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MODELLING OF SIGMA PHASE FORMATION DURING ISOTHERMAL AGING OF A SUPERDUPLEX STAINLESS STEEL

Abstract

An accurate set of experimental data which can describe the kinetics of phase transformations is essential to the reliable determination of thermal cycles for processing of superduplex stainless steels, preventing the formation of deleterious phases such as sigma phase. However, there are different mechanisms of sigma phase formation, which can occur in different thermal cycles, making unfeasible the use of experimentation as the only way of microstructure prediction. Thus, the experimental validation of the models used in simulations of thermodynamic equilibrium and kinetics of phase transformations is essential. This paper aims the modelling and experimental validation of the kinetics of sigma phase formation during isothermal aging at 950 °C a superduplex stainless steel. The thermodynamic equilibrium was modelled through computer simulation using Thermo-Calc software and TCFE6 thermodynamic database, and kinetics of sigma phase formation was modelled through DiCTra software and MOB2 diffusion database, using three different models for sigma phase formation. The results of computer simulations were evaluated and compared with experimental data obtained from samples initially solution treated at 1100°C and then isothermal aged at 950 °C in different time periods.

Keywords

Modelling, kinetics, sigma phase, superduplex stainless steels.

1. Introduction

Duplex stainless steels (DSS) present in their microstructure approximately equal volume fractions of ferrite and austenite, and considering their high chromium, molybdenum and nitrogen contents, and their usually refined grain structure, those steels can be used in situations that demands high corrosion resistance together to high mechanical strength and toughness [1,2]. The Pitting Equivalent Resistance Number (PREN) is an empirical way to classify DSS according to their corrosion resistance [3-5]. Usually calculated by eq. 1, if PREN reaches values lower than 30, the steel is classified as “lean-duplex”; if 30<PREN<40, the steel is a “standard-duplex”, and if PREN is higher than 40 the steel is classified as superduplex. A typical superduplex stainless steel is UNS S32750, which has chemical composition Fe-25%Cr-7%Ni-4%M0-0.27%N, with a PREN of 42.5 [4,6].

\[
\text{PREN} = [(\%Cr) + 3.3(\%Mo) + 16(\%N)]
\]

\text{eq. 1.}

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However, the duplex microstructure is obtained by a solution heat treatment between 1,000°C and 1,200°C followed by water quenching, resulting in a metastable microstructure at temperatures lower than the used at the solution treatment. Specifically between 600°C and 950°C, sigma phase can be formed. Sigma phase is a Cr and Mo rich phase, and its formation leads to the formation of Cr- and Mo-depleted regions in the sigma surrounding phases, compromising corrosion resistance, specially localized corrosion resistance. Furthermore, sigma phase presents brittle behaviour, compromising the excellent toughness commonly related to DSS [7-12].

At least two mechanisms are accepted for sigma phase formation in DSS: eutectoid decomposition of ferrite (with the formation of sigma and austenite, called secondary austenite, with lower Cr, Mo and N contents) and nucleation and growth from ferrite (leaving a Cr- and Mo-depleted ferrite); nevertheless, sigma phase nucleation is essentially found in heterogeneous sites, specially ferrite/austenite interfaces or ferrite/ferrite grain boundaries [6-9].

There is no agreement regarding the kinetics of sigma phase formation; three different studies [10-12] describes sigma phase formation kinetics between 800°C and 850°C of two superduplex stainless steels and one duplex stainless steel, with a large dispersion of results, possibly due different ferrite fractions, different chemical compositions of ferrite, or different ferrite and austenite grain sizes (resulting in different availability of interfaces for heterogeneous nucleation). All those factors can affect the kinetics of sigma phase formation.

Thus, it is essential to study the sigma phase formation kinetics from computer simulations, where differences of initial duplex structure and different microstructure models can be tested. If those simulations were validated by experimental results, they can be an extremely important tool to predict sigma phase and extension of Cr- and Mo-depleted areas after specific thermal histories. In this context, this work is a first approach on the simulation aided by Thermo-Calc® and DiCTra® of sigma phase formation in a superduplex stainless steel after isothermal aging at 950°C, considering the heterogeneous nucleation of sigma and its growth over ferrite.

