EXCHANGE OF EXPERIENCE AND INFORMATION

EXPERIENCE IN PRODUCING REFRACTORY COMPOUNDS UNDER INDUSTRIAL CONDITIONS

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Refractory compounds such as the carbides, borides, nitrides, and sulfides of metals having important physical, chemical, strength, and refractory properties (high melting points, high hardness, high-temperature strength, thermostability, chemical resistance to various corrosive media) are presently finding ever greater use in ferrous and nonferrous metallurgy, machine construction, the chemical industry, and radio and electrical engineering [1]. Therefore, the organization of production of refractory compounds under industrial conditions and the development and implementation of highly efficient technological methods and equipment, which can increase significantly the productivity of labor, lower the cost of refractory compounds and thus accelerate their wider use in the national economy, become an urgent matter.

Underlying the methods we used for producing refractory compounds are the methods worked out by the department of refractory materials of the Institute of Materials Study, Ukraine Academy of Science. They differ from other known methods by their greater simplicity, technological applicability, and availability of equipment.

In collaboration with the Institute of Materials Study, Ukraine Academy of Sciences, we have developed and implemented more than 30 types of refractory compounds: carbides, nitrides, borides, and sulfides of metals.

Production of metal carbides and borides. The production of the carbides of titanium, zirconium, niobium, and hafnium is accomplished by the reduction and carbidization of the oxides of the indicated metals by lamp black according to the reaction:

\[ \text{MeO} + \text{C} \rightarrow \text{MeC} + \text{CO}. \]

The borides of titanium, zirconium, hafnium, lanthanum, calcium, and yttrium are produced by the borothermic method:

\[ \text{MeO} + \text{B} \rightarrow \text{Me}_x\text{B}_y + \text{B}_2\text{O}_3. \]

It is necessary to note that this reaction for the production of borides with the formation of \( \text{B}_2\text{O}_3 \) is still in need of experimental confirmation.

The raw materials for obtaining carbides and borides of metals are the oxides of "pure"-grade metals, "pure" amorphous boron, and lamp black meeting the requirements of GOST 7885-56. Before mixing, the metal oxides are ground to 80-150 mesh size and roasted in muffle furnaces at 800° for 2 h and the lamp black at 400° for 1.5 h. The charge, made up according to the reaction by calculation of the principle substance, is placed in the porcelain drum of a ball mill where it is mixed for 10-15 h, after which it is rubbed through an 80-mesh sieve and pressed in steel molds at a pressure of 15-20 kN/cm² into cylindrical compacts 24 mm in diameter and 35-40 mm long.

The metal carbides and borides are produced in graphite receptacle heaters of laboratory electrovacuum furnaces [2], which have been slightly modified and improved (Fig. 1). Such furnaces are not complex to manufacture, are simple to use, are convenient for working out technological processes, and are suitable for producing small quantities of finished product.

The main units of the furnace are the base 1, metal hood 2 made of 1Kh18N9T stainless steel, water-cooled jacket 3, copper electrodes 4 with copper current-conducting tubes 5, and graphite receptacle heater 6. The last is brought into contact with the copper electrodes along conical surface 7 by means of molybdenum clamp plate 8.
TABLE 1. Production Conditions and Typical Chemical Composition of Carbides

<table>
<thead>
<tr>
<th>Carbide</th>
<th>Temperature, °C</th>
<th>Heating time, min</th>
<th>Metal C bound, %</th>
<th>C free, %</th>
<th>Sum of Me + C total, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiC</td>
<td>1900</td>
<td>120</td>
<td>79.95</td>
<td>99.5—99.7</td>
<td></td>
</tr>
<tr>
<td>ZrC</td>
<td>1900</td>
<td>90</td>
<td>88.36</td>
<td>99.0—100.0</td>
<td></td>
</tr>
<tr>
<td>HfC</td>
<td>2000</td>
<td>60</td>
<td>93.7</td>
<td>99.5—100.2</td>
<td></td>
</tr>
<tr>
<td>NbC</td>
<td>1700</td>
<td>90</td>
<td>88.55</td>
<td>98.5—99.9</td>
<td></td>
</tr>
<tr>
<td>TaC</td>
<td>1700</td>
<td>90</td>
<td>93.68</td>
<td>None</td>
<td>99.5—100.2</td>
</tr>
</tbody>
</table>

This method of clamping the heater between the electrodes ensures reliable contact and makes it possible to change heaters quickly and easily. The different thickness of the walls of the heater (thinner near the cooled electrodes and thicker in the center) provides uniform heating of its entire working part, which is very important for producing a qualitatively homogeneous product. The heaters for the electrovacuum furnaces are manufactured from brand "B" graphite.

The obtained compacts of the finished product were ground, screened through a 80-150 mesh sieve, combined into lots, subjected to analysis, and packed according to the technical specifications. The temperature conditions and chemical composition of the carbide and boride thus produced are given in Table 1 and 2.

The shortcomings of the described method are the rapid destruction of the graphite heaters during boride production (the heater withstands 2-3 operations) and the marked change of resistance of the heater during the operation (evidently as a result of the diffusion of boron into the graphite). All this necessitates changing the operating conditions of the furnace to maintain a constant temperature.

The production of carbide and borides of metals in large quantities in the laboratory electrovacuum furnaces is uneconomical, therefore for the industrial production of these compounds we developed a semi-continuous electrovacuum furnace. The laboratory vacuum furnace described above was the basis for the design of the new furnace. The furnace is powdered by a 220-V alternating-current network through a system of AOSK-25/05 and OSU-40/05 step-down transformers which smoothly regulate the voltage supplied to the loaded furnace heater, which is important for accurate maintenance of the temperature conditions of the furnace.

For the semi-continuous furnace we can use the electrical part of the TVV-4 or TVV-2 electrovacuum furnace produced by Soviet industry but which is intended for research work and is unsuitable for technological purposes. The operating principle of the semi-continuous electrovacuum furnace is as follows: the heating zone of the graphite receptacle furnace is continuously fed for a certain time (25-40 h) a charge in the form of granules measuring 5-8 mm, which, after passing through the heating zone and being there for the required time, then enters a receiving hopper where the reduction product is collected and cooled to normal temperature. The duration of the continuous operation of the furnace is determined by the capacities of the feeding and receiving hoppers. A high productivity is achieved as a result of the continuous process, and this yields a considerable economic effect.

During the production of carbides and borides it is necessary to note the advantages of granulating the charge before compacting. Special equipment (hydraulic presses, molds) is needed for compacting the charge. The process itself is laborious and is poorly amenable to mechanization and automation, whereas for granulating the charge a comparatively simple granulator is needed. The productivity of labor at the charge compression stage is increased several times by replacing compacting by granulation. This is especially effective in the industrial production of refractory compounds.

Fig. 1. Laboratory electrovacuum furnace. Explanation in text.