1. Introduction

Austenitic stainless steels possess very good resistance against general corrosion; however, when heated or cooled through the temperature regime 500–900°C, they can become prone to localized corrosion intergranular corrosion (IGC), intergranular stress corrosion cracking (IGSCC), crevice and pitting corrosion.1,2) Of these, sensitization is responsible for IGC and IGSCC.3) Sensitization can occur during slow cooling from temperatures above 900°C, during the stress relief of fabricated components, or as a result of prolonged service at elevated temperatures. Sensitization can be the result of improper heat treatment or welding conditions, for example.

It has been suggested that sensitization is due to the precipitation of chromium-rich grain boundary carbides that have a detrimental effect either through chromium depletion, local stresses, soluble segregate formation, or microwalvic effects.4–6) However, the initial depletion of chromium adjacent to grain boundaries onto which (CrFe)23C6 carbides (also known as M23C6) have precipitated is now widely accepted as the primary cause of sensitization.7–9) The precipitation of chromium carbides at grain boundaries leads to the formation of chromium depleted zones adjacent to the grain boundaries. The passive layer over the depleted regions is weaker thus making the material susceptible to corrosion when exposed to aggressive solutions.

The phenomenon by which the desensitization of sensitized regions occurs is called self-healing. This occurs by the enrichment of chromium depleted zones with Cr concentration through diffusion of chromium from grain interior to the grain boundary. This results in the concentration of Cr in the depleted regions increasing above the critical level such that corrosion resistance is regained.

Cr depleted zones can be studied in terms of three characteristic parameters: the proportion of grain boundaries that have Cr depleted zones, the width of the zones and the depth of the Cr depletion profiles. The ASTM practices for detecting susceptibility to intergranular attack in austenitic stainless steels10) ignore both width and depth parameters and consider only the coverage of the Cr depletion zones. These are acid immersion tests that are used to measure susceptibility to intergranular corrosion before the electrochemical tests were developed. In these tests, the corrosion rate is evaluated by microscopic and weight loss examinations. The Oxalic acid etch test (ASTM A262 Practice A), the coverage is assessed qualitatively in terms of the appearance of the microstructure after etching in 10% oxalic acid solution. The etched grain boundaries are classified as showing step, dual or ditch structures. Step structure indicates no carbide precipitation, dual structure indicates partial coverage of grain boundaries by precipitates with no single grain completely encircled by the chromium carbides. Under these conditions, the material considered to be resistant to Intergranular Corrosion (IGC). If at least one grain is completely encircled by chromium carbides then it is considered to show a ditch structure, which indicates that the material may be susceptible to IGC. The susceptibility to intergranular corrosion in the other practices (ASTM A262,
Practice B, C, D) is assessed on the basis of weight loss after a recommended period of contact with the test solution ranging from 4 to 240 h.

All the above tests are based on the grain boundary coverage and do not specifically consider the width of the depleted zones nor the depth of the Cr concentration profiles. Earlier depletion profiles have been studied using analytical transmission electron microscopy (ATEM). However, beam broadening and grain boundary orientation make the application of the technique difficult. Also, it is not easy to guarantee statistically representative data. Alternatively, it is possible to quantitatively characterize depletion zones and define a degree of sensitization (DOS) and using electrochemical techniques, i.e., potentiodynamic, potentiostatic or potentiokinetic techniques. Of these, the electrochemical potentiokinetic reactivation (EPR) test is widely used. These tests are non-destructive, rapid and provide a quantitative measure of sensitization based on the average behaviour of a representative area of the material. There are two types of EPR experiments, which differ with respect to the scanning mode: single loop (SL-EPR) and double loop (DL-EPR) methods. In the case of SL-EPR test, it was reported that the solution used in SL-EPR dissolves undepleted regions after the dissolution of chromium-depleted regions, the test requires measurement of the specimen grain size and the reactivation behaviour is sensitive to surface finish. This led to the development of DL-EPR test method. In this method, the sample is polarized anodically through the active region into the passive region, causing the formation of passive layer. The second loop involves scanning in the reverse direction, by decreasing the potential to the corrosion potential thus causing the breakdown of the passive film over the chromium depleted regions. The ratio of reactivation current density (I) to the activation current density (I) gives the degree of sensitization (DOS). The normalization of DOS with grain size is not necessary and a 600-grit surface finish provides reliable data.

