CHARACTERIZATION OF GAS-NITRIDED 31CrMoV9 STEEL

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In this work, gas nitriding of 31CrMoV9 was carried out at three different temperatures, i.e., at (500, 520 and 540) °C for (10, 20 and 30) h. The microstructure of the nitrided layer was examined with light and scanning electron microscopes. Depending on the process temperature and time, the thickness of the compound layer ranged from 8.7 μm to 22.7 μm. The γ′-Fe₃N, ε-Fe₂N and Cr₂N phases formed in the compound layer were determined with the XRD technique. It was found that the hardness of diffusion layer changed from 620 HV to 750 HV. The maximum surface hardness was determined as 920 HV. Depending on the process parameters, the case depth of diffusion layer ranged from 187 μm to 450 μm. Diffusion-coefficient and activation-energy values for the diffusion of nitrogen in the 31CrMoV9 steel were evaluated using studies on the kinetics of the growth of the nitrided layer. The activation energy of the nitriding process of the 31CrMoV9 steel is 150 kJ/mol.

Keywords: gas nitriding, kinetics, nitriding potential, nitride

1 INTRODUCTION

Gas nitriding is a case-hardening process whereby nitrogen is introduced into the surface of a solid ferrous alloy by holding a metal at a suitable temperature (below A₁; for ferritic steels) in contact with a nitrogenous gas, usually ammonia. Quenching is not required for the production of a hard case. The nitriding temperature for all steels is between 495 °C and 565 °C. Because of the absence of a quenching requirement, with the attendant volume changes and the comparatively low temperatures employed in this process, nitriding of steels produces less distortion and deformation than conventional hardening 1. The formation of a nitrided layer, which improves the wear resistance of steel, proceeds in several stages. It starts at the moment of saturation of a matrix with nitrogen. On such an area the nucleation of nitrides can take place. A further development of the layer proceeds through the growth of these nuclei until a connection is made 2. By nitriding Fe–Me binary alloys, where the alloying element (Me) has a strong affinity with nitrogen, i.e., Me = Cr, Al, V and Ti, nanosized nitride precipitates can develop in the ferrite matrix; the nitride precipitation results in a very pronounced increase in the hardness 3 because of the formation of nitrides that are stable at nitriding temperatures. Molybdenum, in addition to its contribution as a nitride former, also reduces the risk of embrittlement at nitriding temperatures 3. The modern, controlled, gas-nitriding process employs pure ammonia or ammonia with one or two additive gases and it is controlled not with the dissociation rate but with the nitriding potential, KN. Controlling the process with the thermodynamic parameter, KN, makes it possible to produce hardened layers that have variable metallurgical properties 4. In the present work, the feasibility of nitriding the 31CrMoV9 steel through gas nitriding in an automatic KN-controlled Nitrex NX-412 model gas-nitriding furnace was investigated. The diffusion coefficient and activation-energy values for the diffusion of nitrogen in the 31CrMoV9 steel matrix were evaluated using studies on the kinetics of the growth of the nitrided layer.

2 EXPERIMENTAL DETAILS

A series of experiments was carried out to investigate the gas-nitriding response of the 31CrMoV9 steel. The chemical composition of the test material is given in Table 1. Specimens had a rectangular shape and the dimensions of 10 mm × 15 mm × 25 mm. The surfaces of the substrates were mechanically ground with the 100, 320, 400 and 600 grit SiC papers. Prior to the gas-nitriding treatment, the 31CrMoV9 steel samples were austenitized at 900 °C and tempered at 630 °C. The parameters for the experimental studies were selected according to the Lehrer diagram 5 given in Figure 1. This diagram shows the areas of nitride phases and the lines of equal nitrogen concentrations.
According to the Lehrer diagram, the values of the KN nitriding potentials were selected as (4.2, 4.9 and 5.6) bar–1/2, providing the same nitrogen concentration on the surface at the selected temperatures (Figure 1). After the nitriding processes, a conventional microstructural examination was made on the ground and polished samples using a light microscope. A more detailed investigation of the metallographic structures was carried out using a JEOL JSM-5600 model scanning electron microscope (SEM).

The hardness profile of the nitrided case was determined using a Leica WMHT-Mod model microhardness tester with a 0.98 N load in terms of HV, and the effective case depth was defined as the distance below the surface, where the hardness was equal to 350 HV. The phases, formed on the surfaces of the nitrided specimens, were identified with a Rigaku X-ray diffractometer using the Cu $K_\alpha$ radiation with a wavelength of 0.15418 nm over a $2\theta$ range of 10° to 90°.

