Nondestructive Evaluation of Thermally Degraded 2.25Cr–1Mo Steel by Electrical Resistivity Measurement

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An attempt was made to evaluate nondestructively the degradation of thermally aged 2.25Cr–1Mo steel by electrical resistivity measurement. Artificial aging was performed to simulate the microstructural changes in 2.25Cr–1Mo steel arising from long time exposure at 540°C. Microstructural parameter (amount of dissolved Mo in the matrix), mechanical property (ductile-brittle transition temperature) and electrical resistivity were measured to investigate the relationship among these parameters. Both the amount of dissolved Mo and the electrical resistivity decreased rapidly in the initial 1000 hours of aging and then changed little thereafter. On the other hand, the ductile-brittle transition temperature (DBTT) increased rapidly in the initial stage of aging and then saturated afterward. Electrical resistivity was found to have linear correlation with the amount of dissolved Mo and DBTT, respectively. Electrical resistivity was suggested as a potential nondestructive evaluation parameter for assessing DBTT of the thermally degraded 2.25Cr–1Mo steel.

1. Introduction

The 2.25Cr–1Mo steel has been widely used for elevated temperature structure applications such as turbine rotors, boilers and pressure vessels in fossil plant and petroleum chemical facilities due to its superiority in high temperature strength, oxidation resistance and hydrogen embrittlement resistance at 300°C–540°C. However, this steel is known to be subject to aging degradation through carbide induced brittleness brought on by precipitation of stable carbides, temper embrittlement brought on by grain boundary segregation and softening of matrix after long exposure to high temperatures.1–7 In order to evaluate the microstructural degradation of Cr–Mo type steel arising from long time exposure to high temperature, composition3–5 or morphology6 analysis of carbides has been performed to identify the different kind of carbides. Comparing the results of diffraction pattern analysis of several carbides with their composition, it was found that carbides had distinct composition depending on the type of carbide such as Cr rich M23C6, Mo rich M6C, Mo23C (M2C), Fe3C (M7C3).3–5 Gope et al.6 and Watanabe and Shoji7 reported an increase in M6C carbide, which had been previously reported by Baker and Nutting8 to be a stable carbide, in thermally degraded 2.25Cr–1Mo steel. The increase of Mo rich M6C in Cr–Mo type of low alloy steel is reported to cause irreversible carbide-induced embrittlement.1,2,7,9 In order to simulate the changes of carbides in 2.25Cr–1Mo steel after prolonged on-site usage, Adbel-Latif et al.3 carried out accelerated artificial aging heat treatment.

Since it is difficult or practically impossible to obtain specimens for mechanical testing without damaging the structure in operation, many researchers have attempted to evaluate the damage of structures nondestructively, for in situ monitoring.9–13 Electrical resistivity,10,11 magnetic,12 and ultrasonic13 methods are currently used for nondestructive evaluation of structures. Electrical resistivity method, which was widely used for evaluating material properties like precipitation behavior,14–18 has recently been applied in the field of non-destructive evaluation of structure.10,11 Maeda et al.11 reported a decrease in electrical resistivity in thermally aged stainless steel. Although some researchers10,11 have reported changes of electrical resistivity in the degraded structure, the correlation between electrical resistivity and microstructural changes in the thermally degraded materials is lacking.

An attempt was made to evaluate nondestructively the thermally degraded 2.25Cr–1Mo steel by electrical resistivity measurement in this investigation. Especially, the correlations among microstructural changes (depletion of solute Mo), mechanical property (DBTT) and electrical resistivity were investigated.

2. Experimental

2.1 Material and heat treatment

A laboratory-made 15 mm thick hot rolled 2.25Cr–1Mo steel (ASTM A387-22-CL2) plate specimen tempered at 720°C for 1 hour after normalizing at 900°C was used, and its chemical composition is given in Table 1. In order to simulate the typical microstructure of the rotor steel in service at 540°C for about 20 years, an accelerated isothermal heat treatment7 was performed at 630°C for up to 4800 hours.

Table 1 Chemical composition of the 2.25Cr–1Mo steel (ASTM A387-22-CL2).

<table>
<thead>
<tr>
<th>Element</th>
<th>Fe</th>
<th>C</th>
<th>Cr</th>
<th>Mo</th>
<th>Si</th>
<th>Ni</th>
<th>Mn</th>
<th>Al</th>
<th>P</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>mass%</td>
<td>bal.</td>
<td>0.138</td>
<td>2.27</td>
<td>0.97</td>
<td>0.142</td>
<td>0.17</td>
<td>0.46</td>
<td>0.007</td>
<td>0.014</td>
<td>0.004</td>
</tr>
</tbody>
</table>
2.2 Measurement of the amount of dissolved Mo in the matrix and X-ray diffraction analysis for electrolytically extracted carbides

In order to analyze the amount of solute element in the matrix, electrolytic extraction technique was employed to dissolve only the matrix, and then the solution was ICP (inductively coupled plasma) analyzed. For electrolytic extraction, a specimen in a solution of 90% methanol and 10% hydrochloric acid was subjected to a voltage of 3 volts. After selectively dissolving the matrix, the remaining residue (carbide) was separated for X-ray diffraction analysis.

