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T.B. Yanko, manager by laboratory

TECHNOLOGIES OF PRODUCTION AND AFFINAGE FOR ZIRCONIUM

SE «State research and project institute of titan», Zaporozhe, Ukraine

There are considered methods of metallic zirconium receipt and also methods of affinage of crude zirconium. It is revealed that a magnesium thermic method allows to get spongy zirconium of enough high-purity.

Keywords: metallic zirconium, technologies of its receipt, crude zirconium, its affinage

It is known that on the supplies of zirconium containing of ore raw material Ukraine occupies one of leading places in the world [1]. In this connection there is expedient creation in the country of complete cycle for zirconium production.

Technologies of receipt of zirconium are characterized by large complication and require the special approach, and also careful study. Among the basic methods of receipt of this metal, having an industrial meaning, it is necessary to distinguish the method of electrolysis, reduction of connections of zirconium fluorides by a calcium and reduction of chlorides of zirconium by magnesium. For the receipt of high-clean zirconium there is use electrolytic or iodide affinage [2].

Method of receipt by zirconium of electrolysis. This method is known a long ago, however complication of appearance and considerable power expenses complicate its wide introduction. Industrial application are had electrolysis of complex fluorides of zirconium, electrolysis of chlorides of zirconium, and also electrolysis in the salt chloride-fluoride systems.

In technology of electrolysis of zirconium chlorides as raw material use its tetrachloride ($ZrCl_4$), got by chlorinating mixture of zircon ($ZrO_2{\cdot}SiO_2$) and graphite by connections of $SiCl_4$, $TiCl_4$ or $AlCl_3$.

At the receipt of feed stock for the electrolysis of K_2ZrF_6 there is carry out decomposition zircon on a reaction:

$$ZrO_2 \cdot SiO_2 + 2KF \cdot SiF_4 \Rightarrow K_2ZrF_6 + 2SiO_2 \ . \qquad (1)$$

The basic reactions of electrolysis process with the use of chloride-fluoride solutions are stated below [3]:

$$K_2ZrF_6 + 4NaCl \Rightarrow Zr + 2KF + 4NaF + 2Cl_2 \ ; \qquad (2)$$

$$ZrCl_4 \Rightarrow Zr + 2Cl_2 \ . \qquad (3)$$

At completion of electrolysis a cathode product, containing 30-50 % crystalline powder of zirconium, is processed by vacuum thermic methods, the where upon washed powder is exposed to drying.

The basic lacks of methods of electrolysis it is been: not high quality of zirconium on content most harmful impurities, complication of instrumental appearance of technological process, considerable charges on electric power, and also substantial extras of harmful connections of fluorine and chlorine in the process of production.

Reduction of zirconium fluorides by a calcium. Technology of receipt of plastic calcium thermic zirconium in the industrial scale of Ukraine was mastered on SSPE «Zirconium». The indicated production is based on realization of calcium thermic reduction of tetrafluoride zirconium on a reaction:

$$ZrF_4 + 2Ca \Rightarrow Zr + 2CaF_2 \ . \quad (4)$$

As a deoxider it is use a calcium as shaving, purged from impurities, first of all from nitrogen.

At realization of reduction process of fluorides of zirconium by a calcium is load necessary components in a reactor, it carry out charge to the necessary temperature and it execute the "primer" of reaction. Foods of reaction (bar of draft zirconium and slag) extract from furnace and divide by a mechanical method. The bar of draft zirconium is exposed to washing by nitric acid, washing by water and drying. Further it is sent to the cathode-ray remelt for an affinage from metallic impurities and receipt of bar, suitable for processing on billets for rolling.

Advantages of this method are relative simplicity of technological process and subzero content of hafnium (< 0.01 %), that answers the generally accepted world standards, and also possibility of receipt of alloys of zirconium directly in the process of reduction. Among defects it should be noted high prime price from the use of expensive reagents, in particular calcium which is not produced in Ukraine, and also the use in the process of reduction of harmful connections of fluorides.

Reduction of zirconium chlorides by magnesium. In basis of this process is underfed:

$$ZrCl_4 + 2Mg \Rightarrow Zr + 2MgCl_2 . \quad (5)$$

Technology foresees chlorinating of zircon, division of chlorides of zirconium and hafnium, reduction of tetrachloride of zirconium, cleaning of foods of reduction byvacuum separation, vacuum treatment of spongy zirconium and it's processing on a commodity product.

