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OPTIMIZATION OF MAGNESIUM' THERMAL REDUCTION TECHNOLOGY OF ZIRCONIUM TETRACHLORIDE

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The problems of getting impurities in zirconium sponge and ways of reducing their amount by preparing starting materials in different ways.

As of 2013 in Ukraine operated 15 nuclear power units with a total installed capacity of 1385 MW. In 2012, they had accumulated about 100 billion kWh, representing about 50% of the total domestic production of electricity. Ukraine's nuclear power requirement in the fuel for BBEP-1000 make up 620 fuel rods per year. Currently, the bulk of Ukrainian NPPs provided nuclear fuel produced by VAT "TVEL" (Russian Federation). This puts Ukraine's energy dependence on Russia, despite of the fact that Ukraine has large reserves of zirconium and uranium ore [1, 2]. For zirconium ore deposits Ukraine is the third largest in the world after Australia and South Africa [3]. To reduce Ukraine's energy dependence from other countries in 1995 was adopted the "Energy Strategy of Ukraine till 2030". One of the areas of its implementation was "Applications of zirconium production by 2030." It included the first phase (2005-2015 years), organization of production rolled zirconium at levels that ensure the needs of the nuclear fuel cycle in Ukraine (150 tons). In the long term (2016-2030 years) was supposed to increase the production of rolled zirconium to 300 tons for manufacturing rolled zirconium alloys used different composition, which are based on metallic zirconium of nuclear purity [4]. Recently, for the production of zirconium alloys zirconium sponge production of magnesium thermal reduction (U.S., France, Russia, China, India), electrolytic zirconium and iodide zirconium (Russia) are used.

According to the Programme planned to make at SSPE "Zirconium" technical re-equipment of existing production zirconium, on SE "State titanium research and design institute" - construction and commissioning of zirconium sponge, on SE "Research and design tube institute" – reconstruction and technical re-commissioning production of zirconium rolled products, tubes, rods and tapes.

By direction of research, design and information support facilities in the nuclear fuel cycle (NFC) provided:

– improve the technology of zirconium dioxide;

– develop technology and equipment for obtaining zirconium sponge by magnesium thermal reduction;

– develop technology for zirconium alloy tubular workpiece;

– improve the technology of cold deformation and getting rolled zirconium.

Top performer scientific, design and information support NFC facilities were identified SE "State titanium research and design institute", ISSP KhPTI MT and SE "RDTI".

SE "State titanium research and design institute" and ISSP MT KhPTI during 2007-2013 years performed a complex of research projects to create technology and equipment for the production of zirconium sponge of magnesium thermal reduction and received experimental batch of zirconium sponge, developed the foundations of technology for domestic zirconium alloy Zr1Nb based on zirconium sponge of magnesium thermal reduction.

Zirconium alloys which have low thermal neutron capture cross section, high radiation and corrosion resistance, is the main structural material for reactor core with water-coolant based on thermal neutrons [5]. Very low additive gas impurities significantly affect the physical and mechanical properties of zirconium alloys and their melting mode, machining and heat treatment. Increasing the oxygen content in zirconium alloys ingots reduces performance pipes for manufacturing fuel cells. Elevated levels of oxygen and nitrogen leads to an increase in σ_v and $\sigma_{0,2}$. In the range of content (0.002...0.40)% oxygen content and (0.002...0.44)% nitrogen ductility decreases respectively for 5 and 10 times. When zirconium sponge of magnesium thermal reduction used for the production of zirconium alloys high content of impurities of chlorine and hydrogen leads to the destabilization of regimes arc and electron- beam melting of consumable electrodes [6].

The main sources of admission to zirconium sponge production of magnesium thermal reduction impurities of oxygen, nitrogen and hydrogen are the raw materials (zirconium tetrachloride, magnesium), auxiliary materials (argon, rubber) and atmospheric air which leaked to apparatus of reduction and separation at their operating. Impurity of chlorine comes in zirconium sponge mainly of magnesium chloride, which is a product of zirconium tetrachloride of magnesium thermal reduction.

To optimize the magnesium thermal reduction process of zirconium tetrachloride and reduce the amount of impurities that come with the feedstock were performed researching of technology of reduction process of zirconium tetrachloride, prepared in different ways:

– of powdery zirconium tetrachloride, which received by double sublimation way of zirconium tetrachloride;

– of molten chloride salt that is received by melting and mixing method;

– with compacted zirconium tetrachloride that received by methods of pressing and over-sublimating of zirconium tetrachloride.

