PREDICTING NITROGEN ABSORPTION IN MARTENSITIC STAINLESS STEELS DURING HIGH TEMPERATURE NITRIDING.

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ABSTRACT
Thermodynamic calculations of the Fe-Cr-N System in the region of the Oas Phase Equilibria have been compared with experimental results of maximum nitrogen absorption during nitriding of two Martensitic Stainless Steels (a 6 mm thick sheet of AISI 410S steel and green powder compacts of AISI 434L steel) under N₂ atmospheres. The calculations have been performed combining the Fe-Cr-N System description contained in the SGTE Solid Solution Database and the gas phase for the N System contained in the SGTE Substances Database. Results show a rather good agreement for total nitrogen absorption in the steel and nitrogen solubility in austenite in the range of temperatures between 1273 K and 1473 K and in the range of pressures between 0.1 and 0.36 MPa. Calculations show that an appropriate choice of heat treatment parameters can lead to optimal nitrogen absorption in the alloy. It was observed in the calculations that an increased pressure stabilizes CrN at the expense of Cr₂N - type nitrides.

1. INTRODUCTION
Nitrogen improves mechanical properties, wear and corrosion resistance of martensitic stainless steels¹. High nitrogen martensitic stainless steels can be obtained by means of high-pressure metallurgy. Nitrogen content of martensitic stainless steels can also be increased by exposure of austenite to high purity nitrogen, under relatively low pressures². This can be done with bulk (case hardening) or particulate materials (powder metallurgy)³.

The beneficial effects of nitrogen on mechanical, corrosion and erosion-corrosion properties can only be obtained if nitrogen remains in solid solution after quenching or is precipitated as coherent and fine chromium nitride particles after tempering. If coarse nitride precipitation is not hindered during high temperature nitriding, chromium and nitrogen depletion of the matrix can impair corrosion and wear resistance of these steels⁴.

When stainless steel is exposed to a nitrogen atmosphere at high temperature, nitrogen may be incorporated in steel through dissolution of nitrogen in the austenitic phase up to its solubility limit, according to equation (1):

\[
\frac{1}{2} \text{N}_2(\text{gas}) \leftrightarrow [\text{N}]_\gamma
\]  
(1)

and through precipitation of chromium nitrides, according to equations (2) and (3):

\[
[\text{Cr}]_\gamma + [\text{N}]_\gamma \leftrightarrow \text{CrN}
\]  
(2)

\[
2[\text{Cr}]_\gamma + [\text{N}]_\gamma \leftrightarrow \text{Cr}_2\text{N}
\]  
(3)

Each of these reactions has its own equilibrium constant, for given temperatures and nitrogen gas pressures.

\[
K_N = \frac{[\text{N}]_\gamma}{\sqrt{[\text{N}]_\gamma}} = \frac{f_N\sqrt{[\%\text{N}]}}{\sqrt{p_{\text{N}_2}}}
\]  
(4)

where \(h_{[\text{N}]_\gamma}\) is the Henryan activity of nitrogen in solution in austenite, and the nitrogen partial pressure \(p_{\text{N}_2}\) represents the activity of nitrogen in the atmosphere. The activity coefficient \(f_N\) relates the chemical activity of nitrogen with its weight percent concentration \([\%\text{N}]\). This relationship leads to Sieverts' law under the domain of validity of Henry's law.

\[
[\%\text{N}] \approx K'' \sqrt{p_{\text{N}_2}}
\]  
(5)
Fig. 5: Isopleth of the Fe-16.2% Cr-N phase diagram and 0.15 MPa N<sub>2</sub> pressure. The nitrogen contents of the samples are shown as small squares.

Fig. 6: Isopleth of the Fe-16.2% Cr-N phase diagram and 0.25 MPa N<sub>2</sub> pressure. The nitrogen contents of the samples are shown as small squares.

Fig. 7: Isopleth of the Fe-16.2% Cr-N phase diagram and 0.36 MPa N<sub>2</sub> pressure. The nitrogen contents of the samples are shown as small squares.

Fig. 8: Isothermal section of the Fe-Cr-N phase diagram at 1273K and 0.1 MPa. The experimental results of Takaki are shown as small squares.
where \( K^\prime = K_N / f_N \).

