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Experimental investigations and DICTRA® simulation of sigma phase formation in a duplex stainless steel

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ABSTRACT

Sigma phase formation in an UNS S31803 duplex stainless steel aged at 940 °C was evaluated by computational simulation in DICTRA® software, using MOB2 diffusion database and TCFE8 thermodynamic database. Simulation results were compared to experimental tests. Two models were tested in DICTRA® software: in model 1 sigma phase are placed between ferrite and austenite, and in model 2 sigma is placed at one side of ferrite region, and austenite on the other. The volume fraction of sigma and ferrite phases obtained in model 1 showed adherence to the experimental results up to 7200 s (2 h) of simulation, indicating the ability of the model in the description of early stages of sigma formation. Model 2 showed good agreement with experimental data up to 86,400 s (24 h) of simulation. The composition profile obtained by the simulation of the model 1 represented better the impoverishment in Cr and Mo in ferrite/sigma and austenite/sigma interfaces, while the profiles obtained by the simulation of model 2 described better the partition of the chemical elements between austenite and ferrite during sigma formation.

1. Introduction

Duplex Stainless Steels (DSS) have a microstructure usually composed by 50% of ferrite (α) and 50% of austenite (γ). The main advantage of their use is the combination of excellent mechanical behavior and high corrosion resistance. The major industrial applications of DSS are in chemical and oil and gas industries [1,2].

However, the exposition of DSS to temperatures between 650 °C and 950 °C may lead to the formation of intermetallic phases, especially sigma (σ) phase. Sigma is a brittle and Cr- and Mo-rich phase, and may be considered the most deleterious phase formed in DSS, especially because of the formation of Cr- and Mo-depleted areas surrounding σ phase [1,3].

Different results concerning the kinetics of sigma formation in DSS are found in literature [4–8], attributed to differences in chemical composition, ferrite and austenite grain sizes and phase fractions. Considering this, it is very helpful the use of computer simulation in the study of sigma phase formation, allowing the evaluation of structural differences of the microstructure prior to aging. Some authors showed the viability of the use of DICTRA® [9] software in studies involving duplex stainless steel [10–13].

The purpose of this paper is the evaluation of the sigma formation in a duplex stainless steel aged at 940 °C by computational simulation in DICTRA®, and the comparison of the simulation to experimental results, validating the proposed models.

2. Experimental procedures

3-mm thickness sheets of UNS S31803 DSS were used for the study, and its chemical composition is given in Table 1. Solution heat treatment was conducted at 1120 °C for 96 h followed by water quenching, in order to obtain a duplex structure. After that, samples were aged at 940 °C between 1200 s (20 min) and 864,000 s (240 h), and aging treatments were also interrupted by water quenching. Heat treatments were conducted in a tubular electric furnace using nitrogen atmosphere to avoid excessive oxidation of the samples.

After heat treatments, samples were mounted in thermosetting resin, parallel to the rolling direction, and metallographic polished in a semi-automatic grounding and polishing machine, with final polishing provided by 1 μm diamond abrasive.

Solution-treated samples were observed in an optical microscope (OM), after two different etching procedures. Beraha reagent was composed by a stock solution of 20 ml hydrochloric acid (HCl) and 80 ml distilled water, and 1 g potassium metabisulfide ($K_2S_2O_5$); to this stock solution, 1 g of ammonium bifluoride (NH_4F-HF), were added just before the etching, for colour differentiation between ferrite and

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Table 1
Chemical composition (wt%) of the UNS S31803 steel.

Cr	Ni	Mo	Mn	N	C	Si	Cu	V	Fe
22.07	5.68	3.20	1.38	0.17	0.017	0.34	0.15	0.13	balance

Table 2
Chemical composition at 1120 °C, calculated by Thermo-Calc.

	Chemical composition [wt%]			
	Cr	Mo	N	Ni
ferrite (1120 °C)	23.93	3.87	0.04	4.33
austenite (1120 °C)	20.23	2.53	0.3	7.02
sigma (940 °C)	31.14	11.33	0	2.55

austenite. Etching of grain boundaries and ferrite/austenite interface of the solution-treated sample was obtained through electrolytic etching in 10 pct. oxalic acid ($H_2C_2O_4$) aqueous solution (6 Vdc during 10 s). The aged samples were observed in an OM after Beraha etching, for distinguish between ferrite, austenite and sigma, and after electrolytic etching in 10 pct potassium hydroxide (KOH) aqueous solution (2 Vdc during 60 s), for sigma phase quantification.

Ferrite content was evaluated by quantitative stereology over OM images after Beraha etching, and sigma content were determined by quantitative stereology over OM images after KOH etching. In each sample, 30 fields were analysed in a computer aided image analysis system.

