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SECONDARY RARE METALS

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The technologies of extraction for zirconium, hafnium, tungsten, tantalum and niobium from various types of secondary materials: waste metals, scrap of refractory materials, waste and scrap of hard alloys, obsolete scrap of capacitors. The possibilities of improving the purity of these metals by electrolytic refining, and cathode-ray melting are indicated.

Keywords: zirconium, hafnium, tungsten, tantalum, niobium, secondary raw materials, extraction technology, electrolytic refining, cathode-ray melting.

An academician A.V. Elyutin brought in a ponderable contribution to development of domestic raremetallic industry. One of parties of his manysided activity was metallurgy of secondary rare metals, which he gave a large value and spared much attention.

In the monograph of A.V. Elyutin etc «Secondary refractory rare metals» [1] technologies of processing for secondary of raw materials recycling, containing zirconium, hafnium, vanadium, niobium and tantalum, and also technologies of affinage of wastes and draft metals are considered. Material of book is complemented by a review [2] of new technologies of extraction for refractory rare, rare-earth and radioactive metals from the different types of secondary raw material.

Works on the affinage of rare metals, as inalienable element of technology of receipt of high-quality raremetallic products is occupied a considerable place in the creative legacy of A.V.Elyutin. Classification and physic-chemical essence of technologies for affinage of the coloured (including. rare) metals are expounded in the teaching aid of national research technological university of «MISandA» of «Basis of affinage of the coloured metals» [3], one of authors of which he is.

A receipt of zirconium from secondary raw material is an additional source for providing of industry by zirconia products. It is possible to consider the real and potential sources of secondary zirconiocontained raw material:

– it is a crow-bar of bacoric (brazilile-corundomic) wares (33.41 % ZrO_2);

– it is a crow-bar and wastes of metallic zirconium and his alloys, low-grade spongy zirconium, wastes, appearing at making and treatment of bars, rolled metal and wares;

– it is marriage and crow-bar of the burnt ceramic billets for condensers and piezoelements: at making of billets from ceramic mass, containing from 5 to 70 % ZrO_2, irretrievable losses make no more than 3 %, and other wastes can be regenerated;

– are wastes of production for zirconia electrocorundum, used at processes of the power polishing; zirconiacontained wastes of this production (to 30 % ZrO_2) are the micronized material (< 10 мкм), appearing at melting of charge, consisting of zirconium dioxide, alumina and zircon concentrate;

– are wastes of production for ferrosilicozirconium and ferroaluminozirconium as slags, containing 7-10 and 10-13 % ZrO_2 accordingly.

Technology of processing of cake bar of glassworking bacoric refractories, appearing at replacement of briakwork of glassworking stoves, includes the three-phase crushing, sitting and magnetic separation. For processing of metallic zirconia wastes use chemical dissolution, hydrogenising, chlorinating and electrolytic affinage in chloride-fluoride electrolytes.

Secondary metallic hafniumcontained raw material is presented by scrap of hafnium and alloys on his basis. Mostly clean hafnium is extracted from scrap by the method of electrolytic affinage with the use of chloride and chloride-fluoride elect-relates.

Secondary raw material of tungsten is presented, mainly, by wastes of metallic tungsten and his alloys, and also wastes of tungstenous carboloies.

For processing of wastes of metallic tungsten and his alloys use oxidization in fusions of alkaline nitrates with a receipt, after lixiviating of salt fusion cake, solution of Na_2WO_4, high temperature oxidization with the receipt of returned materials of WO_3, anodic dissolution in an ammoniac or alkaline electrolyte, and also electrolytic affinage in salt fusions of composition $NaCl$-NaF-WO_3.

Wastes of hard alloys, caked and pulverulent, process also by the methods of oxidization and anodic dissolution in solutions of mineral acids, but apply yet and the high temperature chlorinating and so-called zinc method.

First secondary raw material as a source of receipt of connections of niobium and tantalum is mentioned in the known monograph of A.V. Elyutin etc «Niobium and tantalum» [8]. The basic types of secondary tantalumcontained electrolytes raw material are a crow-bar and wastes of metallic tantalum and his alloys, condensers with a tantalum anode, tantalumcontained hard alloys.

Wastes of metallic tantalum and his alloys are presented by the cakes of bars (for example, by the wreckages of bars crowns for vacuum-arc remelt), shaving, slipping of ready-to-cook foods, marriage of beads, sifting out of powder. Bad quality tantalum metallic wastes returned materials serve as from the screens of cathode-ray and vacuum arc stoves [9].

The most simple and effective method of utilization of caked wastes for tantalum is their direct remelt at bars with pre-cleaning of scrap from superficial contaminations by a liquid calcium or magnesium and subsequent dissolution of metal-getter in hydrochloric acid. The remelt of wastes is carried out, as a rule, by the method of the cathode-ray melting.

Tantalum scrap can be processed on powders with the use of operations of hydrogenising or fluorination. At processing of tantalum scrap with the purpose of receipt of Ta_2O_5 the method of chemical dissolution and reprecipitation or electro-chemical method can be applied.

The oxide of tantalum (V) can be also got by chlorinating of scrap. Appearing $TaCl_5$ of technical cleanness clear of distillation, restore hydrogen to Ta_3Cl_8, delete from him niobium and chlorinate again to $TaCl_5$. Last dissolve in an alcohol with the receipt of tantalium alkochloride, which is exposed to the hydrolysis in presence a carbon. As a result of high-purity Ta_2O_5 got.

The most systematized researches of electrolytic affinage for tantalum are conducted in the institute of SIRM under the direction of A.V. Elyutin [14,15]. It is experimentally shown possibility of the deep cleaning of tantalum from most metallic admixtures, carbon, nitrogen and oxygen.

The tantalum of the highest degree of cleanness can be got with the use of physical methods of affinage, for example zone melting. The area melting provides moving away of admixtures, both at the mechanism of the floating-zone refining and by their evaporation from the surface of molten zone.

Secondary niobiumcontained raw material is presented by wastes of production and application of niobium and his alloys. For wastes of niobium alloys, containing ≥ 90 % parent metal, technology of processing developed on a few directions: electrolytic affinage, chlorinating and hydrometallurgical processing, which allow to dissociate niobium basis from alloying elements and get clean niobium or his compounds. These methods possess by dignity that the questions of processing of wastes of alloys of any compositions decide radically. Another way it is processing of wastes of alloys again to the alloys of niobium. Wastes of niobium alloys with content 50-80 % niobium can be processed directly on a metal by the method of electrolytic affinage or on niobium pentaoxide by oxidization with the subsequent receipt of ligatures of *Al-Nb* or ferroniobium.

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