At the industrial production of zirconium sponge way of magnesium thermal reduction to implement reduction processes mainly sublimated solid and powdered zirconium tetrachloride is used [7-11]. Type of feedstock have a considerable effect to the reduction process indexes, including the productivity of reduction, coefficient of the usage of raw materials, power consumption and the quality of zirconium sponge. It also has a significant effect on the design of the reduction apparatus and its technical and economic parameters: size, weight , reliability and productivity. So when zirconium tetrachloride sublimated solid is used [7-8], design of the reduction apparatus includes an evaporator, a large size and power consumption , low productivity due to difficulties in the cart to block the heat of solid zirconium tetrachloride and low rate of evaporation of zirconium tetrachloride. When powdered zirconium tetrachloride [9-11] is used, design of the reduction apparatus should appended of zirconium tetrachloride powder loading node in the reduction reactor (screw feeder, hopper, etc.) and the evaporators with steam pipes located outside the reactor. It also complicates the design of the device and its reduction operation. In addition, zirconium tetrachloride powder has a low density (0.7…1.0 g/cm^3), which requires the evaporator with large hopper at loading. In the process of loading the powder of zirconium tetrachloride in the evaporator hangs on the walls of consumable container and sealed with screw feeder and screw gets jammed, leading to the shutdown of the feeder and stop the reduction process. Resuming of the reduction process requires cleaning screw feeder. At this moment a part of raw materials has been lost and coefficient of zirconium tetrachloride usage and productivity of reduction process has been reduced. Using the method of loading the powder of zirconium tetrachloride in pneumatic vaporizer, using argon [12], requires spending large amounts of argon. Resulting in the removal of the powder from the evaporator and the reduction reactor, which reduces the coefficient of zirconium tetrachloride usage and productivity of the reduction process, and complicates the design of equipment.

A method of reducing of zirconium tetrachloride from molten chloride salt [13, 14]. The advantages of this method are: the ability to involve waste zirconium production, refining zirconium tetrachloride from impurities, increasing the loading of the reactor due to its higher density in the molten salt (1.8..1.9 g/cm^3) versus with powdered (0.7..0.9 g/cm^3), reduction of losses of zirconium tetrachloride by eliminating the removal of dust, technology effectivity of the original product in storage and transportation (not hydrolyzed and has a slight outgassing at room temperature).

So way of preparation of the feedstock to the process of reduction has an important effect on the productivity and reduction process to develop the technology, which requires more detailed studying of this effect and choose the most effective way to prepare the feedstock to the process of reduction.

Aim of this work was to investigate and to work out of technological modes of obtaining zirconium sponge from zirconium tetrachloride with different type and composition (powdery, melt chlorides, compacted) to determine the best method of preparation of the feedstock to the process of reduction of zirconium tetrachloride to zirconium sponge that provides increased productivity and coefficient of zirconium tetrachloride usage and reduce the content of impurities in zirconium sponge.

To conduct research in laboratory apparatus prepared samples of zirconium tetrachloride and various types of stuff have been prepared:

– powdered, which is obtained by double sublimation of zirconium tetrachloride;

– in the molten chlorides of sodium and potassium, which is obtained by mixing and melting chloride at a temperature of 550 ^{0}C;

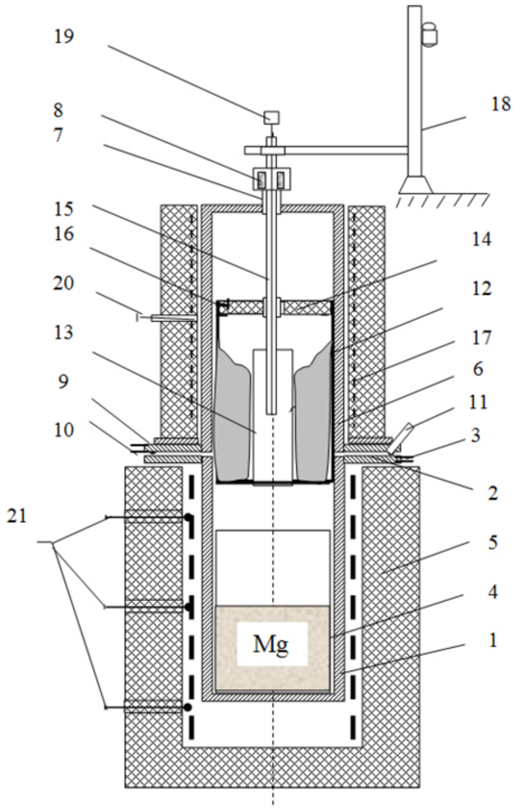
– compacted which is obtained by pressing the powder of zirconium tetrachloride sublimated on a hydraulic press and crushing to the required size;

– compacted that is received by over-sublimating of powdered zirconium tetrachloride with condensation in the solid phase and crushing to the required size.

