DETECTION OF THERMAL AGING OF DUPLEX STAINLESS STEELS WITH SQUID MAGNETOMETER

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Abstract: Thermal aging of several duplex stainless steels was detected by an ultrahigh sensitive magnetic sensor using superconducting quantum interference device (SQUID). It was found that the SQUID output signal pattern in the presence of AC magnetic field applied to the specimen was sensitive to very small amount of material property changes due to thermal aging at the operating temperature of light water reactors (LWRs). The change in the SQUID output strongly depended on aging temperatures and ferrite contents of unaged duplex stainless steel specimens.

Key words: Thermal aging, Duplex stainless steel, Nuclear power plant, Primary piping system, SQUID

1. INTRODUCTION

Cast duplex stainless steels, consisting of a duplex structure of austenite and ferrite, are widely used for primary piping systems in light water reactors (LWRs). Although the cast duplex stainless steels have excellent strength, toughness, weldability and resistance to stress corrosion cracking, thermal embrittlement is a growing concern for long-term-aged components in nuclear power plants [1-6].

The mechanism of thermal aging of duplex stainless steels are considered as follows [1-6]. At the high temperature range such as higher than 600°C, the embrittling mechanism is generally considered to be the formation of sigma phase. While this mechanism is reasonably well understood, the rates of formation of sigma phase at temperatures below 500°C are too slow to explain the embrittlement observed. The mechanism of the embrittlement in the temperature range of 280 to 500°C appears to be very complex and is not well understood. However, the consensus of the opinions expressed in literature is that the embrittling phenomena occur primarily in the ferrite phase of the alloy. The degradation mechanism which appears most likely to be responsible for the deterioration of the mechanical properties is spinodal decomposition of the ferrite into chromium and iron-rich regions.

Since the structure formed through spinodal decomposition is very fine and magnetic change due to the spinodal decomposition is very limited, it is rather difficult to detect the decomposition by conventional methods such as microscopic techniques, X-ray diffraction and normally used magnetic techniques. Thus, an ultrahigh sensitive superconducting quantum interference device (SQUID) magnetic sensor was adopted here as a non-destructive evaluation (NDE) method to evaluate the thermal aging. SQUIDs are known to be the most sensitive detectors of magnetic flux available. Although SQUIDs provide an exquisitely sensitive means to measure magnetic fields, their usage in the past has been chiefly limited to measurement of biomagnetic fields produced by the human heart, brain and other organs [7]. Recently, however, SQUIDs are used for nondestructive evaluation of materials and structures [8-13].

In the present study, a SQUID magnetic sensor was used to detect two different thermal aging mechanisms mentioned above. The SUS329 rolled duplex stainless steel specimens were thermally aged at 800°C to evaluate the detectability of embrittlement due to sigma phase formation. The SUS329 belongs to a relatively new group of duplex stainless steels which are intentionally alloyed and heat treated to produce high ferrite content, and is widely used in various industries. Although the aging temperature of 800°C is much higher than the operating temperature of LWRs (i.e. 280 to 320°C), this evaluation was carried out in order to specify the relationship between measured SQUID value and material properties of the specimen aged at a temperature where the material properties change significantly. On the other hand, SCS16, SCS14A and SCS13A cast duplex stainless steels were aged at relatively low temperature range of 300-475°C for the purpose of evaluating the detectability of thermal aging occurring at the operating temperature of LWRs.

2. EXPERIMENTAL

2.1. Test Specimen

The test specimens were machined from SUS329 rolled duplex stainless steel plates and SCS16, SCS14A and SCS13A cast duplex stainless steel plates. The dimension of the specimens was 80 × 40 × 5 mm³. The chemical compositions and mechanical strength are shown in Table 1 and 2, respectively.
Yoshihiro ISOBE and Toyokazu AOKI

Table 1. Chemical compositions. (wt%)

