Sodium-Water Reaction Characteristics with a Specimen and Target of Ferrite Steel by Water Leakage in Liquid Sodium

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Abstract: In this study, we observed and analyzed the corrosion phenomena of a specimen and target surface caused by the sodium-water reaction from a water (steam) leakage into sodium in a liquid sodium atmosphere. The leak site of the specimen was damaged by the wastage phenomena due to corrosion and erosion; a leak hole of the specimen extended from 150 μm to about 200 μm. The wastage or damage trace at the target surface was observed to have a diameter of ca. 1000 μm. The reopened shape of a specimen was circular and the size of this specimen surface was about 2 mm (diameter) on the sodium side. From the results of EPMA and SEM analysis, the damaged areas are found to be covered with complex compounds, such as (NaOH+Na2O)·FeOy and (NaCrO2+Na2CrO4), mixed with sodium oxides from the sodium-water reaction and Fe or Cr elements from the matrix of the tube material. The temperature of the target surface increased by about 70−80°C with an exothermic reaction, even when the leakage was small (15 mL).

Keywords: wastage, sodium-water reaction, liquid metal

Introduction

Sodium is an alkali metal that can exist in a liquid state at temperatures lower than 100°C. Therefore, sodium is used considerably in an LMFBR (Liquid Metal Fast Breeder Reactor) as a coolant source because it has many advantages, such as superior thermal conductivity, high boiling point, low viscosity at high temperature, maintaining its liquid state in various ranges of temperatures, and a good compatibility with the nuclear reactor’s structural material [1,2].

However, sodium causes a chemical reaction rapidly with water (steam), which is a heat transfer medium in the IHTS (Intermediate Heat Transfer System) of nuclear reactors, and this reaction produces a high amount of heat, corrosion products, such as sodium oxide, sodium hydroxide, and sodium peroxide, and a massive quantity of hydrogen gas. This reaction is a fatal shortcoming that can add danger by raising the pressure and temperature in the heat transfer system [3-5].

An LMFBR is designed by dividing it into the primary and secondary systems including the steam generator, as are other types of nuclear reactors, such as the LWR (Light Water Reactor) or HWR (Heavy Water Reactor).

In the steam generator and the intermediate heat transfer system, heat exchange occurs between the water (steam) at high pressure, about 150 kg/cm², and the sodium maintained by the low pressure of the atmosphere.

If the high-pressure water leaks into the liquid sodium kept at a low pressure, damage to the pin-hole, breach, and welding defects in the heat transfer tube material may occur, and there are rapid chemical reactions such as the following, in the water leaking region [6,7]:

\[
Na + H_2O \rightleftharpoons NaOH + \frac{1}{2} H_2
\]

\[
2Na + H_2O \rightleftharpoons Na_2O + H_2
\]

The heat transfer tube material may become damaged by the heat from the reactions, the hydrogen gases, and the corrosion products, and the erosion phenomenon caused by water leakage resulting from the sodium-water reaction. It progresses continuously until the water leakage
stops. This material damage is the so-called “wastage” phenomenon. In this case, a sudden increase in water leakage occurs and the whole nuclear system could develop a dangerous condition from the expansion of the damaged region [8,9].

In this study, to grasp the wastage and reaction characteristics of the phenomena in the leakage region of the heat transfer tube material, arising from the sodium-water reaction by water leakage, with respect to the safety of the LMFBR steam generator, small water leakage experiments were carried out in a liquid sodium atmosphere.

Leak test specimens and a target were manufactured using 5Cr-1Mo and 2.25Cr-1Mo steel materials. Also, from these water leakage experiments, we studied the corrosion phenomena at the surfaces of the test specimens and target material, leakage characteristics by the sealing and the reopening phenomena of the water leakage path, and the temperature rise phenomena at the target surface from the exothermic heat by the sodium-water reaction.

Experimental

The sodium-water (steam) reaction is violent, produces hydrogen gas, and emits a massive amount of heat. Therefore, to install an experimental apparatus, special attention to the safety of the system must be given. For this purpose, a safety valve that opened automatically to prevent an explosion of hydrogen gas as a result of the pressure increase, was used, and heat tracing and insulation of the piping was needed for the prevention of sodium solidification. Therefore, a lot of expense and difficulties were encountered in the manufacture of the small experimental apparatus.

