Structural characterization of degradation of ODS composite using SEM and XRM techniques

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Abstract

The structural characteristics and mechanisms of corrosion and wear of oxide dispersion strengthened stainless steel composite were investigated. In situ synchrotron x-ray tomography was used as experimental technique for degradation analysis from the corrosion and tribology studies. Corrosion study was carried out using potential dynamic techniques while the tribology experiments were conducted using a tribometer with ball on disc method. The x-ray micro tomography data gave chronological description of crack initiation and propagation in 3D and revealed that pitting did not result from the oxide inclusion. The results also revealed the surface imaging capacity of SEM and XRM’s capability for imaging internal structures. Taber index measurement was used as a complimenting tool for tribology measurements. Tribological behaviour of the sinter Oxide Dispersion Strengthened (ODS) steel composite depends on both the composition of the composite and the loading system.

Keywords

Corrosion; Microstructure; X-ray tomography; Oxide Dispersion strengthening; Composite

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Introduction

Stainless steels are traditional engineering materials utilized for a wide range of applications where high corrosion resistance, formability, weldability and strength are crucial materials design requirements [1-3]. Several engineering service environments require the use of materials that can maintain functionality and performance under extreme conditions. Specifically, applications such as heat exchanger and pumps require the use of stainless steels with improved strength, wear, corrosion and oxidation resistance, and thermal stability [4-6].

Conventional alloy design approaches which explore composition and phase modification to improve properties of stainless steels have been well reported [7,8]. Also, the use of oxide dispersion strengthening (ODS) to improve the mechanical and wear properties of stainless steels has been reported with promising results recorded [9-13]. Being a fairly new composite material, there has been sparse investigation on damage development mechanisms in the composites especially where corrosion and wear are the failure precursor.

Pits and micro-cracks emanating from pitting and intergranular corrosion for instance can be activated to fatigue and stress corrosion cracks which can result in catastrophic failure.

Techniques such as optical microscopy and SEM analysis are conventionally deployed to assess crack and flaws in materials. These techniques are reliable when such cracks develop on the surface but this is known to be less likely as some of the defects due to corrosion are hidden from the surface. In such instances the true orientation and shape of the crack may not be reliably profiled by conventional techniques.

Recently X-ray micro tomography which is a non-invasive technique with capacity to image three – dimension (3D) bulk objects have been adopted for qualitative and quantitative characterization of defects and internal structures of materials. It is well established that observation of a crack by conventional techniques such as optical or SEM on a sample may be misleading particularly for short cracks as the microstructure has a significant effect on the three – dimensional (3D) crack shape. With specifics to oxide – dispersed stainless steels there have been limited researches undertaken to understand from a micro mechanism standpoint, the science of short cracks development.

In the present work, the importance of ceramic strengthening of duplex stainless steel on the corrosion and tribological properties of ODS and a structural assessment of corrosion...
and wear degradations of the ODS composite was investigated using SEM and XRM techniques. This was aimed at a holistic appraisal of damage development in the composites due to corrosion and wear.

Materials and method

The materials used for this research include: atomized polycrystalline 2205, partially stabilized Zirconia (PSZ, 3% yttria, mole fraction), chromium and Nickel powders. The following equipment were also used; electron weighing machine with accuracy of 0.00001g, Turbular T2F mixer, uniaxial hot press (Hp20 Thermal Technology, Autolab potentiostat, Tribometer, Field Emission Scanning Microscope (FESEM) with a link energy dispersive X-ray spectroscopy (EDS) detector attachment, model JEOL, JSM-7600F.

The feed stock powders for the production of the oxide dispersion strengthened duplex stainless steels are 2205 stainless steel, partially stabilized Zirconia (PSZ), Chromium and Nickel. The feed stock starting powders blending was done by dry mixing of approximately 60g per batch of the participating powders, using the Turbular T2F mixer for five (5) hours with the introduction of zirconia mixing balls (3 nos) to maximize homogeneity during the mixing operation.

