Cryogenic Treatment and Combination of Nitriding and Cryogenic Treatment of Hot Forging Tools

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Abstract: - This paper deals with cryogenic treatment and cryogenic treatment combined with nitriding of hot working tool steels. Unlike traditional steel cold treatment generally conducted at the temperatures of about -70°C for several hours, cryogenic treatment at the temperature of about minus -180°C for several dozen hours was performed. Basing on a dilatometric and differential thermal analysis (DTA) the authors made an attempt to explain the process of changes resulting from cryogenic treatment. In addition, the authors, basing on test results, discussed comparatively the effect of cryogenic treatment on the resistance to wear at high temperatures and on the hot working tool steel hardness. The presented results confirm the rise of material durability of drop forging dies after cryogenic treatment or nitriding combined with cryogenic treatment.

Key-Words: - Cryogenic Treatment, Nitriding, Tool Steels, Resistance to Wear

1 Introduction
This paper presents selected researches conducted within the schedule of the European Project Eureka “Advanced Heat Treatment Processing and Surface Engineering of Forming Tools”, No. E! 3030, acronym "FORMING TOOLS". The goal of this study is: the extension of the tool life for specific forming technologies by appropriate selection of materials as well as by optimisation of the tool design and process parameters. From heat treatment methods and thermo-chemical methods as the subject of the study under the said project, the technology of cryogenic treatment and combination of cryogenic treatment with nitriding are presented.

Under this project four tool steel grades were chosen for the study: X38CrMoV5-1, 55NiCrMoV6 and Swedish steel grades Uddeholm HOTVAR and Uddeholm QRO 90 Supreme.

Traditional cold treatment carried out usually at about -70°C for several hours is a process aimed at achieving better mechanical and processing qualities such as hardness or dimensional stability of parts made of steel. Unlike short-term cold treatment, long-term cryogenic treatment is carried out at lower temperatures within the range of -175°C to -196°C for a longer time from several hours to several dozen hours, even up to one hundred hours. This kind of treatment apart from identical effects as in the event of traditional cold treatment is also accompanied by crystallographic and microstructural changes thanks to which as a result of tempering process carried out after cryogenic treatment in the steel microstructure very fine carbide precipitations occur. These precipitations affect both the material strength and its wear resistance [1-6]. The chief convenience of this kind of treatment in contrast to surface treatment, such as nitriding, is the occurrence of changes within the entire structure of the material.

Nitriding of hot forming tools is the processing universally known and used. Combining tool nitriding with cryogenic treatment is the issue for research.

2 Methods of Study
Of steel grades tested under the Eureka Project E! 3030 laboratory samples were made of shapes and dimensions appropriate for the conducted research. All samples were subjected to basic heat treatment consisting in hardening and single high tempering in order to achieve the required hardness. Heat treatment parameters are shown in Table 1.

Toughened samples were then subjected to further versions of cryogenic treatment and/or to thermo-chemical treatment as follows:
- cryogenic treatment;
- nitriding;
- cryogenic treatment + nitriding;
- nitriding + cryogenic treatment.

The comparative test results for the samples processed according to the above methods were compared with those for samples after toughening (without additional processing). Researches comprised among other things surface hardness measurements - HV1 and HV5 determination of the microhardness profile HV0,1 on the
Table 1. Parameters of hardening and tempering of specimens made of tool steels

<table>
<thead>
<tr>
<th>#</th>
<th>Steel grade</th>
<th>Process parameters</th>
</tr>
</thead>
</table>
| 1 | X38CrMoV5-1 to DIN 17350/1980 (equivalent ČSN 419552-69) | • preheating: 600°C – 20 min.,  
• austenitising: 1050°C – 60 min.,  
• cooling – oil,  
• single tempering: 525°C – 2 hours. |
| 2 | 55NiCrMoV6 to DIN 17350/1980 | • preheating: 550°C – 20 min.,  
• austenitising: 860°C – 60 min.,  
• cooling – oil,  
• single tempering: 525°C – 2 hours. |
| 3 | HOTVAR (prod. Uddeholm) | • preheating: 600°C – 20 min.,  
• austenitising: 1070°C – 60 min.,  
• cooling – oil,  
• single tempering: 550°C – 2 hours. |
| 4 | QRO 90 Supreme (prod. Uddeholm) | • preheating: 600°C – 20 min.,  
• austenitising: 1050°C – 60 min.,  
• cooling – oil,  
• single tempering: 600°C – 2 hours. |

cross-section of the material surface layer and determination of the wear resistance at high temperatures.

