INFLUENCE OF NITROGEN ON THE MECHANISM OF AUSTENITIC STAINLESS STEEL HARDENING

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On the example of a C18N12M2 austenitic stainless steel, the influence of nitrogen (whose content varied from 0 to 0.45 wt. %) on the grain boundary hardening coefficient $k_b$ entering into the Hall–Patch equation is analyzed. High values of $k_b$ in steels with and without nitrogen are found. The data of the Auger analysis show that the hardening coefficient in the steel without nitrogen is determined by the grain-boundary segregation of carbon and oxygen. The grain-boundary hardening in the steel with nitrogen is not connected with the predominant segregation of nitrogen at grain boundaries. It is completely governed by intragranular processes – interaction of nitrogen atoms with dislocations.

It is well known that doping of austenitic stainless steels with nitrogen increases the grain-boundary hardening coefficient $k_b$ entering into the Hall–Patch equation. Physical reasons for this phenomenon have yet to be analyzed to the last detail. Norstrom [1] and Zlateva and Mikhnev [2] explain this phenomenon by the influence of nitrogen on the stacking fault energy $\gamma_{sf}$. A decrease in $\gamma_{sf}$ upon doping with nitrogen leads to a decrease in the effective grain size owing to the intense twinning during annealing and to the corresponding growth of the grain-boundary component of the flow stress. Varin and Kurzydlowski [4] disagreed with this viewpoint. Investigating the influence of nitrogen and twin boundaries on $k_b$ in nitrogen austenite, they showed that $k_b$ was independent of the annealing twin density. An alternative viewpoint was put forward by Werner [3]. He explains the increase of the grain-boundary hardening coefficient with nitrogen concentration in steels by the conditions of slip transfer through the grain boundary comprising the segregation of the nitrogen atoms. Both concepts require serious experimental verification.

Taking into account [1–4], we believe that the grain-boundary hardening of the nitrogen steel may increase primarily due to two factors: first, if the creation of dislocations at the grain boundaries is inhibited, and second, if the motion of dislocations emitted by a grain-boundary source is inhibited within the grain volume. The second case corresponds to the nitrogen atoms distributed over the grain volume and their interaction with moving dislocations. In this connection, the problem formulated in the present work is to analyze the feasibility of segregation of impurities, including nitrogen, at the grain boundaries and to study the influence of intragranular processes on the grain-boundary hardening in the austenitic stainless steel doped with nitrogen.

In the 18.0 Cr – 12.4 Ni – 2.3 Mo – 1.2 Mn – 0.013 C – 0.06 Si – 0.005 S – 0.005 P – 0.04 Cu – 0.07 Nb (in wt. %) steel under study the content of nitrogen varied from 0 to 0.45 wt. % (0 – 1.70 at. %) and that of vanadium – from 0.01 to 0.25 wt. %. Plates of appropriate thickness were cut from initial rods and rolled cold to yield a degree of reduction $\varepsilon = 40\%$. Specimens with sizes of their working parts $13 \times 2 \times 1$ mm were cut from the rolled plates. These specimens were recrystallized in an inert atmosphere at temperatures 1423–1573 K with subsequent brine quenching. The microstructure of the annealed specimens was investigated by the methods of optical microscopy, x-ray crystal analysis, and x-ray microanalysis.

Flow curves of steels without nitrogen and with various nitrogen content (0, 0.131, 0.152, 0.181, and 0.45 wt. %) have parabolic shapes typical of polycrystals. These curves are characterized by high values of the yield stress $\sigma_{0.2}$, ultimate strength $\sigma_b$, and elastic limit $\delta$. These characteristics grow as the nitrogen concentration increases. The data on changes in $\sigma_{0.2}$, $\sigma_b$, and $\delta$ in steels with various nitrogen concentration at various test temperatures are given in Table 1. It can be seen that the presence of nitrogen results in significant hardening at low temperatures, which is in good agreement with the published data. According to [3, 5], a nitrogen content of 0.2 wt. % at 77 K leads to the increase of the yield stress by 500 MPa. This value agrees with that obtained by us for the steel with 0.181 wt. % nitrogen (Table 1). The nitrogen hardening under the yield stress decreases as the test temperature increases and becomes weakly pronounced at elevated temperatures.
TABLE 1. Values of the yield stress $\sigma_{01}$, ultimate strength $\sigma_B$, and elastic limit $\delta$ for polycrystals of the C18N12M2 steel with nitrogen at the indicated test temperatures.

