Pitting Corrosion Resistance of CA6NM and 410 Martensitic Stainless Steels in Various Environments

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Abstract. Pitting corrosion is an importance phenomena in power generation steam turbine, as it is one of the main causes for blade failure, particularly in the last row of low pressure blading. In this work, the pitting corrosion resistance of the widely used blading alloy of wrought 410 stainless steel and that of the candidate alloy of cast CA6NM stainless steel were investigated. Cyclic polarization measurements for all samples were conducted in simulated solution of thermal and geothermal power plants. The experimental results show that the pitting potentials of the cast CA6NM steel were higher compared to those of the wrought 410 steel in all simulated solution. Both steels exhibited higher pitting potentials in CO2 containing simulated geothermal water than those in the other solutions. These results were correlated with microstructure of the steels observed by Scanning Electron Microscope (SEM).

1. Introduction

Pitting is one of the localized corrosion attacks on metals surface due to the passive film breaking in corrosive environments. It is an importance phenomena in power generation steam turbine, as it is one of the main causes for blade failure, particularly in the last row of low pressure blading [1-2]. Therefore, the pitting resistance of the steam turbine blade materials is expected to be high for ensuring longer life of the blade. The improvement of pitting resistance as well as mechanical properties of the blade materials has been continuously investigated by chemical composition modification or by optimizing heat treatment processes of the martensitic stainless steel type 403/410 as the standard alloys for steam turbine blades. The Ni and Mo were incorporated and optimized into the standard 403/410 stainless steel and the improved properties were exhibited by the modified alloys [3-6].

The CA6NM alloys is cast martensitic stainless steel originally containing Ni and Mo which is widely used as the blade materials for hydro turbine due to its high cavitation erosion resistance. There were no intensive application of this CA6NM steel for steam turbine blade, although with the high content of Ni (4%) and reasonable Mo (1%). This might be caused by the inferior mechanical properties combination of the cast product (CA6NM) compared to the wrought product (410). However, for the application of low pressure blading, particularly in geothermal steam turbine with lower temperature of steam compared to coal-fired steam turbine, the cast product with better pitting corrosion resistance is appropriate and relatively more economical choice. This work aimed to assess
the pitting resistance of the cast CA6NM in the geothermal environments and in the chloride containing media and compared it to that of the 410 in similar environments. The pitting parameters were determined from the cyclic polarization experiments by using Gamry G750 Corrosion Measurement System (CMS).

2. Experimental

2.1. Materials

The steels for the experiments were cast CA6NM stainless steel prepared by induction melting furnace in the laboratory and the 410 stainless steel rod purchased from the market. The composition of the two steels are shown in the Table 1. Both steels were experienced by similar heat treatment process consisting of quenching and tempering before the cyclic polarization measurement. The steels were austenitized at temperature of 1050°C for 2h and finished by quenching in oil. Subsequent tempering was conducted at temperature of 650°C for 3h and finished by air cooling. The samples from heat treated steels were prepared for the hardness testing (Rockwell C), microstructural observation by optical microscope and cyclic polarization. The samples for microstructural observation were prepared by standard metallographic preparation consisting of mounting, grinding and polishing until 0.3 micron of alumina particle. The polished samples were etched with Kalling’s reagent for revealing the microstructures. The samples for cyclic polarization were machined to the sizes of 1 x 1 cm² and attached with copper cable by soldering before they were mounted with resin. The surface of the mounted samples was then ground with SiC abrasive paper until size 1200.

Table 1. Chemical composition of the investigated steels (wt.%).

| Steel  | C  | S  | P  | Mn | Si | Cr   | Mo | Ni  | Fe  |
|--------|----|----|----|----|----|------|----|-----|-----|
| CA6NM  | 0.04 | 0.008 | 0.02 | 0.40 | 0.35 | 12.83 | 1.02 | 4.17 | Bal. |
| 410    | 0.07 | 0.005 | 0.02 | 0.30 | 0.44 | 10.93 | 0.01 | 0.12 | Bal. |

2.2. Cyclic Polarization Test

The cyclic polarization test was conducted by Gamry G750 Corrosion Measurement System at room temperature in three kinds of solution separately. These solutions were the simulated geothermal solution without CO2, the simulated geothermal solution with CO2 and the NaCl solution. The composition of the simulated geothermal solution is displayed in the Table 2. Three kinds of electrode were used for the measurement, i.e. the working electrode of sample, the auxiliary electrode of graphite rod and the Saturated Calomel Electrode (SCE) as a reference electrode. The cyclic polarizations were carried out for a potential range of -600 to 1200 mV with forward scan rate of 5 mV/s and reverse scan rate of 2.5 mV/s. After the measurement, the samples were clean with water and dried. The pitting occurred in the samples were observed by Scanning Electron Microscope (SEM) imaging.

Table 2. Chemical composition the simulated geothermal solution.

| Chemical Species | g/l |
|------------------|-----|
| NaCl             | 224.60 |
| NaSO4.10H2O      | 12.07 |
| MgCl.6H2O        | 10.62 |
| CaCl2.2H2O       | 6.45  |
| KCl              | 0.39  |
| KOH              | 0.32  |
3. Results and Discussion

The microstructure of CA6NM and 410 stainless steels in quenched-tempered condition are shown in Figure 1. Both steels exhibit dominantly martensite phase as a typical microstructure of the martensitic steels. The difference for the two martensite structures are in the size and fraction, where smaller size and larger fraction are observed in the CA6NM steel. The metal carbides exist in both steels with no distinct appearance in their sizes and distribution due to lack of resolution and magnification of optical microscope imaging. In addition, delta ferrite phase are absence in these two steels due to the absence of Mo (which acting as ferrite stabilizer) in 410 steels and due to the presence of high Ni (4%) in CA6NM steels (with 1% Mo) which suppressed the formation of delta ferrite.