Wear resistance tests were conducted with T-21 tester with ball-disc combination, at the temperature of 600°C, at the sliding velocity \( v = 0.1 \text{ m/s} \) and contact load of 10 N. As counter sample (ball) a ball from ŁH15 ball bearing was used. After performed tests with HOMMEL T-2000 profilograph profiles of sample wear were investigated.

In order to explain structural changes occurring in examined steel grades resulting from cryogenic treatment and the following tempering dilatometric and differential thermal analyses were made.

In addition in parallel with experimental investigations a set of forging dies for hot working was subjected to cryogenic treatment (Fig.6) and one set was nitrided and treated cryogenically (Fig.5). Processed tools were next given to manufacturers for a comparative work life evaluation under manufacturing process conditions.

3 Cryogenic Treatment

The impact of cryogenic treatment on martensitic transformation, stress relaxation and dimensional stabilisation of steel is obvious and unquestionable, as a rule this impact is identical with that of cold treatment, however, in some cases with a possibly greater efficiency due to lower process temperature. Other mechanisms ascribed to the impact of the cryogenic treatment on steel and other materials are not commonly accepted [9].

The best documented cryogenic treatment mechanism affecting steel, other than causing the transformation austenite-to-martensite, is the precipitation of strengthening phases, in particular the carbide phase. In work [1] the precipitation of very fine carbides in martensite resulting from having it treated cryogenically for a long time was named “low temperature conditioning of martensite”. According to [1] long-term low temperature effect can lead to instability of martensite consisting in slow contraction of its lattice, migration of dislocations and generation of carbon atom clusters, which during tempering following after cryogenic treatment turn into nuclei of precipitations of very fine carbides. This mechanism unlike transformation of residual austenite into martensite is not accompanied by hardness growth; however, it can result in the increase of other steel properties, in first line, in growth of the resistance to wear due to friction.

Table 2. Conditions of a cryogenic treatment with single tempering.

<table>
<thead>
<tr>
<th>Process</th>
<th>Process stage</th>
<th>Treatment time [h]</th>
<th>Cooling / warming rate [°C/min]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Below ambient temp.</td>
<td>freezing (20°C → -180°C)</td>
<td>6,4</td>
<td>0,5</td>
</tr>
<tr>
<td></td>
<td>soaking (-180°C)</td>
<td>32,0</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>defreezing (-180°C → 20°C)</td>
<td>9,3</td>
<td>0,35</td>
</tr>
<tr>
<td>Above ambient temp.</td>
<td>warming (20 °C → 350°C)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>tempering (350°C)</td>
<td>2</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>cooling (350°C → 20°C)</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
The process of cryogenic treatment was conducted at IMP, in CRYOTEMPER™ processor, to schedule presented in table 2.

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<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>tempering (350°C)</td>
<td>2</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>cooling (350°C → 20°C)</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

3.1 Wear Resistance Examination

The research conducted in a tester of the ball-on-disc type enabled quantitative evaluation of the wear resistance of heat-treated material surface layers. The evaluation of the wear resistance at high temperatures was based on measurements of friction traces on the surface of samples with the aid of a profilograph. Basing on these measurements the volume of material removed due to friction was calculated and with the relation (1) the surface layer wear rate (factor) was determined:

\[ W = \frac{V}{N \cdot s} \left[ \frac{mm^3}{N \cdot m} \right] \]  

where:
\( W \) - surface wear factor;
\( V \) - worn (removed) layer volume [mm³];
\( N \) - load [N];
\( s \) - friction path length [m].

Fig. 1 shows wear factors obtained for quenched and tempered X38CrMoV5-1 and 55NiCrMoV6 steel samples compared to factors obtained for samples subjected additionally to cryogenic treatment followed by single tempering. The results clearly point to a significantly higher wear resistance of the X38CrMoV5-1 steel, which was cryogenically treated (Fig.1a). Lower wear was also noted for the 55NiCrMoV6 steel grade, however, it was not so substantial as for the X38CrMoV5-1 steel.

![Fig. 1. Wear rates for the X38CrMoV5-1 (a) and 55NiCrMoV6 (b) tool steel, both with and without a cryogenic treatment.](image)

![Fig. 2. Wear rates for HOTVAR and QRO 90 Supreme tool steel, both with and without a cryogenic treatment](image)

Fig. 2 presents the results obtained from a similar test carried out in the Czech Republic by the project partner [11] under identical conditions, however, unlike in the test described above, instead of a steel ball a ceramic ball of \( Si_3N_4 \) was used. Wear indicators obtained for
HOTVAR and QRO 90 Supreme steel grades, which were heat-treated and additionally cryogenically treated over a significantly shorter time of 8 hours and next tempered, are visible there. Substantially lower impact on the augmentation of tribologic properties of tool steel after this ‘shorter version’ of cryogenic treatment, confirms the authors’ observations of the greater efficiency of cryogenic treatment of longer soaking time at -180°C. These results can be the proof that the mechanism of improving wear resistance is of isothermal character, which is confirmed by results available from other authors [7].