<table>
<thead>
<tr>
<th>$C_N$, wt. %</th>
<th>Temperature, K</th>
<th>$\sigma_{01}$, MPa</th>
<th>$\sigma_B$, MPa</th>
<th>$\delta$, %</th>
<th>$\sigma_{01}$, MPa</th>
<th>$\sigma_B$, MPa</th>
<th>$\delta$, %</th>
<th>$\sigma_{01}$, MPa</th>
<th>$\sigma_B$, MPa</th>
<th>$\delta$, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>77</td>
<td>540</td>
<td>1800</td>
<td>52</td>
<td>210</td>
<td>960</td>
<td>62</td>
<td>110</td>
<td>620</td>
<td>34</td>
</tr>
<tr>
<td>0.131</td>
<td>77</td>
<td>590</td>
<td>2140</td>
<td>65</td>
<td>250</td>
<td>1070</td>
<td>67</td>
<td>150</td>
<td>740</td>
<td>40</td>
</tr>
<tr>
<td>0.152</td>
<td>293</td>
<td>745</td>
<td>2200</td>
<td>66</td>
<td>290</td>
<td>960</td>
<td>51</td>
<td>170</td>
<td>770</td>
<td>36</td>
</tr>
<tr>
<td>0.181</td>
<td>623</td>
<td>820</td>
<td>2200</td>
<td>58</td>
<td>320</td>
<td>980</td>
<td>40</td>
<td>190</td>
<td>680</td>
<td>31</td>
</tr>
<tr>
<td>0.45</td>
<td>1150</td>
<td>2110</td>
<td>28</td>
<td></td>
<td>430</td>
<td>1160</td>
<td>37</td>
<td>260</td>
<td>800</td>
<td>28</td>
</tr>
</tbody>
</table>

An analysis of grain-boundary hardening of polycrystals is usually based on the Hall-Patch equation

$$\sigma_{01} = \sigma_r + k_h d^{-1/2},$$

where $\sigma_r$ is the inhibition of dislocation motion for an infinitely large grain, $k_h$ is the grain-boundary hardening coefficient, and $d$ is the grain size.

To estimate the contribution of the grain-boundary term to the nitrogen hardening, we investigated the dependence of the yield stress on the grain size in steels without nitrogen and with 0.131, 0.181, and 0.43 wt. % nitrogen. The grain size (14 ± 1.5, 22 ± 1.5, 30 ± 1.5, and 60 ± 2.5 μm) was varied by two ways: by increasing the recrystallization annealing temperature $T_{rc}$ and the annealing time $t_{rc}$ at 1473 K. In so doing, the dependences $\sigma_{01} = f(d^{-1/2})$ differed. In the first case, the values of the yield stress as functions of $d^{-1/2}$ do not lie on a straight line. As our investigations have shown, this is due to variations in the steel microstructure during the high-temperature annealing used to obtain grains of large sizes. Significant enlarging of particles of secondary phases and structural changes are observed in the vicinity of triple points in the coarse-grained steel. Nonequivalent structural conditions in fine- and coarse-grain materials may be a reason for the two-stage dependence of the yield stress on the grain size found by Kashyap and Tangri [5] in a 316-grade stainless steel.

The structures of steels with various grain size prepared by increasing the recrystallization annealing time $t_{rc}$ do not show noticeable differences. Grain-orientation analysis has shown that steels with and without nitrogen have the same grain orientation. The behavior of the grain orientation in both steels with increase in the grain size $d=f(t_{rc})$ is similar. Qualitatively, it remains unchanged; only some quantitative changes are observed in the content of individual components. Both in steels with and without nitrogen, {112}, {113}, and {110} grains grow at the expense of absorption of {111} grains. In this case, the values of $\sigma_{01} = f(d^{-1/2})$ fall on a straight line (Fig. 1).

From an analysis of Fig. 1 it follows that unlike [3, 4], high coefficients $k_h (10 - 40$ N-mm$^{-3/2}$) are observed in the steel without nitrogen.

These values of $k_h$ correspond to those observed in [4] for alloys with a $(C + N)$ content of 0.7–0.8 wt. % and are characteristic of the alloys with impurity segregation at grain boundaries [3]. This gives us reasons to believe that the grain boundaries in steel without nitrogen are highly enriched with active surface impurities. In the first approximation, the tendency of steel components toward segregation can be characterized by the magnitude of the distribution coefficient $k$ for the binary systems. The values of $k$ for the elements included in the steel composition, namely, S, C, P, Nb, Mn, N, Cu, Mo, Si, Ni, V, and Cr are 0.08, 0.15, 0.2, 0.2, 0.28, 0.5, 0.7, 0.7, 0.82, and 0.91, respectively [6]. Among the readily segregated elements in iron are S, C, P, Nb, Mn, and N, whereas Cu, Mo, Si, Ni, V, and Cr belong to the poorly segregated elements. It is natural that the tendency of a certain element of the steel to form the segregation may be strengthened or weakened, depending on the character of interaction between the components.

Based on the distribution coefficient for the steel without nitrogen, the segregation of sulfur, carbon, phosphorus, niobium, and manganese may be expected at grain boundaries. It is well known [7] that all the elements enumerated above and, in addition, nitrogen and oxygen segregate on the surface of austenitic steels; moreover, the segregation force can be arranged in increasing order as follows: $C < O < N < P < S < Nb < Mn$. X-ray microanalysis has confirmed the enrichment of grain boundaries with carbon (Fig. 2a). In addition, the segregation of oxygen was found at grain boundaries (Fig. 2b).