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MAGNESIUM-THERMAL METHOD OF SPONGE ZIRCONIUM OBTAINING

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The results of research on magnesium-thermal technology of sponge zirconium obtaining on the laboratory apparatus are represented. The magnesium-thermal method for reduction and apparatus are briefly described. The results of research on the optimization of the processes of obtaining zirconium sponge and obtaining zirconium metal are presented. The results of the conducted investigations are recommended for development of industrial technology of sponge zirconium production and equipment for its production.

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INTRODUCTION

In the programs of work carried out in the world to improve nuclear fuel for light-water pressurized reactors (PWR, WWER) and which are aimed at further improving the operational reliability of fuel cells with fuel burn-up to 70…75 MWd/kgU and a campaign length of up to 6–7 years, much attention is paid to increasing the resource characteristics of zirconium fuel element cladding and components of fuel assemblies. Fuel vendors have developed and proposed use of a number of cladding zirconium alloys, such as Zircaloys, and Nb-containing alloys (Table 1 for composition of these alloys) [1, 2]. At high burnup, fuel rods fabricated from conventional Zircaloys often exhibit significant degradation in microstructure. This is especially pronounced in fuel rods fabricated from standard Zircaloy-4 in which significant oxidation, hydriding, and oxide spallation can occur. Corrosion resistance of Nb-containing alloys under normal operating conditions is excellent or superior to that of Zircaloy-4, some of them (E110 and E635) have been known to be susceptible to nodular oxidation under loss-of-coolant accident (LOCA) situations [3, 4]. High-temperature nodular oxidation leads to excessive H uptake and premature loss of post-quench ductility. In contrast, despite the fact that M5 cladding is fabricated from nominally the same type of Zr-1Nb alloy, the alloy has been reported to be resistant to nodular oxidation under LOCA-like conditions, and neither excessive H uptake nor premature ductility loss was observed [5]. Test results reported for Zirlo indicate a behavior similar to that of M5 [6].

The methods of producing nuclear-grade Zr used for E110 and M5 claddings greatly differ [7]. A model [8] was developed that explains contrasting susceptibility of E110 arid M5 cladding to high-temperature nodular or breakaway oxidation under LOCA situations. The model is based on effects of aliovalent elements on the properties of Zr oxide. It predicts that Ca and Al pickup (from Hf purification process) and Mg pickup (from production of sponge Zr by the Kroll process) are beneficial, because they suppress the susceptibility to nodular oxidation. Fluorine pickup (from zircon ore decomposition and Hf purification processes based on fluorine chemistry) and Zr reduction by the electrolytic process are predicted to be deleterious, leading to increased susceptibility to nodular oxidation. Because the typical fabrication procedures used to produce Zirlo, and M5 inherently promote contamination by Ca and Mg but prevent F pickup, it is predicted that susceptibility of these alloys to high-temperature nodular oxidation is inherently suppressed. In recent investigations [9], modified E110 and E635 alloys were fabricated using sponge Zr (Zr feedstock produced with Kroll process). In contrast to their conventional counterparts, the modified alloys performed similar to M5, and Zirlo, and were not susceptible to nodular or breakaway oxidation at high temperature.

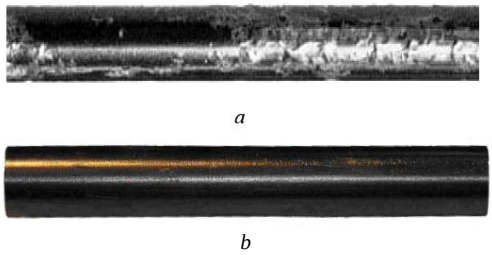
Table 1

Nominal composition of a some fuel cladding alloys

Cladding alloy	Nominal composition, wt.%
Zircaloy-2	Zr-1.5 Sn-0.2Fe-0.1 Cr-0.05Ni-0.12O
Zircaloy-4	Zr-(1.3…1.5)Sn-0.2Fe-0.1 Cr-0.12O
E110	Zr-1Nb (O ≈0.05…0.07)
M5	Zr-1Nb-0.12O
E635	Zr-1Nb-1.2Sn-0.4Fe (O ≈0.05…0.10)
Zirlo	Zr-1Nb-1Sn-0.1Fe-0.12O

