Experimental and computational study on microstructural evolution in 2205 duplex stainless steel during high temperature aging

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2205 duplex stainless steel (DSS) aged at temperatures between 700 °C and 1050 °C for different time intervals (5 min, 0.5 h, 1 h, 2 h) is studied. The evolution of secondary phases and the matrix with variation of aging time and temperature are measured by means of optical metallography (OM), SEM&EDS and BSE. The impact toughness, which reflects the effects of secondary phases, is also measured. It is shown that σ is the dominant secondary phase in the matrix. The σ phase precipitates at the austenite/ferrite boundaries or within ferritic grains, with the volume percent increasing with aging time and maximizing at 850 °C. Aided by Thermo-Calc software, the thermodynamic driving forces for χ phase and σ phase are calculated. Although the driving force for χ phase is larger than that for σ phase between 700 °C and 900 °C, σ phase appears before χ phase because of its rapid growth rate at higher aging temperatures. According to the OM analysis and thermodynamic calculations, 2205 DSS at aging temperatures above 1000 °C is composed of ferrite and austenite, its volume fraction of ferrite increases with the increase of aging temperature. Moreover, the kinetic calculation on the migration of austenite/ferrite interface after different aging time is present. The thermodynamic and kinetic calculation results on the microstructural evolution of 2205 DSS are in good agreement with the experimental results.

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1. Introduction

Owing to its excellent corrosion resistance and mechanical properties, duplex stainless steel (DSS) with a two-phase structure and approximately equal volume fractions of ferrite (α) and austenite (γ) is extensively used in industry. However, a number of undesirable phases such as intermetallic compounds, carbides and nitrides may appear in ferrite and at γ/α interface if the manufacturing processes are not carefully controlled [1–3]. In addition, thermal processing properties of DSS depend on the volume fraction, morphology and distribution of austenite and ferrite [4–6]. So the formation thermodynamic and kinetics of ferrite, austenite and secondary precipitation have been extensively studied. Despite the large amounts of earlier studies, the microstructural evolution process, such as the precipitation sequence and amounts of σ, χ phase and the migration behavior of γ/α interface during high-temperature aging are still not fully understood. Therefore, in this work a detailed study of microstructural evolution during aging is presented combining with quantitative analysis of secondary phases and their effects on impact toughness. While considering the γ/α transformation, particular attention is paid to calculate the migration of γ/α interface during high-temperature aging in the light of Thermo-Calc and DICTRA software [7,8].

2. Experimental procedure

2.1. Materials

The specimens used in this work were commercial 2205 DSS and the chemical composition was shown in Table 1. After 1100 °C × 30 min solid solution treatment, the specimens were water quenched immediately. In order to examine the microstructural evolution of 2205 DSS, aging treatments at temperatures ranging from 700 °C to 1050 °C for different time intervals (5 min, 0.5 h, 1 h, 2 h) were carried out.

2.2. Morphology observation and analysis

Cubic specimens of 15 mm × 15 mm × 15 mm size taken from the aged plates were mechanically polished and electrolytically etched in 40% KOH solution at a voltage of 1 V for approximately 5 s.

Microstructural observations were carried out using a Neophot-21 microscope and Digital Micrograph image analysis software. The average values of volume fraction of ferrite and their relative accuracies were calculated based on measurements on 100 fields.
3. Observation of precipitation and analysis following discussions are divided into four parts to analyze the treatment, where the percent of and no other secondary precipitated phase is found. The volume quantitative metallurgy measurement. were about 2% which are well within the limit value of a successful for each specimen. The relative accuracies for all measurements were about 2% which are well within the limit value of a successful quantitative metallurgy measurement.

The etched specimens were examined by SEM&EDS in order to verify the existence of secondary phases. Distinction between the and phase was made by Quanta 600 FEG SEM, based on BSE images. Thin foils for observation with TEM, which were prepared by using the twin jet method with 80 vol% methanol–20 vol% nitric acid, were examined by JEOL 2100 TEM operated at 200 kV.

2.3. Mechanical properties

10 mm × 10 mm × 55 mm V-notch Charpy specimens were prepared from the aged plates. Charpy test was performed at room temperature and fracture micrographs after impact test were observed in a JSM-6700F SEM&EDS.

