

NUCLEAR REACTOR ZIRCONIUM ALLOYS QUALITY ISSUES

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Abstract. The solution to increase the degree of nuclear fuel burnup and to extend the service life of fuel assemblies (FAs) to 5–7 years is largely related to improving existing production technologies and developing new, more radiation- and corrosion-resistant alloys. This paper analyses the industrial technologies for producing reactor-pure zirconium alloys for producing products operating in the core of thermal neutron reactors (BWR, PWR, VVER). Research demonstrates that the processes of zirconium concentrate opening, the efficiency of zirconium and hafnium extraction separation, and the refining of the alloy by electron beam melting determine the purity of zirconium alloys. It has been established that oxygen is an alloying element, and its optimal concentration should be from 0.10 to 0.14%. The new soda-extraction fluoride-calcium-thermal technology developed in Ukraine has the most efficient refining processes that ensure the purity of zirconium-niobium alloys at $\geq 99.94\%$. This makes it possible to improve the corrosion and radiation resistance of the alloys by reducing the impurity content to 0.05%. Industrial technologies for the production of zirconium alloys for reactor use do not allow achieving a purity level of more than 99.8%. This limits the lifetime of nuclear fuel to 4 years and its burnup rate to 50 mW·day/kgU. Calcium-thermal zirconium and alloys based on it, such as E110, have special chemical compositions and physical and mechanical properties. The data presented in the review show that, in terms of chemical composition, one of the main tasks of researchers and technologists at the present stage is to study the role of oxygen impurity in ensuring the required service characteristics of alloys based on E110. The increased yield strength and hardness values of E110 and E125 alloys raise the challenge of improving the technology of forming pipe billets and the deformation treatment of alloys. More complex are the tasks associated with ensuring radiation and corrosion resistance, reducing radiation embrittlement, and swelling of alloys. The review offers technical solutions and technological methods that can ensure the required quality of alloys under the requirements of national and international quality standards.

Keywords: zirconium, hafnium, alloys, impurities, oxygen, extraction, distillation, sublimation.

1. Introduction

Zirconium with a hafnium content of less than 0.01% is the main component of alloys for the production of products operating in the core of VVER, PWR, BWR, and CANDU thermal nuclear reactors [1]. Tin, nickel, iron, chromium, and niobium are used as alloying components of zirconium alloys [2]. Products made from zirconium alloys of nuclear purity (i.e., those with a low content of elements with a larger thermal neutron capture cross-section than zirconium) include fuel element claddings enriched with ^{235}U and spacer grids for mounting fuel elements.

Alloying zirconium is necessary to improve the chemical and mechanical properties of products used in the high-power radiation zone. At present, the main criterion for the performance of products in the core of nuclear reactors is corrosion and radiation resistance, which should ensure at least a four-year operating cycle at a nuclear fuel burnup rate of 50 mW·day/kgU. The authors of most reviews of nuclear-grade zirconium production focus on the content of hafnium, the main neutron poison, at $<0.01\%$. Methods for separating zirconium and hafnium have received a lot of attention [3], but the main industrial technologies are still based on extraction [4] and fractional crystallisation [5]. The main criteria for the efficiency of the separation process are the content of impurities and the concentration of hafnium in zirconium, which is considered sufficient for the passage of zirconium into nuclear fuel (NF) [6].



The disadvantages of industrial technologies for the production of zirconium for nuclear fuel are incomplete use of raw materials, the presence of non-recyclable waste, and the use of aggressive toxic reagents (chlorine and fluorine compounds) when opening raw materials. The low efficiency of technological equipment leads to numerous studies on its modernisation [7]. The existing technologies and equipment for separating zirconium and hafnium were developed more than 70 years ago and have already exhausted their scientific and technical potential. The quality of zirconium with an impurity content of less than 0.1% cannot be guaranteed. The problem of ensuring the nuclear purity of zirconium must be solved in conjunction with the production and use of hafnium of similar purity since hafnium is not only a major impurity but also a valuable element [8]. Existing technologies do not implement this principle due to the lack of markets.

Hafnium can determine the safety and efficiency of nuclear fuel use. The existing system of compensation for the VVER-1000 jet fuel load does not allow switching to 18- and 24-hour intervals between nuclear fuel overloads. In the United States, up to 75% of NPPs operating with metal In-Cd-Ag alloy absorbers have an overload interval of 18 months and are mastering cycles with an interval of 24 months [9].

The use of hafnium as an absorbing core in the reactor protection control system (RPCS) makes it possible to eliminate the generation and storage of intermediate-level radioactive waste after 30–40 years of operation [10]. Hafnium can be used without overload throughout the entire regulatory life of the reactor. This makes it possible to significantly reduce the cost of electricity generated at NPPs.

Currently, the ideology of producing nuclear-grade zirconium with a purity of 99.7–99.8% and storing excess hafnium due to its limited applications is adopted. In this case, the economics of zirconium production are limited to the plant's capacity of 1,000–1,500 t of zirconium alloy products per year. Hafnium is practically not taken into account in the assessment of the economic efficiency of zirconium production and NPP safety.

Modern science does not consider the issue of reducing the hafnium content in zirconium to <0.005% in a single complex with the production of metallic hafnium. The existing technological equipment for the separation of zirconium and hafnium in the form of extraction columns and fractional crystallisation reactors is not capable of ensuring high specific productivity and product quality. Extraction columns in combination with the use of a chloride-thiocyanate medium are inefficient equipment. They require a large volume of extractant, which increases its losses.

The technology of fractional crystallisation of potassium fluorocarbonate and fluorohafnate is not comprehensive, as up to 50% of zirconium is extracted in hafnium concentrate enriched to 6–10% and stored together with zirconium, reducing overall production efficiency. At the same time, it is impossible to use valuable silicon oxide, which reaches 32% in raw materials, as well as scandium.

The purity of zirconium for the production of Zircaloy, E110 and E125 alloys is determined by the quality of zirconium tetrachloride (ZrCl_4) and potassium fluorocarbonate (K_2ZrF_6) salts used to produce zirconium in sponge or powder form. The quality of ZrCl_4 produced using chloride extraction technology and K_2ZrF_6

produced using fractional crystallisation technology has reached its limit in terms of critical impurities. The low quality of the zirconium produced (concerning the current state of the art) is compensated for by alloying it with zirconium and mechanothermal treatment to obtain a fine-grained structure. Niobium was chosen as an alloying component for zirconium alloys of the E110 and E125 types. Alloying the zirconium sponge with tin, iron, nickel and chromium makes it impossible to clean the sponge from impurities that appear during the magnesium-thermal reduction of zirconium chloride in a stainless retort. A more advanced version of the alloy was implemented in the production of Zirlo alloys (USA) [11].

A feature of the technology for producing zirconium alloys for VVERs (E110, E125, E635) is the use of a charge consisting of zirconium powder and zirconium iodide, which is cleaner than powder but a more expensive metal with a low oxygen and nitrogen content. To produce a homogeneous and fine-grained alloy in ingots weighing up to 5 tonnes, energy-intensive vacuum arc melting is required [12]. The addition of 30–50% zirconium iodide reduces the oxygen content to $<0.1\%$ and ensures high ductility of the alloys. Standards for zirconium alloys such as Zircaloy-2 and Zircaloy-4 do not regulate the oxygen content to the limit of $<0.1\%$.

