Properties of selected materials with non-stoichiometric compounds used for wear-resistant coatings

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In the article were presented the considerations concerning influence of fill ratio of interstitial positions by nitrogen or carbon on technological and functional properties of transient metals of from IVb to VIb groups. Instead of literature data were presented results of own comparative investigations of durability of cutting edges coated with nitrides of transient metals with stoichiometric and non-stoichiometric compounds.

KEYWORDS: wear-resistant coatings, cutting edges, homogeneous range

Introduction

Transition metal nitrides and carbides forming high-melting materials attract much interest due to the possibility of their use on wear-resistant coatings applied on cutting edges [1–8,10–14]. Thanks to its mechanical properties transition metal nitrides and carbides from IVb to VIb group, they are best suited to supporting compressive stress, but they are characterised by high sensitivity to bending and torsional stresses (table I). Most importantly, however, are characterized by high hardness, which has an important impact on their high resistance against abrasive wear.

| TABLE I. Mechanical properties of transition metal nitrides and carbides from groups IVb–VIb [3, 6, 9, 12] |
| --- |
| Carbides | $R_m$ [MPa] | $R_c$ [MPa] | $R_g$ [MPa] | Nitrates | $R_m$ [MPa] | $R_c$ [MPa] | $R_g$ [MPa] |
| TiC | 65 | 1380 | 15 | TiN | – | 1298 | 240 |
| ZrC | 76 | 834 | 75.1 | ZrN | – | 1000 | – |
| HfC | – | – | – | HfN | – | – | – |
| VC | – | 620 | 70 | VN | – | – | – |
| NbC | 67 | 2423 | 70 | NbN | 15.3 | – | – |
| TaC | – | – | – | TaN | – | – | – |
| Cr$_3$C$_2$ | 50 | 1048 | 70 | CrN | – | – | – |
| MoC | – | – | – | MoN | – | – | – |
| WC | 350 | 3600 | 350 | WN | – | – | – |

$R_m$ – tensile strength $R_c$ – compressive strength $R_g$ – bending strength

Thanks to metallic-covalent bonds, those compounds, in most cases, combines high hardness and resistance to brittle fracture - a significantly higher compared to compounds with covalent bonds, in particular ionic.

In the table II and III provides data on physical properties selected transition metal nitrides and carbides. It must however be emphasized that this compounds depending on their degree of interstitial sites filling by nitrogen or carbon for specific stoichiometry can be characterised by other properties than compounds with stochiometric composition [5,6,9]. Below presents considerations regarding this issue.
TABLE II. Selected properties of transition metal carbides from groups IVb–VIb [3, 6, 9, 12, 13]

| Element | Transition group | Compound | Hardness HV [GPa] | Young Modulus [GPa] | Poisson’s ratio |
|---------|------------------|----------|-------------------|---------------------|----------------|
| Ti      | IV               | TiC      | 31.7÷32           | 322÷460             | 0.19           |
| Zr      | IV               | ZrC      | 25.6÷29.5         | 355÷380             | 0.19           |
| Hf      | IV               | HfC      | 27÷28.3           | 350÷461             | 0.18           |
| V       | V                | VC       | 20.1÷27.6         | 430÷434             | –              |
|         |                  | V2C      | 28                | –                   | –              |
| Nb      | V                | NbC      | 19.5÷27           | 276÷345             | 0.22           |
|         |                  | Nb2C     | 19.2÷23.2         | –                   | –              |
| Ta      | V                | TaC      | 17.4              | 440                 | –              |
|         |                  | Ta2C     | 17.2              | 291                 | 0.24           |
| Cr      | VI               | Cr3C2    | 12.7÷20           | 380÷400             | –              |
|         |                  | Cr7C3    | 18.8÷22           | 350÷380             | –              |
| Mo      | VI               | MoC      | 15                | –                   | –              |
|         |                  | Mo2C     | 17.6              | 544                 | –              |
| W       | VI               | WC       | 23÷23.5           | 700÷710             | 0.19           |
|         |                  | W2C      | 20÷29.4           | 428                 | –              |