3. Results and discussion

Secondary phases reported to form in duplex stainless steels above 500 °C are listed in Table 2 [9]. In the present work, the observed precipitates of 2205 DSS are σ, χ, Cr2N, CrN, M7C3 and M23C6. Their forming temperature ranges are similar to those listed in Table 2. The microstructure of 2205 DSS at the aging temperatures above 1000 °C is composed of ferrite and austenite. The following discussions are divided into four parts to analyze the microstructural evolution in 2205 DSS during aging treatment.

3.1. Observation of precipitation and analysis

Fig. 1 shows the initial morphology of 2205 DSS before aging treatment, where the γ islands are embedded in the gray α matrix and no other secondary precipitated phase is found. The volume percent of α phase measured by quantitative metallography is about 42%.

Fig. 2 presents α phase precipitated in 2205 DSS at 800 °C, 850 °C and 900 °C after different aging times. On the optical metallographs, ferrite and σ phases are distinguished by the contrast of gray and dark respectively, while austenite regions are little etched and appear as white areas. It is noted that no distinction could be made between σ phase and χ phase as they are both etched and appear as dark particles. The tetragonal σ phase, enriched in elements like Cr, Mo, Si and poor in Ni and Mn, is thermodynamically stable in DSS in a temperature range between approximately 600 °C and 1000 °C depending on the alloying composition [9].

Moreover, measured by SEM&EDS, it is shown that both σ and χ phase nucleate mainly at the γ/α interphase boundaries above 750 °C. Below 750 °C in addition to γ/α interphase boundary nucleation, some σ precipitates also form within the ferrite grains, as shown in Fig. 3b.

As discussed above, OM cannot identify σ and χ phase. So the volume percentage measured by quantitative metallography refers to the total volume percentage of σ and χ phases, as shown in Fig. 4. It will be discussed in Section 3.2 that χ phase only amounts to about 12% of the total amount and σ phase is dominant. The total amount increases with aging time between 750 °C and 900 °C. This is understandable because σ and χ phases are stable phases at these temperatures and normally the precipitation amount increases with time.

Considering the variation of volume percent of precipitated σ and χ phases with temperature, a peak is observed at 850 °C in Fig. 4. The thermodynamic driving force for the secondary phase precipitation increases as the precipitating temperature decreases, but the mobility of solute elements decreases as the temperature decreases. So the TTP (temperature-time-precipitation) diagram of σ and χ phases is represented by C curve and at intermediate temperature, i.e. “nose temperature”, the precipitation is the fastest. In the present work, the “nose temperature” is about 850 °C according to Fig. 4.

The precipitation of other secondary phases, like Cr2N, CrN, M23C6 and M7C3 can also be observed, as shown in Figs. 5 and 6. But these nitrides and carbides particles are small compared with σ phase because of the low C and N contents in 2205 DSS.

3.2. Analysis of σ and χ phase precipitation

According to Refs. [10,11] the χ phase is a precursor to σ phase by providing suitable nucleation sites and is less detrimental than the σ phase to the properties of DSS. In the present work, only χ

### Table 1

<table>
<thead>
<tr>
<th>Element</th>
<th>C</th>
<th>N</th>
<th>Si</th>
<th>Mn</th>
<th>Cr</th>
<th>Ni</th>
<th>Mo</th>
<th>S</th>
<th>P</th>
<th>Fe</th>
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</thead>
<tbody>
<tr>
<td>Value</td>
<td>0.02</td>
<td>0.16</td>
<td>0.68</td>
<td>1.2</td>
<td>20.94</td>
<td>5.42</td>
<td>3.03</td>
<td>&lt;0.002</td>
<td>0.018</td>
<td>Bal.</td>
</tr>
</tbody>
</table>