Measurements of the mean intercept size of ferrite and austenite phases of the solution-treated sample were made from OM images after oxalic etching. 400 measurements were performed in each phase to obtain the mean value of intercept.

3. Computer simulation

Thermodynamic equilibrium at 1120 and 940 °C was calculated through Thermo-Calc® software, using TCFE8 database. The computer simulation only considered the presence of Fe, Cr, Ni, Mo and N to simplify the simulation of the diffusion controlled formation of sigma. Table 2 presents the expected chemical compositions of ferrite and austenite in equilibrium at 1120 °C and the chemical composition of sigma phase at 940 °C.

Sigma phase formation at 940 °C were simulated through DICTRA® software, using TCFE8 thermodynamic database and MOB2 database for diffusional data.

Two different models were tested, as presented in Fig. 1. The model 1 consider sigma phase as an inactive phase in a ferrite/austenite interface, and DICTRA® software calculates the moment where there is thermodynamic potential for the appearance of the sigma phase, which were then considered as active phase in the model, with initial size of 0.1 μm. Model 2 consider active sigma phase since the beginning of the simulation, growing next to ferrite phase with an initial size of 0.1 μm, allowing alloying element partition between ferrite and austenite throughout the simulation time. The lengths of the ferrite and austenite phases in the beginning of the simulation were assumed to be the mean intercept size measured in the solution-treated sample.

4. Results and discussion

The solution treatment resulted in the microstructure presented in Fig. 2. Fig. 2(a), after Beraha etching, shows the duplex structure, where ferrite appears in black and austenite as the white regions. Fig. 2(b) shows the same sample electrolytic etched using oxalic acid, revealing grain boundaries, interfaces between ferrite and austenite, and twin boundaries inside austenite grains. Quantitative stereology performed over Beraha etched surfaces showed that the solution-treated sample presents 44 ± 2 pct of ferrite. Mean intercept of phases showed that mean ferrite size was 46 ± 8 μm and austenite has mean intercept of 54 ± 16 μm. Those mean intercept values were used as ferrite and austenite lengths in computer simulations.

Fig. 3 presents the microstructural evolution of samples aged at 940 °C. After Beraha etching, sigma phase appears as the white phase, ferrite is the darker phase, and austenite is the light grey regions; in KOH etched samples sigma phase appears dark in a non-etched matrix. In the beginning of the aging treatment, sigma phase was formed preferentially in ferrite/austenite boundaries (Fig. 3(a) and (b)), and its growth occurs mainly over ferrite as shown in Fig. 3(c) through (f). Small dark points in original interfaces after KOH etching (Fig. 3(b), (d) and (f)) are probably related to the hexagonal close-packed chromium nitrides (Cr_2N) formation, without any relation to sigma preferential sites for nucleation. Similar microstructural characteristics were found by other authors [14,15]. In fact, the formation of chromium nitrides reduces the Cr content in those regions, making difficult sigma phase nucleation in those sites.

The measurement of sigma content and its comparison with sigma volume fractions obtained in DICTRA® simulations are presented in Fig. 4. The curves obtained by simulation in DICTRA® shows sigmoidal format according to KJMA studies [4–8]. The major sigma fraction obtained in model 1 simulation was 1.32 pct after 36,000 s (100 h) of simulated aging time at 940 °C, while the model 2 reached 7.89 pct after 864,000 s (240 h).

Model 1 simulation data shows good agreement to experimental results up to 7200 s (2 h) of aging (Fig. 4), although it can not describe the evolution of sigma phase content that takes place for longer aging times. Positions of ferrite/sigma and sigma/austenite interfaces during Model 1 simulation, presented in Fig. 5, show that sigma phase growth preferably into ferrite, according to experimental observations.

Although the sigma volume fraction obtained by the model 1 simulation showed adherence only up to 7200 s (2 h) of aging, Cr and Mo profiles in the beginning of sigma formation describe the depletion in those elements due to sigma phase formation, as showed in Fig. 6. Black lines in Fig. 6 presented the initial condition, were it was assumed that only ferrite and austenite are present, with homogeneous composition of the elements in phases, being the vertical line an indication of the austenite/ferrite interface. Dashed lines represented the profiles when sigma has already been formed, the first vertical line indicate the ferrite/sigma interface and the second the sigma/austenite interface. It can be observed that the displacement of the ferrite/sigma interface to the left is larger than of the sigma/austenite interface to the right. It can be also observed the development of Cr and Mo gradients in ferrite, together to the growth of sigma phase inside ferrite. 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 are faster in the BCC lattice of ferrite if compared to diffusion in the close packed FCC lattice of austenite.

If the compositional gradients in ferrite and austenite are com-

Fig. 1. Models applied in kinetic simulations. (a) Model 1. (b) Model 2.