3.2 Dilatometric And Differential Thermal Analysis (DTA)

In researching the process of steel tempering, at present the DTA and DSC dilatometric methods are prevalingly used. These methods were used to compare tempering processes immediately after hardening or after hardening and cryogenic treatment at temperatures close to that of liquid nitrogen.

The results of dilatometric tests on tool steels showed that cryogenic treatment, directly after hardening, caused the temperature of the first shrinking during continuous warming after hardening to drop. The value of the shrinkage rose also significantly for all other steels. The practice of dilatometric examinations so far shows that the drop of temperature at the beginning of shrinking and the increase of this shrinkage occurred when the carbon contents in austenite and consequently in martensite was significantly higher. Also then most often at low tempering temperatures instead of the ε carbide the η carbide occurs [8]. Because during dilatometric examination the conditions of austenitising of samples subjected after quenching to cryogenic treatment, or not cryogenically treated, were the same, one can surmise that cryogenic treatment affects martensite in a similar way as the raising of the carbon contents in it. Hence one should assume that cryogenic treatment caused the η carbide to precipitate instead of the ε form. Example micrograph of carbide precipitations in a specimen treated cryogenically is shown in Fig. 3.

Establishing the conditions for specific carbon atoms arrangement within the martensite lattice is the prerequisite for the η carbide precipitation. A sub-lattice of carbon atoms situated in the middle of octahedral gaps between carbon atoms in martensite is then generated. Such a lattice does not arise during the ε carbide precipitation [8]. The η carbide precipitation causes larger dispersion of precipitates, hence a higher resistance to carbide spalling and in consequence a higher wear resistance [1-7]. The DTA examination after cryogenic treatment has shown an endothermic effect due to the residual austenite transformation, therefore a minor sample elongation growth during isochronous tempering of hardened and cryogenically treated samples was confirmed. This proves the presence of small amounts of residual austenite, which enhances the impact strength of the material processed in such manner.

One should assume the reasons for heightened steel parameters after cryogenic treatment are the following:
- martensite generated during cryogenic treatment behaving during tempering like high carbon martensite and increasing the product hardness,
- there remained, despite cryogenic treatment, a small amount of residual stable austenite which increases the product impact resistance,
- amount of very small and uniformly distributed carbides precipitated during tempering greater than during traditional treatment. These carbides spall with greater difficulty during work and enhance the abrasive wear resistance under load.

Fig. 3. TEM micrograph of X38CrMoV5-1 tool steel after cryogenic treatment and tempering.
Combination of Nitriding and Cryogenic Treatment

The samples were nitrited both before and after cryogenic treatment in Nitrex Metal Inc. nitriding furnace. The parameters of the three-stage gas nitriding were selected basing on long-term processing practical experience at IMP.

Table 3. Schedule of a nitriding process.

<table>
<thead>
<tr>
<th>Process stage</th>
<th>Temp. [°C]</th>
<th>Treatment time [h]</th>
<th>Atmosphere</th>
<th>Composition</th>
<th>$N_p$ (^{(1)})</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>480</td>
<td>1</td>
<td></td>
<td>100% NH(_3)</td>
<td>40-60</td>
</tr>
<tr>
<td>II</td>
<td>510</td>
<td>2</td>
<td></td>
<td>80% + 20% N(_2)</td>
<td>15-20</td>
</tr>
<tr>
<td>III</td>
<td>510</td>
<td>17</td>
<td></td>
<td>20% + 80% (N(_2) + 3H(_2))</td>
<td>0.3-0.5</td>
</tr>
</tbody>
</table>

\(^{(1)}\) nitrogen potential - $N_p = \frac{p_{NH_3}}{p_{H_2}}^{2/3}$

The applied cryogenic treatment process parameters and those of the following tempering were identical as these for samples solely subjected to cryogenic treatment (Table 2).

4.1 Hardness Tests

Fig. 4 presents average surface hardness values HV5 with 95% confidence intervals obtained for samples subjected to various processing schemes.

By comparison of results obtained for X38CrMoV5-1 steel samples heat-treated and additionally subjected to cryogenic treatment followed by tempering, hardness drop can be observed. This drop is but insignificant and falls within statistical error. Much more interesting are the results obtained for samples, which underwent combined processing of nitriding and cryogenic treatment, since the surface hardness of samples cryogenically treated and tempered and then nitrated is much higher than the hardness of samples subjected only to nitriding or also cryogenically treated after this process.

