

Stress Corrosion Cracking Behavior of Hardening-Treated 13Cr Stainless Steel

Li-Bin Niu¹, Hisamitsu Ishitake², Sakae Izumi³, Kunio Shiokawa³, Mitsuo Yamashita³, Yoshihiro Sakai³

¹Shinshu University, Institute of Engineering, Academic Assembly, 4-17-1 Wakasato, Nagano 380-8553, Japan

²Shinshu University, Graduate student, Graduate School, Toshiba Corp., 1 Toshiba-Cho, Fuchu-Shi, Tokyo 183-0043, Japan

³Fuji Electric Co., Ltd. 1-1 Tanabeshinden, Kawasaki-Ku, Kawasaki 210-9530, Japan

Abstract. Stress corrosion cracking (SCC) behavior of the hardening-treated materials of 13Cr stainless steel was examined with SSRT tests and constant load tests. In the simulated geothermal water and even in the test water without addition of impurities, the hardening-treated materials showed a brittle intergranular fracture due to the sensitization, which was caused by the present hardening-treatments.

1. Introduction

13Cr martensitic stainless steel is widely used as a steam turbine blade material for thermal, nuclear and geothermal power plants due to its well mechanical properties and corrosion resistance. On the other hand, in the power plants, trace amounts of corrosive impurities such as chloride ions (Cl^-) and sulfate ions (SO_4^{2-}) present in the steam are easily carried over into the steam turbine with the steam, which tend to cause corrosion damages of the turbine materials [1-4]. Besides, erosion on the front edges of turbine blades in the wet region of the steam turbine due to the drain attack is also one of the problems [5, 6]. It is very important to improve corrosion resistance as well as erosion resistance of turbine materials.

As a method for suppressing erosion of steam turbine blades in power plants, hardening treatments such as quenching of the blade materials have been applied. However, the microstructure of the material changes due to the hardening treatments such as quenching, and the residual tensile stress occurs at the boundary portion of the heat treatment. For this reason, it is concerned that the stress corrosion cracking (SCC) occurs easily on the blade surfaces of the steam turbine during operation due to the corrosive impurities present in the steam, especially chloride ions (Cl^-). In addition to improving the erosion resistance of the blade material, reduction of the SCC susceptibility is also an important subject in prolonging the service life of the steam turbine. However, the influence of various hardening treatment conditions on the SCC susceptibility of blade materials has not yet been sufficiently clarified. In this work, stress corrosion cracking behavior of the materials of 13Cr stainless steel, which were hardening-treated under different conditions, was investigated in corrosive water environments.



13Cr martensitic stainless steel, which has been used as the steam turbine blade material of power plants, was used in this work. Its chemical composition is as follows (mass%): 0.21 C, 0.32 Si, 0.62 Mn, 13.36 Cr, 0.46 Ni, and the balance of Fe. The as-received steel plates were cut from the virgin steam turbine material. Two kinds of hardening treatment were performed in the present work, in which the steel plates were heated up to 1100°C followed immediately by water quenching (WQ) and air cooling (AC), respectively. After that, they were tempered at 250°C for 2h. The Vickers hardness were measured after the hardening treatments. The average hardness of the water quenched and the air cooled materials WQ and AC were HV522 (100gf) and HV535 (100gf), respectively, and both of them were higher than that of the as-received steel of HV307 (100gf).

The specimens, as shown in figure 1, were cut from the hardening-treated and also the as-received steel plates. The surfaces were abraded using 150-800 grit emery papers. Prior to testing, the specimens were degreased with acetone and rinsed with deionized pure water.

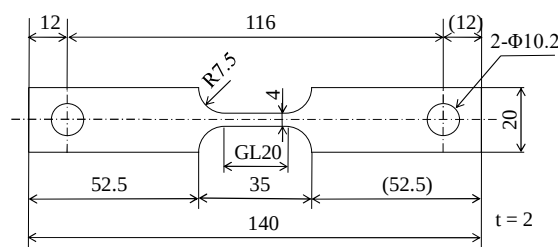


Figure 1. Specimen geometry (dimension in mm).

Table 1. Quality of the test waters.