Sensitization needs to be studied in terms of the characteristics of the chromium depleted zones. They are 1) the depth of the chromium depletion, and 2) the width of the depleted zones. Stawström and Hillert developed a simple model for grain boundary precipitation in 18Cr-8Ni-C (wt.%) stainless steel considering the depth and width of the chromium concentration profiles in the depleted zones, but their treatment only considered the effects of Cr and C, neglecting the effect of nickel on the thermodynamic and mobility parameters. Multicomponent effects were also neglected by Hall and Briant. Was and Krug included a single ternary interaction parameter to model Fe–Cr–Ni–C quaternary system recognizing that the consideration of only binary interaction terms was not sufficient to accurately model the thermodynamics of carbide precipitation. The kinetic modeling was performed to quantitatively describe the Cr depleted zone by solving a discretized Fick’s 2nd law numerically. Bruemmer correlated chromium depletion characteristics directly to DOS as measured using DL-EPR tests and developed a theoretically based empirically modified model for the quantitative prediction of the DOS. However, the chromium concentration in the austenite at the interface with the carbide was calculated based on reaction theory, which does not guarantee the solute atom flux balance at the chromium carbides. Sahlaoui rejected the assumption considered in the previous models, that the carbide nucleation is instantaneous and that thermodynamic equilibrium is achieved immediately at the carbide matrix interface. He developed a two-stage diffusional model taking into account dechromization and rechromization. However, the use of a two-stage description violates the assumption that the carbide-matrix interface should remain in local equilibrium during diffusion-controlled growth. It was assumed that precipitation had finished by the time self-healing began, and this led to inaccurate chromium concentration profile predictions. Sourmail et al. modelled grain boundary precipitation of carbides considering multicomponent effects with the use of MTDATA software for thermodynamic calculations. The interfacial Cr concentration was calculated by solving flux balance equations at the carbide-matrix interface. However, no correlation between the calculated depletion characteristics and DOS was made.

Therefore, a study that relates experimentally measured DOS to grain boundary chromium concentration profiles obtained considering multicomponent thermodynamic and diffusion interactions is required. Earlier, the present authors established a depletion parameter that related DOS to grain boundary concentration profiles; however, there it was assumed that precipitate nucleation was instantaneous. In the present article, the validity of this assumption is examined by including calculations of incubation time and examining its effect on Cr concentration profiles. Compared to the previous work, lower heat treatment temperatures are now included to better explore the extended incubation times for nucleation. Also, longer heat treatment times at higher temperatures are included to extend the study into the self-healing stage. Both DOS obtained from DL-EPR tests and Cr concentration profiles across the M23C6 carbide-austenite matrix interface obtained from diffusion module, represent the overall Cr depletion. The relation between chromium depletion parameter that considers the depth and width of grain boundary chromium depletion profiles and the DOS, that helps in identifying the occurrence and disappearance of sensitization during industrial processing has been established. Comparisons to EPR-DOS measurements enable capabilities to be assessed versus a large, quantitative database. In the present work, the full precipitation sequence with nucleation and growth of metastable carbides during heat treatments at different temperatures is simulated and the input data is provided by CALPHAD databases.

2. Experiments and Methodology

2.1. Materials

The investigated material was a 3 mm thick commercial austenitic stainless steel of grade EN1.4310 obtained from Outokumpu Stainless Oy, Tornio, Finland. The chemical composition of the steel in wt.% was Fe-16.80Cr-6.36Ni-0.10C. The material was first solution treated at 1 100°C for 2 hours followed by water quenching. It is safe to assume that the material is homogenised after this solution treatment. After this, the alloy has been subjected to the isothermal furnace heat treatments given in Table 1. In the present case the
grain size was measured as 72 μm for all the heat treatments.

2.2. DL-EPR Testing

DOS values for the heat treated samples were determined using double loop electrochemical potentiokinetic reactivation testing according to the standard EN ISO 12732 [13], which describes the limits of the DOS values corresponding to highly sensitized, slightly sensitized and unsensitized material. Before the test, the samples were polished to a 600-grit finish. The DOS is not sensitive to surface finish, however, as the forward, anodic polarization scan causes the dissolution of all the surface irregularities and establishes a passive finish. The DOS is not sensitive to surface finish, however, as the forward, anodic polarization scan causes the dissolution of all the surface irregularities and establishes a passive film.\(^{23}\) Polarization in the reverse direction causes the dissolution of this passive layer at any Cr depleted regions, which are susceptible to corrosion, and produces a reaction current peak. The peak current density depends on the extent of Cr depletion.\(^{23}\) 0.5 M H\(_2\)SO\(_4\) + 0.01 M KSCN was used as the medium for the test at ambient temperature with a scan rate of 6 V/h. Each experiment was repeated thrice and DOS values were plotted with the error bars as can be seen below.