Similar relations between applied processing versions were observed for the microhardness distribution on the layer cross-section (Fig.5).

In case of a version being a combination of cryogenic treatment followed by nitriding, surprisingly high hardness was achieved at greater depth from surface; these changes occurred also for the HOTVAR and QRO 90 Supreme steel. The process of cryogenic treatment carried out prior to nitriding and structural transformations associated with this process seem to facilitate the process of diffusion nitriding, thus affecting both the depth and the hardness of the internal nitrogen-hardening zone.

![Image of Fig. 4](image-url)

Fig.4. Averages and 95-% confidence intervals of surface hardness HV5 of X38CrMoV5-1 tool steel specimens after hardening and tempering and after various types of additional treatment.

![Image of Fig. 5](image-url)

Fig.5. Microhardness profiles of X38CrMoV5-1 tool steel specimens after hardening and tempering and after various types of additional treatment.
5 Examination of Dies Under Production Conditions
To confirm the advantageous production work properties obtained for the process versions under investigation, i.e. of the cryogenic treatment and combined ammonia nitriding and cryogenic treatment on dies received from manufacturers and presented in Fig. 6 and 7, the above-mentioned trial processes were conducted. Heat treatment parameters for heat treatment on dies made of the 55NiCrMoV6 and X38CrMoV5-1 steel are presented in Table 4.

 Dies made of the 55NiCrMoV6 steel (Fig.5) received for production trials were mounted in a hammer MPM 1600 HZ seat at the dynamic pressure of 160 T/cm². The dies were heated up to 300°C. The material used for forgings was the RPSi37-2 steel. The forging temperature ranged between 1050°C and 1150°C. The average production life of the same forging dies toughened at manufacturer’s plant was about 5500 pieces. Dies processed according to the process version (Table 4) were capable of forging 6500 pieces and after a minor regeneration are still capable of using them again.

In manufacturer’s opinion, during the forging the material flew without reservations and the forgings were completely filled. Dies shown in Fig. 6, which were heat-treated according to the b version of the process (Table 4), were examined under production condition by the Czech manufacturer. The user determined the life extension of a die in relation to the so-far applied method of quenching and tempering at approximately 40 %.

6. Conclusions
1. Cryogenic treatment is a process which, compared to steel being quenched and tempered, significantly increases the wear resistance of hot work alloy tool steel. This is confirmed by tribologic tests carried out at elevated temperatures. The achieved growth of the wear resistance depends on the steel grade and on the soaking time of the processed part at the temperature close to that of liquid nitrogen.

2. Due to dilatometric and differential thermal analyses it was possible to state that the reason for a tool steel wear resistance growth are precipitation phenomena taking place during tempering following cryogenic treatment, as at this processing stage a significant

Table 4. Heat treatment parameters of drop forging dies made of the 55NiCrMoV6 and X38CrMoV5-1 steel.

<table>
<thead>
<tr>
<th>Version</th>
<th>Steel grade</th>
<th>Treatment version</th>
<th>Treatment parameters</th>
<th>Hardness after treatment</th>
<th>Die life extension</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>55NiCrMoV6</td>
<td>Toughening + nitriding + deep cryogenic treatment</td>
<td>• preheating 650°C - 2.5 h, • austenitising 860°C - 2 h, • cooling – oil; • tempering 520°C - 3 h, • nitriding, • cryogenic treatment -180°C - 32 h, • tempering 350°C - 3 h.</td>
<td>710 HV</td>
<td>ca. 20%</td>
</tr>
<tr>
<td>b</td>
<td>X38CrMoV5-1</td>
<td>Toughening + deep cryogenic treatment</td>
<td>• heat treatment, • cryogenic treatment -180°C - 32 h, • tempering 350°C - 3 h.</td>
<td>42 HRC</td>
<td>ca. 40%</td>
</tr>
</tbody>
</table>
amount of very fine and uniformly distributed carbides precipitates; carbides which during work of a tool spall with more difficulty and increase its friction wear resistance under overloads.

3. The phenomenon of significant growth of both the surface hardness and of the depth of internal nitriding and of the hardness measured on the cross-section of nitrated layers achieved for tool steel, which has been subject before to long-term cryogenic treatment, was observed.

4. Comparative research under production conditions of forging dies subjected to toughening and cryogenic treatment and to the combined process of nitriding and cryogenic treatment have demonstrated a wear resistance growth by 20 to 40% as compared to the heat treatment of dies so far applied by manufacturers.

5. In order to better understand the structural transformation taking place inside the internal nitriding zone, the problem of the hardness growth of nitried layers achieved by combining this treatment with cryogenic treatment must be further researched into.

References: