General paper

Strength Dependence of Intergranular Stress Corrosion Cracking Susceptibility on 3.5% NiCrMoV Steel at 403K

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Abstract: Rotors and discs used in low-pressure turbines must be made of a material possessing high strength and toughness and be capable of manufacturing extremely large components. For these reasons, 3.5% NiCrMoV steel is widely used. It has been previously reported that intergranular stress corrosion cracking in this material is initiated in wet deaerated steam when the temperature reaches approximately 400 K. As no rotor and disc material with high strength and toughness that can serve as a substitute for 3.5 NiCrMoV steel has been found, efforts to resolve this problem have been conducted to reduce material strength and lower the susceptibility to stress corrosion cracking.

The purpose of this study was to elucidate a relationship between material strength and intergranular stress corrosion cracking susceptibility. Slow strain rate tests (SSRT) were performed in a neutral atmospheric environment at a test temperature of 403 K. The results were as follows:

(1) The SSRT found that, as the 0.2% offset strength decreased, the area of the intergranular fracture was reduced. For the test specimen with an 0.2% offset strength of 777 MPa, only a tiny intergranular fracture was observed; at 0.2% offset strengths of 697 MPa and below, cracking disappeared completely. (2) From the precipitation status of the two carbides M_3C and M_7C_3 precipitated at the grain boundaries, it was found that the disappearance of the M_3C carbide coincided with the disappearance of the intergranular fracture. From this observation, it is thought that differences in composition of these carbides have an effect on the susceptibility of 3.5% NiCrMoV steel to stress corrosion cracking. (3) It was confirmed that the M_3C carbide disappears when the 0.2% offset strength is approximately 700 MPa or below, and that these materials achieve the target value for increased resistance to intergranular stress corrosion cracking in neutral environments.

Key words: IGSCC, 3.5NiCrMoV steel, SSRT, Low pressure turbine, Grain boundary carbide, precipitate.

1. INTRODUCTION

The steel used in the large rotors and discs of large-scale, low-pressure turbines must have high strength and high toughness properties and be utilizable for large components, and for these reasons 3.5% NiCrMoV steel is widely used. However, in the late 1970s, intergranular stress corrosion cracking occurred in the United States in wet steam environments at a temperature of approximately 400 K. Since that time, numerous studies have been conducted to evaluate the cause and devise countermeasures. These studies concluded that, for 3.5% NiCrMoV, the cause was not the condensation of free caustic but the initiation of stress corrosion cracking (SCC) in deaerated pure water. Accordingly, crack propagation rates, etc. were evaluated in order to establish reasonable inspection intervals [1~5]. No rotor and disc material with high strength and toughness has been found that can be used in place of 3.5% NiCrMoV steel. However, as the material strength of this steel can be adjusted by altering the tempering conditions, it is now believed that reducing SCC susceptibility will enable long-term, reliable use of this material.

For this reason, with the aim of determining the correlation between SCC susceptibility and material strength, a slow strain rate test (SSRT) was conducted in a neutral environment [6] at a temperature of 403 K to examine the SCC susceptibility of 3.5% NiCrMoV steel.

2. TEST METHOD

2.1. Test Specimens

The test specimens were fabricated from an actual turbine disc made of 3.5% NiCrMoV steel, which was manufactured by means of the vacuum carbon deoxidation and ladle refining processes. The specimens had an outer diameter of approximately 2700 mm and a thickness of approximately 700 mm. Table 1 shows the chemical composition of the test specimens. Five pieces measuring approximately 200 mm square and 400 mm in length were cut away from one section of this disc. After quenching at 1123 K, the pieces were tempered at between 853 K and 908 K to change the strength level. Table 2 shows the mechanical properties of the test specimens. The 0.2% offset strength was between 652 MPa and 952 MPa. The microstructure of each test specimen is shown in Fig. 1; as this figure shows, all of the specimens had a tempered bainite structure. As the tempering temperature increased, the pre-austenitic grain boundary (hereafter abbreviated to "grain boundary") became more clearly visible.

Table 1. Chemical composition of test material (mass%).

C	Si	Mn	P	S	Ni	Cr	Mo	V
0.26	0.07	0.30	0.005	0.002	3.30	1.54	0.35	0.09

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Fig.1. Microstructure of test materials.

Table 2. Mechanical properties of test materials.

0.2% offset strength MPa	Tensile strength MPa	Elongation %	R.A. %	Temper
952	1043	19.9	70.9	853K × 20h
853	958	21.9	71.8	868K × 20h
777	894	25.1	74.2	878K × 20h
697	812	25.4	75.8	888K × 20h
652	754	28.6	76.3	908K × 20h

2.2. Test Procedure

Various test methods can be used to determine SCC susceptibility. For the purposes of this study, the SSRT method, which can be conducted in a comparatively short period of time, was chosen. As noted above, the general temperature of wet steam in a low pressure turbine, 403 K, was used as the test temperature.