	Cl ⁻ (ppm)	SO ₄ ²⁻ (ppm)	CO ₂ or N ₂	DO (ppm)	pH	Temp. (°C)
W1	10,000	50	CO ₂ bubbling	<1.0	3.9	90
W2	0	0	N ₂ bubbling	<1.0	6.4	90

Considering the geothermal steam turbine in a severe corrosive environment, as a kind of test water the simulated geothermal water, named W1, was prepared from ion-exchanged pure water by adding the impurity ions of 10,000 ppm Cl^- and 50 ppm SO_4^{2-} , and by continuously bubbling CO_2 gas into the water before and during test. For comparison another test water without the addition of the above impurities, named W2, was prepared from ion-exchanged pure water by continuously bubbling N_2 gas into the water before and during test to remove dissolved oxygen (DO). Table 1 shows the quality of the test waters. The temperature of the test waters was 90°C .

Slow strain rate tensile (SSRT) tests were carried out on the specimens with a strain rate of $4.2 \times 10^{-7} \text{ s}^{-1}$ in the test waters. Constant load tests were also conducted up to 100h at a stress of 650MPa in the test waters. In SSRT tests and constant load tests, the changes in elongation of the specimen were recorded by a data logger.

After the above tests, the fracture surfaces of the ruptured specimens were observed with a scanning electron microscope (SEM). The gauge portion surfaces were also observed with SEM, after emery-polishing up to #1500 and etching with a solution consisted of 8.4 ml methanol, 1.5 ml hydrochloric acid and 0.1g picric acid.

3. Results and discussion

3.1. SCC behavior of the hardening-treated material

The stress-strain curves of the hardening-treated and the as-received materials obtained from SSRT tests in the simulated geothermal water W1 are shown in figure 2. It can be seen that the three specimens exhibited different stress-strain behavior. For the as-received material, the specimen in the water W1 showed a total elongation of 6.45% with a 0.2% proof stress of 670MPa and a ultimate tensile strength of 798MPa. However, the two specimens of the hardening-treated materials showed a brittle deformation mode. For the hardening-treated material WQ with water quenching, even though the specimen showed the highest rupture stress of 946MPa, it ruptured with almost no plastic deformation. Furthermore, the specimen of the hardening-treated material AC with air cooling ruptured in the elastic deformation region with a lower rupture stress of 436MPa.

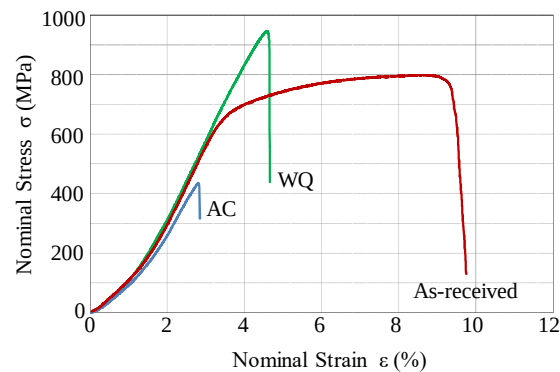


Figure 2. Stress-strain curves of the specimens obtained from SSRT tests in W1.

