Nitrogen improves wear and corrosion resistance of martensitic stainless steels. 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 exposition of austenite to high purity nitrogen, under relatively low pressures. This can be done with bulk (case hardening) or particulate materials (powder metallurgy). Phase diagrams, where equilibrium between austenite, nitrogen gas and chromium nitrides at the metal surface is taken in account, were derived by Thermocalc®. For certain high temperature nitriding conditions, only austenite is in equilibrium with nitrogen gas, and Sievert’s Law describes thoroughly well nitrogen pick up. When temperature is lowered or pressure is raised, nitrogen gas, austenite and chromium nitrides are in equilibrium at the surface. Chromium nitrides can be formed at the surface of the steel leading to different thermodynamic and kinetic conditions of nitrogen absorption. Experimental evidences of this precipitation confirmed the Thermocalc® simulations. A description of the nitriding kinetics was done using a model that takes in account the interaction between Cr and N atoms in austenite and the critical solubility product for precipitation of nitrides. The model, together with Thermocalc® predictions, explained the effect of increasing pressure on nitriding kinetics.

1. Introduction

When nitrogen is incorporated in steel through high temperature nitriding, the nitrogen content of austenite can be increased although chromium nitrides can also precipitate. Whether nitrogen will remain in solid solution or not depends on the thermochemical treatment temperature and nitrogen pressure. Nitrogen loss or pickup may occur according to Sieverts’ law at a given set of temperature and nitrogen partial pressure parameters.

Outstanding beneficial effects of nitrogen can be obtained if nitrogen remains in solid solution after quenching or is precipitated as coherent and fine chromium nitride particles after tempering (1). When profuse precipitation of coarse chromium nitrides occurs during high temperature nitriding, chromium and nitrogen depletion of the matrix can impair corrosion and wear resistance of these steels (2).

Chromium nitrides can precipitate during high temperature nitriding according to reactions describing the equilibrium conditions between nitrogen gas and the surface of the steel (3). Each of these reactions has its own equilibrium constant, for given temperatures and nitrogen gas pressures. The equilibrium of the reaction \( \frac{1}{2} N_2 (\text{gas}) \Leftrightarrow [N]_\gamma (\text{in steel}) \) may be shifted by two other reactions relative to CrN and Cr2N precipitation. 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 and
when convenient databases are selected, the equilibrium between nitrogen gas and steel may be thoroughly described.

Research work on nitrogen absorption in stainless steels during high temperature nitriding has been performed. Thermodynamic modeling using the SGTE Solid Solution (SSOL) database for Fe-Cr-N alloys has been made, leading to reliable phase diagrams that can be accessed through Thermocalc in a rather easy and uncomplicated way. In spite of this the calculated phase diagrams do not agree with experimental values of nitrogen solubility in austenite and nitrogen content absorbed in the steel. The absence of a gaseous phase in the system's description contained in the SSOL database is the main reason for this apparent paradox.

In this work some Fe-Cr-N phase diagrams were computed using the Thermocalc® (version L) program for a system in which equilibrium between austenite, chromium nitrides and \( \text{N}_2 \) gas at the metal surface was considered. This procedure was done by appending the thermodynamic description of the gaseous phase contained in the SGTE Substances 1994 Database - SUB94 - to the system's description contained in the SGTE Solid Solutions – SSOL - Database. The nitrogen contents calculated by this procedure were compared with experimental data and used to assess the kinetics of nitrogen absorption in low carbon martensitic stainless steels (6).

2. Experimental procedure and methods

Two low carbon martensitic stainless steels were high temperature nitrided. Bulk AISI 410 S stainless steel was case hardened, obtaining high nitrogen cases, 0.15 to 1.2 mm thick, which after quenching became martensitic. Previously compacted AISI 434L water atomized stainless steel powder, was simultaneously nitrided and sintered, obtaining homogeneous and dense high nitrogen steels. Table 1 shows the chemical composition of the alloys.

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>410 S</td>
<td>0.07</td>
<td>0.020</td>
<td>13.0</td>
<td>0.27</td>
<td>0.40</td>
<td>-</td>
</tr>
<tr>
<td>434 L 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>

Thermochemical treatments were performed under a high purity \( \text{N}_2 \) atmosphere in a tubular furnace described elsewhere (2), at pressures between 0.15 and 0.36 MPa and temperatures between 1273 K and 1473 K, during 1 to 24 hours.

Nitrogen contents of the powder AISI 434L specimens were evaluated by measuring the increase in weight of the specimens after thermochemical treatment and also by fusion under inert gas method. Surface nitrogen contents of the bulk AISI 410S steel were evaluated by Glow Discharge Optical Spectrometry – GDOS. The nitrogen content of the hardened case was also measured by combustion under inert gas, after sectioning the case in a microtom. Case depths were also evaluated.

Thermocalc® (version L) was used to compute phase diagrams corresponding to the conditions under which thermochemical treatments were performed. The thermodynamic description of the nitrogen gas phase contained in the SGTE – substance SUB – 94 database was appended to the system's description contained in the SSOL database (4).
3. Results and discussion

Figure 1 shows isopleths of the Fe-13wt%Cr-N phase diagrams (a) excluding and (b) including the gas phase. 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 as shown in Figure 1 (b).

Phase diagrams taking in account the gas phase were calculated in order to understand the results obtained during high temperature nitriding of AISI 434L powder material and of AISI 410S bulk material.

Nitriding of the AISI 434 L steel - Nitrogen contents of the 6 hours nitrided and sintered AISI 434L powder specimens are shown in Figure 2. The nitrogen content decreased with increasing temperature and increased with increasing pressure. No significant changes of nitrogen content were observed for treating times greater than 2 hours and temperatures of 1373 K and 1473 K.

