PRODUCTION OF NANOSIZED AND ULTRAFINE METAL AND
COMPOSITE POWDERS FOR VARIOUS APPLICATIONS

L.I. Leontiev¹, V.L. Lisin¹, V.A. Kostilev², S.A. Petrova¹
¹ Institute of Metallurgy, Urals’ Division of RAS. Amundsen St., 101. Ekaterinburg, 620016.
Russia. lis@imet.mplik.ru
² ‘Tantalum Technologies’ Ltd. Lenin St., 131. Upper Pyshma, 624096. Sverdlovsk Region.
Russia., npp-nauka@yandex.ru

ABSTRACT

Creation of qualitatively new functional materials is one of the priority trends in the
development of science and technology. The Institute of Metallurgy UD RAS in cooperation
with Tantalum Technologies Ltd. is engaged in the development of technologies and the
production of nanosized and ultrafine metal and composite powders for various applications.
The developed technology of electrochemical production of metal powders is suitable for
producing any metal powders of various sizes, as well as the production of complex metal
powder mixtures of the given gross composition by electrolyzing the alloy of the desired
composition. A new industrially oriented, currentless technology for the synthesis of high-
purity ultrafine and nanocrystalline powders of carbides, borides and silicides of metals in
ionic melts, that combined the electrochemical process of bulk crystallization of nanopowders
with the process of chemical transport reactions, has been developed. The powders obtained
by this technology correspond to the technical requirements for laser cladding powders and
can be used to improve the mechanical properties of coatings. Another promising application
of nanopowders of carbides and metal borides is their use as modifiers in casting alloys in
order to obtain the effect of dispersed hardening.

Creation of qualitatively new functional materials is one of the priority trends in the
development of science and technology. The Institute of Metallurgy UD RAS in cooperation
with Tantalum Technologies Ltd. is engaged in the development of technologies and the
production of nanosized and ultrafine metal and composite powders for various applications.
To cover the requirements of the modern electronic industry, in the framework of these
studies, electrochemical technologies for the production of tantalum metal powder from
tantalum pentachloride and metallic tantalum and for the agglomeration of nanocrystalline
defect-free tantalum powders of the capacitor grade were developed. The technological
scheme of the process is shown in Fig.1.

The gist of the technology for obtaining nanocrystalline tantalum powders by the
electrochemical method (1-3) lies in creating such conditions for the electrochemical process,
in which the reduction of metals takes place in the volume of the electrolytic bath, and not
only on the surface of the cathode or in the cathode diffusion layer (4-6). Variation of the
current density and temperature makes it possible to obtain powders of different sizes (7).

As a consumable raw material, a tantalum anode with a tantalum content of not less
than 99.92% is used. The electrolyte is a molten mixture of sodium and potassium chlorides
in various proportions in an argon atmosphere. The chemical purity of the powders obtained
is 99.98% (Table 1). The microstructure of the powder obtained (8) is presented in Fig. 2a.
From the obtained powder the pilot batches of were manufactured capacitors (Fig. 2b) and
tested at OJSC ‘Elekond’ (9). The technical characteristics of the manufactured capacitors answered or exceeded the level of foreign analogs.

Figure 1. Technological scheme for producing nanocrystalline powders from metal tantalum

Figure 2. Microstructure of the tantalum powder obtained by electrochemical process (a), and an image of the capacitors produced from this powder (b)
Further investigations showed that the developed technology of electrochemical production of metal powders is suitable for producing any metal powders of various sizes from 10 nm to tens of microns with the content of the basic component up to 99.99%. Table 1 gives the main data on the composition and structure of metals obtained by electrochemical methods.

Table 1. Ultrafine metal powders obtained by electrochemical technology

<table>
<thead>
<tr>
<th>Powder</th>
<th>Average crystallite size, nm*</th>
<th>Particle size, nm **</th>
<th>Sp.gr.</th>
<th>Unit cell parameters, nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti</td>
<td>80±2</td>
<td>165±5</td>
<td>P63/mmc</td>
<td>0.2951(1) 0.4686(1)</td>
</tr>
<tr>
<td>Ni</td>
<td>180±5</td>
<td>-</td>
<td>Fm-3m</td>
<td>0.3523(1)</td>
</tr>
<tr>
<td>Cr</td>
<td>180±5</td>
<td>-</td>
<td>Im-3m</td>
<td>0.2884(1)</td>
</tr>
<tr>
<td>Mo</td>
<td>180±5</td>
<td>-</td>
<td>Im-3m</td>
<td>0.3147(1)</td>
</tr>
<tr>
<td>Co</td>
<td>90±2</td>
<td>15±1</td>
<td>Fm-3m</td>
<td>0.3543(1) 0.3163(1)</td>
</tr>
<tr>
<td>Ta</td>
<td>70±2</td>
<td>78±30</td>
<td>P63/mmc</td>
<td>0.2505(1) 0.4071(1)</td>
</tr>
<tr>
<td>W</td>
<td>115±3</td>
<td>-</td>
<td>Im-3m</td>
<td>0.3163(1)</td>
</tr>
<tr>
<td>Fe</td>
<td>90±2</td>
<td>-</td>
<td>Im-3m</td>
<td>0.2865(1)</td>
</tr>
</tbody>
</table>