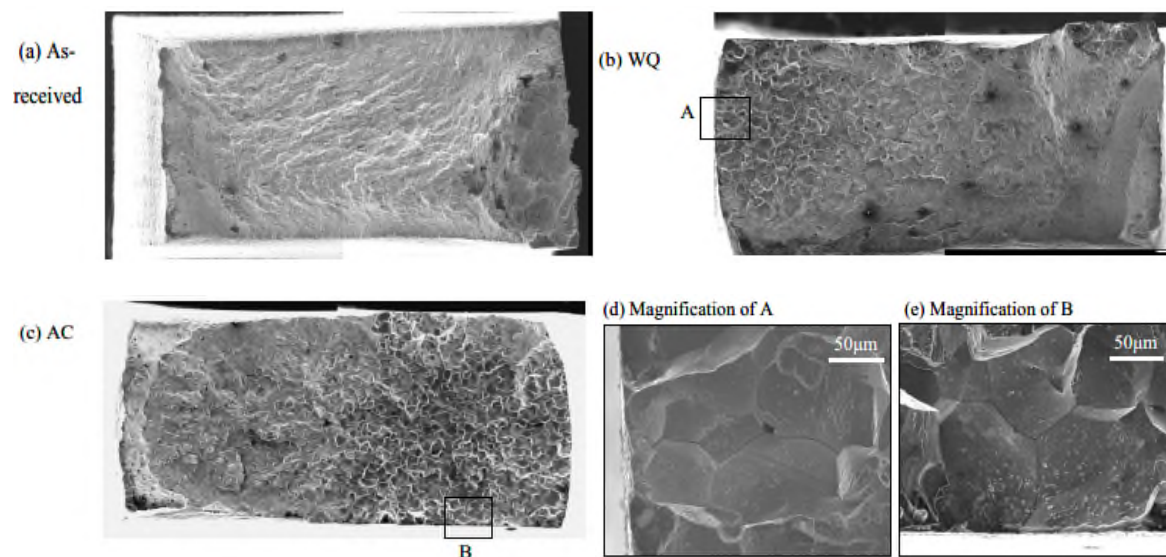


Figure 3. Fracture surfaces of the specimens ruptured in W1.

Figure 3 shows the overall fracture surfaces with partially magnified SEM images of the three specimens of the hardening-treated as well as the as-received materials ruptured in the simulated geothermal water W1. The fractography of the as-received material specimen presented a feature of ductile fracture mode. While the two specimens of the hardening-treated materials WQ and AC showed the mixed mode of ductile fracture with intergranular fracture regions. Particularly, it was observed that the intergranular fracture region on the AC specimen occupied more than half of the fracture surface. Therefore, it is considered that the intergranular crack propagation rate was faster in the AC specimen. Furthermore, as shown in the magnified SEM images of figure 3(d) and figure 3(e), clear grain facets were particularly observed near the specimen surfaces. By the SEM observation on the gauge portions, it was confirmed that many cracks formed on the gauge portion surfaces of the

WQ and AC specimens tested in the simulated geothermal water W1 (figure 4). From the above results, it is inferred that the intergranular cracks nucleation occurred at the surfaces of the WQ and AC specimens. It is considered that sensitization was caused by the present hardening-treatments, especially for the material AC with air cooling, so that the susceptibility of intergranular cracking increased.

The gauge portion surfaces after emery-polishing and etching, of the specimens ruptured in the simulated geothermal water W1, were examined in detail with SEM. No clear cracks were observed on the specimen surface of the as-received material. It is considered that the as-received material of 13Cr stainless steel has a superior corrosion resistance even though in the simulated geothermal water. However, for the hardening-treated materials WQ and AC, many cracks were observed on the gauge portion surfaces of the specimens tested in this water. Furthermore, it was found that most cracks formed in the specimen of the hardening-treated material AC with air cooling were in an intergranular mode along prior austenite grain boundaries (prior γ -GB). It is considered that the sensitization occurred in the hardening-treated material AC was forwarded by the long time air cooling, due to the formation of the Cr-depletion layers along the prior γ -GB in sufficient time. On the other hand, for the hardening-treated material WQ with water quenching it was found that the cracks formed not only in the intergranular mode but also in the transgranular one. Even so, it is considered that the fracture of the WQ specimen in the test water W1 was dominated by the intergranular cracking, which was the same as that of the AC specimen. As an example, figure 5 gives the SEM images near the crack tips on the gauge portion surfaces after emery-polishing and etching of the specimens ruptured in the simulated geothermal water W1. In addition, it is suggested that both the intergranular cracking (figure 5(a), figure 5(b)) and the transgranular cracking (figure 5(c)) occurred on the two hardening-treated materials were SCC (IGSCC and TGSCC), which were caused by the 10,000 ppm Cl⁻ present in the water W1. It has been reported that both of IGSCC and TGSCC occur easily on the sensitized stainless steel in an aqueous solution of chloride [7].

