DIFFERENT DIFFUSION BEHAVIOR OF ALLOY METALS AS A CONSEQUENCE OF MISTAKEN MATERIAL AND USUAL HEAT TREATMENT

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Abstract

Material mistaken is very frequent reason for premature failure in industry. It could be also very interesting source of informations from theoretical point of view. One of these cases were investigated in this work. It was used X5CrNiCuNb17-4-4 stainless steel for production of bolts. The material was heat treated by common way for bolts using carbonitriding. The surface layer with some interesting properties is a result of this procedure. The hardness in this layer slightly increases with growing distance from surface which is absolutely opposite in comparison with theory. The content of nitrogen in this layer is practically zero but on the border between the layer and basic material is a line where content of nitrogen is 1.4 wt.%. The diffusion processes during carbonitriding could be used as a explanation of these results.

Keywords

steel, carbonitriding, diffusion, heat treatment

1. INTRODUCTION

Thermochemical treatment is a common way how to increase hardness of surface and improve mechanical properties. In this paper we focused at carbonitriding. The process of carbonitriding is well known. First papers about this process were published in 30’s of 20\textsuperscript{th} century. The base of carbonitriding is in diffusion of nitrogen and carbon to the structure of material. Nitrogen and carbon are in the structure in form of nitrides, carbides or nitrocarbides with various stoichiometry in dependence on conditions of treatment. The phases with carbon and nitrogen were investigated at first in 40’s by Rengstorff et al. or Jack [1]. Their results were confirmed in next years by many authors [1 - 4]. They described phases with iron such as γ'-Fe\textsubscript{4}N, ε-Fe\textsubscript{2}3(NC), ξ-Fe\textsubscript{2}2(NC) or Fe\textsubscript{3}C. Steels are very often alloyed by various metals. Some of these metals have high affinity with carbon and nitrogen. There were published many papers where were described compounds of nitrogen and carbon with chromium, niobium, tungsten, titanium, vanadium and other metals [1, 3, 5 - 9]. High hardness and brittleness is typical for all these phases.

Carbonitriding (just like other types of thermochemical treatment) is based on diffusion. Theory of diffusion is connected with the name of Adolf Fick who described diffusion and formulated mathematical equations of diffusion (1,2) in 1855:

\[
J_i = -D_i \frac{\partial c_i}{\partial y}
\]

(1)

\[
\frac{\partial c_i}{\partial \tau} = D_i \frac{\partial^2 c_i}{\partial y^2}
\]

(2)
The driving force of diffusion is a gradient of concentration. The mechanism of carbon and nitrogen diffusion is interstitial [1] so the transport of atoms of carbon and nitrogen is made in interstitial positions (see Fig. 1) [10].

**Fig. 1** Interstitial mechanism of diffusion of carbon and nitrogen

### 2. EXPERIMENTAL PROCEDURE

It was used X5CrNiCuNb17-4-4 (or DIN 1.4548) stainless steel for production of bolts. The chemical composition is summarized in Table 1.

**Tab. 1** Chemical composition of X5CrNiCuNb17-4-4

<table>
<thead>
<tr>
<th>Chemical element</th>
<th>C</th>
<th>Si</th>
<th>Cr</th>
<th>Ni</th>
<th>Cu</th>
<th>Nb</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Content [weight %]</td>
<td>0.63</td>
<td>0.30</td>
<td>14.9</td>
<td>3.32</td>
<td>3.12</td>
<td>0.27</td>
<td>&lt; 0.001</td>
</tr>
</tbody>
</table>

This type steel is not usually used for this application. The material was heat treated by common way for bolts using carbonitriding. The cause of failure of bolts was investigated in our department. The investigation showed that this material is not suitable for thermochemical treatment and production of bolts as well. The reason of publishing some of our results is that some interesting phenomena were observed during our investigation. It was investigated microstructure in basic material and in the surface layer using light microscopy. Wave dispersion spectroscopy (WDS) analyzer was used for evaluation of chemical composition in the layer. It was also measured a profile of hardness from surface to basic material using Hanemann micro-hardness tester.