An alternative to the industrial zirconium production technology is the soda extraction-calcium-thermal process. It was developed in Ukraine in the 1970s. The replacement of aggressive fluorine and chlorine during the opening of raw materials with safer soda and alkali made it possible to switch from ZrCl_4 to the more technologically advanced and cleaner ZrF_4 . Magnesium was replaced with calcium, which made it possible to raise the reaction temperature to $2200\text{ }^\circ\text{C}$ and produce a niobium alloy ingot instead of a sponge. The level of technology and equipment made it possible to ensure a stable oxygen content of $0.10\text{--}0.14\%$ in the alloy. The use of nitric acid and tributyl phosphate (TBP) as an extractant made it possible to use more resistant stainless steels to manufacture extraction equipment that could be used for decades without replacement. The use of fluoroplastic, a material that is more resistant to fluoride environments, made it possible to manufacture the main equipment (reactors, pumps, tanks, pipelines, valves) to produce highly pure ZrF_4 suitable for calcium-thermal reduction after sublimation purification from oxygen, nitrogen and several other impurities [13].

Recovery processes are critical to maintaining zirconium purity. Among the industrial methods, it is necessary to distinguish electrolytic and calcium-thermal ones, which are implemented in a garnissage (10 kA or 20 kA electrolyser) and the version of a ‘cold’ water-cooled copper prefabricated crucible, respectively. The calcium-thermal method with induction heating of the charge makes it possible to obtain zirconium alloys with the required content of oxygen, niobium and impurities (C, N) in the reduction process [14].

Magnesium-thermal and electrochemical methods produce zirconium with a purity of $99.7\text{--}99.8\%$, which serves as the main component of alloys after three times of vacuum-arc refining (VAR). This method produces alloy ingots weighing up to 7.5 t, which must be transformed into tubular billets with a diameter of 200 mm and a length of up to 6 m using the energy-intensive forging method. The vacuum arc

process does not allow for refining the alloy from volatile metal impurities. However, it forms a microstructure with grain refinement to improve the mechanical properties of products [15].

The main area of research to improve the durability of zirconium alloy products was to increase fuel burnup to 70–75 MW·day/kgU. This will make it possible to extend the lifetime of the nuclear power plant to 5–7 years and increase the coolant temperature and the thermal load on the cladding. Zircaloy-2 and Zircaloy-4 alloys do not meet these operating conditions, as their quality in terms of impurities remains low. This worsens the corrosion resistance of the cladding, and the thickness of the oxide film can reach more than 100 µm at 40 mW·day/kgU [16].

Thus, the purpose of this work is to analyse the quality of zirconium and its alloys produced by various industrial technologies, to determine critical indicators of technology and product quality, and to identify the main directions for improving the quality of zirconium alloys to ensure an increased degree of nuclear fuel burnup.

2. Theoretical part

2.1 Efficiency criteria for industrial technologies for producing zirconium for reactor use.

The first known process for producing zirconium for reactor use was developed in the USA [17]. The use of cheap and non-scarce chlorine to open zircon concentrate in the presence of a reducing agent (coal) made it possible to convert zirconium and hafnium from insoluble to soluble form with the possibility of deep purification of zirconium and hafnium chlorides from silicon by fractional distillation. The good solubility of ZrCl_4 and HfCl_4 in a chloride-thiocyanate medium made it possible to obtain a complex capable of good extraction with methyl isobutyl ketone (MIBK) and sufficiently complete purification of zirconium from hafnium to 0.01% to obtain pure ZrO_2 . Along the way, $\text{HfO}(\text{OH})_2$ with a zirconium content of less than 4.5% was obtained, which was used to produce superalloys. From ZrO_2 , relatively pure ZrCl_4 was obtained by repeated chlorination in the presence of carbon for magnesium-thermal reduction. Zirconium sponge with a purity of 99.7% was the starting material for the production of Zircaloy-2 and Zircaloy-4 alloys, which showed acceptable corrosion and radiation resistance in lithium-containing coolant. This technology produces up to 80% of all reactor zirconium in the world [18].

An alternative technology was a simpler scheme for separating zirconium and hafnium due to the different solubility of K_2ZrF_6 and K_2HfF_6 in water. It was implemented in simple process equipment in Ukraine in the 1950s. The production of K_2ZrF_6 and K_2HfF_6 salts was achieved by a simpler and safer process of sintering zircon concentrate with K_2SiF_6 produced concomitantly in phosphate fertiliser production. The number of recrystallisation stages (from 11 to 18) made it possible to produce a zirconium salt with a hafnium content of 0.05–0.009%. The salt was useful in developing an electrolysis process from a molten $\text{KCl-K}_2\text{ZrF}_6$ electrolyte in a 10 kA garnissage electrolysis [19]. The availability of iodide technology made it possible to efficiently process up to 50% of oxidised zirconium in the form of oxidised turnovers to return it to the technological cycle. Traditional vacuum arc smelting

makes it possible to produce ingots with a uniform distribution of alloying elements and impurities and the required grain size. Deformation transformations to produce zirconium alloy tubes, sheets, wires and bars allow for a turnover rate of no more than 10%.

The technology of decomposing zircon with soda ash or caustic soda was developed to produce zircon salts for non-reactor use in the USA and Canada. The separation of zirconium and hafnium in a nitrate-acidic environment using TBF extractant was first implemented in Canada, but due to the lack of corrosion-resistant materials, it was not implemented. This technology was first introduced in Ukraine in the 1970s using centrifugal extractors and electron beam vacuum equipment. A comparison of the advantages and disadvantages of each technology is shown in Table 1.

Table 1 – Overview of the advantages and disadvantages of industrial zircon decomposition technologies

| No | Method | Advantages | Disadvantages |
|----|--|--|--|
| 1 | Carbochlorination | <ul style="list-style-type: none"> - availability of reagents; - anhydrous processes; - the simplicity of the equipment. | <ul style="list-style-type: none"> - hazards of chlorine; - multi-stage process; - the need to bury chloride waste; - high process temperature of 850–1100 °C; - losses of Sc_2O_3; - the need to process SiCl_4; - low extraction of Zr ($\leq 95\%$). |
| 2 | Melting with K_2SiF_6 | <ul style="list-style-type: none"> - use of fluorine, a by-product of the production of phosphoric fertilizers; - obtaining the amount of K_2ZrF_6 and K_2HfF_6 with different solubility in water; - corrosion resistance of the equipment; - direct preparation of pure K_2ZrF_6 salt for electrolysis. | <ul style="list-style-type: none"> - loss of SiO_2 with dumps; - high silicon content in zirconium and hafnium compounds; - high process temperature of 800 °C; - losses of Sc_2O_3; - losses of zirconium and hafnium – 10%. |
| 3 | Soda decomposition | <ul style="list-style-type: none"> - safety and availability of reagents; - completeness of decomposition $\geq 99\%$; - corrosion resistance of the equipment; - disposal of reagents in the production of fertilizers; - the possibility of extracting SiO_2 and Sc_2O_3 into a commercial product. | <ul style="list-style-type: none"> - high process temperature of 1100 °C; - the need to regenerate reagents. |
| 4 | Zircon alkaline decomposition in autoclave | <ul style="list-style-type: none"> - reduced process temperature of 300 °C; - completeness of decomposition $\geq 99\%$; - completeness of SiO_2 allocation; - the possibility of extracting SiO_2 and Sc_2O_3 into a commercial product; - possibility of alkali regeneration. | <ul style="list-style-type: none"> - the complexity of the equipment. |

The achievements of modern nuclear science and technology show that the main criteria for the production of reactor zirconium that meet the criteria for sustainable economic development are:

- complexity of zircon processing technology with complete extraction of associated elements;
- complete utilisation of reagents;
- zero waste production and compliance with environmental protection requirements;
- minimal impact of corrosion processes on the purity of zirconium salts;
- minimum specific energy consumption per unit of production;
- maximum efficiency of critical processes of extraction separation of zirconium and hafnium;
- use of acids in a closed cycle;
- availability of energy-efficient equipment for critical processes (extraction, sublimation, fluorination).

