MICROSTRUCTURE AND CHEMICAL CHARACTERIZATION
OF HIGH TEMPERATURE NITRIDED 12%Cr STAINLESS
STEELS

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ABSTRACT

AISI 410 (11.5 %Cr - 0.13 %C) and AISI 410S (13.0 %Cr - 0.07 %C) martensitic stainless steels were gas nitrided in N
atmosphere at 1273-1473 K, 0.02 - 0.38 MPa and 0.9 - 172.8 ks. Nitrogen gradients were determined by chemical analysis through optical
spectroscopy and WDS microanalysis. The average nitrogen content of long-term nitrided thin specimens was measured by optical
spectroscopy and fusion under inert gas. Precipitate extraction was performed by dissolution of the matrix, the precipitates being
analyzed by fusion under inert gas and X-ray diffraction.

The results showed that by increasing nitriding time and pressure, as well as by decreasing temperature, both the nitrogen content at the
surface of the steels and the tendency to form precipitates increased. Thermocalc calculations for the Fe-Cr-N-C system allowed
predicting nitrogen contents, as well as microstructures of the nitrided alloys. Good agreement between calculated and experimental
values was observed. XRD of extracted precipitates confirmed Thermocalc calculations concerning the stability of nitrides.

In specimens containing precipitated nitrides, the nitrogen content dissolved in martensite increased with the distance from the surface,
in the region where precipitation occurs. Beyond this region the nitrogen content decreased towards the core.

1. INTRODUCTION

Nitrogen has been added as an alloying element to
stainless steels to improve mechanical properties and
corrosion resistance. Nitrogen can be introduced in
stainless steels by a high-temperature thermochemical
treatment, which allows introducing nitrogen at
temperatures above Ac3 under nitrogen partial pressures
that typically vary in the range 0.03-0.40 MPa. After
3.6-86.4 ks treatments, a high nitrogen case is formed.
Under these conditions nitrogen remains mainly in solid
solution, without forming a white layer usually found in
low temperature nitriding processes. The gas used
(N2+Ar) is neither explosive nor toxic, and no gas flux
is required.

Depending on the chemical composition of the steel and
the phases in equilibrium at the nitriding temperature,
either high strength austenitic or hard martensitic cases
can be obtained. When applied to martensitic and
martensitic-ferritic stainless steels, this process allows
combining high hardness at the surface with good
impact resistance of the core. The resultant
microstructure after high temperature nitriding
treatment depends on the material and on nitriding
times, temperatures and N2 partial pressures. Several
authors consider the existence of stable equilibrium
between the steel surface and the gas, which implies that
the phases present at the surface as well as their
chemical composition can be read in a phase diagram
including metal-gas equilibrium.

According to Frisk the metal-gas equilibrium during
nitriding of steel powders can be predicted by drawing
in a phase diagram, the nitrogen activity for specific N2
partial pressures. In a similar approach, Tschiptschin proposes that metal-gas equilibrium during high-
temperature nitriding may be predicted by using a
metal-gas equilibrium diagram, constructed for a
specific N2 partial pressure.

There is no systematic study of microstructural changes
at the surface, as a function of time during high-
temperature nitriding. Tschiptschin mentioned that
under some specific nitriding conditions, the assumption

The microstructure of the specimens were examined by optical and scanning electron microscopy and by X-ray diffraction. The prior austenite grain size was determined according to the E112 ASTM standard. The composition of the phases after nitriding was investigated by wavelength dispersive spectroscopy (WDS).

Nitrogen gradients in the thick specimens were determined by chemical analysis through optical spectrometry (OS) and WDS microanalysis. The nitrogen content of long-term nitrided thin specimens was measured by OS and fusion under inert gas.

Precipitate extraction was performed by the chemical dissolution of the matrix, and the precipitates were analyzed by fusion under inert gas and X-ray diffraction. For precipitate extraction, specimens weighing 1-2 g were dissolved in a Berzelius type solution at 300 K for 43.2 ks. The reagent was prepared by dissolving 320 g of CuCl₂·2H₂O, 280 g of KCl, and 20 g of HOOC[CH(OH)₂COOH in 1.85 l of distilled water and 150 ml of HCl. A magnetic wrist-action shaker was used to agitate the specimens inside the reagent in a flask. The solution was suctioned through a 45 mm diameter PTFE filter with 0.45 mm maximum pore size. The residue was washed with 0.25 N hydrochloric acid and water and then transferred to a watch glass and dried at 393 K for 24 h.

