the proportion of CO, was not detected. There are no ordinary gases that correspond to mass numbers 29 and 40, so these might indicate hydrocarbons released from the epoxy resin. The gas compositions measured by the analysis are shown in Table 3. These results indicate that N2 is the main component of the internal gas in the grown blisters.

### 4. Discussion

The nitrogen concentration profiles of the steel surfaces
were analyzed using GD-OES under pre-oxidation conditions. One was heated and held at 950°C for 3 600 s in N₂ gas, and the other was similarly treated in Ar gas. The results are shown in Fig. 8. Nitrogen (N) exists at about 200 ppm at a depth of more than 100 μm when held in nitrogen gas. On the other hand, nitrogen is not detected at a depth of more than 30 μm when held in Ar gas, although nitrogen is distributed near the surface. This indicates that the steel surface is nitrided in N₂ gas at high temperature. When steel is oxidized, alloying elements tend to enrich at the scale/steel interface because iron is consumed for the oxide scale formation. Nitrogen also enriches at the scale/steel interface. The nitrogen component in the steel surface is released as N₂ gas. It causes the blister to grow when the steel is oxidized.

The solubility of nitrogen in solid iron follows Sievert’s law. Its solubility in γ-steel is expressed by Eq. (1). The value at 950°C at a partial nitrogen pressure of 0.8 atm is 230 ppm. This is very close to the measured nitrogen concentration (Fig. 7(a)). This result indicates that the steel surface is nitrided up to its solubility limit.

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\log[\%N]/\sqrt{P_{N_2}} = \frac{450}{T} - 1.955 
\]

Next, the nitrogen gas pressure in blisters is discussed. Oxide scale grows to about 50 μm at 950°C for 40 s, which is the time that the blisters grow, by estimation of the parabolic constant of iron oxidation. The oxidized steel depth is 30 μm. Steel of that depth contains 2.8×10⁻⁷ mol/cm² as atomic nitrogen. It is assumed that the number of blister per unit area and the average blister volume is 3 per cm² and 5×10⁻⁴ cm³, respectively. These are the observed example for blisters. These lead that the potential nitrogen gas pressure of inner blisters is about 1 MPa. This value is close to that of scale adhesion force measured at the same temperature. This can explains nitrogen gas inflates blisters.

There is little work on the effect of nitrogen gas. Griffith mentioned the effects of nitrogen. He showed that the oxidation in pure O₂ does not cause blistering. When N₂ content in O₂–N₂ oxidizing atmosphere more than 30%, blistering occurs. These mean nitrogen in the oxidizing gas is necessary go blister formation.

The results of this work imply that nitrogen within the steel near the surface causes the blisters to inflate. Previous work reveals following findings concerning blistering nucleation and growth process. Internal gases within the blisters are CO, CO₂, and N₂ and the scale is detached at the scale/steel interface at nucleation stage. The steel surface inside blisters is oxidized while the stage changes nucleation to growth. The scale separates at the scale/steel interface and the separated steel surface is not oxidized at the growth stage. An optical microscope image of a cross section of the blistered scale at 950°C is shown in Fig. 9. The center of the blister is oxidized and the non oxidizing steel surface surrounds the oxide scale. From these results the assumed blistering mechanism is shown in Fig. 10. Before the oxidation, steel surface is nitrided by N₂ gas. When the steel surface is then oxidized, carbon and nitrogen are enriched near the scale/steel interface because iron is oxidized to iron oxide. These enrichments cause CO, CO₂, and N₂ gases to be generated beneath the scale. The pressure of these gases detaches the scale. After detachment, the steel surface is oxidized by the dissociative mechanism by CO–CO₂ inside the blisters. Once the scale is detached, oxidation terminates at that site. The enriched carbon starts to diffuse backward into the steel and any CO gas and CO₂ gas disappears. The enriched nitrogen continues to be released in gaseous form. The N₂ gas then inflates the blisters.

It is considered that nitriding of the steel surface always...
takes place. Hayashi et al.\textsuperscript{11)} reported that the steel surface under the oxide scale has aluminum nitride (AlN) when Fe–5%Al alloy is oxidized in air. This indicates that the steel surface is always nitrided at high temperatures even in the oxidation in air.

5. Conclusion

The present study investigated the effect of nitrogen on the growth behavior of blistering when steel is oxidized at high temperatures. The following conclusions are drawn.

1) The atmosphere conditions before oxidation affect blister growth.

2) Blisters nucleate but do not grow, when a steel sample is held in Ar or in vacuum before oxidation. Blisters inflate when a steel sample is held in N\textsubscript{2} gas before oxidation.

3) The gas component within developed blisters is mostly N\textsubscript{2}.

4) The steel surface is nitrided in N\textsubscript{2} gas at high temperatures.

5) It is deduced that the steel surface is nitrided before oxidation, and the nitrogen component causes blister growth by generating N\textsubscript{2} gas at the scale/steel interface.

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