2. Experimental procedures

The studied material, which has the chemical composition presented in Table 1, was obtained as 20 mm diameter hot rolled bars, which is solution treated for 30 min at 1,100°C and water quenched. Isothermal aging at 950°C were then conducted between 300 s and 14,400 s, also followed by water quenching, in order to obtain five different samples: one without aging, containing a duplex ferrite/austenite microstructure, and four other samples with different amounts of sigma phase.

<table>
<thead>
<tr>
<th>Cr (wt.%)</th>
<th>Ni (wt.%)</th>
<th>Mo (wt.%)</th>
<th>Mn (wt.%)</th>
<th>N (wt.%)</th>
<th>C (wt.%)</th>
<th>Si (wt.%)</th>
<th>Cu (wt.%)</th>
<th>Fe (balance)</th>
</tr>
</thead>
<tbody>
<tr>
<td>24.95</td>
<td>6.91</td>
<td>3.79</td>
<td>0.43</td>
<td>0.26</td>
<td>0.015</td>
<td>0.26</td>
<td>0.083</td>
<td>balance</td>
</tr>
</tbody>
</table>

After heat treatments, samples were mounted in thermosetting resin and metallographic polished and then were observed in a scanning electron microscope (SEM) by backscattered electron images (BSC), and sigma content was evaluated by quantitative stereology of BSC since sigma phase, which is Mo-rich, appears brighter in that kind of image if compared to ferrite or austenite phases; an area of approximately 0.224 mm², corresponding to 20 fields at
1000x magnifications, was analysed in sigma quantification. Solution treated sample were also observed in an optical microscope (OM) after electrolytic etching in a 10% oxalic acid solution (6 Vdc for 30s) for better distinguish between ferrite and austenite.

3. Computer simulations

Using the chemical composition presented in Table 2, thermodynamic equilibrium was calculated through Thermo-Calc® software, using TCFE6 database. Table 2 also presents the chemical composition and volumetric fractions of ferrite and austenite in equilibrium at 1,100°C, temperature used in the solution treatment of the samples. The computer simulations only considered the presence of Fe, Cr, Ni, Mo and N to simplify the simulation of the diffusion controlled formation of sigma at 950°C, described in sequence.

Table 2. Chemical composition of the studied steel used in thermodynamic simulations, phases chemical composition and volume fraction at 1,100°C calculated by Thermo-Calc.

<table>
<thead>
<tr>
<th>chemical composition [wt.%%]</th>
<th>Cr</th>
<th>Mo</th>
<th>N</th>
<th>Ni</th>
<th>phases vol%</th>
</tr>
</thead>
<tbody>
<tr>
<td>studied steel</td>
<td>24.95</td>
<td>3.79</td>
<td>0.26</td>
<td>6.91</td>
<td><em>.</em></td>
</tr>
<tr>
<td>ferrite (1,100°C)</td>
<td>26.50</td>
<td>4.65</td>
<td>0.04</td>
<td>5.26</td>
<td>49.4</td>
</tr>
<tr>
<td>austenite (1,100°C)</td>
<td>23.43</td>
<td>2.95</td>
<td>0.47</td>
<td>8.51</td>
<td>50.6</td>
</tr>
</tbody>
</table>

Kinetics of sigma phase formation were simulated through DiCTra® software, using as thermodynamic database for local equilibrium determination the previous cited TCFE6 database, and MOB2 database for diffusional data. Previous work of the author on the kinetics of sigma phase formation in a duplex stainless steel [7] suggested that the fraction transformed in sigma \( f \) after an aging time \( t \) can be described by the Kolmogorov-Johnson-Mehl-Avrami (KJMA) expression (eq. 2), with an exponent \( n \) of approximately 0.9, which can be related to diffusion-controlled growth of particles heterogeneously nucleated. For that reason, it was assumed in the kinetic models that sigma phase is nucleated at ferrite boundaries, with a unidirectional resulting diffusion flux.

\[
f = 1 - e^{-kt^n}
\]

eq. 2.

Three different models were tested, as presented in Figure 1. Models (1) and (2) are similar to the one previous used by other authors [13], and consider that sigma phase as inactive in a ferrite-austenite interface, adopting two different sizes for ferrite and austenite grains. The relative sizes of the two phases in the beginning of the simulation provide the volume fraction of ferrite and austenite predicted by thermodynamic equilibrium calculations showed in Table 2, and the sizes of ferrite and austenite are equivalent to the average grain size of phases in Model (1) and half of the average grain sizes in Model (2). However, models (1) and (2) did not allow re-equilibrium between ferrite and austenite after sigma nucleation, and to analyse this effect Model (3) allows contact between ferrite and austenite throughout the simulation, since ferrite and austenite stays in contact even after sigma formation.
4. Results and discussion

Typical microstructures of the solution-treated sample are presented in Fig. 2a (OM) and 2b (BSC); the average grain diameter of 10 µm can be confirmed in Fig. 2a; round dark spots in Fig. 2 are oxide inclusions, while rod-like dark phases in Fig 2c to 2f are chromium nitrides (Cr₂N), not discussed in the computer simulations.

