Formation of Mesostructure in WC–Co Cemented Carbides – A review

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Abstract: The author considers potential lines in the formation of mesostructures in cemented carbides, analyzes the existing technologies of the formation thereof, describes physical and mechanical properties of cemented carbides with mesostructure and shows the efficiency of such cemented carbides in metal working and rock destruction tools.

Keywords: Cemented carbide; Hard metal; Structure; Mesostructure

1. Introduction

Cemented carbide has a particular hierarchy of the structure which can be described by five levels: atomic, nano, micro, meso, and macro levels. Most in depth results of researches are obtained at micro level – developed physical and chemical bases of structure formation of WC–Co cemented carbide [1], the theory of strength is created [2], features polymorphic transformations of cobalt binder are investigated [3, 4], the mechanism of origin and development of defects is described [5], high technologies of manufacture cemented carbide products are created. These results of researches are base for development of a new direction of creation of mesostructured WC–Co cemented carbides.

Mesostructured WC–Co cemented carbides include a plenty of materials – metals (Co, Ni, Cu, steels, special alloys, etc.), cemented carbides, for example, WC–Co, WC–Ni, WC–(Ti,W)C–Co, Cr3C2–Ni, mono and polycrystals [6]. Each composition has features of structure formation. In connection with the above stated there was a necessity to make classification mesostructured WC–Co cemented carbides, to analyze the problems arising during formation of these materials, to determine ways of development mesostructured WC–Co cemented carbides, to estimate perspective application areas.

2. Structure of mesocompositions

A mesostructure consists of a random ensemble of mesoelements (granules), which are cemented by metal or composite matrix. The matrix it is possible to consider as a binder phase. The mean sizes of the mesoelements are 20–500 μm, while the thicknesses of the binder phase layers between them are 4–50 μm. The author of the present review divides mesostructured compositions into three types. The first type is the compositions consisting of a metal matrix, for example, Co, Ni, special alloys, and mesoelements formed from cemented...
carbides. The mesoelements, as a rule, are prepared from conventional cemented carbides. The second type includes the compositions consisting of mesoelements and a matrix formed from composite materials. For example, the mesoelement is prepared from WC–6Co cemented carbide and a matrix is formed from WC–20Co cemented carbide or W–Fe–Ni heavy metal, etc. The third type is represented with compositions consisting of mesoelements prepared from a mono or polycrystalline and a matrix prepared from WC–Co cemented carbide, for example, a diamond / WC–Co composition. Diamond particles in the sizes 40–500 μm are located in a WC–Co matrix. The diamond / WC–Co composition contains 15–40 vol.% diamond mesoelements. The matrix consists of WC particles in the sizes 1–5 μm and 10 – 20 vol.% Co binder. In the compositions considered above mesoelements can contact with each other, forming a three dimensional structure, or to be in regular intervals located in a matrix, not having contacts. The structure of a mesocomposition can be described by the methods of stereology on metallographic specimens [7, 8]. These methods define the volume fraction, the specific area, the area fraction, the specific perimeter, the contiguity, the average size \( d_{avg} \) of mesoelements, their volumetric contents \( U \) in a composition, the average distance \( L_{avg} \) between the centres of mesoelements, the average thickness \( l_{avg} \) of the bond layers between mesoelements. To calculate \( d_{avg} \), \( U \), \( L_{avg} \), and \( l_{avg} \), the authors [9] have considered the model of a composition which consists of a matrix with spherical particles randomly distributed in it. By applying the probability–statistical methods of calculation they obtained the relationships

\[
L_{avg} \approx \frac{1.19 d_{avg}}{U^{\frac{1}{3}}}, \quad l_{avg} = L_{avg} - d_{avg} \approx \frac{1.19 - U^{\frac{1}{3}}}{U^{\frac{1}{3}}} d_{avg}.
\]

3. Formation of the mesostructure in cemented carbides

3.1. Features of the formation of the structure in the first type mesocomposition

The author of the present review formed mesoelements from the WC–3Co cemented carbide, then was located them in a cobalt powder and processed hot pressing at 1400°C and holding time of 200 s. It was shown through investigations that at 1400°C the WC–3Co mesoelements intensively imbibed the surrounding cobalt melt and after the 200 s holding the mesoelements in the sizes 100 –200 μm disintegrated completely. It has been found that during the formation of mesostructure in the presence of the liquid phase, the metal melt imbibition phenomenon (MMI) takes place in cemented carbides [10]. The phenomenon lies in the fact that sintered pore free mesoelements imbibe a metal melt from the intergranular space. The driving force for this imbibition is the migration pressure \( \Pi \) [11]. The MMI–phenomenon manifests itself under the conditions where the liquid phase is present both in the mesoelements and in the intergranular space. It was found in [12] that the liquid phase interlayers can be located in the bulk of the composition for some time if their thickness is below a particular size \( d_{cr} \).

