SENSITIVITY TO INTERGRANULAR ATTACK KINETICS OF HIGH-ALLOYED AUSTENITIC STAINLESS STEELS WITH COPPER

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Abstract

The sensitivity to intergranular attack of stainless austenitic steels is caused by gradient of chromium concentration in the structure. This is caused by precipitation of carbides on the grain boundaries and thus drop of chromium concentration in the adjacent region.

The degree of sensitization was studied using double-loop electropotentiokinetic reactivation method in 0.5M H₂SO₄ with addition of NH₄SCN. The samples of austenitic stainless steel AISI Super304H were aged at different temperatures (620-720°C) and times (1-1000h). The structure of the samples was studied using optical and scanning electron microscopy. The results showed that even the steel stabilized with Nb is prone to sensitization; the experimental rate of sensitization fits the Larson-Miller equation.

Key words: steel, intergranular, corrosion, precipitation

1. INTRODUCTION

Intergranular corrosion is a localized attack caused by structural inhomogeneity. The inhomogeneity can be either local depletion of certain alloying element, precipitation of secondary phase or segregation. All of these result in concentration gradient of certain element in the structure of the material. If the local concentration of chromium in the case of stainless steels, drops below 14% wt., the material is unable to form passive layer in this area the surface becomes active and it corrodes with high corrosion rates. Material is therefore “sensitized”.

1.1. Sensitization

During the thermal or thermo-mechanical processes, precipitates can form in the steel structure. In the austenitic steel, the precipitated phase causing sensitization is the chromium carbide (Cr₂₃C₆). The precipitation of the carbide causes transport of chromium from surrounding area to the nucleation site.

The combination of precipitates varies with steel compositions, exposure length and temperature. There can be large variety of carbides (M₂₃C₆, M₆C), nitrides (Cr₂N, TiN), carbonitrides (MX), Laves-phases (Fe₅Mo, Fe₅Nb), δ-phase (Fe₃(Fe,Ni)), γ-phase Fe₃₈Cr₁₃Mo₁₀, G-phase (Ti₄C₂S₂) and in the case of copper alloyed steels even the ε-phase [1-9].

The composition of the steel does not only affect the composition of the secondary phases, but mainly their solubility in the solid solution. This is more affected by lattice structure than the element composition. This explains the difference in the sensitization temperature range between ferritic and austenitic steels. The austenitic steels sensitization temperature range is 450-850°C [10, 11], and the range for the ferritic steels is 430-930°C [12]. The differences between the two are different diffusivities of carbon and other elements in the given lattice. The higher carbon diffusivity in the ferritic lattice allows nucleation of the precipitate at lower temperature while the low diffusivity of carbon in austenitic lattice requires higher temperatures to start the nucleation.
1.2. Causes and prevention
The most common cause of sensitization is a wrong thermal treatment regime - i.e. exposure of the material which is prone to sensitization in the temperature zone where carbides with high chromium content can form. The “bulk” sensitization, e.g. exposure in the power plant, causes growth of the carbides on the grain boundaries in all of the material. It should be noted, that chromium diffusion from the grains during long-term high temperature can equalize the differences between the grain boundary and bulk grain chromium concentration, thus causing "self-healing" [3, 4, 13]

1.3. Parameters affecting sensitization/desensitization
The degree of sensitization is proportional to the carbon content (L-grade steels) in the structure and can be prevented by alloying with an element which forms carbides more easily than chromium, such as titanium or niobium. These carbides begin to form at around 800-900°C and deplete the available carbon, which is thus not available to form chromium carbides. The minimizing of carbon content is technically more demanding, requires further raffination of steel and the material can still be sensitized during prolonged exposures [10, 14, 15].

Other parameter known to affect the sensitization/desensitization is cold work prior to the sensitization. According to some authors [13, 16, 17], the cold work promotes both sensitization and desensitization of the material (AISI 304). This is probably due to the increase of both short and long-distance chromium diffusion. This was explained by increase of dislocation density and higher number of vacancies which promote the long-distance transport, and grain refinement which enhances short-distance transport due to shorter diffusive lengths.

1.4. Nucleation of carbides
The intergranular corrosion has severe effect on mechanical properties. The net of chromium carbides alongside the grain boundaries causes drop-off of the grains and provides a net for a potential crack growth. The nucleation of carbides on the grain boundaries is free-energy driven. The grain boundaries are basically lattice imperfections with higher surface energies and thus are the preferential sites for nucleation. The twin-boundary interfaces are generally more resistant compared to the grain boundaries [10].

The aim of the work was to determine the parameters of sensitization of steel AISI Super 304H using the double-loop electro potentiokinetic reactivation. The goal is to determine the maximum sensitization for each temperature and length of exposure.

2. EXPERIMENT

2.1. Samples
The material used for all the experiments was creep resistant austenitic stainless steel AISI Super 304H. The composition is summarized in Tab. 1.