In the early stage of oxidation of E110, white or grayish-white nodules of various size form more or less randomly on the cladding surface. Subsequently, the nodules coalesce to form a continuous white oxide layer. Eventually, the continuous oxide layer delaminates and flakes off (Fig. 1). Frequently, nonuniform color and partial flake-off of the oxide layer lead to a messy-looking surface [7]. Susceptibility of E110 to nodular oxidation in steam is insignificant at oxidation temperatures < 750 °C [10]. Embrittlement of E110 was insignificant after oxidation at 700 and 800 °C, indicating that the material was not susceptible to nodular oxidation or to large H uptake at these temperatures [8]. Susceptibility of E110 to nodular oxidation becomes high at oxidation temperatures in which the beta phase is stable, i.e., > 860 °C [10]. The E110 alloy fabricated using sponge Zr after oxidation at

1100 ºC has a dense, black, non-peeling oxide layer up to a local oxidation 18% (see Fig. 1,b).



a

b

Fig. 1. View of samples of E110 cladding made on based on a mixture of electrolytic and iodide zirconium (a) and spongy zirconium (b) after oxidation in steam at 1100 ºC to local oxidation of cladding 10 and 18%, respectively

In Ukraine, the industrial production of calcium-thermal zirconium (CTZ) of nuclear-grade was carried out by the extraction-calcium-thermal technology [11]. The basic process for the decomposition of zircon ore, used to produce nuclear-grade Zr involves fluorine chemistry, i.e., conversion of the ore to zirconium tetrafluoride (ZrF_4). The separation of Zr and Hf is achieved by solvent extraction using tributyl phosphate as the solvent. After this step, Hf content is reduced to <0.01 wt.%. Zirconium tetrafluoride is reduced to Zr metal through calcium-thermal reduction method and subsequent electron-beam melting (EBM) of the obtained metal for reduces impurities contents. This method allows obtaining zirconium alloys directly in the reduction process.

The calcium-thermal method of producing zirconium has substantial disadvantages and limitations:

– high cost price of CTZ (hydrogen fluoride, hydrofluoric acid, metallic calcium are not produced in Ukraine; the costs of only these three reagents per 1 kg of Zr are 17.2 USD);

– the impossibility of using the CTZ technology to obtain complex alloyed alloys (such as Zircaloy, E635) due to the use of EBM;

– the producing zirconium process is based on fluorine chemistry.

Considering the disadvantages of the calcium-thermal method and the orientation of all world productions of zirconium to chloride technology, a decision was made in Ukraine to re-equip the existing production of zirconium to chloride magnesium technology for the production of zirconium products in the following way [11]:

1. Production of zirconium dioxide at the existing chemical processing.

2. Development of technology for the chlorination of zirconium dioxide with subsequent magnesium-thermal reduction to zirconium sponge.

3. Production of zirconium alloy and pipe billet.

4. Production of zirconium rolled products (pipe, rod, tape, etc.).

The production of sponge zirconium, which is being developed, should include: a process of chlorination of zirconium dioxide; a condensation of zirconium tetrachloride; the magnesium-thermal reduction and vacuum distillation.

In this paper, the state of the art of nuclear grade zirconium production in Ukraine is reviewed. The magnesium-thermal method for reduction to the metal are briefly discussed. The features and characteristics of this method as well as the results of research on the optimization of the processes of obtaining zirconium sponge and zirconium metal are described. This paper aims to provide future directions of research and development for nuclear grade zirconium production.

METHODS AND APPARATUS

To implement the process of obtaining sponge zirconium were developed a process and an apparatus for the production of metal zirconium by the reduction of zirconium tetrachloride by magnesium [12, 13].

The zirconium sponge production can roughly be divided into: chlorination of zirconium dioxide, reduction of zirconium tetrachloride to zirconium metal by Kroll process and vacuum distillation to remove impurities.

Zirconium dioxide chlorination technology is used to produce zirconium tetrachloride. Chlorination of zirconium dioxide has high energy consumption, occurs with heat consumption – for the reaction of interaction of zirconium dioxide with chlorine it is required ~ 102 kJ per 1 mole of zirconium dioxide. When zirconium is added to the charge, a large amount of thermal energy is released, because the reaction of the interaction of metal zirconium with chlorine is exothermic and occurs with the release of ~ 863 kJ of heat per 1 mole of zirconium, which reduces the heat consumption for the chlorination process. The reaction

$$ZrO_2+C+2Cl_2=ZrCl_4+CO_2 \quad (1)$$

is endothermic, the thermal effect of the reaction is determined by the change in the enthalpy of formation and the heat capacity between the final and initial compounds, taking into account the temperature Q_{reac}= -102.303 kJ/mole ZrO_2. The reaction

$$Zr+2Cl_2=ZrCl_4 \quad (2)$$

is exothermic, the thermal effect of the reaction is Q_{reac} = +863.048 kJ/mole Zr.