\[
d_{cr} = K \left( \frac{u}{S_v} \right) \frac{\frac{1}{3} \gamma_{ls} \cos \Theta}{\gamma_{st} - 2 \gamma_{sl}},
\]

where \( d_{cr} \) is the critical size, below which the liquid interlayer and a composition are in the quasi-equilibrium state and above which the former is unTab., \( K \) is the coefficient which takes into account the geometry of high melting particles and the mode of packing thereof, \( S_v \) is the specific surface of high melting particles, \( u \) is the volume fraction of the liquid phase, \( \gamma_{ls} \), \( \gamma_{st} \) and \( \gamma_{sl} \) are the surface tensions at the contact and phase boundaries (solid—solid,
solid—liquid, liquid—vapor), $\Theta$ is the wetting angle. All the above quantities refer to a mesoelement.

The $d_{cr}$ value can be also found experimentally from the filling of a V-shaped capillary with a metal melt [13]. Tab I lists the values of the critical sizes of interlayers of the liquid phase for the most widely used cemented carbides.

**Tab. I** Critical size of the liquid phase interlayer ($d_{cr}$) in cemented carbides [14]

<table>
<thead>
<tr>
<th>Cemented carbide</th>
<th>Composition, mass %</th>
<th>$u$ at 1640 K</th>
<th>$S_c, \mu m^2/\mu m^3$</th>
<th>$d_{cr}, \mu m$</th>
</tr>
</thead>
<tbody>
<tr>
<td>WC–4Co</td>
<td>3.85 96.15</td>
<td>0.09</td>
<td>2.9</td>
<td>5</td>
</tr>
<tr>
<td>WC–6Co</td>
<td>5.90 94.10</td>
<td>0.14</td>
<td>3.0</td>
<td>6</td>
</tr>
<tr>
<td>WC–6CoF</td>
<td>5.90 94.10</td>
<td>0.14</td>
<td>3.6</td>
<td>5</td>
</tr>
<tr>
<td>WC–6CoC</td>
<td>5.90 94.10</td>
<td>0.14</td>
<td>2.0</td>
<td>10</td>
</tr>
<tr>
<td>WC–8Co</td>
<td>7.80 92.20</td>
<td>0.18</td>
<td>3.0</td>
<td>9</td>
</tr>
<tr>
<td>WC–10Co</td>
<td>9.65 90.35</td>
<td>0.22</td>
<td>2.9</td>
<td>12</td>
</tr>
<tr>
<td>WC–10CoF</td>
<td>10.00 90.00</td>
<td>0.22</td>
<td>4.2</td>
<td>11</td>
</tr>
<tr>
<td>WC–15Co</td>
<td>14.30 85.70</td>
<td>0.31</td>
<td>2.6</td>
<td>15</td>
</tr>
<tr>
<td>WC–20Co</td>
<td>20.10 79.90</td>
<td>0.42</td>
<td>2.9</td>
<td>18</td>
</tr>
</tbody>
</table>

In WC–Co and WC–Ni mesocompositions the average thickness $l_{avg}$ of the bond layers between mesoelements is more than critical size $d_{cr}$, therefore will always take place migration of a liquid phase from intergranular space into the mesoelements.

An alternative way to form mesostructures consists in conducting the sintering process at temperature below the melting temperature of the binder in a mesoelement [6]. For example, the mesoelements 100—200 $\mu m$ in size are usually prepared from WC–3Co cemented carbide, while a cementing bond from copper–nickel–manganese alloy (94Cu–4Ni–2Mn (mass %)) the melting temperature of which is about 1080 $^\circ$C. In the WC–3Co mesoelements in the above mesocomposition the cobalt phase is in the solid state at 1080—1300 $^\circ$C, for this reason, the MMI–phenomenon is not observed. This mesocomposition was prepared by the traditional method of hot pressing at 1200 $^\circ$C. The mesostructures can be also formed under these conditions by impregnation of porous compacts formed from cemented carbide granules.

