INFLUENCE OF MARTENSITE FRACTION ON THE EXTENT OF PARTITIONING IN MARTENSITIC STAINLESS STEELS PROCESSED BY QUENCHING AND PARTITIONING (Q&P)

Abstract

The extent of partitioning during quenching and partitioning (Q&P) processing of Fe-0.31C-13Cr (mass pct) martensitic stainless steel was investigated as a function of martensite fraction at quench temperature. In dilatometry cycles, the interval between the quench temperature and the temperature where secondary martensite formation started was used to quantify the extent of austenite stabilization by partitioning. Secondary martensite was defined as the martensite formed during final cooling from partitioning temperature to ambient temperature. Regardless of the solution annealing temperature which influenced the martensite start temperature, stabilization was found to be more pronounced when the primary martensite content was in excess of approximately 50 vol pct. The pronounced stabilization was attributed to a transition in the size and distribution of martensite plates from clusters at low martensite fractions to finer dispersed plates at high martensite fractions. This transition in the course of martensitic transformation caused a rapid increase in the area of austenite-martensite boundaries available for carbon accumulation. The carbon accumulated in such regions enriched the austenite during partitioning and led to its stabilization.

Keywords

Q&P processing, austenite stabilization, primary martensite fraction, carbon diffusion, austenite-martensite phase boundary

1. Introduction

Quenching and Partitioning (Q&P) processing has attracted a great deal of attention in recent years due to its capability to stabilize austenite at room temperature and the associated enhancement of mechanical properties [1–6]. The process involves quenching austenite to a temperature between Mₘ and Mᵓ followed by a partitioning treatment at higher temperatures to allow for the diffusion of carbon from supersaturated martensite to austenite. The stability of retained austenite, which influences the mechanical properties of steels, depends strongly on the extent of partitioning. Hence, extensive efforts have been made to optimize the process of partitioning, such as the close control of partitioning temperature and time [7,8] and the addition of Si and Al to suppress the precipitation of carbides [9–13]. However, no research has been performed to verify the effect of martensite fraction formed during initial quench (primary martensite) on the extent of partitioning. Speer and his co-workers developed a model to predict the carbon content and the fraction of retained austenite at various quench temperatures [14]. In the model, the increase in the carbon content of austenite after

---

1 Institute of Iron and Steel Technology, Technische Universität Bergakademie Freiberg, 09599, Freiberg, Germany
2 Institute of Materials Engineering, Technische Universität Bergakademie Freiberg, 09599, Freiberg, Germany
partitioning is calculated based on the assumption of complete suppression of carbide precipitation and full partitioning of carbon into the austenite. According to the model, the carbon content supplied by the primary martensite is proportional to its fraction. In other words, the contribution of primary martensite to the process of partitioning is only accounted for by its fraction. Obviously, the model does not take the size and distribution of martensite plates into account.

In the present study, Q&P processing of Fe-13Cr-0.31C martensitic stainless steel was simulated by dilatometry. Dilatometry experiments aimed at revealing the relationship between primary martensite fraction and the extent of partitioning. The results are interpreted in view of the microstructural changes occurring in the course of martensitic transformation.

2. Experimental Procedure

AISI 420 type martensitic stainless steel with the chemical composition listed in Table 1 was used in the present study. More information about the alloy may be found in [15]. Dilatometry tests were performed in a Bähr 805 pushrod dilatometer. Specimens with dimensions of 10 × 3 × 3.5 mm³ were machined with their length parallel to the transverse direction of a 3 mm-thick hot rolled sheet. To investigate the effect of martensite fraction at quench temperature on the extent of partitioning, Q&P processing was simulated by dilatometry. Solution annealing of specimens was done at three different temperatures of 1000 °C, 1075 °C and 1150 °C. This enabled to check if results were influenced by $M_s$ temperature. After solution annealing, quench interruption below respective $M_s$ temperatures was followed by reheating to 350 °C for 3 min to accelerate the carbon diffusion in the austenite. Quench temperature ranges shown in Fig. 1 with intervals of 10 °C were selected according to $M_s$ temperature at each solution annealing temperature. The fraction of ferromagnetic $\alpha'$ martensite was measured by a Metis MSAT magnetic saturation device equipped with a Lakeshore 480 fluxmeter.

Table 1. Chemical composition of the investigated AISI 420 type steel (mass pct)

<table>
<thead>
<tr>
<th>Cr</th>
<th>C</th>
<th>Mn</th>
<th>Ni</th>
<th>Si</th>
<th>N</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>13.18</td>
<td>0.31</td>
<td>0.29</td>
<td>0.15</td>
<td>0.47</td>
<td>0.01</td>
<td>Bal.</td>
</tr>
</tbody>
</table>

Fig. 1. Schematic illustration of Q&P processing cycles in dilatometer. AT and QT denote austenitization temperature and quench temperature, respectively. QT ranges have a temperature interval of 10 °C.
3. Results

Prior to Q&P cycles, the M$_s$ temperature of the steel after solution annealing at various temperatures was determined by direct quenching to room temperature (RT). The results and the corresponding martensite fractions at room temperature quantified by magnetic saturation measurements are given in Table 2. Strain offset method [16] at an offset expansion corresponding to 5 vol pct martensite was applied to determine the M$_s$ temperature. Due to the dissolution of Cr-rich carbides at elevated temperatures, which raised the solute Cr and C contents of austenite, the M$_s$ temperature and the martensite fraction at RT decreased at higher austenitization temperatures.