The composition of the powders is as presented in Table 1. The particle sizes of DSS 2205, PSZ; 3% Yttria, Cr and Ni are 22µm, 50 nm, 10 µm and 0.5-3 µm, respectively. Sintering was done by adopting a high temperature high pressure technique using a uniaxial hot press (HP20 Thermal Technology) for the sintering process. A constant uniaxial pressure was applied to the admix powders through the graphite plunger and compaction process was initiated. The furnace was heated to 1100°C at 20°C/min and held at this temperature for 30 minutes while pressure of 30 MPa was applied. The furnace was then allowed to cool to room temperature at 20°C/min after which the graphite pot was removed from the die and the sinter product subsequently removed.

| Table 1. Composition in wt % of 2507 DSS composite |
|----------------------------------------|--------|--------|-------|-------|
| Materials                              | 2205   | Zr2O3(Y2O3) | Cr    | Ni    |
| Composition (%)                        | 97     | 1       | 1.56  | 0.44  |
Corrosion

The electrochemical potential kinetic reactivation test (EPR) was performed using an Autolab potentiostat with general purpose electrochemical system software (GPES 4.9) following ASTM G5 standard [14].

A conventional corrosion cell with three electrodes was used. The test specimen with dimension of 8mm x 5mm x 2 mm was used as the working electrode.

A conducting wire was attached to the working electrode with the help of aluminium tape for conduction of current. It was then placed in a resin, allowed to set for easy handling. Graphite rod from Metrholm was used as the counter- electrode while platinum was used as the reference electrode. The whole set up was placed in a 3.5 % NaCl solution inside the corrosion cell.

Wear Analysis

Dry sliding wear tests were conducted on the sintered ODS composites at room temperature to evaluate the wear behaviour of the composite. Two different sliders namely WC and stainless steel balls were used. The diameter of the respective ball is 10 mm and the original stock of the material was 2mm thick. Wear parameters such as friction coefficient and wear depth were evaluated from the test.

Three experiments were conducted on each for reasonable reproducibility of the results and the average value of co-efficient of friction and wear depth was calculated. Prior to wear experiment, the balls and the specimens were cleaned using acetone and then dried for 10 min. Electronic weighing machine with accuracy of 0.00001g was used to record the mass of the material loss during the tests.

X-ray Tomography

XRT was used to study the corrosion and tribological behaviour of the composites with composition presented in Table 1. Specification of the test specimens is 3 x 3 mm square. The size was thought to be large enough to give full representation of microstructural features expected on larger specimens. A photo source is incident on the test specimen for acquisition of 2D image. Acquisition was carried out at high X-ray energy with a double Si III crystal monochromator. The detector chip was read out with pixels, giving a final 2D practical
resolution. Several 2D radiographs were taken for subsequent 3D images reconstruction using software which is part of the accessory attachments of the XRT instrument.

Figure 1 shows a mounted sample for the XRT investigation.

![Mounted Sample](image)

**Figure 1. Mounted Sample**

**Results and Discussion**

**SEM characterization of the sintered ODS**

Representative back scattered SEM images of the sintered composite presented in Figure 2 shows a fully compacted sinter.

![Sintered oxide dispersion strengthened duplex stainless steel](image)

**Figure 2. Sintered oxide dispersion strengthened duplex stainless steel**
A densification of about 99.193% of the theoretical density as determined using the Archimedes’ method was achieved during the sintering.

The SEM results show a heterogeneous microstructure of large austenite grains with ferrite undergrown. The sinter displayed a sparse dispersion of the oxide particles in the matrix with the presence of some visible pores.

The oxide inclusions were not distinctively seen as particles inclusions in the SEM images but shown in the XRD distinctive peak presented in Figure 3.

Figure 3. Representative XRD diffractograph of the sintered ODS steel

This non-distinctiveness in the SEM images could have resulted from the fact that during the hot consolidation processes of the hot isostatic pressing, yttria and zirconia dissociated and dissolved into the matrix during sintering [15].