TABLE III. Selected properties of transition metal nitrides from groups IVb–VIb [3, 6, 9, 12, 13]

| Element | Transition group | Compound | Hardness HV [GPa] | Young Modulus [GPa] | Poisson’s ratio |
|---------|------------------|----------|-------------------|---------------------|----------------|
| Ti      | IV               | TiN      | 21÷28             | 256÷590             | 0.25           |
| Zr      | IV               | ZrN      | 16÷20             | 400                 | 0.24           |
| Hf      | IV               | HfN      | 15÷20             | 333÷480             | 0.28           |
| V       | V                | VN       | 15.6              | –                   | 0.25           |
| Nb      | V                | NbN      | 14.6              | 493                 | 0.26           |
|         |                  | Nb2N     | 17.2÷21.2         | –                   | –              |
| Ta      | V                | TaN      | 13÷32.4           | 576                 | 0.25           |
|         |                  | Ta2N     | 12.2÷30           | –                   | –              |
| Cr      | VI               | CrN      | 10.9÷21           | 310                 | 0.26           |
|         |                  | Cr2N     | 15.4÷25           | 314                 | –              |
| Mo      | VI               | Mo2N     | 6.3               | –                   | –              |
| W       | VI               | W2N      | –                 | –                   | –              |

Areas of homogeneity of transition metal carbides and nitrides

Almost all transition metals have one of the four types of crystal structure: regular - plane or centered cubic or hexagonal or hexagonal close packed. Transition metal reactions from groups IVb–VIb with free nitrogen or carbon, taking place already below melting temperature lead to formation of carbides and nitrides. During those compounds creation carbon or nitrogen atoms occupy the so called interstitial sites [5,6,9]. The four basic structure types of transition metal with available sites indication for the location of nitrogen or carbon (marked points) are presented in fig. 1. Compounds, in which nitrogen occupy these sites are named interstitial nitrides. They are created when ratio of nitrogen atomic radius to transition metals is lower than 0.59. This rule is referred to Hägga condition [9]:
Fig. 1. Crystal structures of transition metals: a) regular space-centered, b) regular wall-centered, c) hexagonal, d) compact hexagonal [5,6,9]

Interstitial compound formed in this way can have different structure than output metal, and this is one of structure types shown in fig. 1. The positions available for nitrogen or carbon can be occupied in whole or in part. Several types of nitrides and interstitial carbides are known. If nitrogen or carbon takes all interstitial sites, nitride has a composition MN and carbide MC. In case of the half of the interstitial sites is filled arises M$_2$N or M$_2$C, and if third part of interstitial sites is filled - M$_3$N or M$_3$C [6,9].

Almost all interstitial nitrides have areas of homogeneity, which means that compound retain their crystalline structure - despite changes of elemental composition - within a defined scope [3,6,9,12]. In the table IV are shown figures related to homogeneity range of transition metal mononitrides and monocarbides expressed as a percent of N and C atoms and by mass. In the table V provides data on homogeneity range not listed in the table IV transition metal carbides and nitrides.

Areas of homogeneity of transition metal carbides and nitrides expressed as a percent of C atoms are shown in fig. 2, and - areas of homogeneity of transition metal carbides and nitrides expressed as a percent of N are shown in fig. 3.

Indicated gaps in interstitial sites filling prove nitrogen or carbon deficiencies in relation to compound with stochiometric composition. In these compounds are not filled all interstitial sites permitted for specific stoichiometry.

### TABLE IV. Areas of homogeneity of transition metal monocarbides and mononitrides from groups IVb–Vlb [3, 6, 9, 12]

| Carbide | Homogeneity areas | Nitride | Homogeneity areas |
|---------|-------------------|---------|-------------------|
|         | % atoms of N      | % weight| % atoms of C       | % weight |
| TiC     | 32÷48.8           | 11÷20   | TiN               | 29÷52    | 14.9÷22.6 |
| ZrC     | 37.5÷49.4         | 6.6÷11.6| ZrN               | 35÷50    | 7.6÷13.3  |
| HfC     | 37.5÷49.5         | 3.8÷6.3 | HfN               | 42÷52    | 5.4÷7.85  |
| VC      | 41÷47             | 14.7÷17 | VN                | 42÷50    | 16÷21.6   |
| NbC     | 30÷49             | 8.6÷11.5| NbN               | 47÷49    | 13.1÷13.3 |
| TaC     | 36÷49             | 3.1÷3.2 | TaN               | 50       | 5.8÷6.5   |
| Cr      | -                 | -       | CrN               | 50       | 11.8      |
| MoC     | 39÷41             | 7.4÷8.6 | MoN               | 50       | 6.4 ÷ 6.7 |
| WC      | -                 | 2.54÷3.2| WN                | 50       | -         |
TABLE V. Areas of homogeneity of transition metal carbides and nitrides from groups IVb–VIb [3, 6, 9, 12]