Figure 2 show the hardness of the two investigated steels in non quenched-tempered (Non-QT) and in quenched-tempered conditions. The Non-QT condition for CA6NM steel refers to as cast condition, while for 410 steel refers to annealed condition. Therefore, for Non-QT condition the hardness of CA6NM steel is higher than that of 410 steel. This is due to the martensite phase exists in the typical as cast martensitic steels, while for annealed condition the microstructure consists of soft ferrite phase and globular carbides. In QT condition, the CA6NM steel consistently exhibits higher hardness compared to that of 410 steel. The microstructure of the steels in Figure 1 confirms the higher hardness of CA6NM steel due to larger fraction of martensite phase.

![Figure 1](image_url)

**Figure 1.** Optical microscope images of the microstructure of the (a) CA6NM (b) 410 stainless steels in quenched-tempered condition.

The pitting corrosion behaviour of the two martensitic stainless steels can be assessed from the cyclic polarisation measurements. The cyclic polarisation curves of the steels are shown in Figure 3. Both steels display hysteresis curves resulted from forward and reversed scans which describe the passive region of the steels in the respective solution. The pitting behaviour of the steels can be evaluated by determining the pitting potential, repassivation potential and how large the difference between them. The steels with higher pitting and repassivation potentials exhibit higher pitting resistance. Whereas, the steels with smaller potential differences (small hysteresis) will have lower susceptibility to pitting corrosion. At the pitting potential the passive film breaks forming pit and the current density abruptly increases through the forward scan. In the reverse scan the current density...
decreases again and the repassivation of pit occurs when crossing the forward line. As shown in Figure 3 most of the curves do not exhibit this crossing potential indicating that the pits may continue to grow.

Figure 2. Hardness of the CA6NM and 410 stainless steels in non quenched-tempered (Non-QT) and in quenched-tempered (QT) conditions.

The pitting potentials of the steels in difference solution determined from the curves in Figure 3 are shown in Figure 4. The CA6NM steel has pitting potential higher than the 410 steel has in all solutions. This may be due to the higher content of Cr in the CA6NM steel compared to that in 410 steel, where Cr is the element responsible for passive film formation. On the other hand, the pitting potentials of both steels in CO2 containing solution is higher than those in other solutions. The CO2 bubbling into the solution might promote the formation of Na/Mg/Ca carbonates salts in simulated geothermal solution which inhibited the chloride ions attacks. S.A.M Rafae et al reported that the addition sodium carbonates increased the pitting resistance of the stainless steel by the inhibition effect of (Fe,Cr)CO3 film [7]. The lowest pitting potential is exhibited by the 410 steel in the simulated geothermal solution with Epit is -475.3 mV.

Figure 5 and Figure 6 show the SEM images of the surface of the respective stainless steels CA6NM and 410, after cyclic polarisation in the three simulated solutions. The number of pits in CA6NM is larger than that in 410, although the pitting potential of the CA6NM steel is higher. This can be explained by considering other factors such as the carbides content and the quality of the steels. The CA6NM steel with higher content of Mo may have larger content of carbides due to acceleration of carbides precipitation caused by Mo[8]. These carbides are potentially as an initial location for pitting corrosion [9]. With respect to the steels quality, the cast product tends to have inhomogeneity or chemical segregation higher than the wrought product have. In addition, it can be observed also that the pits in 3.5% NaCl are larger and deeper in sizes, particularly in 410 steel. This indicate that higher content of NaCl (in this case 3.5% NaCl is higher than 224.60 g/l in simulated geothermal solution) increases the corrosion severity of the solution. Furthermore, general corrosion are observed in sumulated geothermal solution, particularly in CA6NM steel. This may be due to higher hardness of the CA6NM steel compared to the 410 steel, considering that the hardness value has correlation with the corrosion resistance as reported by S. Weng et al.[10].
Figure 3. Cyclic polarization curves of the (a) CA6NM (b) 410 stainless steels in various simulated solutions.
Figure 4. Pitting potential of the CA6NM and 410 stainless steels in various simulated solutions.

Figure 5. SEM images the surface of the CA6NM stainless steel after cyclic polarisation in (a) geothermal (b) geothermal+CO2 and (c) NaCl simulated solutions.

Figure 6. SEM images of the surface of the 410 stainless steel after cyclic polarisation in (a) geothermal (b) geothermal+CO2 and (c) NaCl simulated solutions.
4. Conclusion
The pitting corrosion resistance of the cast CA6NM stainless steel in the geothermal environments and in the chloride containing media has been assessed and compared it to that of the 410 stainless steel in similar environments. Pitting potential of CA6NM steel is higher than that of 410 steel in simulated geothermal and in 3.5% NaCl solutions, however, the number of pits in CA6NM steel are larger than that in 410 steel according to SEM images observation. The CO$_2$ increases pitting potentials of the two steels in simulated geothermal solution. Furthermore, the pits of two steels in 3.5%NaCl are larger and deeper in sizes than those in simulated geothermal solution.

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