Academician A.V. Elyutin made a substantial contribution to the development of rare-metal industry in the Soviet Union and Russia. One side of the multiform activity by Aleksandr Vyacheslavovich was the metallurgy of secondary rare metals; he considered it significant and paid great attention to it. In this article we represent a short review of publications of A.V. Elyutin and coworkers on technologies of the recovery of rare metals from secondary raw materials.

For example, processing technologies of secondary raw materials containing zirconium, hafnium, tungsten, tantalum, and niobium from various types of secondary raw materials, notably, scrap metal, scrap of refractory materials, wastes and scrap of hard alloys, and obsolete scrap of capacitors, are considered. Possibilities of increasing the purity of these metals by electrolytic refining and electron-beam melting are shown.

Keywords: zirconium, hafnium, tungsten, niobium, secondary raw materials, recovery technology, electrolytic refining, electron-beam melting

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ZIRCONIUM AND HAFNIUM

Obtaining zirconium from secondary raw materials is an additional source of zirconium production for the provision of industrial branches. In addition, it has a much lower prime cost than the production identical in quality but produced from ore raw materials [4, 5].

Secondary Zr-containing raw materials include the following:

(i) scrap of bacor (brazilite–corundum) wares (33–41% ZrO₂);

(ii) scrap and wastes of metal zirconium and its alloys, low-grade sponge zirconium, and wastes formed during the fabrication and processing of ingots, rolled metal, and wares;

(iii) rejects and scrap of roasted ceramic billets for capacitors and piezo elements (with the fabrication of billets of ceramic mass containing from 5 to 70% ZrO₂, irretrievable losses constitute no more that 3%, and other wastes can be regenerated);

(iv) wastes of production of zirconium electrocorundum, which is used in processes of forced grinding. They contain up to 30% ZrO₂ and represent a finely dispersed material (<10 μm), which is formed when melting the charge consisting of zirconium dioxide, alumina, and zirconium concentrate;

(v) wastes of production of ferro silicon zirconium and ferro aluminum zirconium in a form of slags containing 7–10 and 10–13% ZrO₂, respectively.

The technology of processing the lump scrap of vitrified bacor refractory materials, which is formed with the replacement of lining glass-melting furnaces, includes the three-stage crushing, screen sizing, and magnetic separation. The result of the latter is the target product, bacor concentrate, which contains ≤0.2% Fe₂O₃. To produce a refractory materials of the BK–33 grade, the bacor concentrate is charged with 10–15% alumina, zirconium dioxide, and ammonium nitrate. The prepared charge is melted in arc furnaces and then poured into molds to fabricate refractory wares. The use of 1 t of the charge based on the bacor concentrate produced by processing the scrap of bacor refractory materials in the production of BK–33 economizes 400 kg of the zircon concentrate and 500 kg alumina.
To process metal zirconium waste, chemical dissolution, hydrogenation, chlorination, and electrolytic refining in chloride–fluoride electrolytes is applied. The most effective method of using the certified waste of zirconium and its alloys is their involvement into the charge when smelting ingots by various methods. The main volume of recycle metal is smelted in electron-beam furnaces (EBF) in a form of both lump wastes and filing preliminary pressed into briquettes or pellets.

The secondary metallic hafnium-containing raw materials are presented by scrap of hafnium and hafnium-based alloys. Most often, pure hafnium is recovered from scrap by electrolytic refining using chloride and chloride–fluoride electrolytes.

A complex investigation into the electrolytic refinement of hafnium in the melt of sodium and potassium chlorides containing hafnium tetrachloride was performed at GIREDMET [6]. The electrolyzer design made it possible to use crude metal or metal wastes in the form of fillets made from compacted powders or filing, sheet metal, clippings, rods, ingots, and pieces with various contents of impurity elements. The current yield in optimal conditions was 77.0–98.5%. Refined metal had a rather high purity in regards to all impurities excluding oxygen, while hardness of ingots fabricated by EBF of such metal was 102–105 kg/mm².

**TUNGSTEN**

Secondary raw materials of tungsten are presented mainly by wastes of metal tungsten and its alloys, as well as tungsten-containing hard alloys. Technologies of processing tungsten-containing wastes differ depending on their type and physical state [1, 7].

Oxidation in melts of alkali nitrates with obtaining the Na₃WO₄ solution after leaching the salt fusion cake, high-temperature oxidation with obtaining WO₃ distillates, anodic dissolution in the ammonia or alkali electrolyte, and electrolytic refinement in salt melts of the NaCl–NaF–WO₃ composition were used to process wastes of metal tungsten and its alloys.

Wastes of hard alloys, both lump and dusty, are also processed by oxidation and anodic dissolution in solutions of mineral acids; in addition, high temperature chlorination, the so-called zinc method, and Cold-stream process are used.

New processing technologies of tungsten wastes are presented in [7]. These are the hydrochlorination of materials with a low tungsten content in dimethyl formamide, the decomposition of the scrap of superalloys in a melt of the NaOH–Na₂SO₄ salt mixture, hydrometallurgical recycling process of tungsten (and silver) from the scrap of Ag–W powder contact alloys, the electrochemical dissolution of wastes of metal tungsten in ammonia electrolytes with the use of the ac current, and bioleaching tungsten from dead oil-cracking catalysts.

**TANTALUM**

Secondary raw materials as the source of producing niobium and tantalum compounds were mentioned for the first time in well-known monograph [8], where it is particularly mentioned that metal wastes (rejects of fillets; waste of mechanical treatment; and worked-out details made of niobium, tantalum, and their alloys) can serve the starting material for fabricating niobium and tantalum pentachlorides.

The regeneration of tantalum from secondary sources of raw materials ensures up to 10% of the world need for tantalum (up to 25% in the United States). The main types of such raw materials are scrap and wastes of metal tantalum and its alloys, capacitors with a tantalum anode, and tantalum-containing hard alloys. Wastes of metal tantalum and its alloys are represented by rejects of ingots of vacuum-arc remelting, shaving, clippings of half-finished products, green ends and rejects of fillets, and screening of powder. Low-grade wastes are formed by distillates from screens of electron-beam and vacuum-arc furnaces [9].

The simplest and most effective method to utilize lump tantalum wastes is direct remelting into ingots with the preliminary removal of surface contaminations of scrap with liquid calcium or magnesium and the subsequent dissolution of the getter metal in hydrochloric acid. Wastes are usually remelted by electron-beam melting.

Tantalum scrap can be processed into powders using hydrogenation or fluorination. The method of chemical dissolution and repeated precipitation or the electrochemical method can be used during its processing with the purpose of fabricating Ta₂O₅.

To recycle tantalum and other valuable metals from “superalloys,” the alloy is subjected to anodic oxidation in the aqueous solution of organic compounds and salts. Methanol, ethanol, isopropanol, and acetyl acetone are used as the former. Halogenides, sulfates, and nitrates of alkali and alkali-earth metals are recommended as salt additives.

Tantalum(V) oxide can be also fabricated by the chlorination of scrap. Formed TaCl₅ of technical purity grade is purified by distillation and reduced with hydrogen to Ta₃Cl₆; then niobium is removed from the latter, which is chlorinated to TaCl₅ again. The latter is dissolved in alcohol with the formation of tantalum alcochloride, which is subjected to hydrolysis in the presence of carbon. Due to this, high-purity Ta₂O₅ is formed.

The involvement of tantalum wastes in the form of capacitor scrap into processing is very valuable in view of the low use factor of tantalum when fabricating capacitors and large volumes of utilization of war and civil technique taken out of service [10]. The ability of tantalum to form a stable oxide film during electrolytic anodic oxidation is important for applying tantalum in