A buffer solution of acetic acid and sodium acetate was used as the test solution in order to establish an environment of $\text{pH}_{403\text{K}} 6.0$, close to the neutral ($\text{pH}_{403\text{K}} 5.93$) environment.

The solutes were $\text{CH}_3\text{COONa} 10^{-2}\text{M} + \text{CH}_3\text{COOH} 10^{-3}\text{M}$. Figure2 shows the size and shape of the test specimens. Figure3 shows an overview of the test unit used. The strain rate affects the results of the SSRT. Lower strain rates will result in a greater area of intergranular fracture. Accordingly, the strain rate was $1.67 \times 10^{-6} \text{ mm/s}$, the lowest that could be set on the test unit. The strain rate

was set to $8.3 \times 10^{-8}/\text{s}$. After the test, the fracture surface was observed with a scanning electron microscope (SEM).

Fig.2 Test specimen.

Fig.3. Test apparatus.

3. RESULTS

Figure4 shows the load strain chart for the define test. As the strength of the test specimens increased, the maximum load increased as well. Nevertheless, elongation was approximately 4 mm for all five test specimens, and

there were only slight changes due to material strength. As these could not be organized in terms of the changes in ductility normally used in SSRTs, the intergranular fracture surface (for bainite structures, fractures at the pre-austenitic grain boundary are referred to as intergranular fracture surfaces) was observed with an SEM after fracture. The measurement accuracy and sensitivity with respect to the intergranular fracture surface ratio was approximately 1%, and in these results, the value was less than 1% for all of the test specimens except the 952 MPa specimen. Accordingly, SCC susceptibility was judged by the presence or absence of an intergranular fracture surface. Figure 5 shows the largest intergranular fracture surface. However, the SCC fractures themselves were scattered on only the outer circumference, and the area that they occupied was extremely small. Figure 6 shows an enlargement of the intergranular fracture surface section. The area of the intergranular fracture surface decreased as the 0.2% offset strength became lower, and it was practically non-existent for the test specimen with 0.2% offset strength of 777 MPa. For the two test specimens with 0.2% offset strength of 697 or less, it disappeared completely.

Fig. 4. Chart of SSRT.

Fig. 5. Representative fracture appearance after SSRT test.

952 MPa		SCC
853 MPa		SCC
777 MPa		SCC
697 MPa		No SCC
$\sigma_{0.2}$	SEM micrograph	IGSCC

10 μ m

Temp : 403K pH_T : 6 E_{corr} 0.1 μ m/min
Fig. 6. SEM micrographs of the specimens with various strengths.

4. DISCUSSION

4.1. Effect of Material Strength On crack Propagation Rate

The SSRT is designed to simulate crack propagation, so this test was conducted to determine the crack propagation rate in order to study the effect of material strength. The diameter of the test specimen was small (4 mm), but the grain size was much smaller, so the size effect of the test specimen was thought to be negligible. For the pur-

poses of this study, the crack propagation rate was defined as the time until maximum load was reached. However, as this is difficult to determine from Fig. 4, the value was derived by dividing the crack depth by the test time, as shown in Fig. 7. The 0.2% offset strength was used as the material strength. Figure 8 shows the effect of strength on crack propagation rate, derived from the results of test specimens with 0.2% offset strength of 777 MPa or above which had an intergranular fracture surface. From this figure, the following Eq. was obtained:

Fig.7. Crack propagation rate defined in this investigation.

Fig.8. Crack propagation rate obtained by SSRT in a neutral buffer solution at 403K.

$$\ln \left(\frac{da}{dt} \right)_{\text{SSRT}} = 1.000 + 0.01 \sigma_{0.2} \quad (1)$$

where

$(da/dt)_{\text{SSRT}}$: crack propagation rate (mm/h)
 $\sigma_{0.2}$: 0.2% offset strength (MPa)

The crack propagation rate (including material strength) for 3.5% NiCrMoV steel in an actual turbine was reported by W. G. Clark et al[7] using the following equation:

$$\ln \frac{da}{dt} = -4.968 - \frac{7302}{T_R} + 0.0278 \sigma_{yk} \quad (2)$$

where

da/dt_i : crack propagation rate (inch/h)
 T_R : Rankine temperature (°R)
 σ_{yk} : 0.2% offset strength (ksi)

As this Eq. (2) cannot be compared with Eq. (1), unit

conversion was performed, resulting in the Eq.:

$$\ln \frac{da}{dt} = -1.733 - \frac{4057}{T} + 0.00403 \sigma_{0.2} \quad (3)$$

where

da/dt : crack propagation rate (mm/h)
 T : absolute temperature (K)
 $\sigma_{0.2}$: 0.2% offset strength (MPa)

For this test, a constant test temperature of 403 K was used, so the first and second items on the right side in Eqs. (2) and (3) are constant terms.