2.3. Oxalic Etching

Oxalic acid etch test has used for the classification of etch structures in austenitic stainless steels according to ASTM A262 Practice A. This test can only give information whether a specimen is free of susceptibility to intergranular corrosion and thus needs to be used in conjunction with other evaluation tests, in this case, with DL-EPR tests.

3. Experimental Results

Figure 1 shows, as a function of holding temperature and time, the experimentally determined DOS values obtained from the DL-EPR tests. Means and standard deviations based on three repeats are given. It can be seen that at higher holding temperatures, DOS first increases with time and then decreases due to the healing effect. At 820°C and 760°C, the healing effect begins after 24 h of heat treatment, and in the case of 700°C after 120 h. It is also clear that the kinetics of sensitization and healing is faster at higher temperatures. At 600°C, the maximum heating time employed was not enough to produce self-healing. Oxalic etching microstructures quite well complimented the above results as can be seen from the Fig. 3. Step structure has been observed in the sample heat treated at 600°C for 10 h (Figs. 2(a), 2(b)) indicating this sample is free of intergranular corrosion. Ditch structure indicating ditches at grain boundaries can be observed in Figs. 2(c), 2(d) in the sample heat treated at 700°C for 5 days. Figures 2(e), 2(f) shows the etched carbides along the grain boundaries for the samples heat treated at 820°C for 5 days. Even though the sample is desensitized according to DL-EPR, the carbides are still present and are etched during oxalic acid etching.

4. Modelling and Discussion

4.1. Nucleation

The precipitation kinetic simulations were performed using the precipitation module of Thermo-Calc\(^8\), i.e. TC-PRISMA.\(^{26}\) This is based on the Langer-Schwartz theory that adopts the Kampmann-Wagner numerical method for concurrent nucleation, growth and coarsening of precipitate phases.\(^{25,26}\) The vital parameters that are needed for the simulation include the mobilities, interfacial energies and driving forces. These are obtained from the thermodynamic and kinetic databases of Thermo-Calc, i.e. TCFE7 and MOBFE2 respectively. A modified Becker’s model is used for estimating the interfacial energy(\(\sigma\)) of M\(_23\)Cr\(_6\),\(^{25,27-29}\) which gives around 0.1–0.2 J/m\(^2\), as interfacial energy is a function of temperature. This is also in the range reported in the literature.\(^{30,31}\) Molar volumes of phases are calculated based on the work by Qiu and Frisk.\(^{32,33}\) The extension of classical nucleation theory (CNT) for modeling nucleation in a multicomponent alloy system gives the time dependent nucleation rate \(J(t)\).\(^{34}\)

\[
\tau = \frac{1}{2Z^*\beta^*} \quad \text{.......................... (1)}
\]

\(Z\) is the Zeldovich factor, \(\beta^*\) is the rate at which atoms or molecules are attached to the critical nucleus,

\[
\beta^* = \frac{4\pi r^2}{a^4} \sum_{i=1}^{\infty} \left[ \frac{X_i^\beta - X_i^\alpha}{X_i^\alpha D_i} \right]^{1/2} \quad \text{.............. (2)}
\]

\(a\) is the lattice parameter, \(X_i^\beta\) and \(X_i^\alpha\) are the mole fractions of element \(i\) at the interface in the precipitate and matrix.
respectively, \( k \) denotes the number of components, \( D_i \) is the corresponding diffusion coefficient in the matrix, \( r^* \) is the critical radius and is given by

\[
r^* = \frac{2\sigma V_m^{\beta}}{\Delta G_{m}^{\alpha \to \beta}} \quad \cdots \cdots \cdots \cdots (3)
\]

\( V_m \) is the molar volume of the matrix phase, \( \Delta G^* \) is the Gibbs energy of formation of the critical nucleus,

\[
\Delta G^* = \frac{16\pi\sigma^3}{3(\Delta G_{m}^{\alpha \to \beta} / V_m^{\beta})^2} \quad \cdots \cdots \cdots \cdots (4)
\]

Precipitation on grain boundaries is treated by calculating the number of nucleating sites from the density of grain boundary area.\(^36\)

4.2. Growth

The growth of the precipitates is simulated using the diffusion module of Thermo-Calc, DICTRA assuming that growth starts after the time \( \tau \).

