PLASMA METALLURGY OF URANIUM: I. CARBO ThERMIC REDUCTION OF URANIUM FROM OXIDE RAW MATERIAL.

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Abstract

Plasma process of carbothermal slag-free reduction of uranium from oxide raw material is developed as a way for reducing nuclear fuel cycle, and solving ecological problems of the nuclear industry. The plasma pilot plant comprises a shaft furnace supplied with DC hydrogen plasmotrons. Operating parameters of the plasmotron: power ~ 140 kW; efficiency ~ 0.93. In the primary experiments production rate of the shaft was of ~50 kg.U/h. After modification of the hearth a rate of a reduction was of 124 kg/h; power requirements ~ 3 kWh/kg U.

1. Function of carbothermal reduction of metallic uranium in nuclear fuel cycle.

Despite world needs in metallic uranium has been reduced after cessation of producing weapon plutonium, a role of uranium will increase in connection with the new trends in the nuclear fuel cycle: continuing use of uranium as a fuel elements of gas-cooled power reactors; use of enriched uranium in (U–Zr)–fuel elements of the reactors for navy and in the ignition zone of the power (U-Th)–reactors; feasible industrial application of laser technology for uranium enrichment (method AVLIS). Consumption of metallic uranium will drastically increase at inclusion of thorium into the nuclear fuel cycle /1/: designing the reactors VVER-1000T, in which the active zone is heterogeneous. Industrial application of the laser uranium enrichment on isotope U-235 (method AVLIS) must influence considerably on the structure of the nuclear fuel cycle and increase the role of producing metallic uranium.

Current production technology of metallic uranium requires producing uranium dioxide, UO₂, which is then converted to uranium tetrafluoride, UF₄; then uranium is reduced with the use of the calcium- or magnesium- thermal smelting, therefore, according to the route U₂C₃ → U₂O₅ → UF₄ → U. In the processes of reduction of uranium from UF₄ fluorine is transferred into the slags of small value of NaF or MgF₂, of which application is very limited. The concern is not limited with depreciation of fluorine, ecological problems emerged at the uranium metallurgical plants, connected with storing large masses of the slag polluted with uranium.

There is alternative technological route – reduction of uranium directly from oxide raw material -U₃O₈. As a reducing agent, one uses carbon. In this case the problem of slags falls off. Realization of this concept reduces the nuclear fuel cycle; therewith falls off production of uranium dioxide and uranium tetrafluoride as well as producing of auxiliary materials.

2. Thermodynamics of the carbothermal reduction of uranium from oxides.

According to the equilibrium diagram of the system U – C, uranium formates with carbon three compounds UC, U₂C₄, UC₃/2/. UC is stable to the melting temperature; U₂C₃ is stable to 1173 K, at which it decomposes without melting; UC₃ is stable from 1500 K to the melting temperature. At temperature ~1300 C remarkable solubility of uranium in UC was identified, therefore, the alloys corresponding to the portion of the diagram between U and UC are two-phase. Solubility of carbon in solid uranium is low at the eutectic temperature 1116.6 C, but at the transition into the liquid phase the solubility increases rapidly. There is a range of solid.
solutions at the portion between the phases UC and $\beta$-UC$_2$ above 2100°C and down to the solidus line. The process of carbothermic reduction of uranium from oxide raw material is described by the gross equation:

$$U_3O_8 + (x + y)C \rightarrow 3U + xCO_2 + yCO,$$

where $(2x + y) < 8$. Analysis of equilibrium in the system U-O-C was conducted with the use of the program complex “Chemical Bench” developed in RRC “Kurchatov Institute”, which is the user-oriented computer program for modelling, designing and optimization of various processes, reactors and technologies. The complex “Chemical Bench” includes a variety of models of technological processes, the comprehensive basis of data and uses the verified methods of solving. In particular, the model “Metallurgical reactor” used for this purpose, which enables to calculate equilibriums in the systems, characterizing by miscellaneous phase transitions, wide variation of pressure and formation of imperfect alloys and solid solutions.