*High – Resolution Scan of the Corrosion Sample*

Figure 4 shows the potenitio-dynamic polarization curve of the ODS composite in 3.5% NaCl.
Table 2 shows the computed corrosion data by the potentiostat.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Weight (g)</th>
<th>icor (A)</th>
<th>i_cor (A/cm²)</th>
<th>be (v/deg)</th>
<th>ba (v/deg)</th>
<th>Rp (Ω)</th>
<th>Cor Rate (mm/year)</th>
</tr>
</thead>
<tbody>
<tr>
<td>X</td>
<td>162.01</td>
<td>8.408E^-7</td>
<td>1.752E^-7</td>
<td>0.110</td>
<td>0.116</td>
<td>6.611E^3</td>
<td>1.316E^-2</td>
</tr>
<tr>
<td>A5</td>
<td>175.65</td>
<td>4.7765E^-6</td>
<td>1.15E^-6</td>
<td>0.112</td>
<td>0.046</td>
<td>4.836E^2</td>
<td>8.663E^-2</td>
</tr>
</tbody>
</table>

Figure 5 is the typical SEM micrograph showing the corrosion pits. It revealed the surface imaging capacity of the scanning electron microscope (SEM).

Important surface information on pitting corrosion was revealed. However, detail description and morphologies of the pitting corrosion could not be determined; this informed
the choice of x-ray Tomography.

Figure 6 shows the XRM morphology of the corroded and the control samples.

![Figure 6. Morphology of the specimen](image)

The image on the right was from the control sample (the scan condition was the same as the scan of the corrosion sample). The edges of the control sample show no evidence of corrosion structure.

Scanning was carried out on the corroded sample to obtain more buried structural and morphological details on typical region of corrosion (Figures 7-10).

![Figure 7. XZ slice showing the morphology of two corrosion pits](image)

Figure 7 is an example of X, Z virtual cross-section, showing the morphology of the corrosion of the sample. The image on the right is the zoomed-in image of the yellow box on the left. The scan detail shows the morphology of two corrosion pits (Figure 7). The image on
the right is a virtual cross-section of the red line on the left, showing the other perspective of the corrosion pits.

The detail scan as indicated by Figure 7 shows the morphology (grain structures in the middle of the corrosion region.

The morphology of the corrosion sample appears different as the vital cross-sectioning goes into the sample (Figure 8). The image on the right shows the morphology of the pit areas near to the surface. The image on the right is the virtual cross-section of the green line on the left. The image to the left shows the morphology of the pit areas near to the surface. The image on the right is the virtual cross-section of the green line on the left.

![Image](image_url)

Figure 8. The morphology of the corrosion sample appears different as the virtual cross-sectioning goes into the sample

On the other hand, Figure 8 is an example of X, Y slice that shows the morphology in the non-corrosion region. The image on the right is the virtual cross-section of the green lines on the left.

**High – Resolution Scan of the Wear Sample**

Figure 9 shows the plot of coefficient of friction (COF) with time for the sinter when sliding against 302 stainless steel ball and Tungsten carbide (WC) ball (10 mm diameter) in dry condition under wear load of 15N.
Figure 9. Wear behaviour of the ODS steel when abraded with (A1) 302 stainless steel balls and (A5) WC ball.

The COF is determined by the ratio of the friction force to the loading force on the ball. The results show that the COF is much higher when sliding with WC ball compared to that of 302 stainless steel ball this is due to the degree of local debonding [3,16], that COF alone may not be a realistic parameter for wear resistance evaluation especially when there is material transfer between the sliding and the counter body.

Table index measurement is based on weight loss measurement; this technique measures how much material has been removed by abrasion, and is usually reported in milligram. Table wear index indicates the rate of wear, and is calculated by measuring the loss in weight (in milligrams) per thousand cycles of abrasion resistance. The lower the index value, the better the wear resistance of the material.

The calculated wear index for the composite slide with 302 stainless steel ball and WC ball respectively is presented in Table 3.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Weight before (mg)</th>
<th>Weight after (mg)</th>
<th>Taber Index</th>
<th>Wear depth</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>2.62194</td>
<td>2.62160</td>
<td>0.0113</td>
<td>0.005</td>
</tr>
<tr>
<td>A5</td>
<td>2.9372</td>
<td>2.9325</td>
<td>1.57</td>
<td>0.003</td>
</tr>
</tbody>
</table>

The XRM images indicating apparent recessed wear mark by 302 steel and that the structure change induced by 302 steel is different from WC wear (Figure 10).
Figure 10. XRM images

Figure 11 is a 3D view showing reconstructed 2D slices. The coloured lines correspond to slices with the same border colour.