A division of zirconium and hafnium is necessary for providing of minimum content in the active area of materials with the enhanceable coefficient of claw of neutrons, because for hafnium the cross-section of absorption of thermal-neutron is considerably higher, than for zirconium. Industrial scales purchased three methods of division of zirconium and hafnium: on basis of methyl and bytil [4], extraction distillation [5] and shallow crystallization of salts of zirconium and hafnium [6].

One of difficult moments of technology of reduction of tetrachloride of zirconium by magnesium is its supply in a reactor. The different methods of feed of reactor the tetrachloride of zirconium are known [7-9]. Basic from them is a supply of powdery tetrachloride of zirconium in a vaporizer, and then transmission of it's as vapor in the reactor of reduction. There are takes place thus the partial hydrolysis of powder of tetrachloride of zirconium, pickup and hanging up, in the systems of feed. Such method of feed considerably complicates the construction of reactor of reduction, and also reduces the productivity of process. New technical solutions of structural appearance of apparatus of reduction are offered in Institute of titan, and also method of its feed by the tetrachloride of zirconium [10,11], which promote the productivity of process and allow to get spongy zirconium of high quality due to the improvement of preparation of zirconium tetrachloride powder to loading in a vaporizer. In particular, powder of zirconium tetrachloride before a supply in a vaporizer make more compact in granules or pellets of necessary sizes. After heating and evaporation of vapors of zirconium tetrachloride give with the managed speed in a reactor, where a process of its reduction by magnesium at a temperature about 800 °C is behaviored.

Table 1 - Chemical composition of zirconium, processed on different technologies

Element	Technology of receipt			
	mass stake of impurities, % mass			
	maghezium thermic reduction	method electrolysis	calcium thermic reduction	iodide affinage
Aluminium	$7.5\cdot10^{-3}$	$9\cdot10^{-3}$	$5.0\cdot10^{-3}$	$5\cdot10^{-3}$
Beryllium	-	-	$5.0\cdot10^{-4}$	$1\cdot10^{-3}$
Boron	$5.0\cdot10^{-5}$	$5\cdot10^{-5}$	$5.0\cdot10^{-5}$	$5\cdot10^{-5}$
Cadmium	$5.0\cdot10^{-5}$	$3\cdot10^{-5}$	$3.5\cdot10^{-5}$	$5\cdot10^{-5}$
Calcium	-	-	$1.0\cdot10^{-2}$	$2\cdot10^{-2}$
Carbon	$2.5\cdot10^{-2}$	$4\cdot10^{-2}$	$2.0\cdot10^{-2}$	$8\cdot10^{-3}$
Cobalt	$2.0\cdot10^{-3}$	-	-	-
Copper	$5.0\cdot10^{-3}$	$7\cdot10^{-3}$	$5.0\cdot10^{-3}$	$3\cdot10^{-3}$
Chrome	$2.0\cdot10^{-2}$	$5\cdot10^{-2}$	$5.0\cdot10^{-3}$	$2\cdot10^{-2}$
Chlorine	-	-	$3.0\cdot10^{-3}$	-
Fluorine	-	-	$3.0\cdot10^{-3}$	-
Hafnium	$1.0\cdot10^{-2}$	$5\cdot10^{-2}$	$1.0\cdot10^{-2}$	$5\cdot10^{-2}$
Iron	$1.5\cdot10^{-1}$	$8\cdot10^{-2}$	$5.0\cdot10^{-2}$	$3\cdot10^{-2}$
Lead	-	-	$5.0\cdot10^{-3}$	$5\cdot10^{-3}$
Lithium	-	-	$2.0\cdot10^{-4}$	$2\cdot10^{-4}$
Magnesium	$2.0\cdot10^{-3}$	-	-	-
Manganese	$5.0\cdot10^{-3}$	$5\cdot10^{-3}$	$2.0\cdot10^{-3}$	$1\cdot10^{-3}$
Molybdenum	$5.0\cdot10^{-3}$	-	$5.0\cdot10^{-3}$	$5\cdot10^{-3}$
Nickel	$7.0\cdot10^{-3}$	$8\cdot10^{-3}$	$1.0\cdot10^{-2}$	$2\cdot10^{-2}$
Nitrogen	$5.0\cdot10^{-3}$	-	$6.0\cdot10^{-3}$	$5\cdot10^{-3}$
Oxygen	$1.4\cdot10^{-1}$	$(8.12)\cdot10^{-2}$	$1.4\cdot10^{-1}$	$5\cdot10^{-2}$
Potassium	-	-	$4.0\cdot10^{-3}$	-
Silicon	$1.2\cdot10^{-2}$	$3\cdot10^{-2}$	$1.0\cdot10^{-2}$	$8\cdot10^{-3}$
Titan	$5.0\cdot10^{-3}$	-	$7.0\cdot10^{-3}$	$5\cdot10^{-3}$
Tungsten	$5.0\cdot10^{-3}$	-	-	-
Uranium	$3.0\cdot10^{-4}$	-	-	-