The chlorination technology described in [14] was used for production of zirconium tetrachloride. The charge for chlorination consisted of zirconium powder, zirconium dioxide, carbonaceous reducing agent and alkali metal chlorides. The mixture thus obtained was placed in a laboratory installation for chlorination. The installation for chlorination consists of a chlorinator located in a shaft-type electric furnace, a chlorine supply system, a charge loading container, a condenser and a receiver tank for collecting zirconium tetrachloride. After heating a mixture of NaCl and KCl salts to a predetermined temperature, the melt was blown down with chlorine for 10...15 min, and the mixture, which consist zirconium dioxide, carbonaceous reducing agent, alkali metal chlorides and zirconium powder, was charged to the surface of the melt. The steam-gas mixture, which is formed and consists of vapors of zirconium tetrachloride, impurity chlorides of the accompanying metals and gaseous chlorination products, enters the condenser, where it is condensed. After the completion of the experiment obtained

zirconium tetrachloride was analyzed for the content of the main impurities.

The Kroll process is very commonly used on industrial scale for the production of metals from the corresponding metal chlorides. It is currently used for producing nearly all commercial titanium, zirconium and hafnium metal. Ductile zirconium is produced by the reduction of pure gaseous zirconium tetrachloride with molten magnesium in an inert atmosphere, as explained in Eq. (3)

$$2Mg + ZrCl_4 \rightarrow Zr + 2MgCl_2. \quad (3)$$

After the reduction, the formed magnesium chloride and the excess magnesium reductant need to be removed from the zirconium product. The bulk of magnesium chloride is separated mechanically and the obtained metal mass containing residual magnesium chloride and unreacted magnesium is further purified by distillation. The metal ingot is placed in the lower portion of the distillation column which is heated to a high temperature to make the magnesium and magnesium chloride evaporate from zirconium metal and then condense in the cooled upper portion of the column. As the evaporation of the impurities, the metallic zirconium exists as a sintered porous metal mass, which is commonly referred to as zirconium sponge.

The Kroll process is a multi-step process including primary reduction, sponge handling and additional purification, with each individual step being a batch process in itself, and the required apparatus is relatively complicated and expensive. These inherent disadvantages of the Kroll process lead to high production costs. A number of attempts have been made in order to modify and improve the process.

In order to carry out the research, experimental laboratory installations were developed for the reduction and vacuum distillation (separation) processes. In Fig. 2 shows the scheme of the laboratory installation for the magnesium-thermal reduction of zirconium tetrachloride.

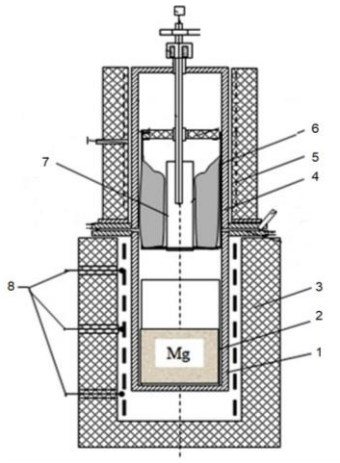


Fig. 2. Laboratory installation of magnesium thermal reduction of zirconium tetrachloride: 1 – retort; 2 – reaction crucible; 3 – electric furnace; 4 – retort-evaporator; 5 – electric furnace; 6 – crucible for purified $ZrCl_4$; 7 – steam pipeline; 8 – thermal sensors for control and regulation of temperature

During the reduction process, the reaction crucible (1) with magnesium-reductant was heated to 800 °C. The retort-evaporator and the crucible (6) with purified zirconium tetrachloride were heated to a temperature of 460…550 °C. In this case, zirconium tetrachloride was sublimated, and its vapors entered the reaction crucible (1) through the steam line (7), where they interacted with magnesium to form sponge zirconium and magnesium chloride. The main part of the spongy zirconium formed was deposited on the bottom of the reaction crucible.