The operating conditions of fuel rods for 1000 MW thermal neutron reactors allow for a service life of 4 years for all grades of zirconium alloys [20]. The durability of E110 and E125 alloy products for VVER-440 makes it possible to increase the service life to 5 years of continuous operation. This makes their use for small modular reactors, which are being actively implemented in many countries, promising. The real radiation and corrosion resistance of zirconium alloy products determines the service life of nuclear fuel under static and dynamic loads, powerful radiation fields, high temperatures and pressures.

Zirconium products are operated in the nuclear reactor core under the following conditions:

- at a temperature of 330 °C;
- under a pressure of 18 MPa;
- the coolant is water with a high content of KOH and H₃BO₃;
- radiation of thermal neutrons, γ -quants and other radionuclides.

2.2 Influence of impurities on radiation and corrosion properties of zirconium alloys.

The nuclear properties of zirconium, its transparency to thermal neutrons, and its radiation resistance depend on the presence of several critical impurities: hafnium, boron, and rare earth elements (REEs). They have a much higher degree of thermal neutron capture and are neutron poisons. Low boron and REE content of 10⁻⁵% is guaranteed by the technology in all industrial production.

The main neutron poison for zirconium is its analogue and constant companion, hafnium, whose content should be reduced from 2% to $\leq 0.01\%$ [21]. The hafnium content of 0.01% in zirconium alloys is the standard limit for all product quality studies. The possibility and necessity of reducing the hafnium concentration in zirconium to $\leq 0.005\%$ is hardly discussed in the literature. Existing industrial technologies are unable to achieve this figure. It is known that reducing the hafnium content in zirconium to 0.005% will allow saving ²³⁵U isotopes during operation. The

electrolytic technology based on potassium fluorocarbonate does not allow reducing the hafnium content in zirconium from 0.05% to 0.01%. For more than 40 years, Ukraine has been forced to operate at an elevated (0.035%) hafnium content in zirconium products, which has resulted in hundreds of millions of US dollars in uranium losses.

The impact of hafnium in E110 and E125 alloys on the economy has not been studied, as the possibility of producing alloys with hafnium content $\leq 0.005\%$ was first demonstrated in Ukraine during the implementation of soda extraction technology. The separation of zirconium and hafnium was carried out under industrial conditions from nitrate-acidic media in centrifugal extractors of the EC-250 and CET-125 types. The depth of separation of zirconium and hafnium was ensured by maximising the theoretical saturation of the extractant with zirconium. This resulted in the displacement of hafnium from the organic phase and a decrease in its concentration in zirconium to $\leq 0.005\%$. Reducing the hafnium content in zirconium to this value reduces the consumption of the ^{235}U isotope by 4% during a nuclear reaction and improves the fuel cycle economy. It is quite possible to include this indicator in the technical specifications for zirconium alloys now (Table 2).

The critical impurities in zirconium alloys that determine their chemical and corrosion properties are carbon, fluorine, chlorine, titanium, nickel, and silicon. Metal impurities are transition metals, the content of which should be 10–3%. The overall purity of zirconium produced by different technologies was determined by calculating the concentration of all the elements except oxygen, nitrogen and hydrogen. It was 99.8% and 99.7% for the electrolysis and magnesium-thermal processes, respectively. In practice, taking into account alloying elements, the zirconium content in Zircaloy alloys is reduced to 98% [22].

The purity of zirconium-niobium alloys obtained by nitrate-acid extraction technology after fluorination of zirconium oxynitrate, sublimation purification of ZrF_4 , calcium-thermal reduction of ZrF_4 and electron beam refining was $\geq 99.94\%$, which is at the level of zirconium iodide purity, except for oxygen and nitrogen. The content of impurity elements (Si, F, Cl, Fe, C) depends on the methods of zircon concentrate processing, in particular, on the use of highly efficient refining processes: extraction, re-extraction, electrolysis, fluorination, sublimation and electron beam melting (EBM).

The purity of reactor zircon also depends on the composition of the zircon concentrate, the type of reagents used to open it, and the efficiency of zircon and hafnium separation. The purity of zirconium compounds will differ when using chlorine, potassium fluorocarbonate and soda, as the aggressiveness of the reagents has a different effect on corrosion processes and the transition of impurities into metal.

The composition of metal impurities contained in zirconium was analysed in [23]. The authors provided a theoretical justification for refining processes based on the degree of separation (β):

- at $\beta \gg 1$, Be, Cd, Ca, K, Li, Mn, Pb, Cl, F and Cu are easily removed by evaporation;

- at $\beta < 1$, Hf, W, Ta, Mn and Nb are not removed;
- at $\beta = 1$, Si, Ni, Ti, V and C are not removed.

Table 2 – Overview of the advantages and disadvantages of industrial zirconium and hafnium separation technologies

| No | Method | Advantages | Disadvantages |
|----|---|--|---|
| 1 | Fractional crystallization of K_2ZrF_6 and K_2HfF_6 in batch reactors | <ul style="list-style-type: none"> - ease of operation; - low specific consumption of reagents. | <ul style="list-style-type: none"> - low separation coefficient; - low extraction of zirconium 50-70%; - output of hafnium in the intermediate concentrate; - the impossibility of obtaining a pure hafnium salt; - high content of hafnium in zirconium $\leq 0.05\%$; - multi-stage and time-consuming process; - high energy consumption; - low purity K_2ZrF_6. |
| 2 | MIBK extraction from chloride-thiocyanate media in columns | <ul style="list-style-type: none"> - low content of hafnium in zirconium $\leq 0.01\%$; - corrosion safety of the environment; - process continuity; - greater productivity per unit area. | <ul style="list-style-type: none"> - loss of extractant; - increased consumption of reagents; - the need to bury $CaCl_2$ waste; - impossibility of obtaining a hafnium salt with a low zirconium content; - loss of scandium; - a large amount of fire-hazardous extractant. |
| 3 | Extraction of TBF from nitric acid media in centrifugal extractors | <ul style="list-style-type: none"> - minimum content of hafnium in zirconium $\leq 0.005\%$; - high process kinetics; - minimum extractant consumption; - high specific productivity; - minimal capital costs; - the possibility of extractant and acid regeneration. | <ul style="list-style-type: none"> - the difficulty of repairing extractors. |

Under these conditions, the main refining method is EBM. This process takes place in a melt under a vacuum with controlled crystallisation of the alloy to refine the grain. The efficiency of zirconium purification from volatile impurities decreases in the order $Zn > Be > Mn > Al > Cr > Cu > V > Fe > Co > Ni > Si$. The EBM process does not purify Ni, Co, Ti, and Si, so their content must be reduced at the extraction stage. Nitrogen forms zirconium nitride, a strong compound that is retained during EBM. Its content at the level of $\leq 0.005\%$ should be ensured by the quality of the reducing metal, zirconium salt, and vacuum conditions at a discharge of 10-5 Pa [24].