The computer calculation of equilibrium in the system UO$_2$ — N was conducted at the account of solid solutions: carbon in uranium and uranium in UC. The composition of the system U$_3$C — C at pressure 0.001 MPa maximum of UC is at $T$—2100 K, maximum of condensed uranium content is attained at $T$—2650 K. At pressure 0.01 Mpa there is remarkable shift of the maximum of the contents of uranium monocarbide, condensed and gaseous uranium to the direction of more high temperatures: UN at $T$—2400 K, condensed uranium — at 3000 K. At temperature 3600 K practically all uranium is in gas phase. At further increase of pressure to 0.1 Mpa the maximum of the contents of UN, U(cond.) and U(gas) are at 2700 K, 3250 K and 4550 K respectively (Fig. 1). Contents of all other potentially possible products (U$_2$C$_3$, UC$_2$, oxide and oxyxcarbide compounds etc.) are negligible above 2000 K.

Thermodynamic calculations indicate that it is impossibly to obtain uranium under equilibrium conditions not containing some quality of uranium carbides; carbon remains in uranium as well at conducting the process under non-equilibrium conditions (e.g. in dynamic vacuum). Therefore, it is necessary to have at disposal the additional chemical or metallurgical conversion for lowering content of carbon in uranium to a specification level.
Beneath the results of large-scale experiments are considered directed to carbothermal reduction of uranium from the oxide raw material.

3. Equipment for plasma shaft reduction of uranium from oxide raw materials.
As the most perspective variant of plasma technology for carbothermal reduction of uranium from oxide raw material was found plasma treatment of briquetted charge of uranium oxides and carbon in the shaft furnace. Metalurgical plasmatron with transferred electric arc operating on hydrogen was used for heating and reduction of uranium. Principal flow sheet of electrical supply of the apparatus is presented in Fig. 2. The scheme includes controlled rectifier, oscillator, DC-plasmatron anode, intermediate cathode, electric arc, melt bath. Flow sheet of the shaft furnaces itself is shown in Fig 3: this is a water-cooled shaft 2, over which the loading appliance 1, filled in with briquettes of uranium oxides and carbon having the composition to be stoichio-metric as applied to reduction of uranium from the appropriate oxide. The charge was briquetted to limit dust carrying away and to prevent disturbance of stoichiometric composition of uranium oxides and carbon. Feeding the briquettes 3 from the hopper 1 is carried out by gravity feed. The lower part of the shaft has conical narrowing to limit feeding the charge into the melt zone (a hearth) 4 and the contrary heat flux. There are several (3 at least) arc plasmatrons 7 of direct action and reverse polarity, so that the melt bath serves as a cathode.

Plasma streams, exiting from the plasmatrons, melted the charge, the
reactions of reducing uranium occurred in it; the melt bath 5 at the furnace bottom of the hearth 4 run down, as the melt accumulated, to the crystallizer, where the ingot 6 moulded. Depending on design of the crystallizer, one can stretch out the ingot with the use of stretching appliance.

As an additional reducing agent for reduction of uranium from oxide raw material, except carbon, one used hydrogen plasma. The plasmatron applied for carbothermic reduction of metals from oxide raw material is shown schematically in Fig. 4. The plasmatron is of reverse polarity comprises inner plasma hollow anode made of copper – tungsten pseudalloy with axial feed of working gas having power of 0.25 MW. The reverse polarity enables to increase length of the inner arc column and to increase efficiency of heating hydrogen fed into the plasmatron. The electric arc is closed up on the metal melt reduced from oxide raw material. The parametric power supply provides decreasing current – voltage characteristics.

Average mass temperature of the (Ar-H₂)-plasma was of 4100 – 5000 K. At the flow rate of hydrogen 10.8 nm³/h power of the plasmatron attained 140 kW, efficiency ~ 93 %.

4. Results of experiments on plasma reduction of uranium from oxide raw material.

The pilot plasma furnace consisted of the water-cooled cylindrical shaft 0.5 m. in diameter and 0.8 m. in height. The furnace mouth comprises the gravity spout, on which the batcher supplied with the hydraulic drive is fastened. The furnace is performed to be hermetically sealed. The hearth with three plasmatrons of reverse polarity was attached to the lower portion of the shaft. The hearth was ended with the water-cooled stool for ingot mold of the reduced uranium; the off – gas went up through the gaps between the charge briquettes and are removed into the scrubbing system.

