Microstructure and fracture mode of a martensitic stainless steel steam turbine blade characterized via scanning auger microscopy and potentiodynamic polarization

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Abstract. The microstructure, the fracture and the resistance to pitting corrosion, in a 10⁻² M (NaCl + Na₂SO₄) solution, of steam turbine blades, made of martensitic stainless steel (12% Cr), were analysed prior and after their utilization (during about 100 000 hours). The unused blades display an inter-granular fracture mode whereas a trans-granular one emerges in used blades. The SAM analysis of the fractured surfaces reveals that this change is concomitant with carbon and chromium redistribution from the grain boundaries to the grain interior. The potentiodynamic polarization curves and the SEM-EDS analysis of the pitting sites show that the used blades are less susceptible to pitting corrosion than the unused ones. These results are interpreted as a further qualitative evidence of an evolution of the microstructure leading to the formation of new precipitates.

1. Introduction

Martensitic stainless steels are widely used as steam turbine blades [1-6]. The corrosion resistance is provided by chromium and the high mechanical performances stem from the martensitic structure. The most commonly used alloy is the Cr-12 (12 % at Cr with 1% at C). Additional alloying elements such as Ni, Mo, Si, V and Nb may improve furthermore the performances [5, 7, 8]. In commercial alloys, inclusions and impurities are always present and they can be deliberately introduced for the purpose of achieving better properties [1, 8].

Failure of steam turbine components is associated with crack initiations, from inclusions located at the free surface that could be, in addition, stimulated by pitting corrosion [4, 6]. However, crack initiations within the bulk, from nonmetallic inclusions, have also been identified after 40000 h service, suggesting that the microstructure has evolved [9]. Different carbide transformations have been identified in gas turbine components exposed for 100 000 h at temperatures in the range 673-723 K [10]. Hence, it appears that long term exposures, even at temperatures as low as 623 K, can result in metallurgical transformations having an effect on the mechanical performances. Here, in contrast with steam turbine components, carbon contamination may also interfere.
In this work, we investigate some microstructural changes induced by long-term service (about 100,000 h) of steam turbine blades made of a 12% Cr martensitic stainless steel via the analyses of the fractured surfaces. We will consider the changes occurring in the bulk of the blades (i.e., far from the surface). To this end, samples machined from unused and used blades will be fractured under ultra-high vacuum, within a Perkin Elmer equipment, at nitrogen temperature. The ensuing observations and the punctual analyses of the fractured surfaces will be performed in-situ, via the coupled Scanning Auger Microscopy (SAM). In addition, potential dynamic cyclic polarization measurements will be carried out. Then, the revealed pitting sites will be characterized by means of scanning electron microscope and energy dispersion spectroscopy (SEM-EDS). The motivation is to provide some qualitative evidence of the metallurgical evolutions, occurring within the bulk of the blades, which could spur further investigations aimed at improving the predictions of life span assessment.

2. Materials and Experimental

2.1 SAM analyses

The steel, from which the blades were manufactured, had undergone an austenization heat treatment at 1323 K for 1 h. After quenching in oil, another heat treatment had been performed at 898 K for 1 h. The composition, given in Table 1, was determined by means of X-Ray fluorescence and comes out almost identical to that reported in reference [4]. The samples were cut from the central part of the blades and machined to identical dimensions. Then, they were notched for in-situ fracturing and characterization, performed under high vacuum ($10^{-10}$torr) at nitrogen temperature, within Perkin Elmer equipment (type PHI 600). Sample 1 and 2 will refer, respectively, to the unused blade and the used one. The service conditions, provided by the plant operator, were the time of utilization (about 100,000 h), the steam temperature (near 673 K), the maximum pressure (250 bars) and the spinning speed (3800 rpm).