The capabilities of EBM were tested on very pure zirconium iodide and Zr1Nb alloy after calcium-thermal reduction. The results of the EBM showed that the micro-

hardness of the metal decreased from 1200 MPa to 800 MPa. The content of metal and gas impurities in the E110 alloy also decreased. The one-time EBM of the Zr1Nb alloy ensured the required quality standards following the specifications. The critical non-metallic impurities in the Zr1Nb alloy are carbon, fluorine and silicon. The carbon content in all zirconium alloys is limited to $\leq 0.02\%$. Higher carbon content can lead to the formation of zirconium carbide, which degrades the fuel rod shell when exposed to irradiation. Carbon is used as a reagent in chloride technology and as part of the degradable anode in electrolytic technology. Both technologies have a low carbon content limit ($\leq 0.02\%$). The carbon content is reduced to $10^{-3}\%$ in the calcium-thermal technology, where its absence at all stages of the technology is mandatory [25].

The fluorine content in electrolytic zirconium powder reaches over 180 *ppm*, and in the charge, up to 100 *ppm*. At elevated temperatures in the reactor core, especially during accidents, this can cause cladding degradation and cladding failure. Its content in the vacuum arc melting (VAR) process does not change, which requires the introduction of an EBM refining process. This process reduces the fluoride content to less than 1 *ppm* [26].

Silicon admixture is an integral part of chloride and electrolytic technology. Silicon is not removed in pyrometallurgical processes and remains in zirconium at the level of its content in zirconium salts. The highest degree of silicon purification is achieved in the process of soda-alkali opening of zircon when its content is reduced from 32–33% to 0.001% after extraction separation of zirconium and hafnium. To ensure a low silicon content in zirconium, its content in water, nitric acid and zirconium salts is controlled. It should be no more than 0.005%.

Impurities in zirconium alloys determine the corrosion and radiation resistance of products in the reactor core. Existing industrial technologies, such as chlorine and electrolysis, cannot ensure the purity of zirconium alloys at the level of 99.9%, because the efficiency of the refining processes of extraction separation of zirconium and hafnium in chloride-thiocyanate media and fractional crystallisation does not provide the required depth of impurity separation. Refining processes in the soda extraction fluoride technology using extraction, vacuum, sublimation, induction melting and EBM processes are more efficient. The products produced using these technologies have successfully passed all stages of pre-reactor and reactor testing.

The achieved scientific and technical level of refining processes can ensure the minimum level of all impurities in zirconium if high-purity zirconium salts are produced and high-purity reagents are used. The best purity (99.9%) was shown by ZrF_4 obtained from high-purity zirconium oxynitrate salt after deep extraction separation of zirconium and hafnium (Table 3).

As can be seen from the comparison of the recovery processes, the indicators of zirconium purification from silicon, metallic and non-metallic impurities are directly related to the environmental safety and economic efficiency of the technology. The highest purity of zirconium compounds (99.9%) is achieved due to the high efficiency of extraction from nitrate-acid media, fluorination of $ZrO(NO_3)_2$, sublimation and reduction of ZrF_4 to produce ingots.

Table 3 – Overview of the advantages and disadvantages of industrial zirconium metal production technologies

| No | Method | Advantages | Disadvantages |
|----|---------------------------------------|---|---|
| 1 | Magnesium-thermal | <ul style="list-style-type: none"> - ease of operation of the melting equipment; - an anhydrous process of separating salts from the zirconium sponge; - possibility of regeneration of magnesium compounds; - greater productivity per unit area. | <ul style="list-style-type: none"> - laboriousness and periodicity of the process; - high content of impurities in the sponge; - hygroscopic $ZrCl_4$; - the need for zirconium doping; - availability of magnesium production; - pyrophoric sponge. |
| 2 | Electrolysis of K_2ZrF_6 -KCl melt | <ul style="list-style-type: none"> - low process temperature of 750 °C; - availability of reagents; - production of zirconium in the form of powder; - the possibility of obtaining fluoroplastic powder; - the possibility of obtaining chlorine and its compounds; - absence of loss of zirconium; - process continuity. | <ul style="list-style-type: none"> - accumulation of KF in the electrolyte; - low (32%) content of zirconium in K_2ZrF_6; - high content of carbon and silicon in the powder; - emissions of freons into the atmosphere; - the need to bury the formed chloride salts; - high (20%) content of oxidized powder in the commercial product; - the need for iodide refining of oxidized powder; - the need for aqueous processing of cathode sediment; - the impossibility of doping the powder with oxygen up to 0.14%. |
| 3 | Electrolysis of the ZrF_4 -KCl melt | <ul style="list-style-type: none"> - high purity of zirconium powder; - high (90%) specific yield of conditioned powder; - higher grain size of conditioned powder; - the possibility of disposal of fluorine and chlorine; - absence of loss of zirconium; - reduction of energy consumption. | <ul style="list-style-type: none"> - increased consumption of graphite for the manufacture of electrodes; - the impossibility of doping the powder with oxygen up to 0.14%. |
| 4 | Calcium-thermal | <ul style="list-style-type: none"> - zero-waste process; - uniform distribution of alloying components in the alloy with niobium; - obtaining compact ingots. | <ul style="list-style-type: none"> - periodicity of the process; - availability of calcium production. |

2.3 Effect of oxygen on the mechanical properties of zirconium alloys.

The oxygen content of zirconium alloys can vary depending on the purity of the starting salts, vacuum conditions during melting, the method of metal production and the purity of alloying components. Zirconium alloys E110 and E125 for VVER reactors contain up to 0.1% oxygen. This determines the ductility of the alloy to reduce energy consumption during deformation and its specific consumption for the production of products. Such an oxygen content is ensured by calculations of the components of a triple charge consisting of electrolytic zirconium powder (up to 60%), iodide metal (up to 50%) after iodide refining of oxidised powder and metallurgical waste [27]. The experience of operating alloy products for VVER-1000 has shown the possibility of reducing the strength of fuel rods due to cladding distortion. This drawback can be eliminated by increasing the oxygen content in the alloy to 0.14% [28].

Increasing the strength of the fuel assembly structure made it possible to reduce the impact of this process on the stability of the products, but in general, it was not possible to exceed the four-year service life of the fuel assembly for VVER-1000. The oxygen content in the alloy is affected by the low concentration of oxygen in zirconium powder, which does not exceed 0.06–0.08%, and the concentration of oxygen in the iodide metal (0.03%). It was impossible to increase the oxygen content in zirconium above 0.1% using this technology. Zircaloy-2 and Zircaloy-4 alloys produced by Westinghouse (USA), unlike E110 and E125 alloys with one alloying component (Nb), are complex alloys. Their ductility and strength are determined by the composition of alloying elements: Ni, Cr, Fe and Sn. Therefore, the oxygen content can reach 0.15–0.18%.