<table>
<thead>
<tr>
<th>Material</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Ni</th>
<th>Cr</th>
<th>Mo</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>SUS329</td>
<td>0.01</td>
<td>0.47</td>
<td>0.46</td>
<td>0.028</td>
<td>0.001</td>
<td>4.49</td>
<td>24.95</td>
<td>1.79</td>
<td>bal.</td>
</tr>
<tr>
<td>SCS16</td>
<td>0.03</td>
<td>1.18</td>
<td>1.40</td>
<td>0.038</td>
<td>0.040</td>
<td>13.27</td>
<td>19.20</td>
<td>2.14</td>
<td>bal.</td>
</tr>
<tr>
<td>SCS14A</td>
<td>0.04</td>
<td>1.11</td>
<td>1.10</td>
<td>0.034</td>
<td>0.005</td>
<td>11.16</td>
<td>18.52</td>
<td>2.34</td>
<td>bal.</td>
</tr>
<tr>
<td>SCS13A</td>
<td>0.05</td>
<td>1.05</td>
<td>1.18</td>
<td>0.018</td>
<td>0.004</td>
<td>8.59</td>
<td>17.81</td>
<td>0.18</td>
<td>bal.</td>
</tr>
</tbody>
</table>

Table 2. Mechanical strength.

<table>
<thead>
<tr>
<th>Material</th>
<th>Yield strength (MPa)</th>
<th>Tensile strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SUS329</td>
<td>573</td>
<td>755</td>
</tr>
<tr>
<td>SCS16</td>
<td>211</td>
<td>429</td>
</tr>
<tr>
<td>SCS14A</td>
<td>224</td>
<td>487</td>
</tr>
<tr>
<td>SCS13A</td>
<td>215</td>
<td>512</td>
</tr>
</tbody>
</table>

2.2. Thermal Aging

The thermal aging of the specimens was performed in an open furnace and the aging conditions are summarized in Table 3. The SUS329 specimens were aged at 800°C for times up to 20 hours. The SCS16, SCS14A and SCS13A specimens were aged at temperatures ranging from 300 to 475°C for times up to 10000 hours.

Regarding temperature effects on thermal aging, it has been reported that the aging embrittlement of cast duplex stainless steels in the temperature range 300-400°C is a thermally activated phenomenon which obeys an Arrhenius law. The equivalent time-temperature aging relationship is given as follows [14]:

\[ \frac{t_1}{t_2} = \exp \left( \frac{Q}{R(1/T_1 - 1/T_2)} \right) \]  \hspace{1cm} (1)

where \( Q \) is the apparent activation energy of the aging process, \( R \) is the gas constant, \( t_1 \) and \( t_2 \) are the aging times giving the same aging level for the aging temperatures \( T_1 \) and \( T_2 \), respectively. With this relationship, knowing the \( Q \) value, it is then possible to simulate the long time aging at the operating temperature with accelerated aging treatments at higher temperature.

Table 3. Aging conditions.

<table>
<thead>
<tr>
<th>Material</th>
<th>Aging temperature (°C)</th>
<th>Aging time (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SUS329</td>
<td>800</td>
<td>20</td>
</tr>
<tr>
<td>SCS16</td>
<td>300, 400, 450, 475</td>
<td>&lt;10000</td>
</tr>
<tr>
<td>SCS14A</td>
<td>300, 450</td>
<td>1500</td>
</tr>
<tr>
<td>SCS13A</td>
<td>300, 450</td>
<td>1000</td>
</tr>
</tbody>
</table>

2.3. SQUID Measurement

The schematic diagram of SQUID system is shown in Fig. 1. The SQUID system consists mainly of a DC SQUID gradiometer of first-order axial type, a superconducting magnet to generate a magnetic field, a nonmagnetic x-y stage, and a data acquisition computer system. The diameter of the gradiometer pickup coil was 6.7 mm with +6 turns and -6 turns and the baseline distance was 10 mm. The pickup coil was located 7 mm above the bottom of the dewar tail. The spacing between the gradiometer pickup coil and the surface of the specimen was 8 mm. The superconducting magnet applied an AC field of maximum amplitude approximately \( 1 \times 10^{-4} \) T at 1 Hz at the position of the surface of the specimen below the bottom of the dewar. Although first-order axial gradiometers are supposed to be sensitive only to changes in magnetic field and not the absolute value of the field, a large AC signal is directly coupled into the system whenever the AC magnet is used, because the gradiometer can not be perfectly balanced. Thus, the SQUID system includes AC nulling circuit with which the gradiometer can be balanced. With this AC magnet nulling system, it is possible to null the SQUID output after placing the specimen under the system. Any defects or changes in the electromagnetic properties of the specimen will then show up as large changes in the AC output.