Grain boundary precipitates are expected to grow after the formation at certain nucleation sites on the grain boundary. They tend to grow into one or both grains as shown in the previous work (or Figure) [36]. The grain boundaries are expected to operate as collector plates for the substitutional atoms diffusion through the matrix to the grain boundaries.
as the mobility of substitutional alloying elements along the grain boundaries is much higher than through the austenite matrix.\(^{37}\)

The DICTRA simulations assume local equilibrium at matrix-carbide interface and are based on a numerical solution of multi-component diffusion equations.\(^{38}\) The problem is reduced to one dimension, by assuming \(\text{M}_{23}\text{C}_6\) grows behind a planar austenite-carbide interface as shown in Fig. 3. The width of the austenite from which C can be withdrawn \(d_a\) is assumed to be one sixth of the grain diameter as suggested by Sourmail\(^{39}\) in order to take into account soft-impingement, i.e. the interference of the diffusion fields around the various grain boundaries. Sourmail’s approach is based on the idea that grains are taken as cubes with six faces making it appropriate to attribute to each calculation volume a sixth of the grain from which C and Cr can be drawn.

4.3. Discussions

Table 2 shows the obtained incubation times for the formation of \(\text{M}_{23}\text{C}_6\) precipitates. \(C_{\text{rin}}\) is the chromium concentration in the austenite at the interface. This value is a result of the local equilibrium condition assumed to exist at the mobile model interface. The value of this interfacial chromium concentration depends on the isothermal holding temperature and changes with holding time as illustrated in Fig. 4. Figures 5–9 show the calculated Cr concentration profiles into the austenite from the carbide-austenite interface at the end of the isothermal treatments. It can be seen how \(C_{\text{rin}}\) increases with time, the increase being most pronounced at the highest temperatures. This means an ever-decreasing depth of chromium concentration profile in the austenite. For 3 h isothermal treatment, at 600°C, \(C_{\text{rin}}\) is around 3 wt.% Cr and this increases to around 10.5 wt.% Cr at 820°C.

Following Yin et al.,\(^{40}\) \(C_{\text{crit}}\) is the critical chromium concentration that determines an effective width \((W_{\text{crit}})\) of the chromium depleted zone at the grain boundary. For this study, it was found that the 12.5 wt.% Cr shown in Figs. 5–9 is the most appropriate value for \(C_{\text{crit}}\) as will be shown below. The width \(W_{\text{crit}}\) initially increases with isothermal holding time and then decreases at longer heat treatment times when the self-healing phase of sensitization becomes

Table 2. Incubation times for the formation of \(\text{M}_{23}\text{C}_6\) precipitates.

<table>
<thead>
<tr>
<th>Holding temperature (°C)</th>
<th>Incubation time (s)</th>
</tr>
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<tbody>
<tr>
<td>600</td>
<td>4 690</td>
</tr>
<tr>
<td>650</td>
<td>740</td>
</tr>
<tr>
<td>700</td>
<td>152</td>
</tr>
<tr>
<td>760</td>
<td>32</td>
</tr>
<tr>
<td>820</td>
<td>10</td>
</tr>
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Fig. 4. Schematic Cr concentration profiles in the austenite ahead of the \(\text{M}_{23}\text{C}_6\) boundary film at the end of isothermal holding for a) different hold temperatures \(T_1 > T_2 > T_3\), b) different holding times \(t_1 > t_2 > t_3\).

Fig. 5. Cr concentration profiles across \(\text{M}_{23}\text{C}_6\) carbide-austenite matrix at 820°C.

Fig. 6. Cr concentration profiles across \(\text{M}_{23}\text{C}_6\) carbide-austenite matrix at 760°C.
operative, i.e. when $C_{\text{crit}}$ starts increasing with time. Sahlaoui suggested that only $W_{\text{crit}}$ need be considered in order to characterize the Cr depletion and thereby the DOS. As can be seen from Figs. 10–11, there is a very poor correlation between measured DOS values and $W_{\text{crit}}$ alone. This conclusion is unchanged irrespective of the value chosen for $C_{\text{crit}}$. Bruemmer suggested that it is reasonable to assume that the degree of sensitization will depend not only on the width of the chromium depleted zone, but also on the depth of the depletion profile. Such is the approach taken in this work.