In cases where metals of the iron group (Fe, Co, Ni) are used as a bond for mesoelements, the mesostructures can be formed by the solid state sintering with the application of pressure [15]. The authors [15] used granules prepared from the traditional WC–6Co, WC–11Co and WC–16Co cemented carbides. The sizes of granules were varied from 60 to 130 $\mu m$. Cobalt was used as a binder (from 0 to 30 vol%). The granules were presintered in a hydrogen atmosphere at a temperature of 1200 $^\circ$C and then mixed with cobalt powder and hot pressed at 1250 $^\circ$C for 2 hours at a pressure of 35 MPa. Under these conditions pore-free mesostructures were formed. This technology is, however, a highly power-consuming one. The application of the intensive technology of electric sintering allows the mesostructures to be formed with the minimum of power consumption. To implement this technology, a special setup has been developed at the Institute for Superhard Materials, which allows one, even at the initial period of sintering, to heat the mixture at a rate of 1000 deg/s at 160—350 MPa. The holding time at the sintering temperature is 2—10 s. With this setup, mesostructures were obtained [16] that consisted of sintered WC–3Co granules 40—100 $\mu m$ in size. The holding time at 1400 $^\circ$C and 220 MPa was 7 s. The sintering process proceeded in the presence of the liquid phase. In the course of high pressure sintering the granules deformed plastically to form a textured mesostructure (Fig. 1). It is necessary to note, under these conditions degradation of mesoelements occurs.
For formation of mesostructures can be used the high technologies of sintering which apply to formation of nanostructures – hot isostatic pressing (HIP) [17], spark plasma sintering (SPS) [18], high frequency induction heated sintering (HFIHS) [19], rapid omni compaction (ROC) [20], pulse plasma sintering (PPS) [21], ultrahigh pressure rapid hot consolidation (UPRC) [22].

Migration metal melt from intergranular space into mesoelement is the main problem during formation mesostructure in the first type mesocomposition.

One more promising method to form mesostructures in cemented carbides, in the author’s opinion, is high temperature treatment of sintered samples with metal melts (MMT–technology). The MMT–technology is based on the phenomenon of the imbibition of metal melts by a pore free sintered composition [23]. On penetration of a metal melt into cemented carbide article the deconsolidation of the high melting skeleton takes place [10]. The process should proceed purposefully to form aggregates of high melting particles separated with thicker layers of a binder. In WC–Co cemented carbides, this was accomplished by squeezing carbide samples before the MMT–process. In this case, the sample deformed elastoplastically and the high melting skeleton became fragmented at the level. On subsequent treatment with metal melts, the liquid phase being imbibed by the sample separated the resulting fragments with the binder layers. The formation of mesostructures in cemented carbides which are used as hard facing materials should be highlighted [24]. The authors of [24] suggested a wear resistant hard facing material which consisted of spherical cast WC/W_{2}C carbide granules of the eutectic composition, polycrystalline granules formed from crystals of WC monocarbide, and a matrix material consisting of cobalt, nickel, iron or their alloys. In the hard facing composition the size of granules was varied from 320 to 640 μm, and the content of them in the matrix from 15 to 50 mass %. The formation of mesostructures in these compositions occurs under the nonequilibrium conditions, with high fluxes of energy delivered into the melting zone and high rate cooling.

**Fig.1.** Mesostructure of the WC–Co composition [16]
3.2. Features of the formation of the structure in the second type mesocomposition


Tab. II. Composition and structure WC–Co cemented carbides [25]

<table>
<thead>
<tr>
<th>No sample</th>
<th>Cemented carbides</th>
<th>WC, mass %</th>
<th>Co, mass %</th>
<th>$d_{ave}$ WC, μm</th>
<th>$u^*$, vol. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>WC–6Co F</td>
<td>94.1</td>
<td>5.9</td>
<td>1.1</td>
<td>14.0</td>
</tr>
<tr>
<td>2</td>
<td>WC–6Co</td>
<td>94.1</td>
<td>5.9</td>
<td>2.0</td>
<td>14.0</td>
</tr>
<tr>
<td>3</td>
<td>WC–6Co C</td>
<td>94.1</td>
<td>5.9</td>
<td>3.2</td>
<td>14.0</td>
</tr>
<tr>
<td>4</td>
<td>WC–20Co</td>
<td>79.9</td>
<td>20.1</td>
<td>2.1</td>
<td>42.0</td>
</tr>
</tbody>
</table>

* at 1400°C

Mesostructured WC–Co cemented carbides were prepared by the traditional method of hot pressing at 1400°C. Distribution Co binder after hot pressing ascertained by X-ray spectrum analysis. Researches (Tab. III) have shown, that during liquid phase sintering the cobalt melt migration occurs, therefore observed redistribution of the Co binder between mesoelements and a matrix.

