AUGER ELECTRON SPECTROSCOPY AND ELECTROCHEMICAL INVESTIGATIONS

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Abstract:

The fractured faces of 12%Cr martensitic stainless steel specimens, virgin material (sample 1) and material having been in service in steam turbine (sample 2), were investigated by Auger electron spectroscopy, scanning electron microscopy SEM. Pitting corrosion behaviour of the same specimens was also examined by potentiodynamic cyclic polarisation techniques. For the samples 1, the brittle and intergranular fracture mode dominates with, however, the presence of some ductile areas. In contrast, samples 2 display a ductile and transgranular fracture mode with a few zones of intergranular fracture. The interpretation of Auger analysis attributes the brittle to ductile transition to the simultaneous diffusion of carbon from grain boundary region (GB) to grain centre (G) and chromium from (G) to (GB). The intergranular crack rupture traces could be assigned to the observed strong phosphorus segregation at grain boundaries. In all samples, cracks do not propagate along ferritic areas. The dominance of intergranular mode (sample 1) is due to the presence of inclusions at GB, such as Si based inclusions. The brittleness after fatigue (sample 2) is attributed to phosphorous segregation and possibly the presence of MnS inclusions. Results from electrochemical cyclic potentiodynamic studies and immersion tests have proved that all the specimens tested showed susceptibility to pitting. In comparison with as received materials, samples 2 showed an improvement in pitting corrosion resistance. Such improvement could be the result of carbides dissolution and chromium redistribution in the matrix.

1. Introduction:

Martensitic stainless steels have been widely used for steam turbine blades [1, 4]. These materials contain up to 1 % carbon and the chromium content is in the range 12 - 18 %. The corrosion resistance is provided by chromium and the high mechanical performances stem from the martensitic structure. The most commonly used martensitic stainless steel is the Cr -12 (12 % Cr). Additional alloying elements such as Ni, Mo, Si, V and Nb improve furthermore its properties allowing withstanding various internal and external stresses [5, 8]. This particular alloy is the subject of our study. We focus on the effects of heat treatments (quenching and annealing) on the final structures and the induced mechanical properties. Under some usage contexts [T=40°C, P= 0.08 Bar], Cr and C segregation can take place in Cr -12 (12 % Cr) alloy resulting in an improvement of its fatigue performances [9]. In commercial alloys, inclusion and impurities are always present. In some cases, they are also deliberately introduced for the purpose of obtaining better properties [1, 8]. Mayes et al [8] and Williams et al [9] have suggested that impurities such as P, C, S and the precipitation of MnS inclusions lead to fatigue crack initiation at grain boundaries. Furthermore, fatigue crack initiation can be favoured by corrosion. Hence, a material that is characterized by excellent fatigue performances can undergo catastrophic crack propagation when corrosion interferes [9, 10].

A thorough characterization of components that have been in service a sufficient time span can give indications about the mechanisms responsible of crack propagation. To this end, a
study using the powerful tools, SEA and SEM in conjunction with cyclic potentiodynamic polarisation has been undertaken. Components that have been in service during about 100 000 hours are investigated making possible the assessment metallurgical evolutions (in particular the segregation) and their induced effects.

3. Experimental procedure:

3.1. Materials:

The material under investigation was the 12%Cr stainless steel. Its chemical composition is shown in table 1. Two types of specimens were studied. The first (sample n°1) is a virgin as manufactured material with characteristics identical to those reported elsewhere [5]. The second one (sample 2) has the same characteristics as the first but has been previously used in a steam turbine at temperature of 40°C for 100 000 hours (the specimens were sectioned from a Turbine Blades).

Table 1: Chemical composition (wt%) of the as manufactured steel.

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>Cr</th>
<th>Al</th>
<th>Si</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>N</th>
<th>Mo</th>
<th>Ni</th>
<th>Cu</th>
<th>Ti</th>
<th>V</th>
<th>Fe</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>0.2</td>
<td>12.4</td>
<td>0.02</td>
<td>0.45</td>
<td>0.74</td>
<td>0.0</td>
<td>0.03</td>
<td>0.01</td>
<td>1.1</td>
<td>0.77</td>
<td>0.1</td>
<td>0.3</td>
<td>0.03</td>
<td>Bal</td>
</tr>
</tbody>
</table>

3.2. Auger electron spectroscopy analysis:

All samples were subjected to Auger electron spectroscopy (A.E.S) analyses using a PHI600 system. For this purpose, specimens were prepared with a notch in the coarse grained zone for in-situ fracturing within the Auger instrument. Fracturing was performed at nitrogen temperature under a pressure less than 10⁻⁹torr.