It is possible to conceive of various depletion parameters that combine the terms $W_{\text{crit}}$, $C_{\text{crit}}$, and $C_{\text{int}}$. Three such depletion parameters are $(C_{\text{crit}} - C_{\text{int}}) \cdot W_{\text{crit}}$, $(C_{\text{crit}}/C_{\text{int}}) \cdot W_{\text{crit}}$, and $W_{\text{crit}}/C_{\text{int}}$. Statistical analyses of the correlations between the experimentally measured DOS values and these potential depletion parameters based on a variety of definitions of $C_{\text{crit}}$ showed that the best correlation is obtained with the following depletion parameter:

$$DP = \begin{cases} 
(12.5 - C_{\text{int}}) \cdot W_{\text{crit}}, & C_{\text{int}} > 10.0 \\
(12.5 - 10.0) \cdot W_{\text{crit}}, & C_{\text{int}} \leq 10.0
\end{cases} \quad (5)$$

i.e. using $W_{\text{crit}}$ values defined by $C_{\text{crit}} = 12.5 \text{ wt.}\%$ and considering the minimum $C_{\text{int}}$ to be 10 wt.%. This corresponds to the assumption that Cr contents below 10 wt.% in the depleted zone have no extra effect on the tendency to intergranular corrosion and DOS values.

Figure 12 shows the variation of DP defined as in Eq. (5) as a function of time for all the temperatures studied. Initially DP increases with time at all temperatures, but for the longer times at 820°C, DP starts to decrease due to a predicted self-healing in a similar way to DOS in Fig. 1. Comparing this with the measured DOS values given in Fig. 1 shows how the current approach is able to reproduce sensitization and self-healing behavior quite well. The considered $C_{\text{int}}$ 12% by wt. in could not able to identify the self-healing although it could able to predict the occurrence
of sensitization. This choice of $C_{\text{int}}$ to be 12.5% by wt, not only predicted the occurrence of sensitization but also the disappearance of sensitization with time. Figure 13 shows a comparison of the measured and predicted values of DOS when 10% Cr cut-off is not considered in the depletion parameter calculations. This shows a very poor correlation with an $R^2$ value of 0.69. Figure 14 shows the correlation of measured and predicted DOS values when the incubation times are not considered. The $R^2$ value for this polynomial trend has found to be 0.76. Now in Fig. 15, the depletion parameter here included the incubation times. The correlation is much better as can be observed from the obtained $R^2$ value is 0.85. Thus the inclusion of a 10% Cr cut-off and the incubation times in the calculation of the depletion parameter reduced the scatter in the correlation between DOS and DP. It should be noted that the polynomial fit has simply been applied to calculate $R^2$ values; it is not implied that such an equation gives a correct functional description, of course and there should be no tendency for DOS to decrease at the highest values of DP like in Fig. 15.

The possible effect of the C, Ni, or Si concentration profiles on the electrochemical properties of the Cr depleted zones and thereby DOS have been ignored. It has been possible to obtain concentration profiles up to the $M_23C_6$ - austenite interface with the aid of thermodynamic and diffusion models. However, an experimental verification of these would require STEM analyses or atom probe tomography measurements that are outside the scope of this work.

Further work is required to explore the validity of the above approach using other stainless steels with different chemical compositions. It is possible, for example, that the critical chromium concentration defining the width of the chromium depleted zone depends on the bulk alloy composition.

5. Conclusions

An austenitic stainless steel with the composition Fe-16.80Cr-6.36Ni-0.10C has been solution treated and isothermally heat treated at varying temperatures in the range 600–820°C for times from 3 to 480 h to produce various degrees of sensitization and self-healing. The degrees of sensitization were measured using DL-EPR tests and correlated to calculated chromium concentration profiles across the $M_23C_6$ - austenite interface obtained.

The following conclusions can be drawn.

- The chromium concentrations at the $M_23C_6$ - austenite interface increase with holding time and temperature before the self-healing begins.
- For the specific alloy composition studied, Cr depletion profile width is best characterized using a critical chromium concentration of 12.5% Cr. This was established by considering the 10% cut-off in the measurement of the interfacial chromium concentration.
- The established depletion parameter shows a good correlation with the experimentally determined degree of sensitization values.
- Both sensitization and self-healing are predicted with the defined depletion parameter.
- The incubation times for the formation of stable $M_23C_6$ precipitates are higher at lower temperatures and their consideration in the growth calculations reduced the scatter in the correlation between degree of sensitization...
Acknowledgements

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