Thermodynamic Modeling and Microstructural Characterization of Precipitation in a Superduplex Steel

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Abstract—In the present work, the precipitation in a superduplex stainless steel was studied via thermodynamical modeling and annealing experiments at 1000 °C, 1100 °C, and 1200 °C and cooled with rates of rates 200 K/s and 0,003 K/s. Thermodynamic modeling of precipitation was done by using the Thermo-Calc software. The microstructural investigations were performed through light/scanning electron microscope and energy dispersive X-ray spectroscopy. The precipitates after homogenization annealing experiments were predicted well by thermodynamical modeling. In order to prevent the precipitation of intermetallic phases, proper annealing parameters were given.

Keywords—Superduplex steels, Precipitation, Intermetallic phases, Thermodynamical modeling

I. INTRODUCTION

Superduplex stainless steels draw attention as a result of their attractive combination of mechanical strength, corrosion resistance in various types of environments, and weldability [1]. Their resistances to pitting and stress corrosion are superior. Superduplex stainless steels with a pitting resistance equivalent number (PREN) above 40 have a microstructure of 50/50 ferrite and austenite [2]. In their application like parts of pumps and tubes for chemical industry and offshore applications, high corrosion resistance and mechanical strength are emphasized [2]. Due to high amount of alloying elements Cr, Mo, and W, the secondary precipitation of intermetallic σ or (Fe,Ni)(Cr,Mo), and χ or Fe₃₆Cr₁₃Mo₁₀ phases may occur during the processing at high temperatures. The secondary precipitates might have an effect on the toughness and the corrosion resistance [3-9]. The purpose of the present study is to model and to investigate experimentally the precipitation in X2CrNiMoCuWN25-7-4 high nitrogen superduplex steel after homogenization annealing. The Thermo-Calc software and database were used for modeling of phase transformation at the thermodynamical equilibrium. The homogenization annealing experiments were performed at temperatures between 1000-1200 °C. In order to determine the morphology and chemical composition of phases, Scanning electron microscope (SEM) attached energy dispersive spectrometry (EDS) were used.

II. EXPERIMENTAL PROCEDURE

The experimental samples were produced from pressurized electroslag remelting (PESR)-blocks of industrial heat. The samples were sectioned from Ø 350 mm hot roll formed bars. The chemical composition of superduplex X2CrNiMoCuWN25-7-4 steel is given in Table 1. All elements present in the Table 1 were also considered in the calculations with the Thermo-Calc software using the TCS Steel Database TCFE5 [10,11]. The aim of the calculations is the prediction of phase equilibrium for various temperatures. The homogenization annealing was carried out in a Bähr DIL805 plastodilatometer in order to investigate the precipitation and phase transformations. The standard specimen size of 5 mm diameter and 10 mm length was used for the dilatometer experiments. The samples were annealed at 1000 °C, 1100 °C and 1200 °C for 15 min, followed by cooling with rates 200 K/s (quenching) and 0,003 K/s (slow cooling). The samples were metallographically prepared. After grinding, they were polished using diamond pastes with particle sizes of 6, 3 and 1 μm. Beraha was applied as the etchant agent. SEM and EDS analysis were used to observe the morphology of secondary phase particles and to analyze their chemical compositions. In addition, metallographic observations were made with a light microscope (LM).

III. RESULTS

A. Thermodynamic calculations

The Thermo-Calc computer program was used to predict the stability of occurred phases and precipitates. Fig. 1a is an isopleth diagram showing stability of phases as a function of temperature and nitrogen content. The dashed line in diagram indicates the relevant nitrogen amount for the steel composition used here. According to the thermodynamic calculations, liquid, ferrite, austenite, M₃N, M₁₇C₆, sigma (σ) and chi (χ) phases are in equilibrium.
In Fig 1b, the computed mass fraction of phases is given as a function of temperature. As indicated in the diagram, M₃N, σ, χ and M₂₃C₆ might precipitate at temperatures below 1100 °C. The intermetallic σ- and χ-phases can precipitate up to about 30 and 15 wt.-percent in equilibrium at 600 °C, respectively. The amount of M₃N is expected about 2 %. The precipitation of M₂₃C₆ carbides may be neglected.