<table>
<thead>
<tr>
<th>Element</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>Cu</th>
<th>Cr</th>
<th>Ni</th>
<th>Nb</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.08</td>
<td>0.2</td>
<td>0.8</td>
<td>3</td>
<td>18</td>
<td>9</td>
<td>0.1</td>
<td>0.1</td>
</tr>
</tbody>
</table>

Tab. 1: Composition of the sample
2.2. Thermal aging

The samples were thermally worked in an induction furnace as follows:

1. solution treatment - heating to 1250°C/30 min, water quenched
2. thermal aging: 620-720°C for 1-1000h.

Thermal aging simulates the exposure in a real power plant. The real exposure does not have stable exposure temperature, fluctuations caused by start-up and failures in the circuit can cause overheating of the material.

2.3. Sensitization quantification

The double-loop electro potentiokinetic reactivation method (DL-EPR) was used to quantify the degree of sensitization. The method consists of anodic polarization of the sample to the passive region and then back to the corrosion potential. The potential range and exact composition of the electrolyte was modified to match the higher corrosion resistance of the material. We used cyclic polarization range -700 to +500mV/E_{cor} and electrolyte composition of 0.5M H_{2}SO_{4} + 0.01/0.001M NH_{4}SCN. The active dissolution and reactivation peak from the curve was integrated (Fig. 1) and the degree of sensitization (DOS) was calculated from electrical charges using:

\[
DOS = \frac{Q_r}{Q_a}
\]  

(1)

2.4. Structure study

The sensitization was assessed from the structure of the material. The samples were ground using grinding paper up to P2500 roughness and then polished with TOPOL solution. As prepared surface was potentiostatically etched in 10% wt. (NH_{4})_{2}S_{2}O_{8} at +6V/E_{cor}. The structure was studied using optical microscope Zeis Axio Observer. The metallography samples were then studied using electron scanning microscope TESCAN VEGA with backscatter electron detector.

3. RESULTS AND DISCUSSION

The sensitization of the samples with different thermal history is visible from Fig.-Fig. It is visible, that the sensitivity results are affected by the composition of testing electrolyte. In the beginning we even used the 0.1M NH_{4}SCN, but the forming oxygen made the sensitization curves unreliable in most cases. The curve support show the previously mentioned phenomenon of sensitization and subsequent "self-healing". It is also visible, that the sensitization time and thus the time to begin nucleation are higher for lower temperatures. The chromium diffusion, which is the limiting process of M_{23}C_{6} forming, is temperature driven and can be fitted by Larsson-Miller parameter:

\[
LMP = T \cdot (C + \log(t))
\]  

(2)
The maximum measured degree of sensitization of the sample aged at 670°C for 100h was 38/50% depending on the composition of electrolyte. The same degree of sensitization for the samples aged at 620/720°C was calculated to be 3.5 hours, resp. 3500h. While the first value (720°C) is in good agreement with the experimental results (Fig. 3-4), the other sample, aged at 620°C (Fig. 2), requires further thermal aging.

The samples with highest degree of sensitization were then prepared to observe the structure. For the sake of keeping this short, we only show the pictures from the scanning electron microscope. The Fig. 5 shows the structure of sample aged at 620°C for 100h. There is clearly visible ditch structure with carbides (dark lines) spread around the grain boundaries and within the grain itself (grain carbide decoration). There are also two twins with carbides on the incoherent interfaces and almost no precipitates at the coherent interfaces (longer sides of the twins). Same phenomenon was observed on twins of the other samples (Fig. 6, 7); however there was almost no grain boundary decoration. All three structures contain bright spots of NbC carbide which is distributed alongside the former deformation texture. The annealing temperature was not high enough to dissolve these.
We have shown the effect of thermal aging on austenitic stainless steel AISI Super304H. Our electrochemical experiments using double-loop potentiokinetic reactivation method showed that the material is prone to sensitization - the time to reach the maximum sensitization can be fitted by Larsson-Miller parameter. The maximum degree of sensitization differs depending on the electrolyte composition - however it seems that electrolyte with the higher activator content (0.01M NH$_4$SCN) is too aggressive for the material and thus yields unlikely results (95% DOS). The maximum degree of sensitization in the other electrolyte was 37.5/50/61% for samples aged at 620/670/720°C. This suggests that higher temperatures cause higher DOS probably due to the higher short-range chromium diffusion rates. The structure all the samples with highest DOS show a ditch structure; in case of the 620°C/1000h aged sample the grain boundary is decorated with carbides.

Our data showed that even the material designed for exposure in aggressive high temperature environments is prone to sensitization and that the sensitization and desensitization is temperature and
exposure time driven. This is especially important for practical application; the start-up or failures cause overheating of the material. In the worst case scenario, the material can be sensitized during the start-up and so-sensitized material can be then operated at much lower temperature - the desensitization (self-healing) in this case can take up to several thousand hours.

The future work, currently in progress, will compare data from this and more conventional methods to determine degree of sensitization (Streich, Strauss, oxalic acid test etc.) and will focus on further mathematical modeling of such processes.

5. ACKNOWLEDGEMENT

This paper was created in the projects of MPO FR-TI1/086 and with financial support from MSMT No 21/2012

6. LITERATURE