Aged samples at 950°C are composed by the microstructures presented in Fig. 2c to 2f, in which the brighter phase are sigma, due to its higher Mo content. Since sigma nucleation is always associated to ferrite interfaces, with grow of sigma over ferrite phase, it is worth noting that ferrite became darker with increase of sigma fraction, as a result of Mo impoverishment of ferrite for sigma formation. It can be observed that increasing of aging time leads to higher sigma fraction. Energy Dispersive Spectroscopy (EDS) analysis on ferrite and austenite of the solution-treated sample allows the quantification of Cr, Ni or Mo contents, and the results are presented in Table 3. While ferrite is Mo-rich, austenite is Ni rich, and for this reason, in the BSC of solution-treated sample (Fig. 2b), for the poor contrast between ferrite and austenite.

Comparison between EDS and Thermo-Calc simulation of chemical composition (Table 2) shows that thermodynamic simulation of equilibrium at 1,100°C is quite faithful to the experimental results. EDS analysis were also performed in the phases of the sample aged for 1,800 s at 950°C, and it can be proved that sigma is a Cr- and Mo-rich phase. However, only the Mo content of ferrite experienced a reduction after aging for 1,800 s at 950°C. This is probably due to two reasons: i) the average measurement possible with point EDS analysis, were the volume of X-ray generation around the electron spot has a diameter of 5-10 µm; ii) the presence of a composition gradient between the interface of sigma and the surrounding matrix, since there is only local equilibrium between phases during the growth of sigma phase. Concerns about local equilibrium and composition gradients will be discussed later on this paper.
Figure 2. Typical microstructures of the studied steel. Solution treated sample in (a) or (b); samples aged at 950°C for (c) 300 s, (d) 600 s, (e) 1,800 s or (f) 14,400 s.

Table 3. Mean chemical composition (wt. %) obtained by EDS for ferrite and austenite in the solution treated sample and in the sample aged for 1,800 s at 950°C.
<table>
<thead>
<tr>
<th>chemical composition [wt.%]</th>
<th>Cr</th>
<th>Mo</th>
<th>Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ferrite (solution treated)</td>
<td>27.3</td>
<td>5.0</td>
<td>5.1</td>
</tr>
<tr>
<td>Ferrite (1,800 s @ 950°C)</td>
<td>28.1</td>
<td>3.9</td>
<td>4.1</td>
</tr>
<tr>
<td>Austenite (solution treated)</td>
<td>24.6</td>
<td>3.3</td>
<td>8.4</td>
</tr>
<tr>
<td>Austenite (1,800 s @ 950°C)</td>
<td>24.6</td>
<td>3.2</td>
<td>8.3</td>
</tr>
<tr>
<td>Sigma (1,800 s @ 950°C)</td>
<td>30.6</td>
<td>9.6</td>
<td>4.3</td>
</tr>
</tbody>
</table>

Thermodynamic equilibrium calculations of the volume fraction of phases as a function of temperature for the studied steel are presented in Fig. 3. It can be observed that volume fractions of ferrite (measured by ferritscope magnetic measurements) and austenite of the 1,100°C solution-treated sample are approximately the same found in Thermo-Calc simulations, showing that the premise of using only Fe, Cr, Ni, Mo and N in the simulations did not have a strong impact in the results for this sample. The small amounts of chromium nitrides found in the sample aged for 14,400 s at 950°C are in agreement with the equilibrium simulations of Fig. 3, since the upper temperature for nitride existence is around 952°C according to simulations; however, the amount of sigma phase found after for 14,400 s at 950°C are smaller than the predicted equilibrium volume fraction, showing that 14,400 s at 950°C was not sufficient for the establishment of thermodynamic equilibrium.