2.3 Measurement of DBTT

The V-notch Charpy impact test was carried out within the temperature range of \(-140^\circ C\) to \(20^\circ C\) using ASTM standard specimens. The DBTT was obtained by fitting under the assumption that the change of absorbed energy with temperature follows the eq. (1):\(^{19}\)

\[
Y = \frac{(P_1 + P_2)}{2} \cdot \frac{(P_1 - P_2)}{2} \cdot \tanh \left( \frac{T - T_a}{T_b} \right)
\]

where, \(Y\), \(P_1\), \(P_2\), \(T_a\), \(T_b\), \(T\) are absorbed energy (J/m\(^2\)), upper shelf energy, lower shelf energy, DBTT (\(^\circ C\)), constant, and test temperature (\(^\circ C\)), respectively.

2.4 Measurement of electrical resistivity

Electrical resistivity was measured using the direct current four terminal potential method.\(^{10,11,20}\) Measurement was carried out at room temperature consistently fixed at \(20^\circ C\). A computer-controlled direct current source was used to supply current \(\pm 1\) A to the specimen and the voltage was measured to \(1\) nV using nano-voltmeter. As the interval between voltage output leads can lead an error in electrical resistivity values,\(^{10}\) a fixture with constant terminal interval was used. A sheet-type specimen of 60 mm in length, 10 mm in width, and 2 mm in thickness was used to measure electrical resistivity. The thickness of the specimen was parallel-abraded to within 2 mm \(\pm 2\) \(\mu\)m. Electrical resistivity was calculated using eq. (2).

\[
\rho = \frac{V}{IL}
\]

where, \(\rho\), \(V\), \(I\), \(A\), \(L\) are electrical resistivity, measured voltage, applied current, cross sectional area of the specimen, and interval between voltage measurement leads, respectively. The electrical resistivity in this experiment was a value averaged over five measurements, and the error range of the measurement was within \(\pm 5\)\(\Omega\)m. These errors in measurement seemed to have been generally caused by the size of specimen and the change of temperature of contact points.

3. Results and Discussion

3.1 Microstructure and mechanical property

Figure 1 is FESEM (field emission scanning electron microscope) micrographs showing the morphologies of carbides before and after aging. Compared to the as-received specimen, the carbides in the aged specimen became coarsened in size and reduced in number. The grain size of the as-received specimen was approximately 20 \(\mu\)m, and the grains did not grow during aging.\(^{21}\) No grain boundary segregation was detected in the artificially aged specimen.\(^{21}\)

Figure 2 shows the change of the amount of dissolved Mo in the matrix with aging time. As aging time increased the amount of dissolved Mo in the matrix decreased rapidly for about 1000 hours of aging and then changed little thereafter. The total amount of Mo in the as-received specimen was about 0.97% (Table 1). It is estimated that the 0.65% of Mo (67% of the total amount of Mo) was dissolved in the matrix
while the remaining 0.32% of Mo was combined to the carbides. As aging time increased the amount of Mo dissolved in the matrix decreased to about 0.3% (46% of the total amount of Mo), the remaining 0.67% is thought to be combined to the carbides. The result of Wada and Biss,4) who reported depletion of Mo in 2.25Cr–1Mo steel used on site for about 100000 hours at 500 to 570 °C, was also plotted in Fig. 2 for comparison. The fact that the 0.28% of Mo was dissolved in the matrix reported by Wada and Biss4) confirmed the similarity to present results.

Figure 3 shows the results of X-ray diffraction analysis of electrolytically extracted carbides. The peaks of M₆C₆, M₃C, M₂C, M₆C carbides are observed along with other unidentified peaks in the as-received specimen. There were a large amount of M₂₃C₆ and a small amount of M₂C and M₆C carbides. The amount of M₂C changed little as aging time increased. This contrasts with reports of extinction of M₃C with aging time from electron diffraction pattern analysis by Gope et al.6) and with reports of increase in M₂C from X-ray diffraction analysis of extracted carbide by Watanabe and Shoji.7) Although M₃C carbide existed in large quantities in the as-received specimen, it rapidly became extinct in the initial stage of the aging. Results of X-ray diffraction analysis of Watanabe and Shoji7) did not report the existence of M₃C (main peak is located very close to the main peak of M₂₃C₆) in the undamaged 2.25Cr–1Mo steel. Gope et al.6) have reported that although M₃C was present in large quantities in the undamaged material, it was undetectable in the aged material. According to the results of X-ray diffraction analysis of this experiment, M₃C existed even in the as-received specimen albeit in small quantities, and M₆C carbide rapidly increased in the aged specimen. Gope et al.6) and Watanabe and Shoji7) have also reported an increase in M₆C carbide with aging time. For Mo rich M₆C carbide to increase, a supply of Mo was needed. From the results of analysis of amount of solute Mo, it was inferred that Mo, which had become depleted from the matrix, had contributed to the increase in M₆C.