The purity of the hygroscopic salt $ZrCl_4$ determines the content of oxygen, nitrogen and carbon in the sponge. The rational oxygen content in zirconium is determined by the requirements developed in Ukraine for:

- electrolytic zirconium powder according to TU 95.259-99;
- iodide zirconium according to TU 95.46-97;
- turnovers of zirconium production according to TU 96.363-97.

Scientists at National Science Center Kharkiv Institute of Physics and Technology (KIPT) studied the evolution and behaviour of zirconium in its alloy with 1% niobium [28, 29]. The choice of oxygen content limits in zirconium alloys was justified by the mechanical properties of the alloy, especially its ductility, which is almost constant within the range of its content from 0.12 to 0.17%. This makes it possible to achieve an optimal combination of ductility and strength of products for the reactor core. In TU U 1.27-8-52-01 (ZrNb alloy pipes), this value is defined in the range of 0.10–0.14%. It was based on an analysis of the actual quality results of alloys E110 and E125, produced by the ZrF_4 calcium-thermal reduction method. The recovery of a particularly pure ZrF_4 impurity was tested under electrolysis and calcium-thermal melting conditions. The results of these processes in terms of oxygen content differ by almost two times (0.08% in the first case and 0.14% in the second) since the first process does not use calcium with an oxygen content of 0.1%.

2.4 Influence of impurities on the mechanical properties of zirconium alloys.

The composition of impurities and their content in zirconium alloys depends on the technology used to produce their base, zirconium. In industrial technologies, the starting materials are zirconium sponge after magnesium-thermal reduction of ZrCl_4 , zirconium powder after K_2ZrF_6 electrolysis, and Zr1Nb and Zr2.5Nb alloys after calcium-thermal reduction of ZrF_4 in the presence of nuclear-purity niobium powder.

The purity of metallic zirconium depends on the purity of the initial salts, ZrCl_4 , K_2ZrF_6 and ZrF_4 . ZrCl_4 and ZrF_4 salts are obtained after the separation of zirconium and hafnium by extraction, so their purity in terms of metal impurities is identical. K_2ZrF_6 is a salt of low purity in terms of Hf, Si and Ni.

All three processes maintain the purity of the salt in different ways, as the conditions for salt reduction depend on the material of the reactor where the magnesium-thermal reduction process takes place. The process is carried out in a reactor made of stainless steel, so the sponge is contaminated with impurities of these metals. It is not possible to clean the sponge from impurities, so a method was found to alloy the sponge with these metals to ensure corrosion and radiation resistance of products in the reactor core.

The sponge is also not purified from oxygen, nitrogen and carbon. The increased nitrogen content is compensated by the introduction of tin up to 1%. Carbon cannot be less than 0.02%, so this value is critical. Oxygen is not an impurity; its content is recommended at $\leq 0.15\%$. Its concentration directly determines the mechanical properties of zirconium alloys before and after irradiation.

The electrolysis process of the K_2ZrF_6 -KCl electrolyte takes place in a sealed garnissage electrolyser. The zirconium powder contains impurities of O_2 and N_2 at the lowest possible level. Replacing the current method of fractional crystallisation to produce the initial zirconium salt K_2ZrF_6 with the extraction technology allows us to significantly improve the quality of Zr powder in terms of all impurities. Unlike metallic-thermal processes, the electrolysis process is continuous, and zirconium powder is a more technologically advanced product than sponge. The transfer of the electrolysis process from K_2ZrF_6 to ZrF_4 makes it possible to reduce the hafnium content in zirconium to 0.005%, i.e. seven times, and the yield of oxidised powder from 20% to 5%, which reduces the cost of zirconium [30].

In the electrolysis process, the main reagent is electric current, which is the most affordable and environmentally friendly product. It does not introduce impurities into zirconium powder. Metallic-thermal processes require the production of nuclear-pure magnesium and calcium, which increases the cost of zirconium. The only disadvantage of the electrolysis process is the destruction of graphite anodes and the contamination of zircon powder with carbon. The carbon separation technology by flotation results in a carbon content of 0.02% in zirconium, which is on par with the magnesium-thermal process.

Analysis of the quality of three zirconium salts, ZrCl_4 , K_2ZrF_6 and ZrF_4 , shows that the purest salt is ZrF_4 , with a zirconium content of 54% (ZrCl_4 contains 40% Zr and K_2ZrF_6 contains 32% Zr). The presence of ballast in the salt requires additional energy costs for its processing and degrades the quality of zirconium.

The only method for the direct production of Zr-Nb alloy with a 99.9% purity is calcination, where the initial purity of ZrF_4 , Ca and Nb is $\geq 99.9\%$. The copper water-cooled prefabricated reactor and argon atmosphere guarantee the purity of the starting materials in the alloy, which distinguishes it from the magnesium-thermal method.

Alloys produced based on sponge, powder and ingot for various nuclear reactors are presented in Tables 4 and 5.

Table 4 – Zirconium alloys of active zones of water-water type reactors

| Brand | Main alloying elements, wt. % | | | | | Purpose (reactor type) | Development terms | Developing country |
|-------|-------------------------------|-------------|---------------|-------|----------------------------|--------------------------------------|----------------------|-----------------------|
| | No | Sn | Fe | O | others | | | |
| E110 | 1 | - | - | <0.16 | - | VVER, RBMK | 1958 | USSR |
| E125 | 2.5 | - | - | - | - | VVER, RBMK, CANDU | 1958 | USSR |
| E635 | 1 | 1.0– 1.5 | 0.3– 0.5 | - | - | VVER, RBMK, CANDU, PWR, BWR | 1971 | USSR |
| Zry-2 | - | 1.2– 1.8 | 0.07– 0.2 | - | Ni < 0.008 Cr 0.05–0.15 | BWR | 1952 | USA |
| Zry-4 | - | 1.2– 1.8 | 0.18– 0.24 | - | Cr 0.05–0.15 | PWR | 1952 | USA |
| Zirlo | 1 | 1 | 0.1 | - | - | PWR | 1990 | USA |
| M4 | - | 0.5 | 0.6 | 0.12 | V 0.3 | PWR | 1997 | France |
| M5 | 1 | - | - | 0.12 | - | PWR | 1997 | France |
| NDA | 0.1 | 1 | 0.27 | - | Cr 0.16 | BWR | 1990 | Japan |
| MDA | 0.5 | 0.8 | 0.2 | - | Cr 0.1 | PWR | 1990 | Japan |

The replacement of vacuum arc melting with electron beam melting fundamentally changes the refining scheme for producing pipe billets. It makes it possible to quickly and efficiently melt billets of the required microstructure in the process of garnissage melting in a copper water-cooled crystalliser [31, 32]. Replacement of alloy ingots weighing 7.5 tonnes and 3 tonnes with 200 mm diameter ingots to produce pipe billets without energy-consuming forging of a 750 mm diameter ingot into a 200 mm diameter ingot weighing up to 50 kg.