Nitrogen will remain in solid solution depending on the temperature of thermo-chemical treatment and nitrogen pressure. Nitrogen loss or nitrogen pickup may occur according to Sieverts’ law at a given set of temperature and nitrogen partial pressure parameters.

The equilibrium of the reaction \( \frac{1}{2} N_2 \text{(gas)} \rightleftharpoons [N]_y \) may be shifted by reactions (2) and (3) relative to CrN and \( \text{Cr}_2\text{N} \) precipitation with equilibrium constants given by equations (6) and (7):

\[
K_{\text{CrN}} = \frac{a_{\text{CrN}}}{h_{\text{CrN}}^{2} h_N} \quad (6)
\]

\[
K_{\text{Cr}_2\text{N}} = \frac{a_{\text{Cr}_2\text{N}}}{h_{\text{Cr}_2\text{N}}^{2} h_N} \quad (7)
\]

Extensive thermodynamic calculations must be carried out to know the nitrogen content in solution in austenite and the amount of precipitated chromium nitrides. Thermocalc® calculations may also be done leading to a good description of the equilibrium between nitrogen gas and steel, provided that convenient databases are selected. Nitrogen contents calculated by this procedure were compared with measured ones after high temperature nitriding of low carbon stainless steels.

2. EXPERIMENTAL

Fe-Cr-N phase diagrams were computed using the Thermocalc® (version L) program for a system in which equilibrium between austenite, chromium nitrides and \( N_2 \) gas at the metal surface was considered. The thermodynamic description of the gaseous phase contained in the SGTE Substances 1994 Database - SUB94 - was appended to the system's description.

Usually the equilibrium between nitrogen gas and steel is described by overlaying \( N_2 \) isobar lines on phase diagrams calculated without considering the gas phase as an equilibrium one, as shown in Figure 1-a, for Fe-13 %Cr-N alloys. It has the advantage of representing phase diagrams for different pressures, all in one.

The method used in this work considers the equilibrium between the gas phase and the steel as shown in Figure 1-b, calculated for a Fe-13 %Cr-N alloy at 0.15 MPa. It gives a realistic representation of the phase fields beyond the solid state.

AISI 410S and AISI 434L stainless steels were high temperature nitrided in a tubular furnace under high purity \( N_2 \) atmosphere at pressures between 0.15 and 0.36 MPa and temperatures between 1273 K and 1473 K, during 1 to 24 hours.

The AISI 410S bulk specimens were thermochemically treated in order to obtain hardened cases 0.15 to 2 mm thick. The AISI 434L stainless steel powder was compacted and simultaneously sintered and nitrided to obtain homogeneous and dense high nitrogen, high hardness martensitic stainless steels. The chemical compositions of the alloys are shown in Table 1.

Thermo-chemical treatments were performed at temperatures between 1273 K and 1473 K and pressures between 0.15 and 0.36 MPa, for 1 to 24 hours.

Nitrogen absorbed during thermo-chemical treatment was evaluated by measuring the increase in weight of the specimens and also by fusion under inert gas analysis to check the results. The nitrogen content at the
Table 1
CHEMICAL COMPOSITION OF THE ALLOYS (wt.%)  

<table>
<thead>
<tr>
<th>Steel</th>
<th>C</th>
<th>N</th>
<th>Cr</th>
<th>Mn</th>
<th>Si</th>
<th>Mo</th>
</tr>
</thead>
<tbody>
<tr>
<td>410S bulk</td>
<td>0.07</td>
<td>0.02</td>
<td>13.0</td>
<td>0.27</td>
<td>0.40</td>
<td>-</td>
</tr>
<tr>
<td>434L powder</td>
<td>0.02</td>
<td>0.018</td>
<td>16.2</td>
<td>0.20</td>
<td>1.20</td>
<td>0.8</td>
</tr>
</tbody>
</table>

Table 2
NITROGEN ABSORBED, NITROGEN DISSOLVED IN AUSTENITE AND PHASES IN EQUILIBRIUM WITH N₂ GAS IN A Fe-13%Cr ALLOY AND AT 0.15 MPa.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>% N_{total}</th>
<th>%Nγ</th>
<th>Phases in equilibrium with N₂ gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>1273</td>
<td>2.30</td>
<td>0.25</td>
<td>γ + CrN</td>
</tr>
<tr>
<td>1373</td>
<td>0.49</td>
<td>0.49</td>
<td>γ</td>
</tr>
<tr>
<td>1473</td>
<td>0.35</td>
<td>0.35</td>
<td>γ</td>
</tr>
</tbody>
</table>