### Table 2

<table>
<thead>
<tr>
<th>Type of precipitate</th>
<th>Nominal chemical formula</th>
<th>Temperature range (°C)</th>
<th>Space group</th>
<th>Lattice parameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ferrite (α)</td>
<td>–</td>
<td>–</td>
<td>Im3m</td>
<td>a = 0.286–0.288</td>
</tr>
<tr>
<td>Austenite (γ)</td>
<td>–</td>
<td>–</td>
<td>Fm3m</td>
<td>a = 0.358–0.362</td>
</tr>
<tr>
<td>σ</td>
<td>Fe–Cr–Mo</td>
<td>600–1000</td>
<td>P43/mnnm</td>
<td>a = 0.879, c = 0.454</td>
</tr>
<tr>
<td>Chromium nitride</td>
<td>Cr2N</td>
<td>700–900</td>
<td>P31m</td>
<td>a = 0.480, c = 0.447</td>
</tr>
<tr>
<td>Chromium nitride</td>
<td>CrN</td>
<td>7 to 1100</td>
<td>Fm3m</td>
<td>a = 0.413–0.447</td>
</tr>
<tr>
<td>χ</td>
<td>Fe86Cr13Mo10</td>
<td>700–900</td>
<td>I43m</td>
<td>a = 0.892</td>
</tr>
<tr>
<td>R</td>
<td>Fe–Cr–Mo</td>
<td>550–800</td>
<td>R3</td>
<td>a = 1.090, c = 1.934</td>
</tr>
<tr>
<td>π</td>
<td>Fe6Mo11N4</td>
<td>550–600</td>
<td>P43,22</td>
<td>a = 0.647</td>
</tr>
<tr>
<td>τ</td>
<td>–</td>
<td>550–650</td>
<td>Fmmm</td>
<td>a = 0.405, b = 0.484, c = 0.286</td>
</tr>
<tr>
<td>M7C3</td>
<td>–</td>
<td>950–1050</td>
<td>Pnma</td>
<td>a = 0.453, b = 0.699, c = 1.211</td>
</tr>
<tr>
<td>M23C6</td>
<td>–</td>
<td>7 to 950</td>
<td>Fm3m</td>
<td>a = 1.056–1.063</td>
</tr>
</tbody>
</table>
Fig. 2. Optical metallographs showing the microstructures of $\sigma$-phase in 2205 DSS at the temperatures of (a) 800 °C, (b) 850 °C and (c) 900 °C after different aging times.

phase was observed in the samples aging at 700 °C within 2 h as shown in Fig. 7, and both $\sigma$ and $\chi$ phases were observed after aging at 750 °C for 0.5 h as shown in Fig. 8. But after aging at 850 °C for 5 min, only $\sigma$ phase can be observed as shown in Fig. 9a and as shown in Fig. 9b, after 1 h soaking at 850 °C, $\chi$ phase was observed. Our observation is in accordance with the report by Duprez et al. [12].

As discussed by Duprez et al. [12], above 750 °C the thermodynamic driving force for precipitation is larger for $\sigma$ than for $\chi$, which explains why $\sigma$ appears before $\chi$ at higher temperatures. However, our calculations show a different scenario. We performed the calculations by using a commercial software Thermo-Calc of latest version and its thermodynamic database for steel (TCFE6) [13], adopting the overall composition as listed in Table 1 and keeping $\gamma$ and $\alpha$ as the stable matrix phases. The steel database (TCFE6) has been assessed based on a large amount of experimental data and verified by many academic and industrial applications. The calculated thermodynamic driving forces for $\sigma$ and $\chi$ precipitates are shown in Fig. 10. Noted that the calculated driving forces are normalized by dividing RT (i.e. gas constant times temperature). The normalized thermodynamic driving force for $\chi$ phase is always larger than that for $\sigma$ phase between 700 °C and 900 °C, which is opposite to Duprez et al.’s conclusion. Moreover, the nucleation of $\chi$ phase is more favourable due to the low lattice coherency stresses [10,11]. Therefore $\chi$ phase should precipitate before $\sigma$ phase if no other fact is considered.

However, in the present work only $\sigma$ phase (no $\chi$ phase) was observed at 850 °C for 5 min aging and in the prolonged aging $\chi$ phase was observed while $\sigma$ phase grew up. According to Fig. 9, the size of $\chi$ phase is about 1.0 $\mu$m at 850 °C for 1 h and the size of $\sigma$ phase reaches 1.5 $\mu$m at 850 °C for merely 5 min. So it can be concluded that the growth rate of $\sigma$ phase at higher temperatures is much larger compared with $\chi$ phase. Although the thermodynamic driving force for $\chi$ phase is larger than that for $\sigma$ phase, the rapid