The reduced mass of zirconium after mechanical separation of $MgCl_2$ is subjected to vacuum distillation operation for removal of entrapped Mg and $MgCl_2$ to get pure zirconium sponge. Purification of the reaction mass is carried out by separation in vacuum at precipitation of magnesium condensate and its chloride in a condenser. Research and development of technological modes of vacuum distillation of spongy zirconium and its high-temperature processing in a vacuum were carried out at a laboratory vacuum distillation installation (Fig. 3).

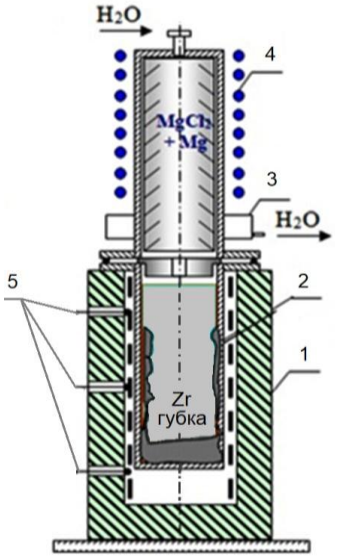


Fig. 3. Laboratory installation of vacuum separation (distillation): 1 – electric furnace; 2 – vacuum distillation apparatus; 3 – water collector; 4 – cooler; 5 – thermocouples

The processes of vacuum separation of the reaction mass are carried out in vacuum at a temperature of 900…950 °C in the upper zone of the furnace and 980…1010 °C in the middle and lower zones of the furnace. The duration of high-temperature exposure in a vacuum was set taking into account the content of zirconium, magnesium and magnesium chloride in the reaction mass within 3…4 h. The reaction mass after distillation is mechanically crushed into small pieces (2…25 mm) of zirconium sponge for further use.

EXPERIMENTAL RESULTS AND DISCUSSION

The purity of zirconium depends on the quality of the initial components (zirconium tetrachloride and magnesium), as well as on the conditions of the reduction process and on the material of the retorts in

which this process is carried out. As is known, all impurities present in zirconium tetrachloride and magnesium are absorbed by zirconium.

In order to improve the quality of initial raw materials, it is necessary to carry out rectification of magnesium before loading it into the reduction reactor. It is also necessary to carry out sublimation purification of zirconium tetrachloride in order to obtain the minimum required impurity content regulated for obtaining reactor-grade zirconium. To protect spongy zirconium from contamination with impurities from the material of the reaction crucible, the optimal solution was proposed to apply a protective zirconium coating by the thermal diffusion deposition method. It is also extremely important to comply with the technological regulations for carrying out the processes of reduction and vacuum separation of spongy zirconium in the process of magnesium-thermal reduction.

Technological regimes for the obtaining and rectification of zirconium tetrachloride using the technology of sublimation purification have been investigated. It has been established that sublimation purification in one stage makes it possible to obtain zirconium tetrachloride with a quality sufficient to obtain reactor-grade spongy zirconium. It should also be noted that a further increase in resublimation cycles improves quality indicators, but leads to an increase in the loss of valuable raw materials. Based on the research results, it is recommended to carry out a one-stage sublimation purification of zirconium tetrachloride to obtain the required content of regulated impurities. The content of impurities in zirconium tetrachloride of various degrees of purification is shown in Table 2.

Table 2

The content of impurities in zirconium tetrachloride of different degrees of purification

$ZrCl_4$	Content of impurities, wt.%					
	Al	Na	K	Si	Ca	Fe
Technical	0.048	0.24	0.36	0.0078	0.00165	0.017
Sublimated	0.0033	0.004	0.003	0.0057	0.00080	0.0066
Double sublimated	0.0030	0.004	0.003	0.0049	0.00069	0.0042
Triple sublimated	0.0023	0.005	<0.001	0.0040	0.00059	0.0040

$ZrCl_4$	Content of impurities, wt.%					
	Ti	Cr	Mg	Cu	Mn	Ni
Technical	0.030	0.0044	0.0011	0.00069	0.00051	0.0024
Sublimated	0.004	0.0046	0.0012	0.0001	0.0003	0.0007
Double sublimated	0.003	0.0031	0.0005	<0.0001	0.0002	<0.0001
Triple sublimated	0.004	0.0033	0.0005	<0.0001	0.0002	<0.0001