Table 3
NITROGEN ABSORBED, NITROGEN DISSOLVED IN AUSTENITE AND PHASES IN EQUILIBRIUM WITH N₂ GAS IN A Fe-13%Cr ALLOY AND AT 0.25 MPa.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>% N_{total}</th>
<th>%Nγ</th>
<th>Phases in equilibrium with N₂ gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>1273</td>
<td>2.6</td>
<td>0.28</td>
<td>γ + CrN</td>
</tr>
<tr>
<td>1373</td>
<td>0.70</td>
<td>0.55</td>
<td>γ + Cr₂N</td>
</tr>
<tr>
<td>1473</td>
<td>0.45</td>
<td>0.45</td>
<td>γ</td>
</tr>
</tbody>
</table>

The surface of the case hardened AISI 410S steel was determined by GDOS.

3. RESULTS

3.1 The Fe-13% Cr - N system and AISI 410S Alloy

Figures 2 and 3 show isopleths of the Fe-13% Cr-N system for 0.15 MPa and 0.25 MPa. These diagrams allow predicting that, when exposed to a N₂ atmosphere, a Fe-13% Cr alloy absorbs larger amounts of nitrogen, at lower temperatures, provided equilibrium is attained. Nevertheless, the amount of nitrogen in solution in austenite increases as the temperature is decreased until the Cr₂N hexagonal nitride becomes stable. From this point on, the solubility limit of nitrogen in austenite decreases with decreasing temperatures. Tables 2 and 3 show for Fe -13% Cr alloys, the total nitrogen content, the nitrogen content dissolved in austenite and the phases in equilibrium with N₂ gas for different temperatures and 0.15 and 0.25 MPa pressures, respectively.

It can be seen that thermo-chemical treatments carried out at 1273K lead to extremely high values of nitrogen absorbed by the alloy, although the nitrogen content dissolved in austenite is low and cubic CrN nitride is present. As the temperature is increased to 1373 K, the total amount of nitrogen is decreased but the content of
Nitrogen dissolved in austenite increases. Increasing pressure stabilizes the Cr$_2$N phase at expenses of the cubic CrN phase.

Figure 4 shows the Fe 13% Cr - N isopleth for 0.20 MPa N$_2$ pressure. The small square plotted in the figure indicates the GDOS measured surface nitrogen content of an AISI 410 S stainless steel after 24 hours of exposure to a 0.20 MPa N$_2$ atmosphere at 1323K. The volume fraction of precipitated CrN at the surface of the alloy was estimated by quantitative metallography as being 3%, leading to a calculated (through mass balance) nitrogen content dissolved in austenite of 0.45%. One can see that the agreement between predicted and measured values is rather good.

3.2 The Fe-16.2% Cr-N System and AISI 434L Alloy

Phase diagrams for Fe-16.2 Cr - N alloys were calculated and Figures 5, 6 and 7 show the isopleths for 0.15 MPa, 0.25 MPa and 0.36 MPa N$_2$ pressures, respectively. One can see that the solubility of nitrogen in austenite increases with increasing temperature until the gas phase becomes stable. From this point on, an increase in temperature leads to a decrease in nitrogen solubility of austenite.

Nitrogen contents of sixteen AISI 434L green compact specimens, nitried and sintered at different temperatures and N$_2$ pressures are plotted as small
4. CONCLUSIONS

1) The calculated phase diagrams were in good agreement with experimental results on nitrogen absorption and nitrogen solubility in austenite obtained in high temperature nitriding experiments.

2) An appropriate choice of heat treatment parameters can lead to optimal nitrogen absorption in the alloy. Extremely high nitrogen levels can be achieved by nitrogen pickup during lower temperature treatments.

3) It was observed in the calculations that increasing pressure stabilises CrN at expenses of Cr$_2$N.

4) The databases SSOL and SUB94 used in the Thermocalc® program describe thoroughly well the thermodynamics of nitrogen absorption in Fe-Cr alloys exposed to N$_2$ atmospheres.

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REFERENCES

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