The experimental apparatus is shown in Figure 1. The materials of the test specimen and target used in the water leakage experiments were 5Cr-1Mo and 2.25Cr-1Mo steels, and the surface of the materials were mapped.

According to the data analysis, water leakage accidents in liquid-metal fast breeder reactor steam generators are known to arise from defects in the tube material, such as pin-holes formed during the manufacturing process or cracks in the tube welding lines.

Two types of water leakage test materials, a specimen and a target, were manufactured to simulate these phenomena. The width, length, and thickness of the specimen were 10, 10, and 3.5 mm, respectively. After making a hole (150-μm diameter) in the center of a specimen using an arc discharge, and then pressing both sides with a 9 ton/cm² pressure, the experiments were undertaken.

The sodium-water (steam) reaction characteristics were observed by the water leakage through the crack of the test specimen into a liquid sodium atmosphere. The surface corrosion phenomenon of a test specimen and the temperature rise at a target surface were also observed. The test specimen used for this experiment has a circular leakage hole, but it was not pressed, and the size is the same as described above. The target material was installed at the front of a water leakage test specimen in a vessel. Thermocouples were used for the measurement of the temperature rise caused by the sodium-water (steam) reaction and they were attached at the back of the target material. The distance between the leak point of a test specimen and the target surface was ca. 20 times that of the leakage hole diameter.

Table 1 shows the properties of the material used in the

<table>
<thead>
<tr>
<th>Elements</th>
<th>2.25Cr-1Mo Steel</th>
<th>5Cr-1Mo Steel</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>0.13</td>
<td>0.32-0.42</td>
</tr>
<tr>
<td>Si</td>
<td>0.37</td>
<td>0.18-1.20</td>
</tr>
<tr>
<td>Mn</td>
<td>0.45</td>
<td>&lt; 0.5</td>
</tr>
<tr>
<td>Mo</td>
<td>0.99</td>
<td>1.00-1.50</td>
</tr>
<tr>
<td>C</td>
<td>2.33</td>
<td>Cr</td>
</tr>
<tr>
<td>Si</td>
<td>0.005</td>
<td>S</td>
</tr>
<tr>
<td>Mn</td>
<td>0.011</td>
<td>&lt; 0.5</td>
</tr>
<tr>
<td>Mo</td>
<td>-</td>
<td>V</td>
</tr>
<tr>
<td></td>
<td></td>
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<td></td>
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<td>Cr</td>
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<td>S</td>
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<td></td>
<td>P</td>
</tr>
<tr>
<td></td>
<td></td>
<td>V</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.80-1.20</td>
</tr>
</tbody>
</table>
Results and Discussion

Corrosion in Reacting Site

When water leakage occurred from the crack of the test specimen, at first the temperature increased by the exothermic heat generated by the sodium-water (steam) reaction at the sodium and water (steam) contact area. The self-wastage phenomenon then occurs by corrosion and erosion from the sodium-water reaction products. The surrounding edges of the leakage path of the material were forecasted to form a halo (deterioration phenomenon caused by the heat of a sodium-water reaction at the leakage path surrounding) [10].

The water (steam), which was heated distilled water, leaked into the liquid sodium through the cracked leakage path of the test specimen made of 5Cr-1Mo steel. The surface of the test specimen was observed using a metallographic microscope, as shown in Figure 2.

The halo phenomenon (round shape) occurred at the surrounding edges of the leakage path of the test specimen. This observation means that the sodium-water reaction occurred in the region where the water (steam) leaked into the liquid sodium through the crack, and the surface of the material was damaged around the leakage path by the heat of the reaction.

On the other hand, whether the water (steam) actually leaked or not was confirmed by observing the leakage path surroundings of a test specimen, using SEM. As for the test result shown in Figure 3, sodium oxide compounds were formed by the sodium-water reaction products at the leakage path surface of a test specimen on the sodium side, which means that a micro or small amount of water at a high temperature and pressure leaked along the leakage path. This phenomenon is similar to that observed in the early experiments conducted by Greene, but those results did not presented in detail with the damage phenomenon and the halo size [11]. Therefore in this study, the results are not compared with those of Greene.