Tab. III. Co binder contents in WC–Co mesocompositions [25]

<table>
<thead>
<tr>
<th>No samples</th>
<th>Mesocomposition*</th>
<th>Co binder content in the initial state, mass %</th>
<th>Co binder content after hot pressing, mass %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>WC–6Co F / WC–20Co</td>
<td>5.9 / 20.1</td>
<td>11.3 / 14.4</td>
</tr>
<tr>
<td>2</td>
<td>WC–6Co / WC–20Co</td>
<td>5.9 / 20.1</td>
<td>9.8 / 16.0</td>
</tr>
<tr>
<td>3</td>
<td>WC–6Co C / WC–20Co</td>
<td>5.9 / 20.1</td>
<td>8.1 / 17.8</td>
</tr>
<tr>
<td>4</td>
<td>WC–20Co / WC–6Co</td>
<td>20.1 / 5.9</td>
<td>13.4 / 12.5</td>
</tr>
</tbody>
</table>

* The numerator indicates the mesoelement and denominator indicates the matrix.

The driving force for the migration process of a liquid phase is the gradient of migration pressure $\Pi$ [26]. The migration pressure $\Pi$ has physical meaning of suction pressure, therefore the liquid moves from volumes with smaller value of pressure $\Pi$ to volumes with its greater value [11]. Migration pressure $\Pi$ depends on the liquid phase content ($u$) and the WC particle size ($d$) of a composition [13]:

$$\Pi = \frac{K}{3d} \left( \gamma_{ss} - 2g \gamma_{sl} \right) \left( \frac{1-u}{u} \right)^{1/3}$$  \hspace{1cm} (1)

where $g$ is the coefficient which accounts for variations of particle geometrics during the period of liquid migration.

Using expression (1), calculated values of pressure $\Pi$ in mesoelements and in matrices (Tab. IV) and established that during liquid phase migration the pressure gradient between mesoelements and a matrix decreases. Knowing value of pressure $\Pi$, it is possible to predict a direction of migration cobalt melt in WC–Co mesocompositions and to define its final state.
Tab. IV. Pressure Ρ in WC–Co mesocompositions [25]

<table>
<thead>
<tr>
<th>No samples</th>
<th>Mesocomposition*</th>
<th>Pressure Ρ in the initial state, MPa</th>
<th>Pressure Ρ after hot pressing , MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>WC–6Co F / WC–20Co</td>
<td>0.64 / 0.18</td>
<td>0.43 / 0.25</td>
</tr>
<tr>
<td>2</td>
<td>WC–6Co / WC–20Co</td>
<td>0.53 / 0.18</td>
<td>0.38 / 0.22</td>
</tr>
<tr>
<td>3</td>
<td>WC–6Co C / WC–20Co</td>
<td>0.32 / 0.18</td>
<td>0.28 / 0.20</td>
</tr>
<tr>
<td>4</td>
<td>WC–20Co / WC–6Co</td>
<td>0.18 / 0.53</td>
<td>0.27 / 0.30</td>
</tr>
</tbody>
</table>

* The numerator indicates the mesoelement and denominator indicates the matrix.

To prevent cobalt melt redistribution between mesoelements and a matrix, formation of structure of a mesocomposition it is necessary produce at temperature below the cobalt phase melting point. Let's note that it is difficult to produce pore free articles under these conditions.

The second way of formation of mesostructures consists in preventing mass transfer of a liquid between mesoelements and a matrix. To achieve this purpose, it is necessary to cover a mesoelement with a layer which is impenetrable for a liquid phase. For example, a mesoelement is covered with TiN layer. In this direction positive results are obtained by authors [27]. It seems perspective to use a combination of materials of a mesoelement and a matrix which form a dense layer at the mesoelement – matrix interface. For example, in a composition consisting of WC–6Co mesoelements and W–Fe–Cu matrix, at the WC–6Co/W–Fe–Cu interface the dense carbide layer is formed (Fig.2). This layer interferes with penetration of a liquid phase from the W–Fe–Cu matrix into the WC–6Co mesoelements.

Fig.2. Structure of the WC–6Co /W–Fe–Cu interface.