Fig. 3. $\sigma$ phase precipitated at (a) 950 °C × 2 h at $\gamma/\alpha$ phase boundaries; (b) 750 °C × 2 h in $\alpha$ grains by SEM&EDS.
It is possible to identify Cr-enriched $\sigma$ phase and the Mo-enriched $\chi$ phase with micron size and to obtain good quantitative estimates by means of SEM based on BSE technique. As shown in Fig. 11 and Table 3 for Spectrum 1 and 6, the weight percentages of Cr are 24.37% and 23.69% and those of Mo are 17.07% and 14.14% respectively, which are almost four times higher than the overall composition (see Table 1). Spectrum 1 and 6 can be identified as $\chi$ phase. The $\sigma$ phase is denoted by Spectrum 2 because of the higher Cr content (28.88%) and lower Mo content (9.00%) compared with $\chi$ phase. Referring to Cr and Ni content, ferrite is denoted by Spectrum 3 and austenite by Spectrum 4 and 5. By quantitative image analysis, the relative amounts of each phase are listed in Table 4. The total volume percent of $\sigma$ and $\chi$ phases is about 4.9% which is close to the measured result of 5.26% by quantitative metallography as shown in Fig. 4. The $\chi$ phase amounts to 12% of the total $\sigma$ and $\chi$ which cannot be identified by OM in Fig. 4.

3.3. Effects of precipitation on impact toughness of 2205 DSS

It is known that the precipitation of intermetallic phases is deleterious to the impact toughness of DSS exposed to temperatures in the range of 600–1100 $^\circ$C [9,14]. Even 1% of intermetallic phase affects impact toughness and the material is very brittle when 10% of intermetallic phase is present. A clear correlation has been found between TTP-curves and iso-impact toughness curves for the steel.
In the present work, the impact toughness of 2205 DSS is measured after different aging treatment in order to testify the amounts and types of intermetallic phases, as shown in Fig. 12. The impact toughness of the solution sample is 303 J. The impact toughness of samples aging at 700 °C and 950 °C after 5 min approximates to that of the solution sample. Moreover, the impact toughness markedly decreases with prolonged keeping time and the impact toughness of samples aging at 850 °C is the lowest.

Fig. 13a presents the fractograph of a solution specimen where a large number of deep dimples can be observed and the size of the dimples is uniform showing the ductile fracture character. Fig. 13b is the fractograph of the same specimen but aged at 900 °C for 2 h.
where many precipitates which form the crack source although fracture character of the matrix for specimen is ductile can be found in the fracture surface. Indicated by an arrow in Fig. 13b, one of the precipitates is analyzed by EDS and shown to be Cr- and Mo-enriched (see Table 5). According to the above experimental results this precipitate is the brittle phase.

### 3.4. Thermodynamic and kinetic calculations on migration of γ/α interface at the aging temperatures between 1000 °C and 1050 °C for 2205 DSS

In the present work, the migration behavior of the γ/α interface during high-temperature aging is investigated since it is related to thermal processing properties of DSS, which depend on volume fraction, morphology and distribution of austenite and ferrite. The average values of volume fraction of α aged at 1000 °C and 1050 °C for 60 min obtained by quantitative metallography are denoted by triangles in Fig. 14 and the solid line denotes calculations by Thermo-Calc software and its steel database. The deviation between calculations and experiments is possible due to the short aging time in the experiments while the calculations are under equilibrium conditions. However, the increasing trend of volume fraction of ferrite phase with the increase of aging temperature is affirmed by both experiments and calculation results.

The effect of aging time on phase composition and γ/α interface boundary was simulated by DICTRA, a flexible software for simulations of diffusion controlled transformations in multicomponent alloys [8,15]. It is closely linked to the Thermo-Calc software, thermodynamic and mobility databases. In DICTRA, the moving boundary model describes the migration behavior of a planar boundary separating two single-phase regions. At the moving boundary the interfacial reactions are assumed to be very fast comparing to the migration of the boundary. Thus thermodynamic equilibrium is assumed to hold at the boundary and the moving