Also, the corrosion phenomenon of a test specimen caused by the sodium-water reaction, owing to the water leakage, was confirmed by analyzing its surface using the EPMA (Figure 4). This figure shows the result of the elemental analysis at each point of the five divided surfaces of the test specimen.

In this Figure, the kinetic energy peaks carbon, oxygen, and iron elements appear at ca. 300, 510, and 680 – 700 eV, respectively. The peak changes of these elements were much broader than those of the other materials, such as Cr, Mo, Ni and V.

This observation may be because the surface corrosion proceeded at the sodium side of the test specimen. Additionally, the Ni and Co peaks appeared at ca. 800 and 700 eV for every minute, respectively, without a big change of the measuring values.

The compositional changes of each element in the test specimen surface, before and after the experiments, were analyzed to confirm the occurrence of the corrosion phenomena. Table 2 shows the compositional changes of each element of a test specimen made of 5Cr-1Mo steel, analyzed using EPMA.
Table 2. Composition Changes at Leak Sike of the Simulator after the Leak Experiment

<table>
<thead>
<tr>
<th>State</th>
<th>Weight %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cr</td>
</tr>
<tr>
<td>Before Experiment</td>
<td>Metal</td>
</tr>
<tr>
<td>After Experiment</td>
<td>Metal</td>
</tr>
<tr>
<td></td>
<td>Oxide</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Also, Na₂O, another reaction product, reacts with Fe again, in a second chain reaction:

\[ x \text{Fe} + y \text{Na}_2\text{O} \rightarrow \text{Fe}_x\text{O}_y + \text{Na} \]

The same reaction occurs continuously, and the iron (Fe) oxide compounds produced from these reactions react with the hydrogen gas:

\[ \text{Fe}_x\text{O}_y + \text{H}_2 \rightarrow \text{Fe} + \text{H}_2\text{O} \]

Finally, complex oxide compounds are deposited onto the reaction site:

\[ \text{NaOH} + \text{Fe}_x\text{O}_y \rightarrow \text{NaOH} \cdot \text{Fe}_x\text{O}_y \]
\[ \text{Na}_2\text{O} + \text{Fe}_x\text{O}_y \rightarrow \text{Na}_2\text{O} \cdot \text{Fe}_x\text{O}_y \]

The reactions of Cr and sodium oxide, which are not well-known, occur under the conditions of an equilibrium phase diagram in high-temperature liquid sodium:

\[ 2 \text{Na}_2\text{O} + \text{Cr} \rightarrow \text{NaCrO}_2 + 3\text{Na} \]
\[ 2 \text{NaCrO}_2 + 3/4 \text{O}_2 \rightarrow \text{Na}_2\text{CrO}_4 + 1/2 \text{Cr}_2\text{O}_3 \]

Conclusively, when the sodium-water reaction occurs by water leakage into the liquid sodium at a temperature higher than 400°C, the corrosion of the ferrite steel material proceeds as follows:
- formation of corrosive sodium oxide compounds: NaOH, Na₂O, and Na₂O₂
- the temperature at some local regions of the water leakage site rises upon the release of heat from the exothermic sodium-water reaction
- some elements contained in the matrix material of the test specimen react with the corrosive compounds above in some local regions at a high temperature
- the wastage continues from corrosion and erosion.

**Leak Path and Reopening**

If micro or small amounts of the water (steam) leak through the leakage path of the test specimen into the sodium, complex compounds of formula (Na₂O+NaOH) · Fe₃O₄ are produced at the leakage site (mainly in
the leakage path) by a reaction of the corrosive sodium-water reaction products and the Fe of the test specimen matrix material.

These solid compounds seal up the water (steam) leakage path of the test specimen, and this phenomenon is termed “self-plugging” [12,13]. The self-plugging advances the corrosion progress according to the circumferential condition of the leakage path, and the sealed leakage path is reopened by the re-dissolution of the solid deposits. If the amount of water leakage is very small, however, the leakage path might remain in a state of plugging [14].

