Wear Resistant Tool Steels with Niobium Carbide Dispersions

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Introduction: Niobium in Steels

Undissolved Carbides and Wear Resistance

Carbide Formation: NbC Size Considerations

Examples of NbC Containing Cold Work and High Speed Steels
Main Roles of Niobium in Steels

- Grain refinement and precipitation hardening of low and medium alloyed steels through thermomechanical rolling.

![Diagram showing the precipitation of niobium carbonitrides in steels.](image-url)
Main Roles of Niobium in Steels

- Grain refinement and precipitation hardening of low and medium alloyed steels through thermomechanical rolling.

- Control of austenite grain growth during hardening, by pinning effect.

Comparison of austenite grain size after hardening in different temperatures. The typical forging temperatures for the balls is highlighted, showing that the grain size for the Nb and V compositions is very different. Adapted from reference: RA Mesquita, CA Barbosa. Effect of Ti, Nb and V on the austenite grain growth of a hot work tool steel. Tecnologia em Metalurgia e Materiais, v. 1, pp. 7-12, 2005.
Main Roles of Niobium in Steels

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- Stabilization of C effect in bake hardening, IF or stainless steels

\[
\begin{align*}
\text{Niobium and Titanium} \\
T_{\text{stabilize}} &= 3.42N + 1.5S \\
N_{\text{stabilize}} &= 7.74C \\
\text{stabilization of nitrogen and carbon via precipitation reactions will be determined by thermomechanical processing on the hot strip mill and during annealing.} \\
\text{care should be taken when selecting annealing cycles as to avoid carbide dissolution}
\end{align*}
\]
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- Formation of carbides, promoting wear resistance

Commercial High Speed Steel, with NbC dispersions:
1%C 1%Nb 2%Mo 2%W 1%V
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Strong Ability of Niobium to Form Carbides

Figure 1: Examples of NbC sizes and their main application in steels: a) with a few nanometers, to promote precipitation hardening and mainly grain refinement of thermomechanically processed microalloyed steels; b) with sizes around 50 nm, stabilizing the dissolved carbon (in BH, IF or stainless steels) or pinning the grain growth during hardening of heat treatable steels; c) with several microns size, used to promote wear and abrasion resistance. Observe that in c the scale bar is in micrometer, while the others are in nanometers. References: [10] for items a and b, and [11] for c.
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Classic Approach of Carbides and Wear Resistance

Key: Hard Matrix + Good Distribution of High Hardness

Examples:

# Carbides in Tool Steels: Hardness

## TABLE 5.2
Data for Undissolved Carbides Typically Found in Cold Work Tool Steels

<table>
<thead>
<tr>
<th>Phase</th>
<th>Rich in</th>
<th>Pure Carbid</th>
<th>Crystallographic System</th>
<th>Lattice Parameters (Reference)</th>
<th>Hardness (Reference)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MC</td>
<td>Nb</td>
<td>NbC</td>
<td>Face centered cubic</td>
<td>$a = 4.47 \text{ Å} [37]$</td>
<td>2300 HV [44]</td>
</tr>
<tr>
<td>MC</td>
<td>V</td>
<td>$V_4C_3$</td>
<td>Cubic</td>
<td>$a = 4.16 \text{ Å} [38]$</td>
<td>2000 HV [45]</td>
</tr>
<tr>
<td>$M_2C$</td>
<td>Mo</td>
<td>$Mo_2C$</td>
<td>Hexagonal</td>
<td>$a = 3.01 \text{ Å}; c = 4.74\text{ Å} [39]$</td>
<td>1800 HV [46]</td>
</tr>
<tr>
<td>$M_6C$</td>
<td>W or Mo</td>
<td>$Fe_3Mo_3C$</td>
<td>Cubic</td>
<td>$a = 11.12 \text{ Å} [40]$</td>
<td>1500 HV [47]</td>
</tr>
<tr>
<td>$M_2C3$</td>
<td>Cr</td>
<td>$Cr_7C_3$</td>
<td>Hexagonal</td>
<td>$a = 13.9 \text{ Å}; c = 4.52\text{ Å} [41]$</td>
<td>1600 HV [48]</td>
</tr>
<tr>
<td>$M_3C$</td>
<td>Fe</td>
<td>$Fe_3C$</td>
<td>Orthorhombic</td>
<td>$a = 5.06 \text{ Å}; b = 6.74\text{ Å}; c = 4.50 \text{ Å} [42]$</td>
<td>1100 HV [49]</td>
</tr>
<tr>
<td>Martensite</td>
<td>0.8%C steel</td>
<td>—</td>
<td>Tetragonal</td>
<td>$a = 2.85 \text{ Å}; c = 2.95\text{ Å} [43]$</td>
<td>900 HV (65 HRC)</td>
</tr>
</tbody>
</table>

*Note:* References shown by each of the data.

