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Stainless Steel Valves with Enhanced Fatigue and Corrosion Performance through Microstructure Optimization

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ABSTRACT

In order to increase the energy efficiency of refrigerators, compressors, valves with new geometries have been developed over the past few years. In addition, higher stresses are increasingly placed upon the valve itself during operation. Hence, higher demands are set on the steel strip used to produce such valves. Today, compressor valves for refrigerators are mainly manufactured from hardened and tempered martensitic stainless steels. The main design criterion for the material selection is the endurance limit of the material under bending. However, impact loads and corrosive atmospheres often act additionally on the valve.

To fulfil the increased demands for such new valves, the microstructure of the most commonly used stainless steel grade is refined. Through this method a new grade Zapp Super-Fatigue is developed, whereby the yield strength, ultimate tensile strength and bending fatigue are increased. In addition, the corrosion resistance of the material is also significantly increased.

All the tests are performed with industrial scale processes and material. The properties are determined with samples taken from various production lots. Tensile properties as well as bending fatigue tests are performed on a strip with a typical thickness for valves used for refrigerators. Current density potential measurements are conducted to confirm and explain the corrosion test results. Finally, the microstructure is characterized using scanning electron microscopy with the electron back scatter diffraction method.

For the first time, the microstructures of the most commonly used stainless steel and the improved grade Zapp Super-Fatigue are compared. It is demonstrated that the fatigue limit and the corrosion resistance of a martensitic stainless steel can be enhanced by tailoring the microstructure.

1. INTRODUCTION

Flapper valves used in full hermetic compressors for household refrigerators are made of hardened and tempered martensitic steels. More and more hardened and tempered chromium martensitic stainless steel is used to reduce the risk of any failure during operation. The use of stainless steel is increasing due to its excellent combination of various properties relevant for flapper valves: high strength, corrosion resistance, high toughness, and very good fatigue properties (Hareland 2014, Nadar 2014). Since their use for flapper valves, publications have reported on the properties of the martensitic stainless steels (Johansson 1976, Lof 2016). Many commercial names are available for the stainless chromium steel X38CrMo14 used for the production of valves. It contains approximately 13.5 weight percent of chromium, 0.38 weight percent of carbon, and around 1 weight percent of molybdenum.

Only a few publications discuss the correlation between the microstructure of the stainless martensitic steels itself and the mechanical properties or corrosion properties. The influence of chromium nitrides on the corrosion-
Table 1: Chemical composition of precision strip used for the investigation
(Zapp 1.4028MO, Zapp SuperFatigue, comparable to X38CrMo14)

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>Cr</th>
<th>Mo</th>
</tr>
</thead>
<tbody>
<tr>
<td>Content in weight percent</td>
<td>0.38</td>
<td>0.38</td>
<td>0.37</td>
<td>13.20</td>
<td>0.93</td>
</tr>
</tbody>
</table>

resistance of AISI 410S was described by Toro et al. (2003). Yuan (2012) demonstrated how, through control of tempering time, the tensile properties of chromium steel with 0.44 weight percent, called X44Cr13 (1.4034, AISI420), can be tailored. The TRIP effect described in the paper is related to reverted austenite. Ardehali et al. (2017) demonstrated the influence of martensite block on the static tensile strength for X38CrMo14 used for valves in compressors. Earlier it was shown for carbon steels that the toughness and fatigue properties can also be controlled by the martensite block size (Ardehali 2007). In this study the influence of the martensite block and carbide size of the stainless martensitic steel on the resulting fatigue properties and the corrosion properties is investigated for 1.4028MO that is widely used in compressors.

2. EXPERIMENTAL

A work-hardened precision strip with a thickness of 0.178mm, typical for valves used in household refrigeration, made out of Zapp 1.4028MO was selected for the investigation. The chemical composition for the coil used for the investigation is given in table 1. With respect to the main alloying elements, the alloy has a comparable chemical composition to X38CrMo14.

Hardening and tempering was carried out in a continuous industrial hardening and tempering line. The line consists of an austenitization furnace, quenching module, and tempering furnace. The heat treatment is schematically shown in figure 1. In order to obtain two distinct microstructures, and hence properties, two different heat treatments were used. Prior to hardening and tempering the original strip was divided into two strips. The first set of parameters consists of the standard heat treatment parameters used at Zapp Precision Metals, for the production of quenched and tempered 1.4028MO. The second set of parameters is applied to reduce the size of the martensite units, to improve the fatigue properties. The samples taken from the first quenched and tempered strip, heat treated with the standard set of parameters, are designated as modification A. The strip heat treated to obtain a refined martensite microstructure, and the samples thereof, are called modification B.

Figure 1: Schematic presentation of the heat treatment
The microstructure was characterized by light and scanning electron microscopy to reveal the different phases and microstructural features. V2A etchant consisting of 100 ml hydrochloric acid, 100 ml water, 10 ml nitric acid was used prior to scanning electron microscopy to investigate the secondary carbide size and their distribution. Electron backscatter diffraction technique was used to investigate the martensite microstructure of the two modifications. Samples in rolling the direction were prepared using standard grinding and polishing procedures. An area of 60 micrometre by 60 micrometre was mapped with a step size of 50nm.

The tensile properties were determined in the longitudinal direction according to standard practice on 10 samples taken from the coil ends, from both the right and left edge and from the centre of the heat-treated strips. Furthermore, the hardness was measured with a Vickers indenter and load of 3kg.

Cyclic fatigue in bending was carried out in three point bending method. Testing was performed in the longitudinal direction. The stress ratio R was 0.1. The test frequency was 10s⁻¹. The testing was stopped if samples passed two million cycles.

Current density potential measurements were carried out in a 0.9 % solution of sodium chloride against a Saturated calomel electrode.

Corrosion resistance was tested by full immersion of samples for 15 hours at room temperature in Strauß solution based on ASTM A262-15 practice E. After the tests, micrographs were prepared using standard grinding and polishing methods.

3. RESULTS

The microstructure revealed by etching and scanning electron microscopy is compared for both samples in figure 2. Scanning electron microscopy is carried out to compare the carbide size distribution for both modifications. No significant differences could be observed, at various magnifications, by visual comparison of the pictures. An area of 88x77µm² is analysed by an automatic picture analysis tool. The Modification B exhibits slightly higher number of smaller carbides and less large carbides (figure 3). The median of modification B is 0.226µm and smaller than modification A (0.245µm).

In figure 4 the area occupied by secondary carbides is shown for each analysed smaller section and presented by false colours. The comparison of both modifications shows that in modification B less area is occupied by secondary carbides than in modification A.
Figure 3: secondary carbide size distributions for both modification A and B

Figure 4: (a) and (b) secondary carbide area per area measured for both modifications A and B in %
(c) and (d) secondary carbide area per area measured for both modifications A and B in % laid over the SEM picture from the total area under investigation
Charaterization and analysis by EBSD shows that the retained austenite fraction for both modifications is below two percent in area and thus comparable. The grain boundary maps are shown in figure 5 for both modifications. A significant difference is not visually discernible. An effective grain size, surrounded by high angle grain boundaries with a misorientation bigger than 15° and consisting at least of 10 points, also revealed no difference. The average effective grain size area of martensite calculated accordingly was 0.24µm² for modification A and 0.25µm² for modification B.

![Grain boundary maps of the two modifications A and B. Black line: high angle grain boundary (15 to 62.8°); blue line: low angle grain boundaries (3 to 15°); red line: sigma 3 grain boundary with a tolerance of 8.7°.](image)

Figure 5: Grain boundary maps of the two modifications A and B. Black line: high angle grain boundary (15 to 62.8°); blue line: low angle grain boundaries (3 to 15°); red line: sigma 3 grain boundary with a tolerance of 8.7°.

The block width was measured by plotting the misorientation perpendicular to the martensite packets and then measuring the distance between grain boundaries with a misorientation larger than 15°. Figure 6 shows the distribution of block width shown as box plots for both modifications. The median block width observed for modification A is 0.42µm and 0.30µm for modification B.

![Comparison of Martensite Block Size](image)

Figure 6: Width distribution of martensite blocks limited by high angle grain boundaries for modifications A and B.
Table 2: Mechanical properties of the samples from modification A and modification B. Tensile testing in longitudinal direction. Averages of ten values.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Modification</th>
<th>Tensile Yield Strength (MPa)</th>
<th>Ultimate Tensile Strength (MPa)</th>
<th>Elongation (%)</th>
<th>Hardness (HV3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zapp 1.4028MO</td>
<td>A</td>
<td>1388</td>
<td>1776</td>
<td>6.3</td>
<td>551</td>
</tr>
<tr>
<td>Zapp SuperFatigue</td>
<td>B</td>
<td>1452</td>
<td>1928</td>
<td>7.1</td>
<td>588</td>
</tr>
</tbody>
</table>

The results of tensile testing together with hardness are presented in table 2. Through modification of the final heat treatment, i.e. the hardening and tempering, the overall mechanical performance is enhanced. The strength values together with the hardness are increased. At the same time the elongation is increased significantly by a value of 0.8%.

In cyclic bending testing modification B exhibits higher fatigue limit (see figure 7). The fatigue limit, determined at two million cycles, was 1020MPa and 140MPa higher than for modification A. Through the modification of the heat treatment, the fatigue limit was increased by 15%.

The corrosion current density at the open corrosion potential is \( I_{\text{corr}} = 0.004 \text{mA/cm}^2 \) for modification A and \( I_{\text{corr}} = 0.0008 \text{mA/cm}^2 \) for modification B. The passivation region was expanded through the heat treatment (see figure 8). The loss of material per unit time measured was 0.07mm per year for modification B and 0.53mm per year for modification A.

4. Discussion

Through the modification of heat treatment parameters, the martensite block width was reduced. This resulted in higher tensile strength values, and at the same time, in higher elongation values. Consequently, the fatigue limit was increased significantly allowing compressor designers to reduce the thickness of the valves, or to increase the loads for current designs. Furthermore, material substitution would offer an additional benefit of reducing the risk for any failure in operation, especially, when the corrosion resistance is considered.

**Figure 7**: S/N curve measured in 3-point bending mode

**Figure 8**: Comparison of corrosion performance of modification A and B in current density potential measurement
In figure 8 the results are summarised with respect to the fatigue limit and corrosion rate. The increase in ultimate tensile strength corresponds to a higher fatigue limit and corrosion rate. The corrosion rate measured in weight loss per year is significantly lower for modification B.

The results for both modifications were obtained in tests on material with the same chemical composition. It is demonstrated that the property improvement is mainly due to the martensite microstructure refinement. The secondary carbide size and frequency is only slightly modified. The retained austenite content is same for both alloys.

5. Conclusion

By reduction of the martensite block size the strength values in tensile testing is enhanced. Concurrently, the fatigue limit in bending of a standard flapper valve grade can be increased by more than 15%. At the same time the tensile yield strength and the elongation are increased. Corrosion measurements performed on both modifications show that the modified flapper valve steel also exhibits better corrosion resistance.

The results generated during the investigation led to the development of a new grade that offers additional advantages for full hermetic compressors. By substituting the material, designers can reduce either the thickness of the valve or reduce the risk of failure for existing designs.

6. Acknowledgement

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REFERENCES