To confirm this phenomenon may occur, water leakage experiments were carried out using the test specimen described in the preceding section. Figure 5 shows an SEM photograph of the sodium side of the surface of the test specimen after ca. 130 min of leakage time and under 20 kg/cm² of pressure. As shown in the Figure 5, the surroundings of the cracked specimen had re-opened with a leakage path to form a circular hole of ca. 2~3 mm. The halo’s size on the other side was ca. 4 mm, and this re-opened size had decreased to 2~3 mm. This phenomenon occurred because the leakage amount was very small in this case, but if the water leaks consecutively, the re-opened size would probably have increased to almost the halo size.

An SEM photograph, shown in Figure 6, displays the corrosion state by presenting the thickness of the test specimen after diamond saw cutting. The size of the crack before water leakage was ca. 70~80 µm. After the sodium-water reaction by water leakage, the re-opening on the sodium side had changed to ca. 2~3 mm in diameter, but the specimen had not penetrated perfectly. From this image, we observe that the corrosion is related to the water leakage rate and the leakage time.

Conclusively, if micro or small amounts of the water leak through the cracked leakage path of the test specimen, the water leakage propagates as follows:

- leakage path is sealed by the products of the sodium-water reaction;
- repetition of the re-dissolution and precipitation phenomena of the deposits occurs at the leak path;
- maintaining the incubation time is maintained;
- the corrosion develops until it reaches a perfect thickness of penetration;
the leakage path expands perfectly.

Temperature Profile

An experiment on the temperature rising effect during the sodium-water reaction was carried out by installing a test specimen and target as shown in Figure 7. Water (steam) was ejected to the target surface in the liquid sodium forming a jet through a test specimen leakage hole while maintaining the conditions of 250°C and 20 kg/cm². The experiment was carried out at a liquid sodium temperature of 400°C, a water leakage of 15 mL, and the sodium in a static state.

The temperature profile of the target surface by during sodium-water reaction is shown in Figure 8. The water (steam) leakage began when the temperature inside the reactor reached ca. 400°C. The temperature distribution of the target surface appears on the left-hand side of this picture. The leaked water quantity of 15 mL vaporized, and the volume was expanded by outside heating with an injector.

After 3–4 seconds of opening the water leakage valve, the temperature of the target surface in a local region increased rapidly from the heat of the sodium-water reaction. Because the water (steam) was injected at 250°C, the temperature of the target surface was predicted to fall
at the initial stage, but this phenomenon did not occur. The temperature at the point where the water (steam) contacted directly, rose to 70~80°C above the liquid sodium temperature, and this time remained at ca. 3~4 s. The temperature around the contact point rose to ca. 470°C. This phenomenon was maintained for ca. 20 s after closing the leakage valve completely, and the sodium temperature inside the reaction vessel increased slightly.

In Figure 9, the shape of the target surface corroded by the water jet is shown. This shape was formed by the injection of high temperature and pressure water (steam) through a leakage hole of the test specimen. The leak size of the test specimen was ca. 150 μm, as shown in Figure 7, but by considering the surrounding size, including the central white part as shown in Figure 9C, the size on the target surface after the water leak is >1000 μm.

**Conclusions**

In a liquid sodium atmosphere, water (steam) leakage experiments were carried out to investigate the phenomena of the sodium-water reaction. The leakage site of the specimen was damaged by wastage phenomena arising from corrosion and erosion, and a leak hole of the specimen extended from 150 μm to ca. 200 μm. The wastage or damage trace at the target surface was observed to be ca. 1000 μm in diameter. The reopened test specimen appeared to have a circular shape and the size of this specimen’s surface was ca. 2 mm in diameter on the sodium side. From the results of EPMA and SEM analysis, the damaged area was found to be covered with a complex mixture of compounds, such as (NaOH+Na₂O) · Fe₃O₄ and (Na₂Cr₂O₇+Na₂CrO₄), mixed with the sodium oxides formed by the sodium-water reaction and the Fe and Cr element in the matrix of the tube material. The temperature of the target surface increased by ca. 70~80°C from the heat of the exothermic reaction, even with a small leakage of only 15 mL.

**Acknowledgment**

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**References**