Figure 11. SEM image for the wear specimen

**Corrosion**

During electrochemical test, the passivation of all analysed steel was not obtained and the usual active – passive transition maximum does not appear (Figure 4). After the passive range, rapid increase of current density occurs and passive layer destruction proceeds and transition to pitting corrosion region.

The corrosive pits were initiated from the open pores then proceed into interior of the bulk. Corrosion resistance of the sinter composite is connected with the density and the pore morphologies. The resistance to pitting corrosion in the test solution was controlled by
balance of ferrite and austenite in the composition [2]. It is apparent that pitting grows in depth and then in length for the examined orientations. The corrosion attack followed the grain boundaries along the longitudinal (depth) and transverse directions as revealed in Figure 7.

It is possible that the corrosion event was initiated by localized corrosion around an intermetallic particle. This susceptibility is not unconnected to the higher defect density present at the surface such as impurities, oxide inclusions, contamination and ultrafine grain structure [10]. This layer was attacked first and caused further delamination of the surface. This study shows that after the first preferential attack, the deformed layer surface does not dissolve further. This was a clear indication of a high uniform corrosion resistance in the electrolyte.

The dissolution of the intermetallic can be explained by the fact that intergranular corrosion can initiate from sites such as clusters of intermetallic particles, and adjacent sites can stifle each other as they are competing for current. If they are not in direct electrical contact with the surrounding matrix, they are no longer cathodic ally protected and can freely corrode [10]. This dissolution can also occur as a result of chemical dissolution due to the aggressively of the electrolyte. This is called DE alloying process.

Micro tomography, however, offers an excellent opportunity to detect the complete dissolution of intermetallic within the bulk as a function of time, which is hard or impossible to verify with conventional methods [3,10,17].

The location of dissolved intermetallic is detected due to the 3D reconstruction, and the corrosion process can be followed as a function of time within the bulk without considering artefacts produced by sectioning or sample preparation.

**Tribology**

The observations from the friction coefficient results indicated that the operating mechanism of 302 stainless steel ball is polishing wear, since 302 steel ball is not as hard as the sinter ODS composite. On the contrary, WC counter body, WC is harder, the wearing mechanism changes due to the plastic ploughing and grooving of the sinter ODS composite that results in local debonding [3,18]. This shows that wear loss increases with the hardness of the counter body.
Figure 10 shows typical images of X, Y virtual cross section of wear mark of abraded surfaces by WC and steel balls obtained from high resolution X-ray microscope scanning.

Results revealed no apparent recessed wear mark on the ODS composite abraded by 302 steel ball as compared with the one abraded by WC ball.

Figure 11 shows the SEM image and its corresponding EDS spectrum under wear condition of 25N and 5Hz is shown in Figure 12.

Figure 12. Typical spectroscopy showing Tungsten in the worn surface

Oxide particles could be seen along the boundary of the micro-cracks formed. This is associated with higher frequency of reciprocation which could increase the heating of the sample and as a result the rate of formation of passive film increases.

The formation of these oxides has an influence on the coefficient of friction, wear depth and tribological performance of the material. EDS spectrum (Figure 12) revealed the presence of tungsten which shows material transfer from the WC ball used.

Other elements presented from the point EDS analysis are C, O, Cr, Fe, Ni and W.
Conclusions

Corrosion and wear damage mechanisms in powder-processed Oxide dispersed 2507 composite have been investigated using x-ray micro tomography. From the results, the microstructure reveals sparse distribution of the Partially Stabilized Zirconia within the matrix of the composite. The tomography data gave chronological description of crack initiation and propagation in 3D. The results also revealed the surface imaging capacity of SEM and XRM’s capability for imaging internal structures for thorough understanding of corrosion and wear damages. SEM revealed important surface information on the mechanism of wear damage while relevant information on pitting corrosion was obtained from XRM technique. Wear behaviour of the sinter ODS composite depends not only on the composition of the composite but also on the loading system, as the deformation behaviour of the matrix and the reinforcement are not similar; 302 steel ball barely affect the composites during tribology experiment unlike WC ball as revealed by the recess mark. COF as a measure of wear property was complimented with Taber index measurement to validate the wear property of the composite.

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References

   *Tribological study of hot pressed oxide dispersion strengthened 2205 DSS composite*,