![Figure 3. Volume fraction of phases in equilibrium calculated by Thermo-Calc® using TCFE6 database and chemical composition of the studied steel presented in Table 2.](image)

Fig. 4 and Fig. 5 present respectively Cr and Mo profiles along phases of Model 1 in five different time periods. Black lines presented the initial condition, were it was assumed that only ferrite (on the left) and austenite (on the right) are present, with homogeneous
composition of the elements in phases, assumed in equilibrium at that point. For time periods up to 1800 s it can be observed the development of a Cr and Mo gradient in the ferrite, together to the growth of sigma phase inside ferrite. The absence of huge differences between chemical compositions of ferrite before and after 1800 s aging, showed in Table 3, is now explained, considering the composition gradients in ferrite, and the average measurement possible with point EDS analysis, were the volume of X-ray generation around the electron spot has a diameter of 5-10 μm. It is interesting to note, however, that Cr and Mo content of sigma are respectively 32%Cr and 10%Mo, values close to those found in EDS analysis (Table 3), validating the simulations of equilibrium.

A sharp gradient of Cr and Mo is also observed in austenite, without any significant growth of sigma over this phase; this was expected, since diffusion in ferrite are at least 2 orders of magnitude higher in the BCC lattice of ferrite if compared to close packed FCC lattice of austenite.

Figure 4. Chromium profile after different aging times at 950°C calculated by DiCTRa® using TCFE6 and MOB2 databases using Model 1.
Figure 5. Molybdenum profile after different aging times at 950°C calculated by DiCTra® using TCFE6 and MOB2 databases using Model 1.

Despite the fact that Model 1 can qualitatively describe the phenomenon of sigma growth from ferrite and the associated composition gradients expected in ferrite and austenite around the formed sigma phase (Fig. 4 and Fig. 5), none of the three studied models were capable of describing the evolution of the sigma volume fraction through aging time at 950°C, as can be seen in Fig. 6. The most important problem is the innability of describe the sharp rise in sigma content between 300 s and 600 s: the slopes of the curves for the three models are smaller than the observed in the experimental results. Model 2, which presents the smaller diffusion distances, is capable of being close to experimental results after 600 s, but fails on describe the initial times of sigma formation, since it predicts 7 times more sigma at 300 s than the observed value.

The major problem concerning the applied models and its poor fit to experimental measurements of sigma phase volume fraction is the ability of only small amounts of sigma to drastically reduce localized corrosion resistance and toughness, and there is the need for determination of the initial steps of sigma formation. Some researches [14,15] described the high rate of sigma formation, and it was found [14] that $n$ exponent of KJMA expression (eq. 2) can reach values up to 7 in the initial times of sigma formation, to values smaller than 0.7.

Higher $n$ exponent of KJMA, which are responsible for larger slopes of the sigmoidal curve described by eq. 2, are related to interface-controlled growth (such as increasing nucleation rates during aging) or related to diffusion-controlled growth of complex shapes of precipitates (coupled to a cooperative nucleation process) [16]. These situations are not included in these three studied models, and future works on this subject must be focused on:

- DiCTra® models that consider the sigma phase growth not only restricted to one-dimensional diffusion, as those that enable radial growth or spherical particles.
- Models in DiCTra® to assess the occurrence of eutectoid decomposition of ferrite in austenite and sigma.
✓ Models to evaluate the effect of different rates of nucleation, as promise to be the models of the new Prisma® software.

Figure 6. Sigma volume fraction after different aging times at 950°C simulated by DiCTra® using TCFE6 and MOB2 databases in the three studied models.

5. Conclusions

The thermodynamic equilibrium of a superduplex stainless steel was modelled through computer simulation using Thermo-Calc software and TCFE6 thermodynamic database, and they were validated experimentally. Kinetics of sigma phase formation was modelled through DiCTra software and MOB2 diffusion database, using three different models for sigma phase formation. Despite the fact that DiCTra models can qualitatively describe the phenomenon of sigma growth from ferrite and the associated composition gradients expected in ferrite and austenite around the formed sigma phase, none of the three studied models were capable of describe the evolution of the sigma volume fraction through aging time at 950°C. Since the studied models only consider unidimensional diffusion flux for the growth of a single heterogeneously nucleated sigma phase, future works on this subject must be focused on models that consider the sigma phase growth not only restricted to one-dimensional diffusion, as those that enable radial growth or spherical particles, models to assess the occurrence of eutectoid decomposition of ferrite in austenite and sigma, and models to evaluate the effect of different rates of nucleation, as the ones possible by Prisma® software.

References