3.3. Electrochemical measurements:

For the potentiodynamic studies, the working electrodes were cut from 12%Cr stainless steel with a rectangular form. In order to provide an exposed surface electrode of 0.7 cm², the specimens prepared from sample 1 and sample 2 were mounted in epoxy resin. Before each anodic polarisation, the electrodes surfaces were polished with silicon carbide paper to 1200 grit, washed in distilled water, degreased in alcohol, and dried in air. The polarisation curves were recorded in cyclic potentiodynamic mode with a potential scan rate of 0.166mV/s using a potentiostat/Galvanostat M273 (EG&G PARC), which is connected to a fully compatible IBM computer and controlled by EG&G Soft corr352 corrosion measurement and analysis software. Polarisation started at -250 mV under open circuit potential. The electrochemical tests were carried out in conventional three-electrode electrochemical glass cell with a saturated calomel electrode as reference (SCE) and platinum wire as counter electrode.

3.4. Solutions:

All solutions were prepared with distilled water and analytical-grade reagents. NaCl and Na₂SO₄ were purchased from Aldrich and were added to distilled water without further treatments. The electrochemical tests were carried out in two electrolytic solutions of different degree of aggressiveness, 10⁻²M (NaCl + Na₂SO₄) and 3%wt NaCl at room temperature. The first solution consists of 10⁻²M (NaCl + Na₂SO₄), which is particularly adapted for the description of pitting of steels with 12%Cr [5]. This solution is close to the real media of operation of the wings of turbine for vapour (treated sea water). The origin of sulfates ion in that media is probably from ion exchange resin used for the water purification system. For
this reason, it is important to study the effect of this species on the corrosion of 12%Cr stainless steel.

4. Results and discussion

a) As manufactured steel (sample 1)

The crack path of the fractured samples under Auger examination is mainly intergranular. One can see from Fig 1a the fracture surface is predominantly smooth. A noticeable carbon and chromium enrichment in the grains boundaries is detected.

![Micrograph showing fracture mechanism during impact fracture: intergranular fracture in steel 1.](image1)

![Micrograph showing fracture mechanism during impact fracture: transgranular fracture in steel 2.](image2)

Only traces of phosphorus are detected by Auger peak localised at 152 eV. For sample 1, the spectra of Fig 2 exhibit low intensity Auger signals for C and Cr at 270 and 490 eV inside the grain structure; Significant changes in the intensity of the Auger peaks for C and Cr can be observed in the grain boundary region (Fig3). The relative AES peak height intensity of the dN(E)/dE spectra for sample 1 and 2 are derived and used to estimate the concentration ratio of C and Cr between the grain centre and the grain boundary region. The
results indicate that the grain boundary region of sample 1 is considerably richer in carbon and chromium than the grain bulk. As indicated in Table 2, the enrichment ratio is found equal to .84 (for C) and .61 (for Cr). The partly high oxygen enrichment at the intergranular area of the fracture specimen is probably due to the fact that some grain boundary were sufficiently separated to provide a connection path to the atmosphere.

![AES spectra of sample 1](image)

**Fig. 2:** AES spectra of sample 1 representing: (a) the grain, and (b) the grain boundary obtained from the intergranular fracture.

**b) Steel specimen from steam turbine (sample 2)**

The same Auger analysis was carried out for sample 2. The appearance of its fracture surface is quite different from that of sample 1 (i.e., sample 1 is predominantly smooth while a dimpled structure emerges from sample 2). The fractographic observations of Fig.1b reveal a number of facets and cavities, which are associated with a transgranular structure fracture with the presence of brittle areas. The Auger line profile (Fig. 3) and the punctual Auger analysis (Fig 5) point out a significant increase of chromium and a pronounced decrease of the concentration of carbon in the grain boundary region as compared to that of the grain with an average ratio of 0.68 and 1.78.
Therefore, the change in the structure could be attributed essentially to the segregation of carbon from the grain boundary region to the grain centre during the life service of the material. It was also shown in this study, that the intergranular region was enriched by chromium and carbon, which leads to the rupture by embrittlement of original steel. For steel 2, at the early stage of the fatigue test, the segregation of carbon and chromium respectively at the grain centre and at the grain boundary regions permits a ductile behaviour of the material to take place with high resilience characteristics. The relative enrichment of the grain in carbon after fatigue induces a high segregation of phosphorus at G and GB as shown by the AES punctual analysis (Fig 2 and 3). The inclusions associated to these fracture modes were too small in most cases to be detected by integral Auger analysis. The results obtained from Auger analysis fractured samples were as follows: samples fractured in situ in the Auger instrument were:

a) Fracture mode:
- for steel 1: the fracture was brittle with an intergranular mode and the presence of ductile areas.
- for steel 2: the fracture was ductile with a transgranular mode and presence of traces of an intergranular mode fracture.

b) Auger analysis:
Furthermore, the heavy segregation of phosphorus at the grain boundaries could explain the intergranular crack rupture traces observed in steel 2.

4.2. Electrochemical behaviour:
The corrosion behaviour of specimens cut from steel n°1 and steel n°2 in two solutions 10^-2 M (NaCl + Na_2SO_4) and 3%wt NaCl was investigated by electrochemical measurements and tests of immersion.