Table 2. M$_s$ temperatures and martensite fractions obtained after austenitization at various temperatures

<table>
<thead>
<tr>
<th>Austenitization temperature, °C</th>
<th>M$_s$, °C</th>
<th>Martensite fraction, pct</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000</td>
<td>302</td>
<td>96.1</td>
</tr>
<tr>
<td>1075</td>
<td>247</td>
<td>93.6</td>
</tr>
<tr>
<td>1150</td>
<td>222</td>
<td>91.9</td>
</tr>
</tbody>
</table>

The dilatometry length changes in Q&P processing with austenitization at 1000 °C are shown in Fig. 2(a). After quench interruption and partitioning, martensitic transformation in the final cooling step (secondary martensite formation) clearly occurs at temperatures lower than the respective quench interruption temperature. The interval between these two temperatures, marked θ for the quench temperature of 250 °C in Fig. 2(a), was used to quantify the extent of austenite stabilization in the present study. It is clearly shown that θ increases as quench temperature decreases. The stabilization of austenite reflected in measurable θ values has been justified by the diffusion of carbon from supersaturated martensite to austenite during partitioning [17–19]. The curve with solid squares in Fig. 2(b) shows the relationship between θ and the primary martensite fraction, f$_{α'}$. The latter was calculated from the dilatation curves in Fig. 2(a) using the lever rule in a manner analogous to that described in [15]. As f$_{α'}$ increases, θ increases slightly at small martensite fractions before accelerating at fractions larger than approximately 50 vol pct.

Fig. 2(b) also shows θ values calculated according to the Q&P processing model of Speer and co-workers [14]. The model assumes full partitioning of carbon from martensite to austenite without carbide precipitation. The calculated θ values in Fig. 2(b) were calculated using the following equations:

\[ C_γ = C_{nominal} / f_γ \]  
\[ θ = \text{quench interruption temperature} - 510(C_γ - C_{nominal}) \]

The constant 510 in Eq. 2 denotes the magnitude of M$_s$ depression by each percent of carbon enrichment in the austenite [20]. As shown in Fig. 2(b), calculated θ values are much larger than the experimental values due mainly to the inevitable carbide precipitation in the martensite. Other factors such as non-zero solubility of carbon in martensite, non-uniform distribution of carbon in austenite after the partitioning step, and presence of undissolved Cr-rich carbides at solution annealing temperatures, particularly in the case of austenitization at
1000 °C and 1075 °C, might also be responsible for the observed differences. The calculated \( \theta \) values increase monotonically at higher martensite fractions without any remarkable transition.
Fig. 2 Relative length changes during Q&P processing of dilatometry specimens austenitized at 1000 °C (a), 1075 °C (c), and 1150 °C (e). Experimental θ values based on dilatometry curves at left are shown in (b), (d), and (f) as a function of primary martensite fraction. Calculated θ values based on the full partitioning assumption according to Eqs. (1-2) are also included for comparison.

The dilatometry length changes for Q&P cycles involving austenitization at 1075 °C and 1150 °C and the corresponding θ values are shown in Fig. 2(c) - (f). In spite of different Ms temperatures, the variations with fα of θ resemble that of experiments with an austenitization temperature of 1000 °C. In other words, a transition in θ values similarly occurred at a martensite fraction of around 50 vol pct.

A similar phenomenon was observed upon continuous cooling at different rates of dilatometry specimens (Fig. 3). The specimens were austenitized at 1075 °C followed by cooling to room temperature at the rates of 10 °C/s, 0.5 °C/s, and 0.05 °C/s. Stabilization of austenite clearly occurred during cooling. At a cooling rate of 0.05 °C/s, even though the transformation began at a higher temperature, a smaller contraction occurred during cooling to RT compared to the higher cooling rates. Similar results have been reported for an Fe-0.8C steel [21]. In the latter work, the smaller expansion at lower cooling rates was explained by the contraction associated with auto-tempering of martensite as it proceeds to a larger extent at lower cooling rates. This explanation is, however, not applicable to the present work since reheating of specimens cooled at different rates resulted in comparable tempering contractions suggesting a similar extent of auto-tempering at different cooling rates. Therefore, a difference in the extent of auto-tempering could not be responsible for the smaller expansions at reduced cooling rates for the present alloy. Besides, quantification of martensite in specimens of the present steel cooled in different media has indicated lower martensite fractions at reduced cooling rates [15]. Comparison of dilatometry length changes obtained at various cooling rates (Fig. 3) indicates that, in agreement with the results of quench interruption cycles, pronounced stabilization of austenite initiates at temperatures where martensite fraction is above nearly 50 vol pct.
4. Discussion

In Q&P processing, the supersaturated carbon in martensite can segregate to the austenite-martensite phase boundaries already at the quench temperature. The low-temperature segregation of carbon to austenite-martensite boundaries has been demonstrated in recent atom probe tomography investigations [22–24]. During partitioning, the segregated carbon at boundaries supplies the carbon needed for the enrichment of austenite. Considering that the stabilization of austenite depends strongly on the amount of carbon available for the enrichment, the rapid rise in $\theta$ at martensite fractions larger than nearly 50 vol pct is thought to be a consequence of significant increase in the amount of accumulated carbon. This increase could be either due to a lower loss of carbon by competing carbon-consuming reactions or due to a higher abundance of carbon accumulation sites before partitioning. The likelihood of these possibilities is discussed in the following.