3.3. Features of the formation of the structure in the third type mesocomposition

Features of the formation of the structure in the third type mesocomposition we shall consider on an example of a diamond/WC–Co composition. The diamond/WC–Co composition prepare on the technology of hot pressing briquettes consisting of powders of diamond, WC, and Co. The hot pressing is processed at temperature above the Co phase melting point. To manufacture of these mesocompositions apply also high technologies [28, 29]. During manufacturing a mesocomposition it is necessary to provide good adhesion of diamond particles and a matrix. To obtain good adhesion of diamond particles and a matrix, diamond particles cover with a layer of metal, as a rule Co, Ni, Mo. This layer is necessary for keeping at a surface of a diamond particle during hot pressing. In this connection the problem
of stability of metal layers in a WC–Co mesocomposition is important. Conditions of stability of metal layers are given in articles [12, 30]. The author [30], using a thermodynamic method of research, obtained the following expression for the change in the Helmholtz free energy (∆F) which describes process of migration of a liquid from a layer in a matrix.

\[
\Delta F = \frac{1}{3} (2\gamma_{13} - \gamma_{11}) \Delta S_{11} + S_c \gamma_{34} \cos \Theta_2 + S_2 \gamma_{34} \cos \Theta_3,
\]

(2)

where \( \gamma \) is the surface tension; \( S \) is the surface areas; \( S_c \) is the cavity surface area; indexes: 1 is the WC particles, 2 is the diamond crystal, 3 is the liquid phase, 4 is the gas, 11, 13, 23, 14, 24, 34 indicate to which phase or surface a value relates; \( \Theta_2 = \gamma_{14} - \gamma_{13} \), \( \cos \Theta_3 = \frac{\gamma_{24} - \gamma_{23}}{\gamma_{34}} \); \( \Theta \) is limiting wetting angle.

In expression (2) the first term describes energy changes which occur within the volume of the composition during migration of liquid from the cavity, the second term describes those in the cavity, and the third those in phase 2. It is noted that in the composition always \( \Theta_2 < 90^\circ \), i.e., \( \cos \Theta_2 > 0 \). This is a necessary condition for existence of a composition as a physical object.

From expression (2) follows, that in compositions which exhibit migration pressure liquid metal interlayers are stab. with any values of \( \Theta_3 \) only in a cavity whose size is less than the critical size, and they are unstab. with cavity dimensions greater than the critical size and also with mesoelements not wetted by liquid, \( \Theta_3 > 90^\circ \). If a mesoelement is wetted by liquid, interlayers are stab. in the case when their thickness is less than critical \( \delta_c \) determined from the equality of composite migration pressure and capillary pressure which arises with substitution of the interlayer by a gas phase. With \( \delta > \delta_c \) under these conditions the interlayer is unstab. External pressure (pressure of hot pressing) promotes stability of a metal layer.

During formation of a diamond / WC–Co mesocomposition polymorphic transformation diamond – graphite occurs. This process takes place at a surface of diamond crystal therefore the graphite film divided a diamond crystal and a matrix is formed. To eliminate the graphite film, in a metal layer enter the chemical elements having high affinity to carbon. Positive results have been achieved at addition Cr, Mo, B [31].

4. Properties

The formation of the mesostructure allows one to produce cemented carbides with particular properties by varying sizes and compositions of mesoelements, their properties as well as the content, composition and properties of a cementing bond. Special purpose alloys, various steels and subsequent heat treatment of an article, dispersion hardened materials, etc., are used as a bond.

The most comprehensive findings of an investigation into the effect of the composition and structure of the mesostructured cemented carbides on the fracture toughness \( K_Ic \), hardness \( HV_{100} \) and wear resistance were obtained for the WC–Co cemented carbide [15] (see Tab. V). The authors of [15] have found that cemented carbides with mesostructure are characterized by an excellent combination of the fracture toughness and wear resistance which is far superior to the identical combination of the properties of the commercial WC–Co cemented carbides. A high fracture toughness ranging up to 37.9 MPa\( \cdot \)m\(^{0.5} \) was obtained thanks to rather thick interlayers of a bond between mesoelements, and a high wear resistance was assured by low cobalt mesoelements.
Tab. V. Mechanical properties of mesostructured WC–Co cemented carbides [15]