Thermocalc® was used to predict phase stability and chemical composition of the nitrided specimens. The gas-metal equilibrium was calculated for one specific N₂ isobar allowing predicting the phases present and the maximum nitrogen content at the surface of the steel. The stability and the compositions of the phases in other regions inside the case were calculated assuming...
Table 2

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Calculated (wt%)</th>
<th>Measured (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1473</td>
<td>0.09</td>
<td>0.11 ± 0.05</td>
</tr>
<tr>
<td>1373</td>
<td>0.12</td>
<td>0.16 ± 0.05</td>
</tr>
<tr>
<td>1353</td>
<td>0.15</td>
<td>0.20 ± 0.05</td>
</tr>
<tr>
<td>1273</td>
<td>0.20</td>
<td>0.22 ± 0.05</td>
</tr>
</tbody>
</table>

Three zones with different microstructures were observed from the surface towards the center of the specimens: a martensitic surface layer, a transition zone, and a dual-phase martensitic-ferritic inner zone. The microconstituents in the martensitic surface layer were the same observed in the high-nitrogen case of AISI 410 steel. The transition zone was consisted of a martensitic matrix with isolated regions of untransformed ferrite, as shown in Fig. 2. No precipitates were observed under SEM. The inner zone showed a dual phase martensitic-ferritic microstructure containing 40-50% ferrite.
Table 3 shows the microconstituents at the surface of XRD and WDS techniques. Lowering the temperature the thick specimens nitrided at 0.25 MPa, identified by

**Table 3**

MICROCONSTITUENTS AT THE SURFACE OF THICK SPECIMENS NITRIDED AT 0.25 MPa

<table>
<thead>
<tr>
<th>T (K)</th>
<th>Time (ks)</th>
<th>Micro constituents</th>
<th>Time (ks)</th>
<th>Micro constituents</th>
</tr>
</thead>
<tbody>
<tr>
<td>1473</td>
<td>0.9/1.8/3.6</td>
<td>α'</td>
<td>0.9</td>
<td>α'</td>
</tr>
<tr>
<td>1473</td>
<td>7.2/10.8/86.4</td>
<td>α' + γretained</td>
<td>1.8/3.6/10.8/86.4</td>
<td>α' + γretained</td>
</tr>
<tr>
<td>1373</td>
<td>3.6</td>
<td>α'</td>
<td>3.6/6.3</td>
<td>α'</td>
</tr>
<tr>
<td>1373</td>
<td>6.3/10.8/21.6/86.4</td>
<td>α' + MX</td>
<td>10.8/21.6/86.4</td>
<td>α' + M2X</td>
</tr>
<tr>
<td>1353</td>
<td>3.6/10.8/21.6/86.4</td>
<td>α' + MX</td>
<td>3.6</td>
<td>α' + M2X</td>
</tr>
<tr>
<td>1353</td>
<td>6.3/10.8/21.6/43.2</td>
<td>α' + MX</td>
<td>6.3/10.8/21.6/86.4</td>
<td>α' + MX</td>
</tr>
<tr>
<td>1273</td>
<td>1.8/3.6/63</td>
<td>α' + M2X</td>
<td>3.6</td>
<td>α' + M2X</td>
</tr>
<tr>
<td>1273</td>
<td>10.8/21.6/86.4</td>
<td>α' + MX</td>
<td>6.3/10.8/21.6/86.4</td>
<td>α' + MX</td>
</tr>
</tbody>
</table>

enhanced nitride precipitation; the volume fraction increased with increasing nitriding time, as shown in Figs. 3 and 4 for the AISI 410 steel (nitrided at 1273 K, 0.25 MPa).

In the precipitate-free specimens (nitrided at 1473 K) grain growth occurred reaching a size of 2-4 ASTM. On the other hand, in specimens with intense precipitation (nitrided at 1273 and 1353 K) grain growth was inhibited, and grain sizes of 5-6 ASTM were obtained. Fig. 5 shows the effect of nitriding time and temperature on prior austenite grain size for the AISI 410 steel nitrided at 0.25 MPa.

Table 4 shows the precipitates formed inside the entire case of specimens nitrided at 0.25 MPa for 21.6 and free cases were obtained in both the steels. For the other nitriding temperatures, MX and M2X precipitates were identified in AISI 410S steel, while only MX type precipitates were found in AISI 410 steel.