The $f'_\alpha$ increases as quench temperature deceases. Hence, as shown in the schematic of Fig. 4, the two regimes of $f'_\alpha$ below and above 50 vol pct can be referred to as high and low quench temperature regimes, respectively. One may argue that the abrupt increase in $\theta$ at low quench temperatures (high $f'_\alpha$) might be due to the suppression of a carbon-consuming reaction which is operative at higher quench temperatures. In the present steel, carbides form in a sequence of transition carbides ($\varepsilon$- or $\eta$-carbides) and cementite ($\theta$-carbide) with increasing temperature [15]. Accordingly, two hypothetical scenarios as marked in Fig. 4 present themselves. The transition in $\theta$ might be related to the occurrence of transition carbides at high quench temperatures and its suppression at low quench temperatures. This scenario might arise because in the absence of transition carbides formation, the boundary segregation of a larger fraction of original carbon in martensite will be enabled. In the second scenario, the transition is assumed to be caused by a competition between transition carbides and cementite. The higher solute carbon content of martensite in equilibrium with transition carbides might then enable the segregation of a larger fraction of carbon in martensite to the austenite-martensite boundaries than that would be possible at higher temperatures in
equilibrium with cementite. Assuming that both of the hypothetical scenarios are effectively operative, they must give rise to two transition temperatures. In order for the transitions in the plots of \( \theta \) vs \( f_{\alpha'} \) in Fig. 2(b,d,f) to be attributable to transitions in the type of precipitation reactions as discussed in the above scenarios, at least two of the quench temperatures corresponding to the transition points in Fig. 2(b,d,f) must be identical. Considering that transitions observed in the three series of experiments correspond to three different quench temperatures of 270 °C, 200 °C, and 160 °C, it is contrary to the scenarios discussed in the preceding discussion and schematically shown in Fig. 4. Therefore, possibilities other than a change in the type of carbide precipitation reactions must be sought to explain the transitions in Fig. 2(b,d,f).

Fig. 4. Hypothetical reasons based on the type of precipitation reactions in martensite for the segregation of less carbon to austenite-martensite boundaries at \( f_{\alpha'} < 50 \) vol pct than at \( f_{\alpha'} > 50 \) vol pct.

The transition in \( \theta \) values as a function of martensite fraction could be most likely ascribed to the significant increase in the availability of carbon accumulation sites, namely austenite-martensite boundaries, at martensite fraction above 50 vol pct. Due to the refinement in the size of martensite plates during martensitic transformation, the phase boundary area does not follow a linear relationship with \( f_{\alpha'} \). In-situ observation of martensite laths occurring in a low-alloy steel [25] indicated that transformation initiates with the fragmentation of austenite grains into several parts. The early coarse plates were found to form in clusters to minimize the shear component of the shape deformation associated with the martensitic transformation. Therefore, the early clusters only slightly increase the austenite-martensite boundary area. At later stages of transformation, individual plates which are also finer in size form in the untransformed austenitic regions. A change in the size and distribution of martensite laths is proposed as the main reason for the rapid increase in the area of carbon accumulation sites and the associated transition in \( \theta \) vs \( f_{\alpha'} \) plots of Fig. 2(b,d,f).

5. Conclusions
The influence of martensite fraction at quench temperature on the stabilization of austenite after partitioning was studied in Fe-0.31C-13Cr martensitic stainless steel subjected to Q&P processing. The following conclusions were drawn.

1. Regardless of the Ms temperature, the stabilization of austenite was more pronounced in the presence of more than 50 vol pct martensite.

2. Stabilization of austenite similarly occurred at reduced cooling rates during continuous cooling to room temperature. Clear deviation among dilatometry curves obtained at various cooling rates occurred when the martensite content was in excess of approximately 50 vol pct.

3. The pronounced stabilization of austenite at martensite fractions above 50 vol pct cannot be attributed to the suppression or a change in the type of carbide formation reactions during quenching. It is rather caused by a transition in the size and distribution of martensite plates from clustered coarse plates to dispersed individual plates. It is proposed that the rapid increase in the area of austenite-martensite boundaries serving as carbon accumulation sites is responsible for the more efficient carbon enrichment of austenite at high martensite fractions. It is likely that the ratio of austenite-martensite boundary area to the volume fraction of untransformed austenite plays an important role in the stabilization of austenite.

Acknowledgement

The authors gratefully acknowledge the financial support of German Research Foundation (DFG) under grant number MO 2580/1-1.

References