<table>
<thead>
<tr>
<th>Co, vol%</th>
<th>Mesoelement</th>
<th>Matrix</th>
<th>$K_{IC}$, MPa⋅m$^{0.5}$</th>
<th>$HV_{100}$</th>
<th>Wear resistance, ASTM units*</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0</td>
<td>10.9</td>
<td>1620</td>
<td>14.8</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>10</td>
<td>17.6</td>
<td>1250</td>
<td>7.3</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>20</td>
<td>23.5</td>
<td>1050</td>
<td>4.7</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>30</td>
<td>34.5</td>
<td>856</td>
<td>4.3</td>
<td></td>
</tr>
<tr>
<td>18</td>
<td>0</td>
<td>13.4</td>
<td>1350</td>
<td>4.6</td>
<td></td>
</tr>
<tr>
<td>18</td>
<td>10</td>
<td>19.9</td>
<td>1080</td>
<td>3.5</td>
<td></td>
</tr>
<tr>
<td>18</td>
<td>20</td>
<td>27.7</td>
<td>899</td>
<td>2.7</td>
<td></td>
</tr>
<tr>
<td>18</td>
<td>30</td>
<td>35.7</td>
<td>732</td>
<td>2.0</td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>0</td>
<td>16.7</td>
<td>1100</td>
<td>2.5</td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>10</td>
<td>22.7</td>
<td>930</td>
<td>1.8</td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>20</td>
<td>31.5</td>
<td>804</td>
<td>1.5</td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>30</td>
<td>37.9</td>
<td>667</td>
<td>1.4</td>
<td></td>
</tr>
</tbody>
</table>


Unfortunately, in Ref. [15], there is no information on such important characteristics as bending strength $R_{bmm}$, compression strength $R_{cm}$, the total work of deformation $A_{tot}$, and plastic deformation $\varepsilon$. The values of these mechanical properties of WC–15Co,Ni were obtained in [32]. Tab. VI lists the properties of the WC–15Co,Ni cemented carbide of homogeneous structure and the properties of the WC–15Co,Ni (MMT) with the mesostructure obtained by the MMT technology. It should be noted that the WC–15Co,Ni (MMT) samples consisted of mesoelements from 10 to 20 $\mu$m in size separated with interlayers of the cobalt bond.

Tab. VI. Mechanical properties of cemented carbides [32]

<table>
<thead>
<tr>
<th>Sample</th>
<th>$K_{IC}$, MPa⋅m$^{0.5}$</th>
<th>$R_{bmm}$, MPa</th>
<th>$R_{cm}$, MPa</th>
<th>$A_{tot}$, kJ/m$^3$</th>
<th>$A_{pl}$, kJ/m$^3$</th>
<th>$\lambda$</th>
<th>$\varepsilon_{tot}$ %</th>
</tr>
</thead>
<tbody>
<tr>
<td>WC—15Co,Ni</td>
<td>16.6</td>
<td>2460</td>
<td>3740</td>
<td>114.9</td>
<td>90.1</td>
<td>3.6</td>
<td>4.1</td>
</tr>
<tr>
<td>WC—15Co,Ni (MMT)</td>
<td>19.8</td>
<td>2610</td>
<td>3500</td>
<td>165.7</td>
<td>143.6</td>
<td>6.5</td>
<td>4.8</td>
</tr>
</tbody>
</table>

The mean thickness of the Co interlayers in the mesoelements was 0.1 $\mu$m, mean size of WC particles 1.5 $\mu$m and the binder content of 8 mass %. The mean thickness of the Co intergranules was 2 $\mu$m. A correlation between mechanical properties of WC–15Co,Ni and WC–15Co,Ni (MMT) with the mesostructure has shown that the formation of the latter involved an increase in bending strength, total work of deformation, its plastic component and plasticity of cemented carbides (Tab. VI). To assess the dissipation of energy delivered to the material, the energy absorbability coefficient $\lambda$ was used. It is defined as the ratio between the plastic and elastic components of the work of deformation ($\lambda = A_{pl}/A_{el}$) [35]. It follows from Tab. 6 that mesostructured cemented carbides are characterized by a higher ability to absorb energy.

From the above stated follows, that at present only limited experimental data on physic–mechanical properties of cemented carbides with the mesostructure are available. These data have been obtained using cemented carbides with different mesostructures and compositions and cannot be used for the construction of correlation maps of cemented carbide mesostructure–macroproperties relations. This problem can be partially solved by the
computer–aided modelling of mesostructures and subsequent calculating of physico–mechanical properties of mesostructured cemented carbides.