An analysis of the ways of formation of substandard products of magnesium-thermal production of spongy zirconium and methods of their processing was carried out. Processes of processing of chloride substandard products of magnesium-thermal production of zirconium by hydrolysis of zirconium chlorides with subsequent decomposition of zirconium oxychloride into high-quality zirconium dioxide ZrO_2 and processing of metallic substandard products of magnesium-thermal production of zirconium by hydrogenation and comminuting are investigated [14]. It has been established that the quality of zirconium tetrachloride, obtained by processing substandard products of magnesium-thermal production of zirconium spongy, exceeds in some indicators zirconium tetrachloride, obtained by conventional technology. The chemical composition of the obtained purified zirconium tetrachloride in comparison with the typical products of the world-leading manufacturers ATI (Allegheny Technologies Incorporated), USA [15] and CEZUS (Areva), France [16] are shown in Table 3. As can be seen from the Table, according to the results of chemical analysis, the quality of purified zirconium tetrachloride is acceptable even at the level of world manufacturers. The quality of zirconium tetrachloride, obtained by processing substandard products of magnesium-thermal production of spongy zirconium, is not inferior, and in some indicators exceeds the purified zirconium tetrachloride, obtained by conventional technology.

A study was carried out to optimize the modes of the main technological processes of magnesium-thermal reduction from raw materials of different composition and high-temperature vacuum processing of spongy zirconium obtained under various conditions [17]. The study of technological modes of magnesium-thermal reduction of zirconium tetrachloride and vacuum separation was carried out on laboratory installations (see Figs. 2 and 3). For the magnesium-thermal reduction process, the optimal temperature values in the reduction furnace and the evaporation furnace, the residual pressure in the reduction apparatus, the average loading rate and the magnesium utilization factor were determined. For the process of vacuum sublimation (distillation), the optimal temperature values of the separation furnace, residual pressure and duration of the process are determined.

Table 3

The chemical composition of purified zirconium tetrachloride

Impurity	Content of the component in zirconium tetrachloride, wt.%		
	Purified	ATI	CEZUS
Al	0.002…0.0072	<0.01	<0.0050
Fe	0.0040…0.0056	<0.01	<0.0040
Si	0.0091…0.0170	<0.01	<0.0020
Ti	0.0002…0.0011	<0.0050	<0.0010
Cr	0.0003…0.0007	<0.0050	<0.0010
Mg	<0.0010	–	<0.0010

Technological regime for using the operation of pouring out of magnesium chloride in the process of magnesium-thermal reduction of zirconium tetrachloride have been studied and developed. It is shown that the use the operation of pouring out of magnesium chloride allows reducing the duration of vacuum separation by 30%, which in general leads to an increase in the productivity of vacuum separation equipment and energy savings.

The chemical analysis of the obtained magnesium-thermal zirconium is given in the Table 4. Comparing the chemical composition of the resulting zirconium sponge with the chemical composition of magnesium-thermal zirconium from other manufacturers, we can see that the quantitative composition of impurities present in Ukrainian magnesium-thermal zirconium only for some impurities exceeds the data for ASTM B350. The content of nitrogen and oxygen impurities in the obtained spongy zirconium is higher than in the commodity metal of foreign manufacturers. This is due to the lower quality of the zirconium tetrachloride used. The content of carbon, iron, magnesium in some batches of sponge exceeds the permissible content of these elements.

The method of electron-beam melting was used to study the change in the content of impurities during the refining of a magnesium-thermal zirconium sponge of domestic production. Researches refining of test samples of magnesium-thermal zirconium sponge have shown that an increased content of impurities in all research sponge parties not allow effective use the method of EBM for obtaining high quality zirconium ingots nuclear grade [18, 19]. It was established that in some samples of magnesium-thermal zirconium sponge a content of certain impurities exceeds allowable their content, in particular titanium, iron and interstitial impurities.

The increased content of oxygen in almost all research sponge parties leads to spattering of starting materials during EBM due to a significant amount of gas-forming impurities and the formation of refractory compounds which are not allowed to fully melt the sample and thereby obtain a high quality ingot both content of impurities and on structure. To reduce the gases and other easily volatile impurities a preliminary annealing of the initial sponge was carried out.

Initial sponge was annealed at temperatures of 700...900 °C. Preliminary annealing of samples positively influences on the carrying out of EBM: spattering of the sponge is reduced, warm-up time of initial materials decreases and, as a consequence, melting time is significantly less for the annealed sponge as compared with the sponge in the initial state.