In Fig.3 the micrographs of tungsten and nickel powder obtained by the developed electrochemical technology (10) are presented.

The main advantages of the electrochemical technology over the other known technologies are as follows:
1. High purity of the powders obtained.
3. Low production cost.
4. Practically non-waste production.
5. Production portability, the possibility of automation.

The next step in the development and improvement of the worked out technology was the production of complex metal powder mixtures of the given gross composition by
electrolyzing the alloy of the desired composition. Table 2 presents the chemical composition of the initial 12H18N10T steel and the powder obtained by electrolysis of the cast alloy (recalculation according to XRD data).

<table>
<thead>
<tr>
<th>Initial material (GOST 5632 – 72)</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>Ni</th>
<th>S</th>
<th>P</th>
<th>Cr</th>
<th>Cu</th>
<th>Ti</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>≤0.12</td>
<td>≤0.8</td>
<td>≤2</td>
<td>9 - 11</td>
<td>≤ 0.02</td>
<td>≤ 0.035</td>
<td>17 - 19</td>
<td>≤ 0.3</td>
<td>≤ 0.8</td>
<td>осталльное</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>The powder obtained by electrolysis (recalculated from XRD data)</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>Ni</th>
<th>S</th>
<th>P</th>
<th>Cr</th>
<th>Cu</th>
<th>Ti</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.1</td>
<td>9.6</td>
<td>17.3</td>
<td>73.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Later on, when creating composites such as "refractory metal carbide in a complex metal matrix," this made it possible to use as the matrix the powder obtained electrochemically from an alloy of the required composition (10).

Another area of research became the production of new functional materials suitable to manufacture products by additive technologies. The advantage of additive technologies is the possibility of "growing" blanks of molds, special tools, original parts of complex configuration that are difficult or impossible to obtain by casting or mechanical treatment. One of the key problems to actively introduce the additive technologies into the domestic industry is the expansion of the range of domestic metal powders suitable for laser cladding.

In particular, the creation of functional powder composite materials containing carbides, borides and silicides of metals which are intended to be used for the manufacture of cutting tools; creation of products by laser prototyping; application as protective wear and heat resistant coatings by various methods (laser surfacing, plasma spraying).

For this purpose, a new industrially oriented, currentless technology for the synthesis of high-purity ultrafine and nanocrystalline powders of carbides, borides and silicides of metals in ionic melts, that combined the electrochemical process of bulk crystallization of nanopowders with the process of chemical transport reactions, has been developed.

Chemical transport reactions are widely used in metallurgy for producing high-purity metals (including monocrystals), intermetallic compounds, carbides, borides, surface metallization of various materials etc. In general, the process is as following. The metal, being in liquid or solid state, interacts reversibly with gaseous material, and generates only gaseous products which, being transferred into another part of the system with differ conditions, are decomposed with metal formation. The concentration gradient due to the difference in temperature and pressure, as well as diffusion and other factors, is the necessary condition for the metal transfer. An ionic melt is the homogeneous medium, while for the chemical transport reactions, heterogeneous schemes are used as a rule. Nevertheless, currentless transfer of one metal onto another one can be considered as the chemical transport reactions taking place in ionic melts. The transfer mechanism is described in details in numerous publications; see for example (11). For two different metals placed into an ionic melt, the more electronegative metal will be transferred onto the more electropositive one. The concentration gradients of the potential-determinate ions with different oxidation state is a driving force for the transfer that realized through diffusion and convection. Without diffusion the process will be quickly stopped due to the electrochemical potential equalizing. In the system where alloys formation is available the transfer process will last till the end.
The energy of the alloy formation is the only driving force for the transfer process under isothermal conditions.