4.2.1. Open circuit potential behaviour
Figure 4 presents the open circuit potential (OCP) transients for type CR12w% steels (as received and used state) in 10^-2 M (NaCl + Na_2SO_4) solution. As can be seen, open circuit
potential of each type steel decreases as function of time and both reach a time (about 1000sec) where no significant change in OCP values are observed. The decrease in OCP can be attributed to weakening of steel passivity or surface activation, for example due to an air-formed oxide transformation and yielding of less compactness and diffuse layer that does not protect the metal from further corrosion. The OCP curves are shifted parallel to less noble direction (cathodic) with time, but that of the steel n°1 (as received) is lowered more than that of steel n°2 (used).

Consequently, from the open circuit potential transients obtained just after immersing specimens, it is concluded that the type steel n°2 (used) surface film appears to resist better than that of type steel n°1 (as received) surface film in $10^{-2}\text{M (NaCl + Na}_2\text{SO}_4$ solution.

4.2. 2. Potentiodynamic cyclic polarisation
The tendency to pitting behaviour of specimens from steel n°1 (as received) and steel n°2 (used) in solutions of $10^{-2}\text{M (NaCl + Na}_2\text{SO}_4$ was investigated by electrochemical measurements and tests of immersion in 3%wt NaCl. It is known that concentration of the aqueous salt solution clearly controls the onset of pitting of the martensitic steel which is previously exposed to fatigue conditions [9].

The potentiodynamic cyclic polarisation curves of the two type steels are shown in figures 5 and 6. It may be seen that there are no marked differences in anodic curves obtained in the above media. Both of the tested steels show spontaneous passivity in this solution after the onset of anodic current and a wide region of steel passivity ($\Delta E = \text{E_{pit} - E_{cor}}$) which extended up to the Break down potential can be clearly seen in potentiodynamic curve measured at positive potential scan (approx. 0.6V and 0.88V for steel n°1 and 2 respectively). During further positive scan in applied potential an anodic current increased. Upon the reverse anodic scan, the current decreased slowly to its protection potential $E_{prot} < E_{cor}$ (see the table n°2). Marked hysteresis, which was detected between anodic curves measured at positive scan and back scan for both steels (as received and used), can be attributed to pitting phenomenon [12, 13]. The micrographs in Fig. 9 and 10 show an example of such pitting corrosion.
Breakdown (Epit) and protection (Eprot) potentials measured in cyclic polarisation curves were much more positive for type steel n°2 sample (Epit = 587mV and Eprot = -323mV) than those for type steel n°1 sample (Epit= 292mV and Eprot = -424mV).

Analysing the electrochemical parameters above, we can see that tiredness has a positive effect on the pitting corrosion resistance of the martensitic steel. This improvement of pitting resistance of the used stainless steel compared to that of as received steel is probably attributed to redistribution of Chromium and carbon segregation during life service as demonstrated by auger spectroscopy above.

It is believed [14, 15] that the dissolution of carbides MxCy types during the life service induced a carbon and chromium excess in the martensitic matrix. The segregation of these elements can thus transforms a low part of martensitic to the austenitic phase and enrich martensitic phase with chromium. It should be noted that the segregation of chromium to the grain boundary will consolidate the grain boundary due to the ferrite formation [16, 17]. Consequently, all these transformations partly explain the improvement of the corrosion resistance of the used steel as depicted in the figure 8.
Figure 6: Cyclic anodic potentiodynamic curves of used martensitic steel measured after OCP exposure in 10^{-2}M (NaCl + Na_{2}SO_{4}) solution

Table n°2: Electrochemical parameters obtained from figures 2, 3.

<table>
<thead>
<tr>
<th>Type</th>
<th>Steel</th>
<th>Ecor (mV)</th>
<th>Epit (mV)</th>
<th>Eprot (mV)</th>
<th>Corrosion rate (MPY)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As received (n°1)</td>
<td>-328</td>
<td>292</td>
<td>-424</td>
<td>0.873</td>
<td></td>
</tr>
<tr>
<td>Used       (n°2)</td>
<td>-298</td>
<td>587</td>
<td>-323</td>
<td>0.135</td>
<td></td>
</tr>
</tbody>
</table>

4. Conclusion:
The results obtained in this work showed that:
a) Fracture mode:
   - for steel 1: the fracture was brittle with an intergranular mode and the presence of ductile areas.
   - for steel 2: the fracture was ductile with a transgranular mode and presence of traces of an intergranular mode fracture.
b) Auger analysis:
The Auger results allowed us to understand the brittle to ductile transition for the material by showing the simultaneous diffusion of carbon from grain boundary region (GB) to grain centre (G) and chromium from (G) to (GB).
Furthermore, the heavy segregation of phosphorus at the grain boundaries could explain the intergranular crack rupture traces observed in steel 2.
Results from electrochemical cyclic potentiodynamic studies and immersion tests have proved that all the specimens tested showed susceptibility to pitting. The improvement in corrosion resistance of those of steel 2 is probably attributed to carbides dissolution and chromium redistribution in the matrix.
References