The mechanical properties of all zirconium alloys before irradiation are virtually identical, despite the different quality of zirconium. Their main production technologies differ in complexity, technical and economic indicators, product quality and process equipment. Each process has its technological shortcomings, but in general, they solve the main task of ensuring the standard level of chemical impurities and mechanical properties to maintain the product life of 4 years. Ukraine has a choice in the technology of producing zirconium and its alloys with niobium due to the versatility and frequency of the ZrF_4 feedstock and the methods of its processing.

Of all the zirconium salts, K_2ZrF_6 is the least technologically advanced, as it contains up to 40% of ballast. This is a result of the inefficient technology of fractional crystallisation of zirconium and hafnium fluorides. The low quality of

K_2ZrF_6 creates preconditions for criticising the highly efficient and cheapest zirconium electrolysis process.

Table 5 – Content of impurities in iodide and calcium-thermal zirconium metal

| Impurity | Content of impurities, mass % | | |
|-----------------|-------------------------------|---------------------------------------|--|
| | Starting | After the first electron beam melting | After the second electron beam melting |
| Iodide | | | |
| O | 0.04 | 0.008 | 0.007 |
| N | 0.006 | 0.004 | 0.0006 |
| C | 0.035–0.04 | 0.025 | 0.011 |
| H | 0.0045 | 0.002 | 0.0008 |
| Fe | 0.025 | 0.01 | - |
| Al | 0.004 | 0.003 | - |
| Cu | 0.0035 | 0.0006 | - |
| Ni | 0.0065 | 0.004 | - |
| Cr | 0.005 | 0.002 | - |
| Ti | 0.0023 | 0.0001 | - |
| Si | 0.006 | 0.005 | - |
| Calcium-thermal | | | |
| O | 0.17–0.19 | 0.10–0.12 | 0.050–0.036 |
| N | 0.007–0.008 | 0.007–0.008 | 0.007 |
| Fe | 0.1 | 0.032 | 0.0012 |
| Al | 0.018 | 0.0008 | 0.0008 |
| Cu | 0.02 | 0.00054 | 0.00025 |
| Ni | 0.01 | 0.0061 | 0.0024 |
| Mn | 0.0013 | 0.0001 | 0.00009 |
| Cr | 0.006 | 0.0025 | 0.00025 |
| Ca | 0.01 | 0.0065 | 0.003 |
| Si | 0.0035 | 0.0017 | 0.0017 |

The technological properties of zirconium alloys are determined by the method of their production and the ability to purify alloys from critical impurities. The selected methods of producing zirconium alloys from sponge and powder involve mandatory VAR of alloy components. It is not a refining process but determines the microstructure of the alloy. The effect of zirconium quality on the mechanical properties of the alloy is shown in Table 6.

Table 6 – Dependence of the mechanical properties of zirconium on its purity

| The total content of impurities, wt. % | Ultimate tensile strength, MPa | Yield strength, MPa | Elongation, % | Obtaining method |
|--|--------------------------------|---------------------|---------------|--------------------------------------|
| $5 \cdot 10^{-2}$ | 200 | 120 | 28.0 | Electron beam melting |
| $1 \cdot 10^{-2}$ | 130 | 85 | 34.0 | Zone melting |
| $5 \cdot 10^{-3}$ | 103 | 25 | 49.5 | Zone melting + electron beam melting |

To achieve the content of impurities of the order of $10^{-2}\%$ and below, additional purification of ZrCl_4 is required (Table 7) [33].

Table 7 – The content of impurities in zirconium tetrachloride of various degrees of purification

| ZrCl_4 | The total content of impurities, wt. % | | | | | | | | | | | |
|--------------------|--|-------|--------|--------|---------|--------|-------|--------|--------|---------|---------|---------|
| | Al | No | K | Si | Ca | Fe | Ti | Cr | Mg | Cu | Mn | Ni |
| Technical | 0.048 | 0.24 | 0.36 | 0.0078 | 0.00165 | 0.017 | 0.030 | 0.0044 | 0.0011 | 0.00069 | 0.00051 | 0.0024 |
| Sublimated | 0.0033 | 0.004 | 0.003 | 0.0057 | 0.00080 | 0.0066 | 0.004 | 0.0046 | 0.0012 | 0.0001 | 0.0003 | 0.0007 |
| Double sublimation | 0.0030 | 0.004 | 0.003 | 0.0049 | 0.00069 | 0.0042 | 0.003 | 0.0031 | 0.0005 | <0.0001 | 0.0002 | <0.0001 |
| Triple sublimation | 0.0023 | 0.005 | <0.001 | 0.0040 | 0.00059 | 0.0040 | 0.004 | 0.0033 | 0.0005 | <0.0001 | 0.0002 | <0.0001 |

Achieving a purity of 99.95% is possible based on the sodium-extraction technology of direct production of the Zr-Nb alloy in the process of self-propagating high-temperature synthesis from reagents of a similar level of purity. Additional cleaning of the alloy is carried out in electron-beam processes, which significantly reduce the amount of metal turnover when obtaining a pipe blank.

The mechanical properties of Zr alloys strongly depend on several parameters, such as composition, texture, and metallurgical state (Table 8).

Table 8 – Short-term mechanical properties of Zr1Nb alloy ring samples without and with the addition of oxygen up to 0.13% in the initial state and after irradiation [36]

| Material | T, °C | Ultimate tensile strength, MPa | Yield strength, MPa | Elongation, % |
|------------------------------|-------|--------------------------------|---------------------|---------------|
| Zr+1%Nb+0.08%O 580°C, 3 h | 20 | 370 | 320 | 11.5 |
| | 350 | 190 | 170 | 12.0 |
| Zr+1%Nb+0.13%O 580°C, 3 h | 20 | 470 | 400 | 9.1 |
| | 350 | 210 | 180 | 8.2 |

For practical purposes, the properties at 300–400°C are the most important, and the behaviour at room temperature is used mainly for comparison (Table 9).

Table 9 – Mechanical properties of the Zr1Nb alloy

| T = 20 °C | | | | T = 380 °C | | | |
|--------------------------------|---------------------|---------------|----------------------------|--------------------------------|---------------------|---------------|----------------------------|
| Ultimate tensile strength, MPa | Yield strength, MPa | Elongation, % | Loop storage efficiency, % | Ultimate tensile strength, MPa | Yield strength, MPa | Elongation, % | Loop storage efficiency, % |
| 440–450 | 385–395 | 14.0–15.0 | 49.0–50.5 | 150–175 | 120–135 | 16.0 | 70.0–79.5 |

At room temperature in the annealed state, pure oxygen-free Zr has a low yield strength of about 150 MPa. However, the yield strength can be increased by solution hardening using oxygen, tin or niobium. Tin causes only a small increase in tensile strength, but is effective in increasing the creep strength; Nb increases both the yield strength and creep strength [34].

Oxygen is highly soluble in the α -phase and stabilises at high temperatures. Oxygen should be considered as an alloying element. The use of oxygen for hardening is rare in metallurgy compared to the use of nitrogen. However, the use of nitrogen for strengthening severely degrades the corrosion resistance, so nitrogen is

removed whenever possible. The purpose of adding oxygen is to increase the yield strength through solution hardening without compromising corrosion resistance. The oxygen content is not specified in ASTM standards, but it is usually added at concentrations in the range of 600–1200 *ppm*. High O concentrations (> 2000 *ppm*) reduce the ductility of alloys, so O additions above 1500 *ppm* are not recommended. In addition, O atoms interact with dislocations at moderate temperatures, which leads to age hardening in temperature ranges that depend on the strain rate [35]. The addition of 1000 *ppm* oxygen increases the yield strength to 300 MPa.