![Fig. 1. Schematic diagram of SQUID system.](image)

The SQUID measurement was carried out on the same specimens in the presence of AC magnetic field generated by the superconducting magnet with periodic interruption of thermal aging. Figure 2 illustrates a typical example of SQUID output signal. The x- and y-axes of Fig. 2 indicate the AC current flow in the superconducting magnet and SQUID output voltage, respectively. Among several possible parameters such as slope, peak-to-peak and area of SQUID output signal pattern (Fig. 2), slope that means the ratio of change in SQUID output to change in applied field was selected and evaluated whether it is a sensitive indicator to detect thermal aging. The reason of selecting the slope as a candidate indicator is that it was a high S/N parameter and that it was sensitive to changes in material properties in our preliminary research elsewhere [15]. It should be noted that the slope value increases as the permeability increases. The meaning of slope value is shown both experimentally and theoretically later in this paper.
DETECTION OF THERMAL AGING OF DUPLEX STAINLESS STEELS

2.4. Material Characterization

Following material characterization was carried out for the purpose of correlating measured SQUID value with material properties of the specimens. The transition in magnetic permeability and electric resistivity during thermal aging of SUS329 specimens were evaluated by destructive methods. Quantitative analysis of phase transformations of SUS329 was conducted through field emission scanning electron microscope (FESEM) observation and the subsequent image processing of SEM photographs. The room-temperature impact value of aged specimens were evaluated by Charpy impact tests.

3. RESULTS AND DISCUSSION

Figure 3 indicates typical examples of the slope value of unaged SUS329 rolled duplex stainless steel specimen and SCS14A, SCS16 and SCS13A cast duplex stainless steel specimens after setting the slope value as practically zero with no specimen under the SQUID gradiometer. The slope of SUS329 specimen revealed a much higher value than those of SCS14A, SCS16 and SCS13A specimens. This indicates that SUS329 specimen contained more ferrite phase than SCS14A, SCS16 and SCS13A specimens. As for the cast stainless steels used in this study, SCS14A was most magnetic and SCS13A was least magnetic.

3.1. SUS329 Rolled Duplex Stainless Steel

As mentioned in the introductory part, examinations for SUS329 rolled duplex stainless steel were performed for the purpose of specifying the relationship between measured SQUID value and material properties of the specimen at a temperature where the material properties change significantly, namely, at 800°C. The changes in the slope value of SUS329 rolled duplex stainless steel aged at 800 °C are shown in Fig. 4. The slope value decreased rapidly up to 10 hours and gradually decreased after that.

Results obtained by Charpy impact value revealed a sharp drop at 1 hour of aging, followed by a gradual decrease up to 20 hours (Fig. 5).
A relationship between SQUID slope value and thermal embrittlement is shown in Fig. 6, suggesting that the slope value is a promising indicator to detect the change in Charpy impact value of aged SUS329 specimen.

Transition in the area ratio of the ferrite, the austenite and the sigma phases of SUS329 specimen during aging measured from SEM photographs are shown in Fig. 7, indicating that the sigma and the austenite phases increased while the ferrite phase decreased.

Figures 8 and 9 show changes in electromagnetic properties of aged SUS329 specimens. The decrease in permeability in Fig. 8 corresponds to the decrease in ferrite phase ratio in Fig. 7, because the ferrite phase is ferromagnetic and the austenite and sigma phases are non-ferromagnetic. The change in resistivity was saturated after one hour of aging as shown in Fig. 9.

The effects of the change in permeability and resistivity on the change in SQUID slope value are discussed theoretically in the next section.

### 3.2. Theoretical Consideration on SQUID Parameter

In order to correlate the slope value in the SQUID output signal pattern with electromagnetic properties of the specimen, namely, permeability and resistivity, theoretical evaluations were performed analytically through Hankel transformation method using an axially symmetric model illustrated in Fig. 10. The definitions of the parameters in Fig. 10 are summarized as follows.

