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Technology Features an Electrochemical Obtain Powdered Zirconium

Z.M. Protsenko*

Sumy State Pedagogical University, 87, Romenska Str., 40001 Sumy, Ukraine,

The work is devoted to technology electrochemical obtain powder of zirconium ion fluoride melts (setting parameters of the electrolysis method of washing powder Zr impurities from salt mixture components) on different substrates. Phase and element composition and cell size distribution of powdered zirconium was investigated.

Keywords: Powdered Zirconium, Electrolysis, Phase and Elemental Composition.

1. INTRODUCTION

Now there are several methods for preparing zirconium in powder, and massive state. Zirconium is widely used in nuclear energy, space technology, electronics, chemical industry and other branches of engineering. Ability to use zirconium in many cases depends on its purity. For nuclear power to create structural reactor blocks them (shells of fuel elements fuel, ducted pipes) are requirements for purity zirconium a relatively oxygen, nitrogen, carbon (less than 0.05, 0.006, 0.005 at.%, respectively). For example, in works [1, 2] paid attention to obtaining high-purity and nuclear-purity zirconium. To obtain high-purity metals, including zirconium, the authors of work [1] proposed the application at various stages of refining of complex chemical or physical and chemical methods. To obtain nuclear-pure zirconium and alloys based on zirconium with magnesium thermal or iodide zirconium devoted to the work [2].

For the reprocessing of spent nuclear fuel, promising electrochemical method for electron electroreduction Zr fluoride of salt melts. Although the problem electroreduction of Zr salt melts considerable attention in the work of domestic and foreign authors [2-6], there are still many unexplored and clarified points, so the subject study on the electroreduction of fluoride Zr alloys is important.

The aim of this study was to establish the optimal process parameters of electrolysis, obtaining powdered Zr, washing it from impurities and establishment of phase and elemental composition and granule size distribution of powder product.

2. EXPERIMENTAL METHODIC

For the electrolysis was elected two eutectic mixtures based on $NaF-ZrF_4$: NaF (50,5 ml.%) - ZrF_4 (49,5 mol.%), 500 °C and NaF (59,5 ml.%)-ZrF_4 (40.5 ml.%), 512 °C. Anode served graphite was used as the cathode plate of copper, brass, bronze, zirconium, stainless steel. Electrolysis was carried out for 2-4 hours in the galvanic static mode under argon. Temperature was asked within 570-770 °C, cathode current density

of 0.2 - 0.5 A/cm². Purified from salt impurities by decantation in hot water, acidified hydrochloric acid powder residue analyzed by X-ray diffraction (DRON diffractometer - 4.0 in $К_\alpha$ radiation Cu) and mass spectrometry (mass spectrometer MS-7201) analysis. The elemental and granule composition of the product was determined by scanning microscope REMMA-102-02.

3. EXPERIMENTAL RESULTS

Selection to melt electrolysis caused by both physical and chemical properties of the salt mixture (relatively high melting point, no volatility, resistance to heat, the solubility of zirconia in it), and associated with the possible use of these systems in nuclear power. The experiment was conducted in order to choose the material electrode - cathode, not corroded in the studied salt mixture is not formed from zirconium deposition temperature of its chemical compounds. The important point was to establish the parameters of the process of electrolysis to produce dense precipitate of zirconium powder with minimal salt impurities minimum loss (dissipation) powder in the melt and subsequent easy removal of it from the substrate.

Dependence of mass increase cathode (for different materials) of the current density with a parabolic form, indicating the diffusion control process electroreduction zirconium.

When choosing the optimum current density and the cathode material into account primarily mass of sediment (at the same time and temperature electrolysis), the content in the sediment of salt impurities, the density of sediment and the ease of its removal from the substrate. Note that in all cases the deposit on the substrate was in the form growths dendrites that are removed mechanically. As follows from the experimental data, the best results are obtained when using as substrate zirconium (the largest daily gain, the smallest impurities including salt), but it was great complications in the removal of sediment from the substrate, so we can recommend to use as a cathode substrates, brass, or copper. In addition, based on experimental data and Faraday's law was calculated output current for powdered zirconium, this value is 86%

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* zoya.protsenko@i.ua

(cathode-zirconium), 80% (brass), 74% (steel).

Reduced value of the output current can be explained by the partial loss of zirconium in the melt and in washing.

Obtained and purified from salt impurities zirconia powder was analyzed by X-ray diffraction analysis to determine the phase composition of the product. For example, Figure 1 shows a fragment of the X-ray pattern obtained on the substrate of zirconium.
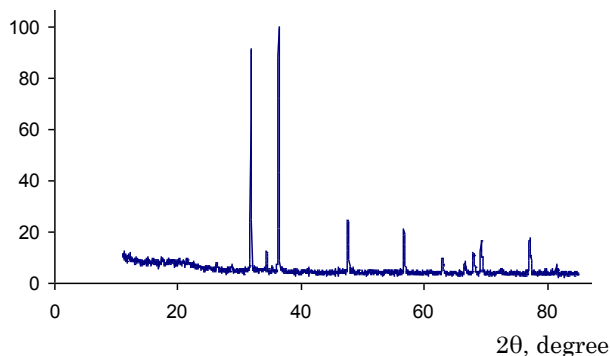

Fig. 1 – X-ray pattern for powder product of electrolysis obtain on zirconium substrate

After decoding of radiographs, found that all the lines correspond to the same phase - the phase of zirconium impurity phases were found, although the X-ray analysis reveals no trace. Similar results we obtained in the case of a substrate with brass. In Table 1 for example the results of XRD analysis, the resulting powder lined with brass. Found that all the lines correspond to the phase of zirconia, but recorded each radiograph as several lines (on the background), which can be attributed to the phase of ZrO_2, ie powder contained not a large percentage of impurity phase (less than 1%).