### 3 RESULTS AND DISCUSSION

Light microscopy examinations revealed that there are three distinct layers on the cross-section of a nitride sample; i) the fine external compound layer of nitrides, ii) the internal diffusion layer and iii) the matrix (Figure 2). The compound layer is formed on the top of the diffusion zone where dense and fine precipitates of iron nitrides are present and it preferentially grows in the whisker form through the grain boundaries (Figure 3).
the nitriding conditions are presented in Table 2. The hardness profiles for the nitriding samples as a function of the case depth are given in Figure 5 for different nitriding conditions. The hardness of the nitride layer is much higher than that of the matrix due to the formation of hard Fe₄N, Fe₃N and Cr₂N nitrides in the compound layer as determined with the XRD analysis. At all the nitriding temperatures and times, the hardness continuously decreases from the surface to the core due to the decreasing nitrogen concentration. The maximum surface hardness, 920 HV, was obtained for the nitriding time of 10 h at 500 °C. The surface-hardness values decrease due to the increasing process temperature and time. The decrease in the surface hardness seems to be mainly associated with the white-layer thickness. As the increase in the white-layer thickness makes the compound layer more brittle, the surface hardness decrease is also due to the brittleness increase.

Table 2: Variation of the compound-layer thickness, case depth, diffusion coefficient of the case layer and surface hardness with the nitriding temperature and time

<table>
<thead>
<tr>
<th>Nitriding temperature (°C)</th>
<th>Time (h)</th>
<th>Compound layer thickness (μm)</th>
<th>Case depth (μm)</th>
<th>Diffusion coefficient (10⁻⁸ (cm²/s))</th>
<th>Surface hardness (HV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>500</td>
<td>10</td>
<td>8.70</td>
<td>210</td>
<td>0.614</td>
<td>920</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>14.8</td>
<td>250</td>
<td>0.608</td>
<td>908</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>17.1</td>
<td>350</td>
<td>0.595</td>
<td>870</td>
</tr>
<tr>
<td>520</td>
<td>10</td>
<td>12.8</td>
<td>230</td>
<td>1.153</td>
<td>914</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>17.4</td>
<td>320</td>
<td>1.144</td>
<td>895</td>
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<tr>
<td></td>
<td>30</td>
<td>20.4</td>
<td>370</td>
<td>1.135</td>
<td>860</td>
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<tr>
<td>540</td>
<td>10</td>
<td>17.0</td>
<td>250</td>
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</tr>
<tr>
<td></td>
<td>20</td>
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<td>350</td>
<td>1.93</td>
<td>891</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>22.7</td>
<td>450</td>
<td>1.92</td>
<td>821</td>
</tr>
</tbody>
</table>

As it can be seen from Table 2, the compound-layer thickness and the case depth increased with the increasing nitriding temperature and time (Figures 2 and 3). An increased time provides more atomic nitrogen diffusion towards the core while the increasing temperature raises the diffusion coefficient of nitrogen, providing the same effect. The solid-state diffusion of atomic nitrogen into the α-Fe matrix is assumed to obey Fick’s second law. The growth of the nitrided layer is a consequence of the nitrogen diffusion perpendicular to the sample surface. The layer growth kinetics is enhanced when increasing the surface nitrogen concentration. This effect is more pronounced with a rise in the temperature since the process becomes more active.

Primarily, diffusion-coefficient values were calculated using the $d^2 = Dt$ equation, where $d$ is the case depth (μm), $t$ is the process time (s) and $D$ is the diffusion coefficient (cm²/s). The variation in the square of the case depth ($d^2$) as a function of the nitriding time is shown in Figure 6a for each temperature. The calculated diffusion-coefficient values are given in Table 2. To obtain the activation energy $Q$, connected to the effective diffusion coefficients, the Arrhenius plots, In $D$ versus...
The activation energy for the gas-nitrided 31CrMoV9 steel was found to be 150.48 kJ/mol. This is in reasonable agreement with the values in the other investigations\(^8\),\(^9\).

4 CONCLUSIONS

In this work, the effect of the nitriding temperature and time on the development of the compound layers during the KN controlled gas nitriding of the 31CrMoV9 steel was investigated. It was found that the process parameters of gas nitriding considerably affect the diffusion-layer hardness and diffusion-zone thickness of a workpiece. They increased with the increasing nitriding temperature and time. The XRD analysis confirmed the presence of the \(\gamma'\)-Fe\(_3\)N and \(\alpha\)-Fe\(_2\)N phases. The kinetic study showed that the effective diffusion coefficient for the nitrided 31CrMoV9 steel depends considerably on the process temperature, and the diffusion coefficient increased with the increasing temperature. The activation energy of nitriding of the 31CrMoV9 steel was found to be 150 kJ/mol.

5 REFERENCES