Figure 3 shows isopleths of the Fe-16 wt% Cr-N phase diagram, for (a) 0.15 MPa and (b) 0.25 MPa N₂ pressure. The measured nitrogen contents presented in Figure 2 are indicated by squares in Figure 3. A good agreement between experimental and calculated nitrogen contents in the solid can be seen for 1373 K and 1473 K. At 1273 K the equilibrium nitrogen content could not be reached due to the reduced treatment times used.
Figure 2 - Nitrogen content of AISI 434L powder specimens simultaneously nitrided and sintered for 6 hours as a function of temperature and N$_2$ pressure.

Figure 3 - Isopleths of the Fe-16wt% Cr-N phase diagram for (a) 0.15 MPa and (b) 0.25 MPa. The measured nitrogen contents are indicated by squares.

Nitriding of the AISI 410S steel – Figure 4 shows the variation of (a) the nitrogen content of the case and (b) the case depth with temperature and N$_2$ pressure after high temperature nitriding of AISI 410 S bulk specimens during 6 hours. Nitrogen absorption increases with decreasing temperature and increases with increasing N$_2$ pressure. Case depth increases with increasing temperature and increasing N$_2$ pressure. Isopleths of the Fe-13wt% Cr-N phase diagram for 0.15 MPa and 0.25 MPa N$_2$ pressure were calculated giving the total amount of nitrogen absorbed in the steel, the nitrogen content dissolved in austenite and the phases in equilibrium at the temperatures and N$_2$ pressures shown in Table 2.
Figure 4 – Variation of (a) the nitrogen content of the case and (b) the case depth of AISI 410 S bulk specimens nitrided at different temperatures and N$_2$ pressures for 6 hours.

Table 2 – Nitrogen absorbed in steel, nitrogen dissolved in austenite and phases in equilibrium with nitrogen gas at given temperatures and N$_2$ pressures.

<table>
<thead>
<tr>
<th>T (K)</th>
<th>% N</th>
<th>%N$_\gamma$</th>
<th>P (MPa)</th>
<th>Phases in equilibrium</th>
</tr>
</thead>
<tbody>
<tr>
<td>1273</td>
<td>2.30</td>
<td>0.25</td>
<td>0.15</td>
<td>γ + CrN</td>
</tr>
<tr>
<td>1373</td>
<td>0.49</td>
<td>0.49</td>
<td>0.15</td>
<td>γ</td>
</tr>
<tr>
<td>1473</td>
<td>0.35</td>
<td>0.35</td>
<td>0.15</td>
<td>γ</td>
</tr>
<tr>
<td>1273</td>
<td>2.60</td>
<td>0.28</td>
<td>0.25</td>
<td>γ + CrN</td>
</tr>
<tr>
<td>1373</td>
<td>0.70</td>
<td>0.55</td>
<td>0.25</td>
<td>γ + Cr$_2$N</td>
</tr>
<tr>
<td>1473</td>
<td>0.45</td>
<td>0.45</td>
<td>0.25</td>
<td>γ</td>
</tr>
</tbody>
</table>

The isopleths show that CrN precipitates during nitriding at 1273K for 0.15 and 0.25 MPa N$_2$ pressures and Cr$_2$N precipitates during nitriding at 1373 K and 0.25 MPa N$_2$ pressure. No precipitation of Cr$_2$N can be foreseen at 1373 K and 0.15 MPa. When nitriding is performed at 1473 K only austenite is present in equilibrium with N$_2$ gas, although the nitrogen contents of austenite are not very high (0.35 wt.% at 0.15 MPa and 0.45 wt.% at 0.25 MPa).

Figure 5 – Calculated apparent diffusion coefficients for a 6 hours nitriding treatment of AISI 410 S steel at 1273 K, 1373 K and 1473 K, 0.15 and 0.25 MPa N$_2$ pressures.
The calculated nitrogen contents and the measured case depths of Figure 4 (b) were used to evaluate the kinetics of high temperature nitriding of the AISI 410 S stainless steel (5) using an internal oxidation model proposed by Lightfoot (5):

\[ \xi^2 = \frac{2[N]}{r[X]} Dt \]  (1) \[ \xi \] is the case depth. 
\[ N \] is the nitrogen at% concentration at the surface. 
\[ X \] is the chromium at% concentration in the steel. 
\[ r \] is the at% N/at% Cr ratio in the nitride. 
\[ D \] is the nitrogen diffusion coefficient through the matrix.

Figure 5 and Table 3 show the diffusion coefficients and activation energies calculated in this work as well as those reported by Heger (5). The calculated activation energy (280.1 kJ/mol) is compatible with nitrogen diffusion through the matrix.

3. Conclusions

1) Thermocalc® calculated phase diagrams, taking in account the gaseous phase were in good agreement with the experimental results on nitrogen absorption and nitrogen solubility in austenite during high temperature nitriding of stainless steels.

2) Nitrogen absorption increases with decreasing temperature and increasing nitrogen pressure. Optimization of thermochemical treatments, leading to high nitrogen contents dissolved in austenite and absence of precipitated chromium nitrides, may be accomplished by careful analysis of the calculated phase diagrams.

3) Case depths attained after high temperature nitriding increase with increasing temperature and \( \text{N}_2 \) pressure due to higher nitrogen contents in the steel.

4. References

6) A.P.Tschiptschin – Habilitation Thesis for becoming Associate Professor, 2000, pp. 142.

5. Acknowledgements

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