Table 1 – X-ray analysis of the electrolysis products (powdered zirconium) on brass substrate

№	Experimental data			Table data for Zr	
	2θ, degree	d, Å	I, %	d, Å	I, %
1	31,85	2,8096	54	2,780	33
2	34,45	2,6033	51	2,573	32
3	36,35	2,4714	100	2,459	100
5	47,65	1,9084	47	1,894	17
6	56,70	1,6234	50	1,616	17
7	62,95	1,4764	46	1,463	18
8	68,05	1,3777	45	1,368	18
9	69,20	1,3576	41	1,350	12

Elemental and granular size distribution of powder precipitate Zr was determined by X-ray microanalysis (PMA) and electron microscopy. Microstructure on Fig. 2a clearly shows that dust does not have a clear crystalline structure, their size is (2 - 20) microns. On Fig. 2b presents EDAX spectrum of powder products of electrolysis, shot wave dispersion spectrometer. In the inset is represented the elemental composition (wt.%) zirconium powder precipitate corresponding Zr and doped elements K, Cl (artificially brought about during washing) and F, indicating a lack of clean sediment cathode.
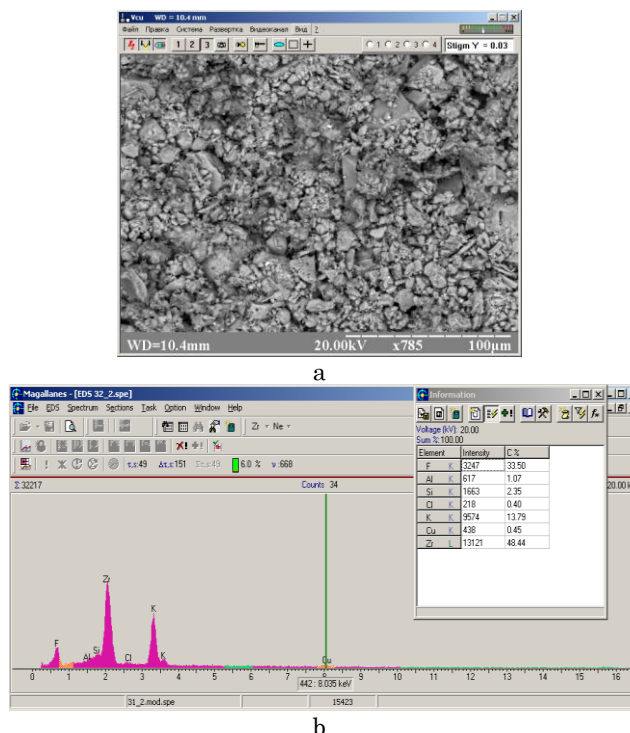

Fig. 2 – Microstructure of powder using secondary electrons (a) and EDAX spectrum of powder products of electrolysis (b)

The elemental composition of the powders as set by mass - spectrometric analysis method. Results of mass spectrometric analysis and X-ray diffraction data confirm the microanalysis of the presence of zirconium in the product and no other impurity phases. In the mass spectrum clearly recorded five peaks, which corresponds to the natural prevalence of zirconium, with the main peak corresponds to ^{90}Zr.

4. CONCLUSION

Thus on the basis of the studies found the various factors on the electroreduction of zirconium. Thus, with increasing temperature of the electrolyte on current yield partially reduced.

This can be explained by increasing the intensity of the chemical interaction of metals with salt phase, the formation of reaction products and other factors. Therefore, there is an optimum temperature at which the least likely occurring secondary and indirect processes that reduce output by current, while maintaining constant other physic and chemical properties of the electrolyte. This temperature for each different salt mixtures, in our case we can recommend temperatures of 580-650 ° C.

Exit from current increases with increasing current density. The main reason for the significant difference between the output current from Faraday's law of electrolysis in molten salts are metal loss due to its dissolution in the electrolyte or dispersion in the melt in the

case of the formation of loose sediments. Very high current density increases the voltage drop in the electrolyte layer and increases power consumption. Moreover, with increasing cathode current density increases accordingly and anode current density at the anode and the anode effect occurs that violates the normal course of electrolysis (in our experiments at high anodic current density observed effect).

At high current densities also possible occurrence of side processes - selection of the cathode along with the base metal in the metal present in the electrolyte, such as alkaline Na or K.

The optimal process parameters of electrolysis for substrates of different materials: $i = (0,1 - 0,3)$ A/sm^2, U = (2,8-3,0) V, T = 600-650 °C (zirconium); $i = (0,2-0,4)$ A/sm^2, U = 2,6 - 2,8 V, T = 600-650°C (brass), $i = (0,3-0,45)$ A/sm^2, U = 2,7 -2,8V, T = 580-630 °C (steel).

Investigated the microstructure of powdered zirconium, calculated crystallite sizes that are roughly equal to 2 - 50 microns, depending on the conditions of electrolysis. Determined the elemental composition of the powder corresponding zirconium.

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