Being included in various ionic compositions, the carbon can be transferred onto metals by means of chemical transport reactions. In the other words, metals can be carbonized in ionic melts. This way has some advantages in comparison to the others. The process takes place at lower temperatures than the other, as a rule (500-1000 °C). The poor solubility of gases in ionic melts (~10^{-4}-10^{-5}%) prevents metal oxidation.

However, in such a process, the granulometric composition of the carbides is always limited by the initial size of the carbide-forming element powder. If one creates the conditions under which the transfer of the carbide-forming metal would take place in atomic form to carbon, the grain-size distribution of the carbide powders would be given by the carbon particles size. It greatly simplifies the task of producing nanopowders of carbides as nanosized carbon powder is produced commercially.

![Figure 4 Micrograph of the TiC powder obtained by transferring the carbon onto the metal (a) and the metal onto the carbon (b)](image)

To realize the process of transporting the carbide-forming metal to carbon, we used the long-known phenomenon of direct spontaneous metal transfer by their ions through an ionic melt without electrolysis (11). The pilot batches of the stoichiometric TiC, WC, TaC, NbC, ZrC, Al3C2, Cr3C2 nanopowders were produced. For comparison, Fig. 4 shows micrographs of two titanium carbide powders obtained by transferring the carbon onto the metal (Fig. 4a) and transferring the metal onto the carbon (Fig. 4b).

In addition, an electrochemical method for coating carbide particles of refractory metals with one or more metal layers has been developed, that contributes to solve the problem of the wettability of carbides by certain metals or alloys and to create a binder suitable for relaxing the stresses, transferring loads to carbide particles, and providing braking in the development of cracks during the destruction of carbides. By combining the electrochemical process of bulk crystallization of nanopowders and the process of chemical transport reactions, nanosized and submicron carbides of TaC, WC and TiC, as well as titanium diboride TiB2, coated with one or several metal layers were obtained. In Fig. 5 an image of WC powder coated with Cr and Ni, made by magnetic force microscopy is presented, and Table 3 shows the results of a layer-by-layer phase composition analysis of the powder made by the XRD method under grazing beam conditions. The choice of metals for coating is determined by the ultimate use of the powder.
Table 3 Phase composition

<table>
<thead>
<tr>
<th>Grazing angle α, grad</th>
<th>Layer thickness х, mkm</th>
<th>WC wt%</th>
<th>Cr wt%</th>
<th>Ni wt%</th>
<th>W wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>0.02</td>
<td>44.1</td>
<td>3.7</td>
<td>50.4</td>
<td>1.8</td>
</tr>
<tr>
<td>0.5</td>
<td>0.08</td>
<td>51.0</td>
<td>4.6</td>
<td>41.7</td>
<td>2.7</td>
</tr>
<tr>
<td>1.0</td>
<td>0.15</td>
<td>49.3</td>
<td>5.3</td>
<td>43.0</td>
<td>2.4</td>
</tr>
<tr>
<td>1.5</td>
<td>0.25</td>
<td>52.0</td>
<td>6.9</td>
<td>38.2</td>
<td>2.9</td>
</tr>
<tr>
<td>2.0</td>
<td>0.30</td>
<td>52.6</td>
<td>5.9</td>
<td>39.5</td>
<td>2.0</td>
</tr>
<tr>
<td>2.5</td>
<td>0.40</td>
<td>51.8</td>
<td>6.4</td>
<td>38.9</td>
<td>2.9</td>
</tr>
<tr>
<td>3</td>
<td>0.45</td>
<td>53.57</td>
<td>6.97</td>
<td>37.78</td>
<td>1.68</td>
</tr>
<tr>
<td>Volume content</td>
<td></td>
<td>53.74</td>
<td>4.67</td>
<td>39.63</td>
<td>1.96</td>
</tr>
</tbody>
</table>

Figure 5 – Microstructure of the WC powder coated with Cr and Ni

Figure 6. A cross-section of a stock steel with composite covering deposited by laser fusion
The resulting composite powders containing refractory metal carbides have been tested in laser cladding technology to produce wear-resistant coatings. In Fig. 6 a cross-section of the stock steel with a composite covering of a powder mixture based on tungsten carbide, obtained by our electrochemical technology, and deposited by laser sintering (fusion) is shown.