### 3. RESULTS AND CONCLUSIONS

At first, it was investigated the microstructure in the center of material and in the layer – see Fig. 2 and 3. The structure of material is formed by martensite with precipitated phases of carbides around grain boundaries. The structure in surface layer is different – formed by plated martensite and white phase precipitated around boundaries of original austenitic grains. The thickness of this layer is mostly between 32 - 40 µm but on the head of the bolt was about 100 µm. There is a line which cannot be etched using Villela - Bain on the border between the layer and basic material. The similar problem with etching was described in work of Wells – see Fig. 4 [2]. It was proved in Wells’s work that hardly etched layer is made by carbonitrides.
The next part of our investigation was measuring of micro-hardness in surface layer. We expected the highest values of hardness right on the surface and gradual decrease in direction to the center of material. Typical hardness profile in thermochemical treated material published in [3] could be used as example – see Fig. 5. The line in Fig. 6 shows the hardness profile from our measuring. The difference between expected and real results is obvious. The hardness in the layer increases with growing distance from surface. The highest value is on the border between the layer and basic material. This point responds to non-etched line at Fig. 3. Behind this point is very fast drop of hardness right to the hardness of basic material. The thickness of this drop is only 10 μm.
The main information source about diffusion behavior of chemical elements in surface layer is from WDS analysis. The analysis was performed at the place where thickness of layer is 100 μm. The content of most analyzed elements is the same in the whole layer and in the basic material. The differences across the layer were found, of course, in cases of nitrogen and carbon but also surprisingly in case of niobium. The results of measuring for these three elements are summarized in Fig. 7. First values at the point of 10 μm are affected by passivation in nitric acid as a last step of production of bolts. These values are most probably misleading. The thickness of layer in measured
place is 100 µm so the values at points 110 and 120 µm could be considered as a basic material. The content of carbon slightly decreases with growing distance from surface to 90 µm. This agrees with theory. The problem is significantly higher content at point 100 µm. In case of niobium is average value in first 90 µm about 0.2% which is little bit smaller value than in basic material. There is also significantly higher content at the point 100 µm. But the content at points 110 and 120 µm is only 0.07 % and 0.12 %. These values are smaller than should be in basic material. The most extraordinary concentration profile is in case of nitrogen. If we forget the first value because of passivation than in first 90 µm form surface is content smaller than 0.001 %. The situation at the point 100 µm is the same with other two elements — large increase. The content in basic material is again under 0.001%. The point at 100 µm agrees with non-etched line which was mentioned above.

The explanation of these results could be seen in diffusion processes during carbonitriding. The diffusion processes must be affected by chosen material. The behavior of niobium is connected with martensitic structure in material. Martensitic structure is not equilibrated. There is a strain in the structure. The atomic radius of niobium is bigger than iron. So our theory is that niobium is forced out of material. On the other hand, there is a process of carbonitriding in opposite direction. These two processes met at the point 100 µm. The diffusion of nitrogen and carbon is very limited. The interstitial positions for their diffusion are smaller because of higher content of big atoms of niobium in metal lattice. So we could expect presence of nitrocarbides. This assumption agrees with worst etchability in this place and highest micro-hardness.

A different problem is how to explain very low concentration of nitrogen in the layer in first 90 µm. The answer to this question could be seen in high affinity of niobium to create nitrocarbides as instrument to get equilbrium. The content of nitrogen in carbonitriding layers is much smaller then carbon content. So if we expect that the content in at. % of carbon and nitrogen in nitrocarbides is the same than there is deficiency of nitrogen to create carbonitrides. Atomic content of nitrogen and carbon at point 100 µm is very similar so the deficiency against usual conditions could be balanced by transport of nitrogen from surface layer to place of deficiency at point 100 µm. This theory would also agree with decrease of carbon content. In this time, there is missing bulletproof evidence of this theory. The layers of niobium carbide and carbonitride are used in tool steels for increasing their tribological properties so understanding of mutual influences between niobium, carbon and nitrogen could have potential interesting for progress in this field.

REFERENCES