The SSC KIPT has developed a technology for producing Zr1Nb alloy ingots based on calcium-thermal zirconium, pipe production turnover, and zirconium iodide with an oxygen content of less than 0.10 wt.%. The developed technology includes:

- smelting of initial consumable electrodes from CTZ110 alloy;
- assembling an electrode from a triple charge for the first VAR in a 160 mm diameter crystalliser;
- performing the first VAR, producing ingots with a diameter of 160 mm and a length of 450–480 mm;
- assembling the electrode for the second VAR;
- second VAR, producing ingots with a diameter of 200 mm and a length of up to 450 mm.

The chemical composition of the alloy meets the requirements of TU 95.166-98 for zirconium alloys used in nuclear power (Table 10).

Table 10 – Impurity content in Zr alloy ingots after double VAR, wt.%

| Impurity | Zr1Nb | E110 |
|----------|-----------------|---------|
| Al | 0.00011–0.00022 | 0.008 |
| B | <0.00001 | - |
| Be | <0.00001 | 0.003 |
| C | 0.008–0.01 | 0.02 |
| Ca | <0.0005 | 0.03 |
| Cd | <0.00001 | 0.00003 |
| Cl | <0.0005 | 0.003 |
| Cr | 0.001–0.0016 | 0.02 |
| Cu | 0.0024–0.0045 | 0.005 |
| F | <0.0005 | 0.003 |
| Fe | 0.012 | 0.05 |
| Hf | 0.015–0.036 | 0.05 |
| K | <0.0005 | 0.004 |
| Li | <0.00001 | 0.0002 |
| Mn | <0.0005 | 0.002 |
| Mo | <0.001 | 0.005 |
| N | 0.0008–0.0014 | 0.006 |
| Ni | 0.002–0.003 | 0.02 |
| O | 0.07–0.93 | 0.1 |
| Pb | <0.001 | 0.005 |
| Si | 0.001–0.002 | 0.02 |
| Ti | <0.0001 | 0.005 |
| Nb | 0.94–1.02 | 0.9–1.1 |

Studies have shown that the microstructure of Zr1Nb and E110 alloys is identical. The hardness of the Zr1Nb alloy is 1600–1720 MPa, and the hardness of the E110 alloy is 1580–1680 MPa [37]. The mechanical properties of the metal obtained by the double VAR method were studied in the transverse direction at temperatures of 20 and 380 °C [38]. A comparative analysis of the data on the mechanical properties of the obtained alloy and E110 alloy showed that the values of the tensile and yield strengths, as well as ductility, are close.

2.5 Factors affecting the stability of the shape and properties of products under conditions of nuclear fuel operation in NPPs.

The physical and mechanical properties of products under conditions of nuclear fuel operation in NPPs are mainly influenced by the following factors

- temperature, which depends on the ratio of energy release and heat removal;
- chemical composition of the coolant, radioactive products of nuclear reactions, coolant gases after radiolysis;
- cyclic nature of heat supply and mechanical loads;
- the combined effect of thermal and mechanical loads under conditions of radiation exposure on structural elements;
- the presence of a neutron flux with a fluence of 10^{22} cm² of a wide energy spectrum, γ -activity of radioactive isotopes (Cs, Sr etc.) and induced radioactivity.

Pressurised water-cooled thermal reactors (PWR, BWR, VVER) will be developed and supplemented by fast neutron reactors operating on regenerated uranium in a closed fuel cycle. The main results of improving the properties of zirconium alloys should be an increase in fuel burnup to 70 MW·day/kgU for BWR and VVER-1000 and to 75 MW·day/kgU for PWR.

Given the scarcity and cost of zirconium, its recovery into finished products in all zircon concentrate processing processes should be maximised, and all the turnovers should be returned to the process cycle and recycled with minimal losses. Recycling of turnovers determines not only the cost of zirconium but also the content of impurities in it. This circumstance requires quality control of each turnover to ensure that the level of impurities in the finished alloy ingot does not exceed the requirements of the technical specifications.

The most critical impurities in the process are oxidised metal turnovers containing high levels of oxygen and nitrogen. These impurities can only be removed by iodide refining, an expensive and inefficient process that increases the cost of zirconium. In the technology for producing zirconium alloys for VVER, the volume of iodide metal must be at least 30%, which is a consequence of the low quality of K₂ZrF₆ for the electrolysis and the presence of turnover in the production of pipe billets and tubes.

The technology for obtaining and processing a 7.5 t ingot at “Western Zirconium” (USA) is based on efficient physical processes of cutting a 500 mm diameter ingot with a water jet up to 1000 at, and chip removal during processing of a 700 mm diameter ingot without oxidation. The chips contaminated with impurities are melted down at an electron beam unit into an alloy ingot that can be returned to the process

cycle. This made it possible to eliminate iodide redistribution and reduce the cost of products.

A higher oxygen content in zirconium sponge (up to 0.18% as allowed by the manufacturer's specifications) makes it possible to maintain the metal's ductility by alloying it with iron, nickel, chromium and tin [39, 40]. Maintaining the quality of metal turnovers at a given level for all types of impurities requires only their compacting into ingots that are convenient for processing.

Thus, the level of technology determines the quality of the alloy for the manufacture of reactor core components. In all technologies, up to 10% of the turnover is chemically contaminated, including oxides, which are sent for chemical processing and recycled via dissolution in acids and extraction. Alloying components are not recovered and are irretrievably lost. The number of refining processes in each industrial technology determines the composition and quality of impurities in reactor-pure zirconium alloys. A comparative analysis of different technological refining processes for producing zirconium alloys is shown in Figure 1.