Figure 4 shows the change of Charpy impact-absorbed energy with testing temperature. The absorbed energy of the aged specimen was lower than that of the as-received specimen at all temperatures and the impact-absorbed energy curve in the aged specimen was shifted to higher temperature. Figure 5 shows the change of DBTT and electrical resistivity with aging time. The DBTT increased sharply for initial about 1000 hours, then it changed little thereafter. This change of DBTT is consistent with the results obtained from the thermally degraded turbine rotor steel by Yu et al.10) and Viswanathan and Gehl.22) In our previous research21) the fracture surface of the specimen that had been impact-fractured in liquid nitrogen after being aged for 4800 hours showed complete intragranular cleavage fracture surface indicating that the grain boundary had not been weakened due to temper embrittlement caused by grain boundary segregation. Consequently, the increase of DBTT in this investigation seems to be mainly due to carbide-induced embrittlement. The irreversible carbide-induced embrittlement in 2.25Cr–1Mo steel has been reported to be related to formation2,9) or coarsening7) of Mo rich M₆C carbides. On the other hand, the irreversible embrittlement in the aged 2.25Cr–1Mo–1V steel has been reported to be related to coarse M₆C carbide.1)
3.2 Change of electrical resistivity and correlation with DBTT

As shown in Fig. 5, the electrical resistivity rapidly decreased in the initial 1000 hours of aging and then changed little thereafter. Electrical resistivity, which results from conduction electron scattering, is affected by phonon scattering, impurities, and lattice defect etc. In particular, the defect of atomic unit size has been found to be a predominant microstructural factor affecting electrical resistivity.23 In this respect, the reduction of electrical resistivity with increasing aging time is thought to be closely related to the depletion of Mo dissolved in the matrix. Electrical resistivity has been reported to be linearly proportional to the amount of Mo dissolved in the matrix and electrical resistivity.24 Therefore, the decrease of electrical resistivity in the thermally aged 2.25Cr–1Mo steel is mainly due to decrease of conduction electron scattering arising from the solute Mo.

As shown in Fig. 5, the DBTT increased greatly in the initial stage of aging while the electrical resistivity decreased drastically. Figure 7 shows the correlation between electrical resistivity and DBTT and a linear correlation between these two can be seen. From the results of linear regression analysis, the relationship can be represented as eq. (4).

\[ DBTT = 75.5 - 0.449 \times (\rho) \]  

Here, the DBTT is ductile-brittle transition temperature in °C unit. The depletion of Mo dissolved in the matrix increases the amount of Mo carbides and decreases the electrical resistivity. As a result, the decrease of electrical resistivity is seen to reflect the increase of Mo carbides. By measuring electrical resistivity, the DBTT change arising from carbide-induced embrittlement in the aged 2.25Cr–1Mo steel, could be estimated within ±3 °C of error. Therefore, the electrical resistivity is proposed as a potential non-destructive evaluation parameter for assessing DBTT of the thermally degraded 2.25Cr–1Mo steel.

4. Summary and Conclusion

From the research to evaluate the thermally degraded 2.25Cr–1Mo steel by electrical resistivity measurement nondestructively, the following conclusions were drawn:

1) The Mo was rapidly depleted in the initial 1000 hours of aging and then hardly changed. The amount of Mo carbide increased by thermal aging. The DBTT increased rapidly in initial about 1000 hours of aging and then changed little afterward.

2) The electrical resistivity decreased rapidly during about 1000 hours of aging and then tended to level out. It showed a linear correlation with the amount of Mo dissolved in the matrix. The marked decrease of electrical resistivity in
the initial stage of aging is thought to be mainly due to decrease of conduction electron scattering arising from the depletion of Mo dissolved in the matrix.

(3) The change of electrical resistivity showed a linear correlation with that of DBTT of the thermally aged 2.25Cr–1Mo steel. Therefore, the DBTT change arising from carbide-induced embrittlement of aged 2.25Cr–1Mo steel, could be evaluated nondestructively by measuring electrical resistivity.

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REFERENCES