| Carbide | Areas of homogeneity | Nitride | Areas of homogeneity |
|---------|----------------------|---------|----------------------|
|         | % atoms of N         |         | % atoms of C         |
| Ti₂C    | 33                   | Ti₃N    | 33                   |
| V₂C     | 33                   | V₂N     | 27±33                |
| Nb₂C    | 33                   | Nb₂N    | 28±33                |
| Ta₂C    | 33                   | Ta₂N    | 29±33                |
| Cr₃C₂   | 33                   | Cr₂N    | 29±33                |
| Mo₂C    | 33                   | Mo₂N    | 29±34                |
| W₂C     | 33                   | W₂N     | 33                   |

Fig. 2. Areas of homogeneity of transition metal carbides from groups IVb–VIb [3,6,9,12]

Fig. 3. Areas of homogeneity of transition metal nitrides of groups IVb–VIb [3,6,9,12]

Comparative tests results

Structure of transition metal nitrides and carbides, discussed above, has a close link with physical characteristics MEX compounds, as shown in the example microhardness measurements (fig.4).
Fig. 4. Change of microhardness of transition metal carbides in the area of homogeneity [3,5,6]

Own research [5,6] confirmed change the properties, incl. titanium nitride microhardness according to the proportion of nitrogen atoms to titanium. Schiller, Holleck and own studies [3,5,10] have been proven that form among transition metals nitrides the widest possible application to manufacture anti-wear coatings on cutting edges might have especially nitrides from group IV with stoichiometric composition, which have the highest hardness and thus, the highest resistance against abrasive wear.

It must however be emphasised that this rule is subject to exceptions. But it is not hardness alone that determines operational properties of coatings on cutting edges. As own research have discovered [5,6], during gear slotting those properties are impacted by some blade load nature during machining. Among tools working in impact conditions, greater durability was showed by more ductile and less hard (more resistant to brittle fracture) coating based on titanium nitride with nitrogen deficiency with respect to stoichiometric composition (table VI). These coatings were manufactured incl. impuls-plasma method developed by Institute of Materials Science and Engineering of the Warsaw University of Technology [7,8,11].

**TABLE VI. Selected examples of the use of TiN coatings with a composition close to stoichiometric (Ti/N = 1.0/0.98) and significantly different from it (Ti/N = 1.0/0.85) with an indication of durability measured by the fold increase average durability compared to uncoated edges [6]**

| Tool dimension | Type of coating | Colour of coating | Workpiece material | Increase of average durability |
|----------------|-----------------|------------------|--------------------|------------------------------|
| module gear shaper cutter SW7M/HS 6-5-2 | NNMb 3/20° | TiN0.85 | silver | 40H/1.7035 | 2.2 |
| | NNMb 2.5/20° | TiN0.98 | gold | 1.6 |
| | TiN0.98 | silver | 2.0 |
| | TiN0.98 | gold | 1.5 |

**Summary**

The studies carried out by the author indicate that there is a need for precise selection of anti-wear coatings on cutting edges, taking account of cutting conditions. Ensuring stoichiometric composition of coat material is not always a sufficient requirement. Transition metal nitrides and carbides from IV group with stoichiometric composition - although they are characterised by the highest hardness, so also high wear resistance - working in impact conditions do not guarantee highest durability. In that case the more important is resistance to brittle fracture [6]. On the other hand, coat material stoichiometric composition is not always related to obtaining the highest composition hardness. In the case of transition metal carbides from Vb-Vlb group their highest hardness exists at reduced carbon contents (from 75% to 85%) with respect to stoichiometric composition. Therefore, it is to be concluded that under abrasive wear conditions of blades during continuous cutting they should have the highest durability.
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