Table 1: Chemical composition (in wt %) of the blades obtained by means of X-Ray fluorescence

| C   | Cr  | Al | Si  | Mn | P  | S   | N  | Mo | Ni | Cu | Ti | V  | Fe |
|-----|-----|----|-----|----|----|-----|----|----|----|----|----|----|----|
| 0.21| 12.4| 0.02| 0.45| 0.74| 0.05| 0.003| 0.01| 1.1 | 0.77| 0.12| 0.35| 0.03| Bal |

As mentioned above, the characterizations of the fractured faces (i.e., the micrographs and the Auger spectra) were performed in-situ by means of the SAM. As a result, any surface contamination, during these characterizations, was de facto precluded. The Auger spectra were acquired with Cylindrical Mirror Analyser in derivative mode. We systematically observed the variations of the peak height intensities related to the $dN(E)/dE$ spectra for carbon, chromium, iron and oxygen. The peak intensities were translated into concentrations of elements taking into account their respective sensitivity coefficient. The quantification of the composition is facilitated using peak-to-peak heights of the $dN(E)/dE$ signal corrected by sensitivity factors. The Auger peak-to-peak heights of C (272 eV), O (510 eV), Fe (703 eV), Cr (529 eV) and P (120 eV) were measured.

2.2. Electrochemical measurements

The solution, $10^{-2}$M (NaCl + Na$_2$SO$_4$), was prepared from distilled water and analytical-grade reagents. The choice of this solution was furthermore motivated as it appears particularly adapted for the study of pitting corrosion of 12% Cr stainless steel [5]. Incidentally, its composition is close to the actual operating environment of the blades (i.e., because the vapor was obtained from sea water and sodium sulfate was present in the ion exchange resin used in the water purification system).
The rectangular working electrodes were machined with an exposed surface of 0.7 cm² and then mounted in epoxy resin. Before each anodic polarization, the electrodes surfaces were mechanically polished with silicon carbide paper to 1200 grit, degreased, rinsed and dried.

The electrochemical tests were carried out, at room temperature, in a conventional three-electrode electrochemical glass cell with a saturated calomel electrode, as reference (SCE), and platinum sheet, as counter electrode. The polarization curves were recorded in cyclic potentiodynamic mode, with a potential scan rate of 0.166 mV/s, using a potentiostat/Galvanostat A273 (EG&G Princeton Applied Research) that was connected to a fully compatible IBM computer and controlled by EG&G Softcor M352 corrosion measurement and analysis software. Polarization starts at -250mV under open circuit potential. The samples used in cyclic polarization were observed by means of a Scanning Electron Microscopy (SEM) (Philips environmental: FEI/PhilipsXL30 FEG ESEM). The qualitative punctual analysis of the pitting sites was performed by means of Energy Dispersion Spectroscopy (EDS).

3. Results and discussion

3.1. Observations of the fractured faces
The micrographs of the fractured faces are shown in figure 1 and 2. One can see that the crack path of the fractured sample 1 (unused blade) is dominantly inter-granular and the fractured surface appears smooth. In contrast, the fractured sample 2 (used blade) reveals a trans-granular fracture mode with the presence of facets and cavities. Three samples of each blade were fractured and the dominant fracture mode persisted. Therefore, the reproducibility of the experiments can be anticipated.

3.2. AES line profiles and punctual analyses
The typical Auger spectra acquired from the above fractured surfaces are shown in figure 3 and 4. It seems straight forward to assign the periodicity of the Auger transition to the effects induced by the grain boundaries. Hence, a noticeable carbon and chromium enrichment in the grain boundary region arises in sample 1 (figure 3). On the contrary, sample 2 exhibits a depletion of these elements as seen in figure 4. The analyses were repeated over a few zones and a periodicity was always observed. However, we hasten to point out that the reported period (i.e., the distance between two consecutive depletion or enrichment lines) cannot be interpreted as an average value of the grain size as this would require a statistical treatment. The results of the punctual analyses are shown in figure 5 and 6.
A comparison of the spectra of figure 5 (sample 1) with those of figure 6 (sample 2), shows a salient evolution of the intensities of the Auger signals pertaining to C and Cr (located, respectively, at 270 and 490 eV). Clearly, the service conditions have induced a significant redistribution of C from the grain boundaries to the grain interior. The extent of Cr redistribution is however less pronounced.

The relative AES peak height intensities of the dN(E)/dE spectra, for sample 1 and 2, allow to estimate the ratio of the concentration of C (and Cr) at grain boundaries (GB) to their respective counterpart within the grain interior (G). The estimates, derived from the Seah formula [11], are given in table 2.

**Figure 3.** Typical AES line profile of carbon and chromium as a function of distance over the inter-granular fractured surface of sample 1 (unused blade). The enrichment of carbon and chromium at grain boundaries emerge.