When Eqs. (1) and (3) are compared, the coefficient for the material strength term is slightly greater for the former than the latter. However, considering the fact that this is an SSRT and such matters as the time from crack initiation until the end of propagation remain unclear, this is not considered to be a significant difference. As a result, Eq. (1) can be considered to show the effect of material strength on the crack propagation rate in an actual turbine environment.

In Fig. 6, there was no intergranular fracture surface in the test specimens with 0.2% offset strength of 697 MPa or less, distinct change from the test specimens with 0.2% offset strength of 777 or greater. In other words, at around 700 MPa the crack propagation rate decreases significantly, and for all practical purposes further crack propagation does not occur. The data was consistent with the results of tests conducted by Itoh et al [8] with U-bend test specimens in an actual turbine environment for 100,000 h. In both cases, SCC was initiated in 3.5 NiCrMoV steel at 0.2% offset strength of approximately 700 MPa.

4.2. Effect of Microstructure on SCC Propagation

As noted above, the existence of a threshold around 700 MPa after which crack propagation can be discounted for all practical purposes was suggested. Equation (2) is derived from the Arrhenius Eq., and it does not take into consideration changes in microstructure, such as changes in the type of precipitates at the grain boundary. As a result, if the microstructure at the grain boundary is changed, the temperature range for tempering in Eq. (2) will naturally become narrower.

With the 3.5% NiCrMoV steel examined in this study, SCC was initiated at the grain boundary, and it is very likely that the microstructure of the grain boundary was changed in the course of the heat treatment performed to change the material strength. The grain size for large forgings does not change greatly, so for the purposes of this study it is assumed that the grain size had no effect on SCC.

These changes to the grain boundary may result from either of two causes. One is segregation at the grain boundary. The other is the precipitation of intergranular carbides. One example of segregation at the grain boundary might be a concentration of P, etc. which becomes temper brittleness in this type of alloy. There are two views with regard to SCC on the high basic side; some researchers think that segregation at the grain boundary results in acceleration [9], while others think that it has no

effect [10]. In the neutral region, on the other hand, the effect disappears as the material strength increases [4], so segregation at the grain boundary is not thought to be a significant factor in SCC.

Regarding the second possible cause, a change in the intergranular carbides, each of these test specimens has a tempered bainite structure with carbides precipitated in both intergranular and intragranular regions. Figure 9 shows the results of a determination of whole precipitates. The determination was made by performing electrolytic extraction for the test specimens in a solution of alcohol with 5% HCl and then performing X-ray diffraction to identify the residue. A comparison of extraction performed for the matrix is also shown in the figure. The result was 1.1% for the test specimen with 0.2% offset strength of 952 MPa. When the tempering temperature increased and the 0.2% offset strength was 652 MPa, the result increased as well to 3.7%. The major peak for precipitates was M_3C for only the test specimen with 0.2% offset strength of 952 MPa; it was M_7C_3 for all other material strengths tested. Nevertheless, the reason for this is thought to be not that the carbide changed to M_7C_3 as the tempering temperature increased, but rather that precipitation of the latter carbide gradually increased as the tempering temperature increased until it became the major peak.

For this reason, in order to exclude the impact of the

Fig. 9. XRD results of whole precipitates extracted in 5% HCl solution.

intragranular carbides, an extraction replica was used to observe and identify the intergranular carbides. The extraction replica was achieved by sampling carbides etched with nital after the surface had been polished. In the course of sampling from the extraction replica, the carbides sometimes moved, but the shape of the carbides and their location with respect to the grain boundary was confirmed during the identification process. Figure 10 shows a typical observation of the grain boundary. As the tempering temperature increased, the intergranular carbides tended to become both coarser and clearer. Two types of carbide were identified as intergranular carbides by means of X-ray diffraction: M_3C and M_7C_3 . In the process of identifying these carbides using this electron diffraction and an energy dispersive spectroscope (EDS), a major difference in the composition of the carbides was confirmed. Both were made up of Fe, Cr and Mo, but the former carbide had a cubic system structure made up primarily (75% - 95%) by Fe. As shown in Fig 11, in contrast, the latter carbide had an orthorhombic or triclinic structure, so streaks were visible in the electron diffraction and Cr was the primary element, with Fe making up only 30% - 50%. There was no difference in Mo content; it was approximately 5% for both carbides.

Fig. 11. Chemical composition of M_3C and M_7C_3 analyzed by EDS.