<table>
<thead>
<tr>
<th>Spectrum</th>
<th>Si</th>
<th>Cr</th>
<th>Mn</th>
<th>Fe</th>
<th>Ni</th>
<th>Mo</th>
<th>Phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spectrum 1</td>
<td>1.30</td>
<td>24.37</td>
<td>1.25</td>
<td>53.44</td>
<td>2.57</td>
<td>17.07</td>
<td></td>
</tr>
<tr>
<td>Spectrum 2</td>
<td>1.13</td>
<td>28.88</td>
<td>1.33</td>
<td>56.77</td>
<td>2.90</td>
<td>9.00</td>
<td>γ</td>
</tr>
<tr>
<td>Spectrum 3</td>
<td>0.89</td>
<td>24.22</td>
<td>1.27</td>
<td>66.48</td>
<td>3.37</td>
<td>7.77</td>
<td>Ferrite</td>
</tr>
<tr>
<td>Spectrum 4</td>
<td>0.80</td>
<td>19.95</td>
<td>1.48</td>
<td>68.84</td>
<td>6.51</td>
<td>2.41</td>
<td>Austenite</td>
</tr>
<tr>
<td>Spectrum 5</td>
<td>0.83</td>
<td>20.12</td>
<td>1.42</td>
<td>68.67</td>
<td>6.58</td>
<td>2.39</td>
<td></td>
</tr>
<tr>
<td>Spectrum 6</td>
<td>1.16</td>
<td>23.69</td>
<td>1.26</td>
<td>56.56</td>
<td>3.18</td>
<td>14.14</td>
<td>χ</td>
</tr>
</tbody>
</table>
rate is controlled by the diffusion rate of the components to and from the boundary. Within each single-phase region, the Fick’s laws are applied numerically which allows to handle complex diffusion problems, such as multicomponent systems and concentration variations of diffusion coefficients. This model is suitable to treat problems where diffusion causes a phase transformation, e.g. γ/α transformation in stainless steel during aging. The initial volume percent of ferrite and austenite in 2205 DSS is 42% and 58%, respectively, detected by quantitative metallography and the initial width of austenite and ferrite are 40 μm and 26 μm, respectively. The initial carbon and nitrogen content in austenite and ferrite are obtained by Thermo-Calc calculations. The initial contents of other elements are taken as the average in the steel since EPMA detection of these elements in the present work does not show any difference in ferrite and austenite.

Fig. 15 shows the calculated Cr-concentration profiles in γ and α at different temperatures after different diffusion time. The vertical line represents the interface between γ and α phases, the left side to the interface corresponds to the γ phase region and the
right side to the α phase region. The volume fraction of each phase corresponds to the ratio of the distance at the abscissa axis. The simulation reveals that the volume percent of γ decreases with aging time at 1000 °C and 1050 °C, as shown in Fig. 15. The comparison between the calculated and experimental results of the volume percent of α is made in Fig. 16 and the agreement is satisfactory.

Calculation reveals that the γ/α interface boundary migrates from γ-region to α-region with prolonged aging time at 1000 °C and 1050 °C, as shown in Fig. 15. The interface boundary migration is caused by the simultaneous movement of Cr, Mo, et al. to α-region, and Ni, Mn to γ-region. The diffusion of these elements proceeds until their chemical potentials in both phases are equal. When this is fulfilled, the driving force for diffusion disappears and the equilibrium condition is reached as represented in Fig. 14.

The thermodynamic and kinetic calculation results on the microstructure evolution of 2205 DSS are in good agreement with the experimental results.

4. Conclusion

(1) σ phase is the dominant secondary phase due to the low content of N and C and nucleates at γ/α interphase boundaries or within ferrite grains for 2205 DSS. The precipitation of σ phase increases with the increase of aging time and the maximum volume percent of σ phase is observed after aging at 850 °C.

(2) At the temperature of 850 °C, σ is the first phase to be observable while at the temperature of 700 °C and 750 °C, χ is the first. The thermodynamic driving force for χ phase is always larger than that for σ phase between 700 °C and 900 °C calculated by Thermo-Calc software. This fact can be explained by the rapid growth rate of σ phase. Impact toughness of steel is remarkably affected by the volume percent of σ phase but not χ phase because of its small amount.

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Fig. 14. Effect of aging temperature on volume fraction of ferrite and austenite in 2205 DSS, triangles denoting experimental results for ferrite and solid line denoting calculated results.

Fig. 15. Concentration profile of Cr in γ and α phases at different aging temperatures (a) 1000 °C and (b) 1050 °C after different diffusion time (in s) in 2205 DSS.

Fig. 16. Comparison between the measured and calculated amounts of ferrite at different aging temperatures (a) 1000 °C and (b) 1050 °C after different aging time in 2205 DSS, triangles denoting experimental results and black circles denoting calculated results.
According to the OM analysis and thermodynamic calculation results, the microstructure of 2205 DSS at the aging temperatures above 1000 °C is composed of ferrite and austenite and the volume percent of ferrite increases with the increase of aging temperature. Moreover, the kinetic calculation on the migration of γ/α interface after different aging time is present. The thermodynamic and kinetic calculation results on the microstructure evolution of 2205 DSS are in good agreement with the experimental results.

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References