Table 4

The content of impurities in the original magnesium-thermal zirconium sponge, wt.%

Impurity	Zirconium sponge	ASTM B350
Al	0.005…0.02	0.0075
B	<0.002	0.00005
C	0.04	0.027
Ca	<0.0012	–
Cl	0.06…0.13	–
Co	0.0002	0.002
Cr	0.01…0.02	0.02
Cu	0.002…0.004	0.005
Fe	0.22…0.57	0.15
Mg	0.05…0.25	0.002
Mn	0.002…0.003	0.005
Mo	0.0025	0.0025
Nb	0.009	-
Ni	0.007…0.01	0.007
Pb	<0.003	-
Si	0.003…0.02	0.012
Sn	<0.001	0.005
Ti	0.0035	0.005

The refining processes are actively occurring during EBM. Evaporation of metallic impurities is determined by the melting temperature of zirconium. Therefore impurities whose melting temperature is lower melting temperature of zirconium (Al, Ti, Cr, Mn, Fe, Ni, Cu, Ca, etc.) during EBM evaporate. The content of impurities in magnesium-thermal zirconium after double EBM is given in the Table 5 [11, 19].

Appearance of magnesium-thermal spongy zirconium and microstructure of magnesium-thermal zirconium after electron beam melting is shown in Fig. 4. As can be seen microstructure of magnesium-thermal zirconium is similar to microstructure of iodide zirconium. It is the same large grains, clean boundaries and set of colors when considering of zirconium grains in polarized light.

Table 5

The content of impurities in the magnesium-thermal zirconium after double EBM, wt.%

Impurity	Zr after double EBM	ASTM B350	CTZ-110*
Nb	< 0.00005	–	0.9…1.1
Hf	0.1	0.01	< 0.01
Cd	< 0.00001	–	< 0.00003
Si	0.0006	0.012	< 0.02
Al	0.0001	0.0075	< 0.008
Ni	0.07	0.007	< 0.02
Cu	0.00002	0.005	< 0.005

(Table 5) continued

Ca	< 0.0001	–	< 0.03
Mn	0.00002	0.005	< 0.002
Pb	< 0.0001	–	< 0.005
Ti	0.0092	0.005	< 0.007
B	< 0.00001	0.00005	< 0.00005
Be	< 0.00001	–	< 0.003
Fe	0.035	0.15	< 0.05
Cr	0.00045	0.02	< 0.02
O	0.14	–	0.06…0.1
C	0.008	0.027	< 0.02
N	0.0009	–	< 0.006
F	0.00015	–	< 0.003
Mo	< 0.0005	0.0025	< 0.005
Li	< 0.00001	–	< 0.0002
K	< 0.0001	–	< 0.004
Cl	< 0.0001	–	< 0.003

*Alloy Zr-1Nb based on calcium-thermal zirconium

a *b*

Fig. 4. Appearance of magnesium-thermal spongy zirconium (a); microstructure of magnesium-thermal zirconium after EBM (b)

Microhardness of magnesium-thermal zirconium is 900…1150 MPa. The value of hardness of magnesium-thermal zirconium after electron beam melting is 1350…1450 MPa. It is slightly higher than for electrolytic zirconium after EBM. Apparently the more high oxygen content in the initial sponge of magnesium-thermal zirconium is affected.

CONCLUSIONS

The technology of magnesium-thermal production of spongy zirconium on laboratory installations has been studied. The processes for obtaining spongy zirconium are considered: reduction of zirconium tetrachloride and high-temperature vacuum sublimation of the reaction mass. Installations for their implementation are described. A zirconium sponge was obtained from domestic raw materials. The change in the content of impurities during the refining of magnesium-thermal the zirconium sponge was investigated using the electron beam melting method. It is shown that the content of impurities, except for gaseous ones, in the obtained sponge and the quality of metal zirconium slightly differ from the sponge zirconium of other manufacturers. The results of the research can be used to develop an industrial magnesium-thermal technology for the production of spongy zirconium and equipment for its production.

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МАГНІЄТЕРМІЧНИЙ МЕТОД ОТРИМАННЯ ГУБЧАСТОГО ЦИРКОНІЮ

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Наведено результати досліджень магнієтермічної технології отримання губчастого цирконію на лабораторних установках. Коротко описано магнієтермічний метод відновлення та обладнання. Наведено результати досліджень з оптимізації процесів отримання губчастого цирконію та отримання металевого цирконію на його основі. Результати проведених досліджень рекомендовані для розробки промислової технології виробництва губчастого цирконію та обладнання для його виробництва.