Power supply of the plasmatrons included three parametric current sources with power of 140 kW each. The system of gas supply of the plasmatron is divided to three parallel circuits supplying three plasmatrons with argon and hydrogen. There were on the board the control buttons of the DC- and AC-contacts, oscillator, autotransformers and hydraulic drives, the emergency detaching bottom and measuring instruments.

The plasma furnace hearth is provided with auxiliary capacity designed for intake of molten metal from the shaft. The auxiliary capacity was heated by one plasmatron. Two other plasmatrons operated on the hearth. The auxiliary capacity is supplied with overflow channel covered by the water-cooled shutoff. It was found at testing the hearth, that intensive reducing uranium took place in the shaft with a rate of 50 kg U/h. The reduced uranium flowed out into the auxiliary capacity and formed as an ingot of ~40 kg. Partial drain of uranium was carried out into the ingot mold.

The charge had the gross composition U₂O₅ + C, where x was of 2.3...2.4. The initial components were batched in the ratio of 1 kg U₂O₅: 0.12-0.13 kg. of the coal pitch, the blend was loaded into the hopper-mixer, the latter was inserted into the grip of the mixing machine and the blend was mixed in crushing into pieces the coal pitch. The charge was pressed on the heated matrix with simultaneous extrusion through the dies with cell sizes of 18 – 20 mm. Then the charge was loaded into the container of stainless steel and calcinated in the electrical furnace at temperature 700 – 800°C during 3 hours. According to the X-ray analysis, during calcination of the charge uranium is reduced from U₂O₅ practically to UO₂, so that composition of the charge briquettes corresponds approximately to the formula UO₂ + 2N. The charge briquettes were loaded into the shaft through the feeding hatch. Then installed the plasmatrons into the hearth, sealed the furnace, pumped out...
the furnace by to the residual pressure 0.04 Pa and filled in with argon, ignited the plasmatrons, and established the gas flow rate. After feeding the charge into the furnace intensive carbothermic melting started in the hearth. After descending the charge the metal reduced was subjected to degassing. Feeding of hydrogen was stopped, the plasmatrons were switched off, the shaft was filled in with argon. The ingot was taken out, the remainders of the charge and the lining slag were loaded to the next melting. The results of the meltings are presented in Table 1.

In the course of the tests of the pilot plant 2.423 t. of metallic uranium were produced. Direct output of uranium to the crude ingot was 95%, other 5% were collected at trimming the shaft, the hearth and the filter. Composition of the crude uranium ingots – in Table 2.

<table>
<thead>
<tr>
<th>Melting</th>
<th>Charging, kg</th>
<th>Time of melting, h</th>
<th>Obtained, kg</th>
<th>Content of (N(%) \text{ in U}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>15.5</td>
<td>30</td>
<td>7.30</td>
<td>2.90</td>
</tr>
<tr>
<td>2</td>
<td>15.0</td>
<td>40</td>
<td>8.25</td>
<td>2.90</td>
</tr>
<tr>
<td>3</td>
<td>19.4</td>
<td>40</td>
<td>10.0</td>
<td>3.30</td>
</tr>
<tr>
<td>4</td>
<td>12.9</td>
<td>40</td>
<td>7.5</td>
<td>3.5</td>
</tr>
<tr>
<td>5</td>
<td>15.0</td>
<td>35</td>
<td>7.1</td>
<td>4.8</td>
</tr>
<tr>
<td>6</td>
<td>16.0</td>
<td>50</td>
<td>9.0</td>
<td>3.6</td>
</tr>
<tr>
<td>7</td>
<td>16.0</td>
<td>30</td>
<td>11.7</td>
<td>0.55</td>
</tr>
</tbody>
</table>

Table 2. Chemical composition of the crude uranium ingots.