At a laboratory device (Figure) were made 6 processes of zirconium tetrachloride reduction, which is prepared in various ways , including 2 processes using sublimated zirconium tetrachloride powder, 2 processes using zirconium tetrachloride in the chloride salt melt, a process using compacted on hydraulic press zirconium tetrachloride and one process using zirconium tetrachloride compacted by over-sublimating to the solid phase .

As can be seen from the data shown in the table, the highest proportion of zirconium tetrachloride in achieved productivity in the reduction process 5 and 6, in which compacted zirconium tetrachloride was used as a feedstock. In reduction processes 1 and 2 relative productivity on zirconium tetrachloride close to this index in the processes 5 and 6. Lowest relative productivity on zirconium tetrachloride in the reduction process 3 and 4. This can be explained by the fact that when zirconium tetrachloride in the chloride salt melt was used as a feedstock its rate of evaporation at a temperature of 450…550 ^{0}C lower than the temperature of the evaporation of compacted powder and zirconium tetrachloride. Subject to this, and the fact that using zirconium tetrachloride powder rather complicated operation on his load in the evaporator and equipment for the transportation and storage of powder more efficiently compacts zirconium tetrachloride powder to tablets or granules optimal size prior to loading into the evaporator.

Conditions of reduction processes and the results are shown in Table.



Laboratory installation of the process of zirconium tetrachloride reduction by magnesium
1 – retort; 2 – cooled flange; 3 – tubes for feeding and water drainage; 4 – reaction crucible; 5 – shaft electric furnace; 6 – boiler evaporator; 7 – pipe; 8 – gland seal; 9 – cooled flange; 10 – tubes for supply and drainage water; 11 – connection for degassing, argon flow and relief; 12 – cup for refined $ZrCl_4$; 13 – steam line; 14 – insulated lid; 15 – hollow rod; 16 – binder screw; 17 – electric furnace tube , 18 – drive rod; 19, 20 – temperature sensors for the control and regulation of temperature in retort – evaporator; 21 – temperature sensors for control and temperature regulation height retort from the reaction crucible

№ process	Type of output $ZrCl_4$			Loaded Mg into reactor, kg	The temperature in the reduction reactor, ^0C	Pressure in the reduction reactor, kPa	Duration of the reduction process, h	Obtained Zr in reaction mass, kg	Specific output of reduction by $ZrCl_4$, kg/h
	powder	salt melt	compacted						
	loaded into the evaporator / used in the reduction process, kg								
1	0.84 / 0.71	-	-	0.36	800-850	98-150	4.0	0.28	0.180
2	1.05 / 0.97	-	-	0.31	800-850	101-135	5.5	0.38	0.177
3	-	0.9 / 0.43	-	0.30	810-850	100-150	3.5	0.17	0.124
4	-	1.1 / 0.56	-	0.40	810-850	103-136	4.0	0.22	0.140
5	-	-	0.5 / 0.39	0.22	810-850	100-125	2.10	0.15	0.183
6	-	-	1.0 / 0.87	0.36	810-850	98-130	4.1	0.34	0.212

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УСОВЕРШЕНСТВОВАНИЕ ТЕХНОЛОГИИ МАГНИЕТЕРМИЧЕСКОГО ВОССТАНОВЛЕНИЯ ТЕТРАХЛОРИДА ЦИРКОНИЯ

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Рассмотрены вопросы попадания примесей в губчатый цирконий и способы уменьшения их количества за счет подготовки исходного сырья разными методами.

ВДОСКОНАЛЕННЯ ТЕХНОЛОГІЇ МАГНІЄТЕРМІЧНОГО ВІДНОВЛЕННЯ ТЕТРАХЛОРИДУ ЦИРКОНІЮ

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Розглянуто питання надходження домішок у губчастий цирконій та способи зменшення їх кількості за рахунок підготовки вихідної сировини різними способами.