- D1: outer diameter of the superconducting magnet
- D2: inner diameter of the superconducting magnet
- H: height of the superconducting magnet
- I: current in the superconducting magnet
- L: spacing between the superconducting magnet and the infinite plate specimen
- T: thickness of the infinite plate specimen
- C1: center point of lower pickup coil of +6 turns
- C2: center point of upper pickup coil of -6 turns

Fig. 10. Geometrical definition of SQUID gradiometer model.
Using the model in Fig. 10, relationships between the slope value and the electromagnetic properties of the specimen were evaluated under the same condition of AC magnetic field used in the experiments in this study, namely, AC magnetic field of maximum amplitude approximately $10^{-4}$ T at 1 Hz at the position of the surface of the specimen. In the evaluation, the slope value was obtained as

$$\text{slope value} = \frac{[B(C1) - B(C2)]}{1}$$

where $B(C1)$ and $B(C2)$ are the magnetic flux densities at C1 and C2, respectively. It should be noted that the conversion ratio of the SQUID output voltage per magnetic flux density in this study was $10^6$ (V/T).

The theoretical evaluations were carried out based on data of permeability and resistivity of the aged and unaged SUS329 specimens measured destructively in this study (Figs. 8 and 9).

3.3. SCS16, SCS14A and SCS13A Cast Duplex Stainless Steel

The change in the slope value of SCS16 cast duplex stainless steel specimens aged at 300-475°C are summarized in Fig. 12. As can be seen in Fig. 12, the slope varied during aging process depending strongly on the aging temperatures. The specimen aged at 475°C indicated a slight increase in the slope at 10 hours of annealing and then a sharp fall up to 100 hours. In the case of aging temperature at 450°C, after an increase in the initial period, the slope decreased up to 10000 hours. At the aging temperature of 400°C, the initial increase in the slope was more evident and, again, the slope started to decrease. The specimen subjected to the aging at 300°C revealed a gradual increase up to 1000 hours followed by a gradual decrease up to 7000 hours. In general, the slope of SCS16 specimens aged at temperatures above 300°C showed an increase first followed by a decrease depending on the aging temperatures. The decrease of the slope value was possibly due to the formation of paramagnetic Cr-rich phase through spinodal decomposition during aging [16].

Results obtained by Charpy impact tests for SCS16 specimens aged at 450 and 300°C indicated that the value of the specimen aged at 450°C revealed a slight decrease in the course of aging up to 6000 hours, while that of the specimen aged at 300°C showed no detectable change up to 3000 hours.
Figure 13 shows the changes in the slope value of SCS14A cast duplex stainless steel specimens aged at 300 and 450°C, indicating that the change in the slope for SCS14A was more evident compared with SCS16 specimen aged at the same temperatures. Since the amount of the ferrite in the duplex structure controls the extent of thermal embrittlement [1-6], it is highly probable that SCS14A, which was most magnetic among the cast duplex stainless steels in this study, revealed the biggest change in the slope value.

The SCS13A specimen, which was the least magnetic specimen in this study, indicated the least change in the slope value among other cast duplex stainless steel specimens aged at the same temperatures for aging period up to 1000 hours (Fig. 14).

4. CONCLUSIONS

SQUID magnetometer was adopted for the detection of thermal aging of several types of duplex stainless steels, namely, SUS329 rolled duplex stainless steel and SCS16, SCS14A and SCS13A cast duplex stainless steels. The SUS329 specimens were aged at 800°C for times up to 20 hours, while the SCS16, SCS14A and SCS13A specimens were aged at temperature range from 300 to 475°C for times up to 10000 hours.

It was found that the SQUID output signal pattern in the presence of AC magnetic field applied to the specimen was sensitive to the material property changes due to the thermal aging. In the case of cast duplex stainless steel specimens, the change in the SQUID output varied according to the amount of ferrite in the duplex structure.

Using the slope value in the SQUID signal pattern which means the ratio of the change in SQUID output to the change in applied field, it has been found that SQUID magnetometer can be a promising NDE method to detect thermal aging of the duplex stainless steels.

REFERENCES