<table>
<thead>
<tr>
<th>Melting</th>
<th>Content of chemical elements, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 x</td>
<td>(10^1) (10^2) (10^3) (10^4) (10^5) (10^6)</td>
</tr>
<tr>
<td>1</td>
<td>96.5 (10^1) 7.9 (10^2) 2.8 (10^3) 2.8 (10^4) 4.2 (10^5) 0.4 (10^6)</td>
</tr>
<tr>
<td>2</td>
<td>96.5 (10^1) 6.6 (10^2) 3.2 (10^3) 2.0 (10^4) 4.6 (10^5) 0.3 (10^6)</td>
</tr>
<tr>
<td>3</td>
<td>96.4 (10^1) 2.3 (10^2) 1.9 (10^3) 2.0 (10^4) 4.2 (10^5) 0.3 (10^6)</td>
</tr>
<tr>
<td>4</td>
<td>96.0 (10^1) 2.3 (10^2) 1.1 (10^3) 2.0 (10^4) 6.1 (10^5) 0.3 (10^6)</td>
</tr>
<tr>
<td>5</td>
<td>96.3 (10^1) 2.3 (10^2) 1.1 (10^3) 2.0 (10^4) 5.9 (10^5) 0.1 (10^6)</td>
</tr>
<tr>
<td>6</td>
<td>95.8 (10^1) 2.0 (10^2) 1.0 (10^3) 2.0 (10^4) 6.8 (10^5) 0.2 (10^6)</td>
</tr>
<tr>
<td>7</td>
<td>96.1 (10^1) 2.3 (10^2) 3.2 (10^3) 2.0 (10^4) 10.7 (10^5) 0.3 (10^6)</td>
</tr>
</tbody>
</table>

In the industrial apparatus for carbothermic reduction of uranium from oxide raw material a hearth was designed in such a way, that uranium reduced was collected in the bath with following pouring melt into the detachable ingot molds without stopping the process. A quantity of a single pouring was 0.2 t. U. The overall quantity of the charge loaded into the shaft was ~ 3 t., average rate of the process was of 124 kg/h; power consumptions - 3 kWh/kg.

5. Selection of heat carrier for plasma carbothermic reduction of uranium from oxides.

Various gases have been tested as heat carriers in the process aforesaid.

**Hydrogen.** Using hydrogen results in improving heat- and mass exchange of plasma with charge briquettes, but hydrogen facilitates to elimination of oxygen from uranium oxides in the form of water vapor; this results in more high content of residual carbon in the uranium. Thermodynamic study demonstrated that practically there was no influence of hydrogen on
the temperature dependence of the reduction products composition. It is connected with more high thermodynamic stability of CO – molecules above 2500 C as compared to I2 ; I – molecules, i.e. at T > 2500 C hydrogen loses its reduction ability. It means, that one can select as a plasma gas not without fail hydrogen: for this purpose one can use any neutral gas.

Nitrogen. Use of nitrogen as heat carrier results in synthesis of uranium nitrides. At availability of oxygen and carbon in uranium there are solid solutions UN, UC, UO. It is very difficult to eliminate chemically bonded nitrogen at the stage of refining.

Argon. Use of argon does not create technological problems, improves operation conditions of electric arc plasmatrons, but increases cost of the process.

Carbon dioxide. Carbon dioxide is chemically compatible with the charges U3O8+x C but output of uranium lowers drastically at using this plasma heat carrier.

Therefore, analysis of various gases as plasma heat carriers for carbothermic reduction of uranium from oxide raw material demonstrated that it was the most convenient to use either hydrogen or hydrogen in mixture with argon.

6. Modern level of plasma technique and technology for realizing plasma carbothermic process of uranium reduction from oxide raw material

Power of DC electric arc metallurgical plasmatrons with tubular electrodes made of copper alloys (copper alloyed with Zr, Ag, Cr) or graphite is up to 1 MW. The metallurgical plasmatrons with tubular electrodes made of copper alloy have controlled power in the range 250 – 4500 kW; voltage on the electrodes 600 – 900 V, current – 420 – 5000 A /5/.

For obtaining metallic uranium from oxide raw material one should be orientated to the most available raw material – U3O8 – stable chemical compound, obtained after completion of extraction purification of uranium. At integral energy consumption of 3 kW h/kg.U, for producing 0.5 t U/h one must have available the furnace with installed power of 1.5 MW. Operating mode is continuous or semicontinuous depending on drawing off uranium ingots.

At plasma carbothermic reducing uranium from uranium oxides content of carbon in uranium exceeds the level of 550 ppm /4/; as well as content of oxygen, i.e. uranium obtained needs in refining, therefore the uranium ingots are transported to the appropriate remelting.

References.