**Figure 4.** Typical AES line profile of carbon and chromium as a function of distance over the trans-granular fractured surface of sample 2 (used blade). The depletion of carbon and chromium at grain boundaries emerge.

**Figure 5.** AES spectra of sample 1 (unused blade) corresponding to: (a) the grain interior and (b) the grain boundary

**Figure 6.** AES spectra of sample 2 (used blade) corresponding to: (a) the grain interior and (b) the grain boundary
Table 2. Ratio of the concentration of carbon (C) and chromium (Cr) at grain boundaries (GB) to their respective counterpart within the grain interior (G) for sample 1 (unused blade) and 2 (used blade) calculated by means of Seah formula [11] and the sensitivity factors.

| Steel Type | Sample 1 | Sample 2 |
|------------|----------|----------|
| X_c(GB)/X_c(G) | 1.19     | 0.56     |
| X_cr(GB)/X_cr(G) | 1.63     | 1.47     |

It appears that the grain boundary region in sample 1 is richer in carbon and chromium than the grain interior. The enrichment ratio, resulting from the fabrication process, is found equal to 1.2 (for C) and 1.6 (for Cr). In the case of materials after utilization (sample 2), the grain boundary region is no longer richer in C. Instead, the ratio, X_c(GB)/X_c(G), is drastically decreased (by nearly a factor of 2) to 0.6. However, the reduction seems less noticeable for Cr.

As mentioned above, the analyses were performed over a few different zones that were taken randomly. The degrees of carbon and chromium redistributions kept the same trend. Since a carbon contamination through the external surface of the blades has to be ruled out, due the composition of the blade environment (water vapour), the rather conspicuous carbon redistribution can be assigned, with reasonable confidence, to intrinsic metallurgical transformations that were induced by the service conditions.

3.3. Electrochemical studies (open circuit potential and potentiodynamic cyclic polarization)

The results of figure 7 show the open circuit potential (OCP) versus time obtained with samples 1 and 2 in a 10^{-2}M (NaCl + Na_2SO_4) solution. It can be seen that the OCP curves of both samples decrease with time until reaching their respective quasi-stabilization limit. These curves evolve towards the negative less noble direction. However, the curve of sample 1 (unused blade) lies well below that of sample 2 (used blade). Accordingly, these results could already suggest that the used material is more resistant to corrosion in the 10^{-2}M (NaCl + Na_2SO_4) solution.

The cyclic polarization curves of sample 1 and 2, after exposure in the foregoing solution, are shown in figure 8 and 9. Both curves exhibit spontaneous passivity after the onset of anodic current and a wide passivity domain between the corrosion potential, E_{cor}, and the pitting potential, E_{pit}, above
which stable pits initiate. Figure 8 and 9 also display the reverse anodic scans. The cycle is furthermore characterized by the area of the hysteresis loop and the protection potential \( E_{prot} \) below which no pitting occurs. The electrochemical parameters are given in Table 3.

In comparison with the unused blade, the used material is characterized by:
- nobler pitting and protection potentials;
- a hysteresis loop, of slightly smaller area, that closes at a more positive potential;
- a smaller difference between \( E_{prot} \) and \( E_{corr} \);
- a greater difference between \( E_{pitting} \) and \( E_{corr} \).

![Figure 8. Cyclic potentiodynamic curves of sample 1 (unused blade) measured in 10^{-2}\text{M} (\text{NaCl} + \text{Na}_2\text{SO}_4) \text{ solution after stabilization of OCP.} E_{pit}, E_{corr}, \text{ and } E_{prot} \text{ stand for pitting potential, corrosion potential and protection potential.}](image)

![Figure 9. Cyclic potentiodynamic curves of sample 2 (used blade) measured in 10^{-2}\text{M} (\text{NaCl} + \text{Na}_2\text{SO}_4) \text{ solution after stabilization of OCP.} E_{pit}, E_{corr}, \text{ and } E_{prot} \text{ stand for pitting potential, corrosion potential and protection potential.}](image)

| Type Steel | \( E_{corr} \) (mV) | \( E_{pitting} \) (mV) | \( E_{prot} \) (mV) | \( E_{prot} - E_{corr} \) (mV) | \( E_{pitting} - E_{corr} \) (mV) |
|------------|---------------------|---------------------|---------------------|--------------------------|---------------------|
| Sample 1   | -328                | 296                 | -424                | -96                      | 620                 |
| Sample 2   | -298                | 587                 | -323                | -25                      | 885                 |

Table 3. Electrochemical parameters obtained from figure 8 and 9. \( E_{corr} \), \( E_{pitting} \) and \( E_{prot} \) stand for corrosion potential, pitting potential and protection potential.