### Table 1. Chemical composition (wt-%) of the examined steel.

<table>
<thead>
<tr>
<th>Steel grade/Alloy</th>
<th>C</th>
<th>Mn</th>
<th>Cr</th>
<th>Mo</th>
<th>Ni</th>
<th>W</th>
<th>Cu</th>
<th>Nb</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.4501 / X2CrNiMoCuWN25-7-4</td>
<td>0.022</td>
<td>0.62</td>
<td>25.6</td>
<td>3.65</td>
<td>6.15</td>
<td>0.55</td>
<td>0.90</td>
<td>0.009</td>
<td>0.256</td>
</tr>
</tbody>
</table>

**B. Homogenization annealing**

Two series of experiments were performed to evaluate the precipitations and phase transformations. The samples were heated to temperatures of 1000 °C, 1100 °C, and 1200 °C, and then held at these temperatures for 15 min in order to dissolve all precipitates. Finally, the samples were cooled to room temperature at two different linear cooling rates of 0.003 K/s (slow cooling) or 200 K/s (quenching). The aim of used cooling rates was to reveal the secondary precipitates with slow cooling and to determine their dissolving temperatures after quenching.

In investigations of samples cooled at 0.003 K/s, intermetallic phases were observed with ferrite and austenite grains, as shown in Fig. 2. The precipitates were appeared within grains or at grain boundaries of the ferrite, but not within the austenite. According to studies at literature [12,13], the precipitation of intermetallic phases in austenite is very sluggish due to the ferrite forming elements Cr and Mo and takes thousands of hours.

In order to determine the chemical compositions, SEM and EDS analysis of selected precipitates were performed. In Fig. 3, measured compositions of the precipitations were given. EDS analysis indicated σ, χ and secondary austenite (γ₂) phases. As well-known, the formation of σ-phase leads to depletion in Cr and Mo and to enrichment in Ni of the neighboring ferrite, which becomes unstable and transforms into γ₂. The overall result is the co-precipitation of γ₂ and σ. On the other hand, Mo rich χ phase also formed.

After quenching (200 K/s) from temperatures above 1000 °C, the secondary precipitates was dissolved as seen in Fig. 4. The microstructure after quenching contains a mixture of ferrite and austenite phases. Ferrite phase is free of precipitated intermetallic phases. Thermo-Calc is also consistent with the results. However, M₃N precipitation was also predicted.
Figure 2. Microstructures after slow cooling (0.003 K/s); (a) 1000 °C/15 min, (b) 1100 °C/15 min, and (c) 1200°C/15 min (LM).

Figure 3. Precipitates after slow cooling (0.003 K/s); (a) SEM image, (b-d) EDS analysis for γ2, σ, and χ phases (1100 °C/15 min).
Figure 4. Microstructure after quenching (200 K/s); (a) 1000 °C/15 min, (b) 1100 °C/15 min, and (c) 1200°C/15 min.

IV. DISCUSSION

Superduplex steels may exhibit a secondary precipitation during high temperature processing such as shaping and welding, which detrimental to mechanical properties. In this study, the secondary precipitation was studied by thermodynamic modeling and annealing experiments. The results can be summarized as follows:

- In ferrite phase, the intermetallic \( \sigma \) and \( \chi \) phases were precipitated with \( \gamma_2 \) phase. Thermodynamic calculations were also consistent with the experimental results.

- \( \text{M}_{23}\text{C}_6 \) and \( \text{M}_2\text{N} \) phases were also calculated at thermodynamic equilibrium. However, they were not observed because of prolonged equilibrium conditions and their small amounts.

- Intermetallic \( \sigma \) and \( \chi \) phases can be avoided by quenching (200 K/s) from temperatures above 1000 °C.

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REFERENCES