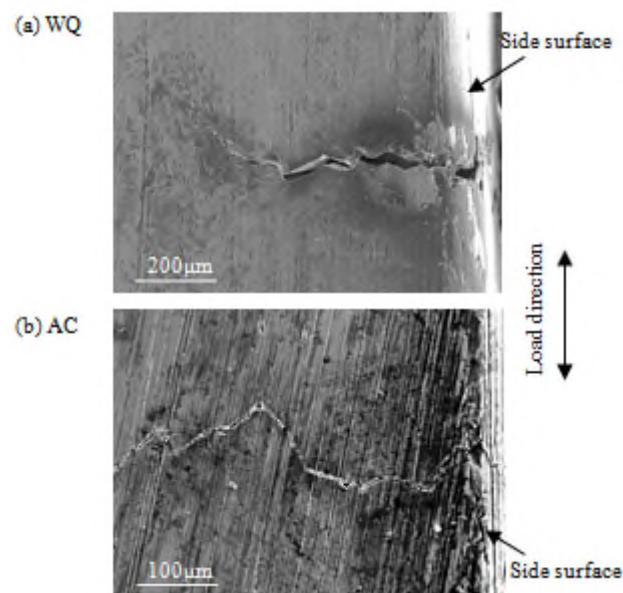


Figure 4. Cracks formed on the gauge portion surfaces of the specimens tested in the simulated geothermal water W1.

3.2. Effect of impurities on cracking behavior

To investigate the effect of corrosive impurities on the cracking behavior of the hardening-treated materials, SSRT tests were also conducted in the test water W2 without the addition of impurities. figure 6 shows the stress-strain curve of the hardening-treated material WQ with water quenching in the test water W2. For comparison, the stress-strain curve of the same hardening-treated material in the

simulated geothermal water W1 was also plotted in this figure. As shown in figure 6, the WQ specimen in the test water W2 without the addition of impurities exhibited a brittle deformation mode. It showed a rupture stress of 741MPa, which is lower even than that of the WQ specimen in the simulated geothermal water W1.

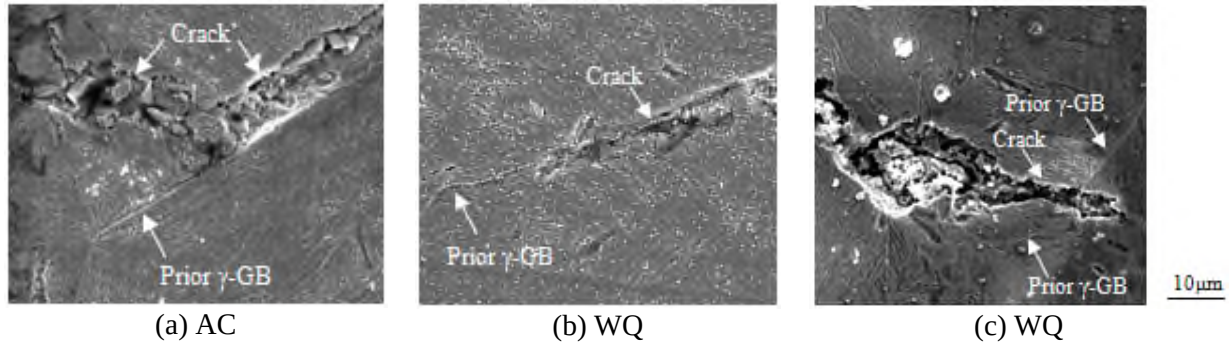


Figure 5. SEM images showing the crack tips on the gauge portion surfaces after emery-polishing and etching of the specimens ruptured in W1.

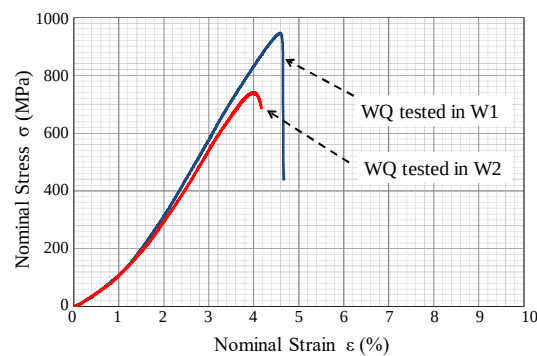


Figure 6. Stress-strain curves of the WQ specimens tested in the simulated geothermal water W1 and in the test water W2 without impurities.