The block of spongy zirconium in a reactor is formed as a result of the joint behavior of processes of reduction of tetrachloride of zirconium and formation of zirconium and chloride of magnesium, crystallization and sintering of zirconium in the environment of liquid magnesium and liquid chloride of magnesium.

For the division of foods of reaction of reduction there is apply vacuum separation of reactionary mass at a temperature about 1000 °C. At this temperature and low pressure magnesium and its chloride evaporate from the block of spongy zirconium, and then condense in the cold area of apparatus of separation. At completion of a vacuum treatment spongy zirconium is unloaded from an apparatus and is pound to commodity factions.

Quality of spongy zirconium, got on masgnezium thermic technology, as compared to zirconium, made on different technologies (table. 1), is inferior to zirconium, subjected iodide affinage, however is acceptable to the use in alloys without the impurity cleaning. In addition, the results of technics and economy analysis showed that prime price of zirconium, got on technology of masgnezium thermal reduction of tetrachloride of zirconium, less than, and process of receipt - more rapid with providing of considerable energy-savings [12].

Technologies of zirconium affinage. The affinage of zirconium is applied for cleaning of substandard polluted metal, processing of wastes of zirconium and its alloys, and also at the production of zirconium from a draft metal, got by a cheap method.

The methods of electrolytic and iodide affinages are used at industry conditions [13]. The process of electrolytic affinage insignificantly differs from the production of zirconium electrolysis. A difference consists of level of temperature for these processes and more high demands, produced to the electrolyzers, and also cleanness of the applied materials. An initial polluted metal is used as a soluble anode. At electrolysis more electropositive, as compared to a basis metal, impurities are remained in anode slime, and more electronegative is accumulated in an electrolyte. The cleared zirconium is besieged on a cathode.

The method of iodide affinage or method of Van-Arkel (by the method of transport reactions) is get high-clean zirconium. A draft metal in a vacuum pressed apparatus is heated to the temperature, providing sufficient speed of satiety it’s by iodine. Thus appearing tetriiodide zirconium passes to the gas phase, carried to the hot tungsten filament and on its surface, heated to the temperature 1200-1300 °C, dissociated on an iodine, returning on oididing of draft metal, and also metal, besieged on a filament.

The process of iodide affinage is described by equation:

$$Zr_{(tech)} + 2J_2 \overset{200-500°C}{\Rightarrow} ZrJ_4 \overset{1500-1800°C}{\Rightarrow} Zr_{(clen)} + 2J_2 \,. \quad (5)$$

Such method is the effective method of cleaning of zirconium from impurities which do not form volatile connections with iodine at the conditions of realization of zirconium affinage, in particular from such impurities, as oxygen and nitrogen, which assist fragility of metal. As a feed stock use the metal of high degree of cleanness, because at processing some metallic impurities remain in the same quantity, what initial metal.

Magnesium thermic spongy zirconium contains the fair quantity of impurities, both gaseous and related with the process of receipt of metal (magnesium, chloride of magnesium et al). Affinage of the cleared magnesium thermic zirconium by cathode-ray melting [14] allows considerably to reduce content of aluminum, iron, silicon, magnesium, manganese, copper, and titan and to get zirconium of high-purity.

Conclusions. The analysis of the above-mentioned methods shows that the receipt of the cleanest zirconium is possible by methods electrolytic and iodide affinages. However the indicated technologies are characterized by high expense coefficients and complication of implementation. In addition, their realization requires the presence of initial draft metal. At the same time technology of magnesium thermic reduction of tetrachloride of zirconium allows to get zirconium of high enough quality. Thus the prime price of the got zirconium less than thus, and process is more rapid with a considerable energy-savings. Taking into account it, and also orientation of world production of zirconium on the use of chloric technology, becomes obvious, that with magnesium thermic technology of receipt of zirconium in Ukraine development of production of this metal must be constrained.

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