To form mesostructures, sintered carbide granules [15], cast granules of the WC–W₂C eutectic composition [24], and granules produced by crushing cemented carbide waste are used. Granules of the first two types are spherical, those produced by crushing are of arbitrary shapes with sharp edges and on oxidation in air these particles also acquire the near spherical shape. This allows authors [34] to suggest the regular structural model of a mesostructured cemented carbide. The structural unit cell of the model is a combined (two phase) cube of side $a$, the surface of a sphere of diameter $D$ is an interface. A part of the sphere which is inside the cube is a granule of the WC-Co cemented carbide and the rest of the cube volume is filled with cobalt (Fig. 3). The $D$ value is chosen such that the volume fraction of the cemented carbide within the cell equals the volume fraction $c$ of cemented carbide granules in a mesocomposite. Correspondingly, the volume content of cobalt that bounds granules is $V_{Co} = 1 - c$. An advantage of the periodic model is the possibility of a rigorous approach to predicting properties of a composite by the statement and solution of boundary value problems for a structural cell that at the same time is a representative volume of a composite. In this case, the problem of the conversion from micro to macrolevel is eliminated and the reliability is assured of predicting both micro structural fields (of concentration of stresses, in particular) and the macro characteristics of a composite over the whole range of variations of properties and volume content of phases. Another but no less important advantage of the model is its ability to take into account the parameters of the microstructure like packing of particles of the discrete phase, particle shape, the existence of zones of the phase interaction, etc. It should be noted, however, that in the known papers on theoretical analysis, on the basis of the above model of elastic [35] and plastic [36] properties of dispersion–strengthened composites, the condition of noncontacting and nonintersection of spherical particles of the discrete phases is assumed, which restricts their volume content to the $c = c_{max} = 0.52—074$ value depending on the mode of packing.

In the mesostructured cemented carbide under consideration, the volume content of granules of the WC–Co cemented carbide is, however, in the range from 0.6 to 0.95, which is possible only in the case of $D > a$, i.e. when granules have finite spots of contact. Such a material belongs to the category of composites with interpenetrating (cobalt and cemented carbide) skeletons. Its structural cell is given in Fig. 3 and the whole volume may be obtained by repeating it in three mutually perpendicular directions. This model is true for the range of $0 < c < 0.95$ and the corresponding value of $D(c)$ is defined by solving one of the equations

$$\frac{\pi ( \frac{D}{a} )^3}{6} = c, \quad D < a, \quad c < 0.524;$$

$$\frac{3\pi}{4} \left[ \left( \frac{D}{a} \right)^2 - \frac{1}{3} \right] \frac{\pi}{3} \left( \frac{D}{a} \right)^3 = c, \quad D > a, \quad c > 0.524;$$

![Fig. 3. Unit cell of a model of the mesostructure: structural cell(I), carbide mesoelement (II), cobalt binder (III) [34.]](image-url)
At present the finite element method is the most versatile as regards a consideration of geometrical and physical nonlinearity. This method is used in the work [34] for the solution of model three dimensional boundary–value problems of elastoplasticity.

Figure 4 shows the curves of the dependence of the effective elastic modulus \( E^* \) of a cemented carbide with the mesostructure on the cobalt volume content \( V_{Co} \) (Co matrix). We would like to remind that the \( V_{Co} \) value takes no account of cobalt entering into mesoelements of cemented carbide which is considered as a homogeneous material. As would be expected, the WC–15Co + Co matrix (see Fig. 4, curve 1) is more pliable as compared to a similar mesocomposite containing mesoelements of WC–6Co (see Fig. 4, curve 2). In both the cases, the elastic modulus decreases as \( V_{Co} \) increases.

**Fig. 4.** Dependence of the elastic properties of the mesostructured cemented carbide on the cobalt volume content: 1 — WC–15Co + Co matrix, 2 — WC–6Co + Co matrix, 3 — homogeneous WC–Co cemented carbides, • — experimental data for WC–6Co, WC–8Co, WC–10Co, WC–15Co cemented carbides [34].

**Fig. 5.** The \( \langle \sigma_z \rangle = f(\langle \varepsilon_z \rangle \) function for WC–6Co + Co matrix (—) and WC–15Co + Co matrix (---) mesocompositions: \( V_{Co} = 0.1 \) (1), 0.2 (2), 0.3 (3), the dot–dash lines indicate the trajectories of unloading, coordinates: \( \langle \sigma_z \rangle \) is the stress, \( \langle \varepsilon_z \rangle \) is the deformation [34].
The effect of the cemented carbide mesostructure on its elastoplastic properties can be judged from the deformation curves shown in Fig. 5 (up to $\epsilon_z = 0.02$) for the WC–6Co + Co matrix and WC–15Co + Co matrix mesocompositions. From here on the value of the deformation $\epsilon_z$ is given in fractions of unit. A comparison between curves 1, 2 and 3 shows that the material becomes more plastic as $V_{Co}$ (Co matrix) increases.