Table 4. EDX results

<table>
<thead>
<tr>
<th>Elem.</th>
<th>At.%</th>
<th>Wt.%</th>
<th>At.%</th>
<th>Wt.%</th>
<th>At.%</th>
<th>Wt.%</th>
<th>At.%</th>
<th>Wt.%</th>
<th>At.%</th>
<th>Wt.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>46.21</td>
<td>49.89</td>
<td>16.85</td>
<td>12.69</td>
<td>19.00</td>
<td>19.85</td>
<td>12.00</td>
<td>13.00</td>
<td>18.61</td>
<td>22.00</td>
</tr>
<tr>
<td>Fe</td>
<td>28.03</td>
<td>28.79</td>
<td>14.31</td>
<td>10.25</td>
<td>8.32</td>
<td>8.27</td>
<td>33.02</td>
<td>34.03</td>
<td>58.43</td>
<td>65.72</td>
</tr>
<tr>
<td>Si</td>
<td>8.80</td>
<td>4.54</td>
<td>-</td>
<td>-</td>
<td>33.22</td>
<td>16.61</td>
<td>-</td>
<td>-</td>
<td>5.52</td>
<td>3.12</td>
</tr>
<tr>
<td>Cr</td>
<td>6.29</td>
<td>6.01</td>
<td>36.53</td>
<td>24.37</td>
<td>12.79</td>
<td>11.84</td>
<td>32.04</td>
<td>30.75</td>
<td>3.37</td>
<td>3.53</td>
</tr>
<tr>
<td>C</td>
<td>5.30</td>
<td>1.17</td>
<td>9.83</td>
<td>1.51</td>
<td>13.52</td>
<td>2.89</td>
<td>16.08</td>
<td>3.57</td>
<td>13.43</td>
<td>3.25</td>
</tr>
<tr>
<td>Co</td>
<td>3.72</td>
<td>4.04</td>
<td>1.13</td>
<td>0.85</td>
<td>1.12</td>
<td>1.18</td>
<td>2.01</td>
<td>2.18</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>W</td>
<td>1.64</td>
<td>5.56</td>
<td>21.34</td>
<td>50.33</td>
<td>12.03</td>
<td>39.36</td>
<td>4.85</td>
<td>16.47</td>
<td>0.64</td>
<td>2.38</td>
</tr>
</tbody>
</table>

The tests carried out by OOO NTO ‘IRE-Polus’ showed that the powders obtained correspond to the technical requirements for laser cladding powders and can be used to improve the mechanical properties of coatings (such as hardness and wear resistance).

Studies have shown that the addition of these composite powders to industrially produced powders that do not contain carbides significantly increases the hardness of the applied coatings. For instance, by laser cladding of the mixture contained 70% powder Hoganas 1360 (Ni-based) + 30% composite (composition 85% WC + 9% Cr + 3% Co + 1% Ni) a coating with microhardness up to 1522 HV was obtained, while the microhardness of the layers melted with pure powder HOGANAS 1360, is within 520-616 HV. The increase in microhardness becomes clear after analysis of the microstructure of the formed coating. In Fig. 7 the microstructure of individual sections of surfacing is shown. The local chemical composition of the main structural components of the coating is given in Table 4.

The coating has a cellular dendritic structure typical for coatings of this type. The matrix (point a-1) is a nickel-based supersaturated solid solution. As we approach the steel base, the iron content increases (Table 5). The columnar dendrites (Fig. 4d) are oriented along the front of the thermal wave, while close to the steel base the longer dendrites are observed. The solid (not melted) tungsten carbides of the equiatomic composition (Fig. 4b, point 1) are also localized along the front of the thermal wave. Being well-moistened they will not crumble out during abrasion wear. The structure of the molten zone generally contains two types of structural elements (Figure 4a). There are recrystallized precipitates of a complex composition enriched with chromium and tungsten (point a-2) in the matrix of lighter elements (point a-1). This structure determined the magnitude and behavior of the microhardness over the thickness of clads made by powder of series 1. Depending on the amounts of additives, the microhardness of the obtained coatings increased by a factor of 1.5-2 compared with the use of pure HOGANAS 1360 powder.

Another promising application of nanopowders of carbides and metal borides is their use as modifiers in casting alloys in order to obtain the effect of dispersed hardening. At
present, we are working on the development of aluminum based foundry alloys to be used for the modification of aluminum casting alloys.

References

[1]. L.I. Leontiev, V.A. Kostilev, V.V. Chebikin, R.S. Karimov, G.A. Panov. Electrochemical Technology for Producing Metal Nanopowders. 3rd All-Russian Conference on Nanomaterials, Ekaterinburg, UD RAS, 2009 (in Russian)
[7]. Baraboshkin A.N. Electric Crystallization of Metals from Melted Salts. Moscow, Nauka, 1976 (in Russian)