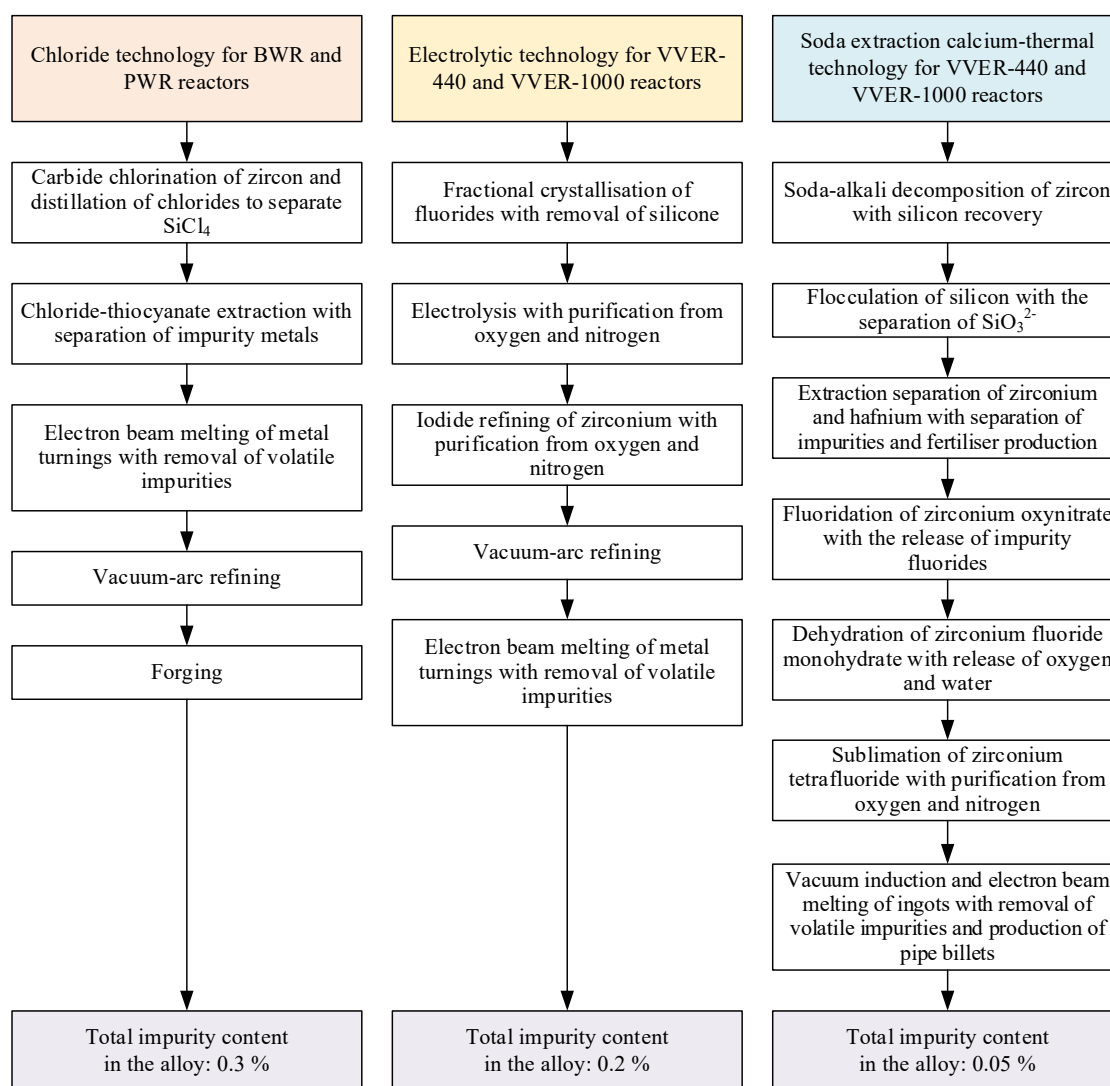


Figure 1 – Comparative analysis of different technological refining processes for the production of zirconium alloys for steam and water nuclear reactors

3. Conclusions

1. The analysis of the quality of zirconium alloys used in the nuclear fuel of thermal neutron reactors produced by different industrial technologies showed that the composition of impurities and purity of alloys significantly depends on the type of reagents used for the zirconium concentrate processing.

2. The main indicator of the nuclear properties of zirconium alloys is the hafnium content, which is set by the international ASTM standard at $<0.01\%$. The soda extraction fluoride calcium-thermal technology for the production of zirconium from ZrF_4 reduces the hafnium content in alloys to $\leq 0.005\%$.

3. The purity of the zirconium sponge used to produce Zircaloy-2, Zircaloy-4 and Zirlo alloys, obtained using carbochloride technology, is 99.7% of the total amount of impurities. This is due to the increased content of iron, chromium and nickel in the zirconium sponge due to corrosion of the reactor material. Alloying the zirconium sponge ensures the ductility and strength of the alloy and the operational stability of the LWR fuel cladding.

4. Oxygen in zirconium alloys is an alloying element that, at a content of $0.12\text{--}0.17\%$, provides the required ductility of the alloy with maximum strength.

5. The electrolytic method of producing zirconium powder from potassium fluorocarbonate reduces the oxygen content to $0.06\text{--}0.08\%$ and ensures zirconium purity of 99.8% , with hafnium content $\leq 0.035\%$.

6. The main method for producing industrial zirconium alloys of reactor purity is vacuum arc melting of ingots weighing from 3.0 to 7.5 t, which is not an affinage process. Three vacuum-arc melts and an energy-intensive forging process is required to ensure uniform distribution of alloying elements, which increases electricity consumption.

7. Affinage processes (extraction from nitric acid media, fluoride sublimation, EBM) to produce oxygen-doped Zr-Nb reactor alloys reduce the content of critical impurities and increase the purity to 99.94% .

8. The proposed Ukrainian technology for producing zirconium-niobium alloys ensures the highest zirconium recovery in the pipe billet. This reduces the amount of metal waste and maintains high purity of alloys.

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ПРОБЛЕМИ ЯКОСТІ СПЛАВІВ ЦИРКОНІУ РЕАКТОРНОЇ ЧИСТОТИ ДЛЯ ЯДЕРНОЇ ЕНЕРГЕТИКИ

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Анотація. Вирішення завдань підвищення ступеня вигорання ядерного палива і збільшення терміну служби тепловиділяючих збірок (ТВЗ) до 5–7-річного періоду багато в чому пов'язане з удосконаленням наявних технологій виробництва та розробленням нових більш радіаційно- і корозійностійких сплавів. У цій роботі проведено аналіз промислових технологій отримання сплавів цирконію реакторної чистоти для виробництва виробів, що працюють в активній зоні реакторів на теплових нейтронах (BWR, PWR, ВВЕР). Показано, що чистота сплавів цирконію залежить від процесів розкриття цирконового концентрату, ефективності екстракційного поділу цирконію і гафнію, рафінування сплаву методом електронно-променевої плавки. Встановлено, що кисень є легуючим елементом, а його оптимальна концентрація має становити від 0,10% до 0,14%. Нова содово-екстракційна фторидно-кальцієтермічна технологія, створена в Україні, має найбільш ефективні афінажні процеси, що забезпечують чистоту сплавів цирконій-ніобій на рівні $\geq 99,94\%$. Це дає змогу підвищити корозійну та радіаційну стійкість сплавів за рахунок зниження вмісту домішок до рівня 0,05%. Промислові технології отримання сплавів цирконію для реакторного застосування не дають змоги досягти ступеня чистоти понад 99,8%. Це обмежує термін експлуатації ядерного палива 4 роками і ступінь його вигорання 50 мВт·добу/кгU.

Кальцієрмічний цирконій та сплави на його основі, на кшталт E110, мають особливі хімічний склад і фізико-механічні властивості. Наведені в огляді дані показують, що за хімічним складом одним з основних завдань дослідників і технологів на сучасному етапі є дослідження ролі домішки кисню в забезпеченні необхідних службових характеристик сплавів на основі E110. Підвищені значення меж текучості та твердості сплавів E110 і E125 ставлять завдання вдосконалення технології формування трубної заготовки і технології деформаційної обробки сплавів. Складнішими є завдання, пов'язані із забезпеченням радіаційної та корозійної стійкості, зниження радіаційного окрихтіння і розпухання сплавів. Огляд пропонує технічні рішення та технологічні прийоми, які здатні забезпечити необхідну якість сплавів відповідно до вимог вітчизняних та міжнародних стандартів якості.

Ключові слова: цирконій, гафній, сплави, чистота, домішки, кисень, екстракція, дистиляція, сублімація, корозія.