The above data also allow one to assess the level of residual plastic macrostrains $\epsilon^{pl}_z$, which may be found either by the direct solution of the model boundary–value problem under the boundary conditions corresponding to unloading, or by the use of previously obtained data on the effective elastic module (see Fig. 4). The point of intersection of the trajectory of unloading with the abscissa axis gives the value of the residual plastic deformation (see Fig. 5).

The development of the theory of strength of mesostructured cemented carbide on the basis of the model under consideration is one of possible applications of the latter. The calculated values of the limiting deformation and compression strength are listed in Tab. VII.

**Tab. VII.** Limiting characteristics of the mesocompositions in compression predicted on the basis of the suggested model [34]

<table>
<thead>
<tr>
<th>$V_{Co}$/</th>
<th>WC–6Co + Co matrix</th>
<th>WC–15Co + Co matrix</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\epsilon_{lim}$, %</td>
<td>$\sigma_{com}$, GPa</td>
</tr>
<tr>
<td>0</td>
<td>1.35</td>
<td>5.10</td>
</tr>
<tr>
<td>0.1</td>
<td>1.47</td>
<td>4.52</td>
</tr>
<tr>
<td>0.2</td>
<td>1.58</td>
<td>3.94</td>
</tr>
<tr>
<td>0.3</td>
<td>1.72</td>
<td>3.43</td>
</tr>
</tbody>
</table>

It is seen from the tabulated numerical values that the accepted condition of the transition of the material to the limiting state predicts an increase in the deformability and a decrease in the compression strength with increasing the volume fraction of the cobalt phase similar to those observed in conventional hard alloys. This suggests that the model under discussion, which is free of simplifying assumptions, is a reliable basis for the development of advanced theories of strength of cemented carbides of mesostructure.

5. Applications

According to researches [37, 38], mesostructured WC–Co cemented carbides are highly effective in rock destruction tools – a roller cone drill bit, a percussion or hammer bit, a drag bit. Using MMT–process, authors [39] obtained mesostructured WC–TiC–Co cemented carbide. Because of the establishment of mesoelements cemented by thick layers of binder metal, the material acquires a higher viscosity. The stresses arising under impact cyclic loads were thus distributed over a considerable depth compared with conventional WC–TiC–Co cemented carbide, i.e. an increased volume of material entered into the cutting operation, this not only having improved physico–mechanical properties, but also being able to absorb a larger quantity of critical energy. It has allowed increasing mill service life in 3 times [40].

The second type mesostructured compositions can be effective at manufacturing materials for electric contacts. Good electric conductivity in a combination to high wear resistance is obtained by the author of the review in the composition consisting of a W–Fe–Cu matrix and WC–6Co mesoelements. Researchers [31] have produced drag bits comprising inserts prepared from a diamond / WC–Co mesocomposition. In this mesocomposition at a surface of diamond particles created the Co layer alloyed with B and Cr. Service life of new bits were in 2 times more in comparison with conventional drag bits. It is the author’s opinion
that mesostructured WC–Co cemented carbides can be highly efficient in friction couples. The above described examples have shown that application of mesocomposite materials is perspective in rock destruction and metal working tools as well as in mechanical engineering.

6. Conclusions

Analysis of the literature data shows that at present several lines in the formation of mesostructures in cemented carbides are being developed. They are: sintering in the presence of the liquid phase, solid-state sintering at pressure, treatment of carbide articles with metal melts. During liquid phase sintering mesocompositions of the first and second types mean a problem is penetration metal melt in a mesoelement therefore degradation of structure of a mesoelement takes place. One of methods of the decision of this problem is creation at a surface of a mesoelement of a layer which interferes with penetration metal melt in a mesoelement. Formation of mesostructure of the third type compositions is necessary for carrying out under the conditions providing good adhesion of a mesoelement and a matrix.

For wide practical application of mesocompositions it is necessary to solve a number of scientific and technological problems. One of them is development of scientific base of formation of mesocompositions, prediction of their properties, studying of the mechanism of occurrence and development of fatigue cracks at a mesolevel, and to find the correlation between the mesostructure and the macro properties of cemented carbide.

6. References


Садржај: Аутор разматра формирање мезоструктура у цементираним карбидима, анализира постојеће технологије за њихово добијање, описује физичка и механичка својства цементираних карбиди са мезоструктуром и указује на њихову ефикасност у обради метала и као алате за дробљење стена.
Кључне речи: цементирани карбид; чврсти метали; структура; мезоструктура