Carbides in Tool Steels: Stability

**NbC**: highly stable, due to the very strong chemical attraction between C and N.
**NbC**: lower alloy content is necessary to form 1 vol% in a tool steel microstructure based on solubility data and results from high speed steels (for W and Mo, \(M_6C\) carbide) and cold work steels (for Cr, \(M_7C_3\) carbide), from ref. [13], considering austenitizing at 1200°C (which is typical for reheating temperatures for forging or rolling). All carbides according to stoichiometry of Fig. 3a. all.
Carbides in Tool Steels: Inter-dissolution of Alloy Elements

**NbC:** dissolve small amounts of Mo, W and V

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*Figure 5: Mapping of elements in two different high speed steels: a) the traditional composition of M2 (0.9%C, 2%V, 5%Mo, 6%W) and a modified Nb high speed steel (1.1%C, 2%V, 3%Mo, 3%W, 1.8%Nb). Observe that the Nb-rich carbides (point by arrow) tend not have other alloy elements. See text for explanation. From Ref. [15].*
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Formation of Carbides in High Carbon High Alloy Tool

SEQUENCE OF SOLIDIFICATION
1- Delta ferrite from liquid: $L \rightarrow \delta$
2- Peritectic reaction: $L + \delta \rightarrow \gamma$
3- MC precipitates directly form Liquid: $L \rightarrow$ MC
4- End of solidification, with eutectic of carbide + austenite: $L \rightarrow M_2C + \gamma$ or $L \rightarrow M_6 + \gamma$

Critical for Final MC Size

Pseudo-binary diagram for M2 high speed steel.
Primary MC Carbides, V or Nb-rich

High V or High Nb steels: carbides will be eutectic or primary, which is determined by the solidification interval.

Content of V or Nb is the first factor determining the presence and size of primary MC:

M3:2 high speed steel (1.2%C 4%Cr 3%V 5%Mo 6%W).
Control of MC Primary in Nb-rich MC

1. Nb Content (previous slide): between 1 and 2%, for 1% C
2. Control of Nitrogen: < 120 ppm N
3. Additions of Cerium: 500 ppm
Innovate, Respect, Compete

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Examples of NbC Containing Tool Steels

Table 1: Example of tool steels with addition of Nb to form undissolved hard carbides. The literature source for each one is presented in the table. All composition in wt.%.

<table>
<thead>
<tr>
<th>Designation</th>
<th>C</th>
<th>Cr</th>
<th>Nb</th>
<th>Others</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Modified D3</td>
<td>2.2</td>
<td>19</td>
<td>2.0</td>
<td>0.5Mo</td>
<td>[18]</td>
</tr>
<tr>
<td>8%Cr</td>
<td>0.9</td>
<td>8.0</td>
<td>0.15</td>
<td>2Mo 0.5V 1Si</td>
<td>[19,20]</td>
</tr>
<tr>
<td>Nb mod HSS</td>
<td>0.9</td>
<td>4.0</td>
<td>1.2</td>
<td>2Mo 2W 1V</td>
<td>[21]</td>
</tr>
</tbody>
</table>

Example 1: Modified D3 Cold Work Steel

<table>
<thead>
<tr>
<th>Type of test material</th>
<th>Material loss</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nr. 1A: 19.5% Cr 1.9% V</td>
<td>650 mg</td>
</tr>
<tr>
<td>Nr. 1B: 19.5% Cr 4.0% V</td>
<td>320 mg</td>
</tr>
<tr>
<td>Nr. 2A: 19.2% Cr 2.0% Nb</td>
<td>200 mg</td>
</tr>
<tr>
<td>Nr. 2B: 19.2% Cr 4.0% Nb</td>
<td>– 14 g (weight increase)</td>
</tr>
</tbody>
</table>

Figure 8: a) Increase in abrasive wear resistance of traditional high Cr high C cold work tool steels, after the addition of Nb. b) NbC carbides (lighter) and Cr-rich M₇C₃ carbides (darker) formed in the same microstructure. From reference [18]

Comment: strong increase in abrasive wear resistance, which may be a solution for pure abrasive tooling applications, such as shaping of refractory bricks. The same reference studied the possibility of V in forming the same carbides, but it was found that V tends to dissolve in the M₇C₃ carbides and then not form the own carbides of MC type.
Example 2: 8%Cr Cold Work Tool Steel

Comment: 8%Cr better toughness is directly dependent on the reduction of the Cr-rich M7C3 carbides, as shown in Fig. 9b and Fig. 9c. However, in order to not compromise the wear resistance, the addition of small contents of Nb is often applied in 8%Cr cold work tool steels, leading to carbides that are finer and harder than the M7C3 carbides.
Example 3: Low Alloy High Speed Steel

Figure 10: Results from semi-high speed steel modified with Nb (see composition in Table 1). a) graphic representation of the reduction in alloying elements. b) performance results, comparing to other standard semi-high speed steels. c) dispersion of NbC carbides in the microstructure of this new Nb-alloyed high speed steel, showing a fine dispersion of particles. From ref. [21] and [11].

Comment: The composition developed with this concept, according to reference [21], shows however that NbC, with the advantage of low solubility, may replace completely the role of the undissolved carbides of Mo, W or V, and these last three elements may then used only for the precipitation hardening
OVERAL CONCLUSIONS

✓ Niobium has different roles in steels, but the ability to form hard and stable carbides may be used in wear resistant tool steels, for cold work or high speed tool steels.

✓ When compared to other carbides, NbC is harder and also less soluble, enabling formation of undissolved carbides even for small added contents.

✓ Other elements do not dissolve in large extent in NbC and Nb also does not dissolve in other carbides than the MC type. This brings a unique role of Nb to form NbC carbides without interfering with the role of other alloying elements in the matrix hardening of tool steels.

✓ The control of the sizes of primary MC may be done by tuning or optimizing the Nb Content, with i) Nb content not exceeding 2% and in most cases less than 1.5%. Additional control of carbide growth may be done by ii) reducing the amount of free nitrogen, by overall nitrogen reduction or addition of rare earth elements.

✓ The examples of properly designed Nb-containing tool steels show that the formed NbC carbides, due to the high hardness, may be used to contribute in increasing the wear resistance. In some cases, this advantage may lead to reduction of other alloying elements, Cr, Mo, W or V, leading to an increase in toughness or cost advantages.

✓ Niobium may thus be considered as a potential alloy element for new or modified tool steels for wear resistant applications.
Thank you very much for your attention!

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