**Table 4**

PRECIPITATES IN THE CASE OF SPECIMENS NITRIDED AT 0.25 MPa

<table>
<thead>
<tr>
<th>T (K)</th>
<th>AISI 410 steel</th>
<th>AISI 410 S steel</th>
</tr>
</thead>
<tbody>
<tr>
<td>1473</td>
<td>None</td>
<td>None</td>
</tr>
<tr>
<td>1373</td>
<td>MX</td>
<td>M2X</td>
</tr>
<tr>
<td>1353</td>
<td>MX</td>
<td>MX + M2X</td>
</tr>
<tr>
<td>1273</td>
<td>MX</td>
<td>MX + M2X</td>
</tr>
</tbody>
</table>
Figure 6 shows the relation between nitriding time and nitrogen content at the surface of the specimens nitrided at 0.25 MPa, 1273 - 1473 K. The nitrogen content increased with nitriding time up to a saturation value, which decreased with increasing nitriding temperature.

The nitrogen content decreases towards the core, as shown in Fig. 7 for three representative specimens. In specimens containing precipitated nitrides, both nitrogen and chromium contents in martensite increased with the distance from the surface in the region where intense precipitation occurs. Beyond this region the martensite nitrogen content decreased towards the core while the chromium content remained almost constant, as shown in Fig. 8 for the AISI 410S steel nitrided at 1273 K, 0.25 MPa for 21.6 ks.
decreases with nitriding time reaching a limit value. Fig. 9 shows the relation between nitriding time and nitrogen and chromium contents in martensite, at the surface of the AISI 410 steel nitrided at 1273 K, 0.25 MPa.

The chromium content of the precipitates, measured through WDS technique, was between 50 and 70 wt%. The WDS-measured nitrogen contents of the MX and M₂X were 22±1 wt% and 13±1 wt%, respectively.

Figure 10 shows the experimental and the Thermocalc® calculated nitrogen and chromium contents in martensite as a function of total nitrogen content at the surface of the AISI 410 steel, nitrided at 1273 K, 0.25 MPa. The experimental points were obtained by correlating the total nitrogen content at the surface, for different nitriding times, with the chromium and nitrogen contents of austenite shown in Figs. 6 and 9. Each point was taken for the nitriding times indicated in the graph. The Thermocalc curves were calculated assuming that stable equilibrium was reached for given nitrogen contents at the surface. The nitrogen content in martensite at the surface increases with the total nitrogen content up to a maximum value (0.54 wt% N for the mentioned steel), and then decreases reaching an equilibrium limit value. The chromium content in martensite remains almost constant for low nitrogen contents at the surface. As the nitrogen content increases with nitriding time the chromium content starts to decrease, reaching an equilibrium limit value, as a consequence of the precipitation of nitrides.

3.2 Thin Specimens Gas-metal Equilibrium

OS and fusion under inert gas measurements showed that the long-term nitrided thin specimens were chemically homogeneous. In addition, quantitative metallography and XRD of the collected residues showed that the amount and type of precipitates at the
surface and inside the specimens were the same. Thereafter, it was considered that the stable equilibrium conditions were reached.

<table>
<thead>
<tr>
<th>Nitriding temperature (K) and pressure (MPa)</th>
<th>AISI 410 Predicted precipitates</th>
<th>AISI 410 Identified precipitates</th>
<th>AISI 410 S Predicted precipitates</th>
<th>AISI 410 S Identified precipitates</th>
</tr>
</thead>
<tbody>
<tr>
<td>1473 K-0.25 MPa</td>
<td>None</td>
<td>None</td>
<td>None</td>
<td>None</td>
</tr>
<tr>
<td>1373 K-0.10 MPa</td>
<td>None</td>
<td>None</td>
<td>None</td>
<td>None</td>
</tr>
<tr>
<td>1373 K-0.25 MPa</td>
<td>None</td>
<td>MX</td>
<td>M2X</td>
<td>M2X</td>
</tr>
<tr>
<td>1353 K-0.25 MPa</td>
<td>M2X</td>
<td>MX</td>
<td>M2X</td>
<td>MX</td>
</tr>
<tr>
<td>1273 K-0.25 MPa</td>
<td>MX</td>
<td>MX</td>
<td>MX</td>
<td>MX</td>
</tr>
</tbody>
</table>

The predicted precipitates were read in an isobar line for each temperature studied, obtaining a rather good agreement with the experimental results.

The nitrogen contents analyzed by fusion under inert gas of the extracted precipitates were 19±2 wt% and 11±2 wt% for the MX and M2X, respectively.

In Fig. 12 the (%N_s / %N_eq) ratio (total nitrogen content / equilibrium nitrogen content ratio) at the surface is plotted as a function of the nitriding time for the AISI 410 steel nitrided at 0.25 MPa, 1273 - 1473 K. The time necessary for reaching the nitrogen content...
corresponding to equilibrium metal-gas decreased with the temperature.

![Nitrogen content at the surface of thin specimens as a function of (a) nitriding temperature and (b) N2 partial pressure.](image)

Fig. 11: Nitrogen content at the surface of thin specimens as a function of (a) nitriding temperature and (b) N2 partial pressure.

![Effect of nitriding time and temperature on the total nitrogen content/equilibrium nitrogen content ratio (%N_s/%N_eq) at the surface of the AISI 410 steel nitrided at 0.25 MPa.](image)

Fig. 12: Effect of nitriding time and temperature on the total nitrogen content/equilibrium nitrogen content ratio (%N_s/%N_eq) at the surface of the AISI 410 steel nitrided at 0.25 MPa.

### 3.3 Discussion

The results disclose two basic characteristics of the microstructure of high temperature nitrided martensitic stainless steels:

(i) The microstructure at the surface reached the metal-gas equilibrium condition after nitriding times of the order of hours. This time is much greater for nitriding conditions in which precipitates are formed.

(ii) In precipitate-free specimens, the microstructure in a region of the nitrided case can be predicted by assuming equilibrium. Depending on the nitriding time and the amount of precipitates in the microstructure, that assumption could not be valid for specimens containing nitrides.

In precipitate-free specimens the nitrogen content at the surface increases very quickly during nitriding, given that after 3.6 ks the surface has already attained 80% of the nitrogen equilibrium content. On the other hand, in specimens with intense precipitation, the nitrogen content at the surface increases very quickly for lower nitriding times (when the amount of precipitates is small) and very slowly for longer times. As an example, when nitriding was carried out at 1273 K the nitrogen content at the surface after 3.6 ks was about 20% of the equilibrium content, and a value of about 85% was reached only after 86.4 ks.

The increase in the total nitrogen content at the surface with time is related to the nitrogen uptake reaction \( \frac{1}{2} N_2(gas) \rightarrow [N]_y \) and to the nitride precipitation rate. In the specimens with intense precipitation, when the amount of precipitates is still small (shorter times), the controlling reaction is the absorption of nitrogen in austenite, which is a very fast reaction. For higher times, the controlling reaction is the precipitation of chromium nitrides, which strongly depends on the diffusion of chromium in austenite. This precipitation reaction strongly reduces the rate of nitrogen increase at the surface.

During nitriding, chromium depletion of austenite occurs in the specimens containing precipitates. This depletion changes the ratio between total nitrogen content and nitrogen content in martensite (as shown in Fig. 10), thus explaining the time variation of nitrogen content at the surface shown in Figure 9. Moreover, the austenite nitrogen content / total nitrogen content ratio cannot be calculated by assuming stable equilibrium conditions, because the time necessary for nucleation and growth of precipitates is not negligible. This fact explains the differences between the experimental and calculated values in Figure 10.

### 4. CONCLUSIONS

(1) The microstructure of the nitrided steels near the surface was mostly martensitic. Depending on the
REFERENCES


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nitriding conditions, different volume fractions of retained austenite, MX and M₂X precipitates were also observed.

(2) The nitrogen content at the surface and the tendency to nitride precipitation were increased by increasing nitriding time and pressure and by decreasing temperature.

(3) In the specimens containing precipitated nitrides, the martensite nitrogen content at the surface increases with the nitriding time up to a point where the volume fraction of precipitates is still small; from this point on, it decreases reaching a limit value. In the same specimens, the martensite nitrogen content increased with the distance from the surface in the region where intense precipitation occurs, decreasing beyond this region towards the core.

(4) For the precipitate-free specimens the assumption that all components are in equilibrium is useful to predict the microstructure in a region of the nitrided case.

Depending on the nitriding time and the amount of precipitates, this assumption is not valid for specimens containing nitrides.

(5) Thermocalc® calculations described fairly well the phase stability in high temperature nitrided martensitic stainless steels.

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