All the above mentioned characteristics are in accord to express a better resistance to pitting corrosion of the utilized blades [12].

The SEM observations, of the surfaces of the samples after the cyclic potentiodynamic experiments are shown in figures 10 to 12. The qualitative punctual analyses (i.e., the typical EDS spectra) of the pitting sites are also given. Noticeably, the responses of the samples are quite different. First, the pits in the unused blades are much larger. Next, the EDS spectra depend on both the sample and the pit size. For instance, in the case of the unused blades, the Si peak is more noticeable in smaller pits than in the larger ones. Finally, in used blades, the presence of Nb is systematically associated with smaller pits.

4. Discussion
It is recognized that the alloy microstructure can have strong effects on the tendency for pitting corrosion and that the pits more likely initiate at some heterogeneities such as inclusions and
precipitates [12]. The detailed description of the physical and chemical processes involved during a potentiodynamic cyclic polarization test, in the considered materials, is beyond the scope of this paper. In spite of that, the curves of figure 8 and 9 along with the SEM-EDS analyses can be interpreted as the fingerprint of the microstructural state as it is also suggested for other types of stainless steels [13, 14].

Accordingly, the better resistance to pitting of used blades may stem from the microstructural evolution resulting from long time exposure to the service conditions. The differences in the EDS spectra extracted from the pitting sites somewhat reflect the formation of new precipitates or the modification of the vicinities of the existing heterogeneities due, for instance, to fatigue damage accumulation. However, it must be pointed out that these spectra do not display the actual composition.
of the precipitates or inclusions because the dissolution of elements and the passivation/re-passivation also interfere during the polarization tests [15]. Nevertheless, in the light of the noticeable differences that are mentioned just above, one can connect the spectra to the nature of the heterogeneities that have spawned the pits.

The marked carbon redistribution from the grain boundaries to the grain interior (cf. section 3.2), derived from the Auger analyses, highlights that the long-time exposure to the service conditions can lead to changes of the grain boundaries structure. It could also induce small carbide precipitates within the grain such as those linked to NbC whose formation is expected due to the strong affinity of Nb for C. Indeed, the presence of Nb, which is systematically associated with smaller pits (of sub-micron size) distributed within large pit clusters (diameter of about 7 μm), emerges in the EDS spectra (figure 12). This, incidentally, indicates that Nb, although not identified by X-Ray fluorescence (table 2), is present as a trace element.

The change of the fracture mode (from inter-granular in the unused blade to trans-granular in used blades), which is well illustrated by figure 1 and 2, more likely originates from the microstructural evolutions suggested by the preceding interpretations. However, the contribution of fatigue damage is expected to play a triggering role in the occurrence of the trans-granular fracture. Indeed, it has been pointed out that fatigue damage can lead to the initiation of micro-cracks in the grain interior at microstructural heterogeneities [16]. Hence, these micro-cracks may favour the dominance of the trans-granular fracture mode that is provoked by the fracture tests. Since the samples were taken from the bulk of the blades (section 2), the foregoing interpretation implies that the failure of steam turbine blades, which is commonly associated with crack initiations at their surface [4, 6], could also originate from cracks located within their bulk [9].

5. Conclusion

This work shows that steam turbine blades made of martensitic stainless steel (12% Cr) undergo metallurgical changes under the service conditions. The change of the fracture mode from inter-granular (in unused blades) to trans-granular (in used blades) is associated with the formation of new precipitates in the grain interior along with the initiation of micro-cracks induced by fatigue damage accumulation.

We acknowledge that further experiments are required for the characterization of the exact nature of the metallurgical transformations. Nevertheless, the micrographs of the fractured faces and the potentiodynamic cyclic polarization curves concur to reflect the evidence of a microstructural evolution. This inference, although qualitative, could be of interest for those who seek refinements of life span assessment of turbine blades.

6. References

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