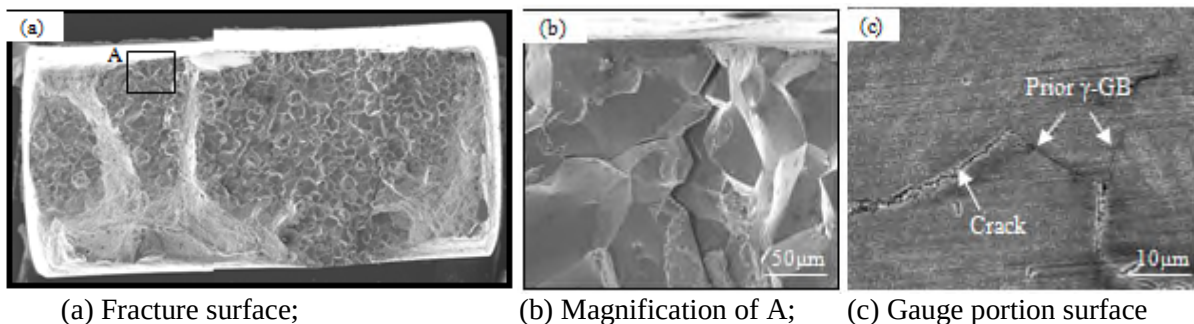


Figure 7. SEM images showing the fracture surface and the gauge portion surface after emery-polishing and etching of the WQ specimen ruptured in W2.

The overall fracture surface and a magnified SEM image of the fracture surface as well as the gauge portion surface after emery-polishing and etching of the specimen ruptured in W2 are shown in figure 7. Most of the fracture surface exhibited a feature of intergranular fracture mode. The cracks along prior γ -GB were observed on the gauge portion surface near the rupture surface. From the above results, it is assumed that the hardening-treated material WQ in the test water W2 without addition of impurities ruptured with other behavior than SCC.

Constant load tests were also conducted on the specimens of the hardening-treated material WQ in the simulated geothermal water W1 and in the test water W2 without impurities. Figure 8 shows the time variations of nominal strain of the two specimens loaded at 650MPa. The specimen in W1

ruptured in 8.3 h, while the specimen in W2 did not rupture up to 100h. The gauge portion surfaces of the two specimens after emery-polishing and etching were examined with SEM. It was found that the cracks along prior γ -GB formed on the specimen ruptured in W1, while no cracks were observed on the specimen tested in W2. It is considered that most of the cracks formed on the specimen in the constant load test in the simulated geothermal water W1 were intergranular SCC (IGSCC), which were the same as those formed in the above SSRT test and were caused by the 10,000 ppm Cl^- present in the water.

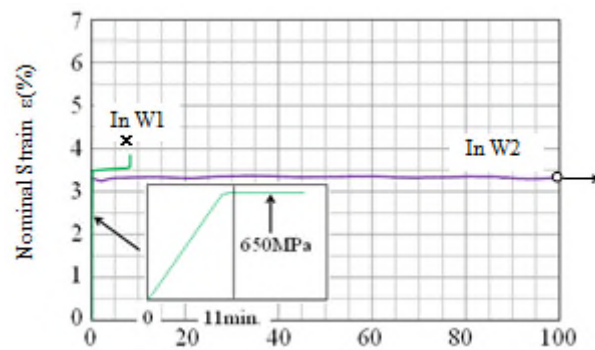
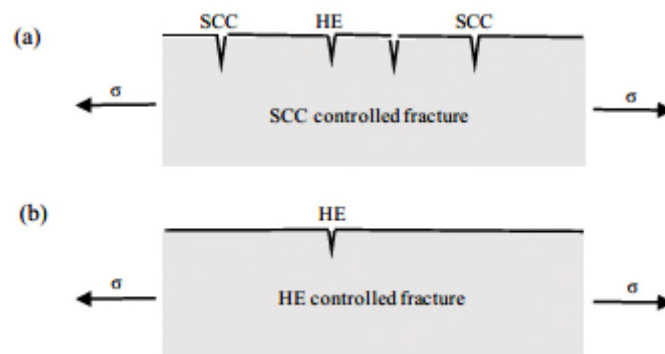


Figure 8. Time variations of nominal strain of the WQ specimens tested at a constant load of 650MPa in the simulated geothermal water W1 and in the test water W2 without impurities.