Fig. 10. Representative TEM micrographs of grain boundary.

A comparison of the precipitation status of these two carbides, as shown in Fig. 12, with the results of the SSRT reveals that, although a bit of M_3C carbide was observed in the 697 MPa test specimen, the precipitation of M_3C matches almost exactly the disappearance of the intergranular fracture surface. This indicates that the difference in carbide composition has an impact on the SCC susceptibility of 3.5% NiCrMoV steel. In this case, the Cr content of the matrix itself is low (approximately 1.5%), so no Cr-depleted layer has formed in the area around the M_7C_3 carbide in which Cr is the primary element, as in the case of austenitic stainless steel. In contrast to M_7C_3 , in which a spinel containing Cr and Mo is formed, M_3C has a large Fe content, so it is thought that only a film of Fe_2O_3 with low corrosion resistance is formed, making it easy for cracks to propagate.

Fig.12. Grain boundary carbide distribution of 3.5% NiCrMoV steel.

4.3. SCC Susceptibility of 3.5% NiCrMoV Steel

The NiCrMoV steel used in low-pressure turbine rotors and discs is equivalent to ASTM A470 classes 5, 6 and 7 and A471 classes 1 to 6. The material strength is specified in levels, from 0.2% offset strength of 520 MPa to 1035 MPa. To satisfy the desired values for material strength, manufacturers do not simply perform adjustments using the tempering conditions (temperature and time) during the final heat treatment but suitably adjust the chemical composition, in particular the C content. C itself is an element that is easily segregated, so improvements have been made to the refining, ingot-making and thermal pre-treatment processes in order to reduce segregation. The C content varies widely in the range of about 0.2 to 0.3%, so the heat treatment conditions have such broad possibilities that the materials can be thought of as different steels. For this reason, the question remains as to whether the aforementioned test results can be applied to all types of 3.5% NiCrMoV steel.

Recently, integral rotors, in which the discs and rotor form a single unit, have become the mainstream, as opposed to rotors in which several discs are shrunk-on. Whereas tempering of a disc can be completed in a single day and night, the latter method requires a period of several days for tempering. In such cases, as tempering takes a long time, the C content is inevitably low. The lower C content changes the CCT curve, with the formation of a bainite nose being delayed to the extent that the C content has been reduced. However, the cooling rate is lowered to

the extent that the mass of the rotor has increased, so in overall terms the differences in the microstructure during quenching are reduced.

Nevertheless, if the tempering conditions change, it is possible that material strength may be affected. Accordingly, test specimens measuring $70 \times 50 \times 15$ mm were sampled from actual turbine materials of several types and, after oil quenching from 1223 K, a check of the effect of tempering conditions on material strength was conducted. The tempering temperature was 823 K to 923 K, and the tempering time was made constant at 20 h. The results are shown in Fig. 13. As the tempering temperature increased, the 0.2% offset strength decreased, but within the scope of this test, the change in 0.2% offset strength due to differences in C content were within the range of variations. A check of intergranular carbides was conducted for some of the test specimens; the results are shown in Fig. 14. It was confirmed that, in materials with 0.2% offset strength of around 700 MPa or less, the M_3C had disappeared entirely, and materials of around 700 MPa or less achieved the target value of increased resistance to intergranular stress corrosion cracking in a neutral environment.

Fig.13. Correlation of temper temperature and 0.2% offset strength.

Fig.14. Disappearing of M_3C in grain boundary related by temper and 0.2% offset strength.

5. CONCLUSION

A slow strain rate test (SSRT) was conducted for the 3.5% NiCrMoV steel used for the rotor and discs of low-pressure turbines, in a neutral environment at a test temperature of 403 K, in order to study the correlation between intergranular stress corrosion cracking (SCC) and material strength. The following results were obtained:

- (1) In the SSRT, the SCC fractures were scattered on the outer circumference only, and the area that they covered was extremely small. The lower the 0.2% offset strength was, the smaller the area of the intergranular fracture surface became, until it was almost nonexistent for the test specimens with 0.2% offset strength of 777 MPa, and disappeared entirely for the test specimens with 0.2% offset strength of 697 MPa or below.
- (2) When the precipitation status of the two carbides (M_3C and M_7C_3) precipitated at the grain boundary is combined with the results of the SSRT, the precipitation of M_3C matches almost exactly the disappearance of the intergranular fracture surface. Accordingly, the difference in the type of carbide is thought to affect the SCC susceptibility of 3.5% NiCrMoV steel.
- (3) For materials with 0.2% offset strength of approximately 700 MPa or less, M_3C disappeared, and these materials achieved the target value of increased resistance to intergranular stress corrosion cracking in a neutral environment.

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