(a) In the simulated geothermal water W1
(b) In the test water W2 without addition of impurities

Figure 9. Schematic illustration of cracking behavior of the WQ specimens in SSRT tests.

As stated above, no cracks were observed on the WQ specimen in the constant load test in the test water W2 without addition of impurities. However, as shown in figure 7, the cracks along prior γ -GB were observed on the WQ specimen ruptured in the SSRT test in the W2. Therefore, it is wondered if the cracks formed in the SSRT test in the W2 without Cl^- were IGSCC or not.

In both of the test water W1 and W2, the cathodic reactions should be mainly the reduction reaction of hydrogen ions (H^+), because the dissolved oxygen (DO) were removed by continuously bubbling of CO_2 gas (W1) or N_2 gas (W2). As atomic hydrogen (H) were generated and adsorbed on the specimen surfaces, it is considered that hydrogen embrittlement (HE) occurred on the specimens of the hardening-treated materials. It has been known that in high strength steels HE occurs easily even if a very small amount of hydrogen [8]. It has been also reported that in high strength steels HE occurs easily in an intergranular mode [9]. In this work, it is considered that the WQ specimen in the SSRT test in W2 ruptured unexpectedly due to the occurrence and rapid growth of HE cracking. On the other hand, for the present hardening-treated materials in the simulated geothermal water W1, it is considered that IGSCC controlled the cracking behavior due to the presence of the 10,000 ppm Cl^- , even though HE occurred also on the specimen surfaces. It is also assumed that for the specimen of the hardening-treated material WQ in SSRT test in the simulated geothermal water W1, due to many IGSCC occurred on the surface the plastic restraint was relaxed the specimen showed a higher stress to

rupture than that in the test water W2 (figure 6). Figure 9 schematically illustrates the cracking behavior of the WQ specimen in the simulated geothermal water W1 and in the test water W2 without addition of impurities.

4. Conclusions

Stress corrosion cracking behavior of the hardening-treated materials of 13Cr stainless steel was examined with SSRT tests and constant load tests, in the simulated geothermal water and in the test water without addition of impurities. The results obtained are as follows.

(1) Both the two hardening-treated materials, WQ with water quenching and AC with air cooling, showed a brittle deformation mode in the test waters due to the sensitization caused by the hardening-treatments. Especially the hardening-treated material AC showed a more brittle fracture mode, as the sensitization was forwarded by the long time air cooling.

(2) In the simulated geothermal water, IGSCC with a part of TGSCC occurred on the hardening-treated material WQ with water quenching, while most of IGSCC occurred on the hardening-treated material AC with air cooling. In the test water without addition of impurities, the hardening-treated material WQ in the SSRT test exhibited a brittle fracture mode. It is considered that HE cracking occurred on the WQ specimen in the test water.

References

- [1] Bellows J C 1999 *PowerPlant Chem.* **1** 26-30.
- [2] Jonas O 1985 *Mater. Perform.* **24** 9-18.
- [3] Jonas O, Machemer L 2008 *Steam turbine corrosion and deposits problems and solutions* Proc 37th Turbomachinery Symposium, (Houston, USA, 2008), 211-28.
- [4] Sakai Y, Yamashita M, Sakata M 2000 *Geotherm. Res. Counc. Trans.* **24** 521-6.
- [5] Sakai Y 1999 *Therm. Nucl. Pow.* **50** 778-83.
- [6] Kato H, Shiokawa K, Sakai Y 2004 *Turbomach.* **32** 599-606.
- [7] Oki T, Okido M, and Kanamatsu H 1985 *Boshoku Gijutsu* **34** 546-51.
- [8] Shiraga T 2011 *Zairyo-to-Kankyo* **60** 236-40.
- [9] Nakasato F 1982 *Bull. Japan Inst. Met.* **21** 441-8.