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Perspectives of Zirconium Carbide in the Modern World

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Abstract

Nowadays scientists try to not only improve the process of quality, but also reduce cost and substitute foreign materials for domestically-produced ones. In this paper, an analysis of the state of zirconium carbide was carried out and information on its production was systematized. Carbothermic synthesis is the basis for the synthesis of zirconium carbide. Self-propagating high-temperature synthesis is not used widely, but it can be claimed for multifunctional nanostructured films containing zirconium carbide. Nanocrystalline zirconium carbide is obtained by using mechanosynthesis, but in small quantities. Due to its characteristics, plasmosynthesis should be considered as the most promising of the known methods for producing zirconium carbide in the nanostate. An analysis of world production of zirconium carbide suggested that the nanocrystalline market segment is fully provided by foreign suppliers is also carried out.

Keywords: Plasmosynthesis, production, nanotubes, zirconium carbide, ZrC, carbothermic synthesis, mechanosynthesis;

1. Introduction

The current transition to an innovative model of development and modernization of the economy enables the country to create fundamentally original cross-scientific technologies for material synthesis based on a complex of academic research results. One of the most important tasks of modern materials science is the creation of materials for working in extreme conditions - at high temperatures and voltages, aggressive environments impact, and so on [9].

Using refractory metals and their compounds, such as carbides, which have high hardness, refractoriness, heat resistance, as well as certain physical and chemical properties solves these problems. Among carbides of refractory metals, zirconium carbide has high operational properties, which makes it potentially suitable for solving many problems of modern materials science: as components and alloying additives of hard alloys, versatile composite materials, and also for protective coatings[2].

2. Research

Zirconium carbide is a chemical compound of zirconium metal and carbon with the formula ZrC. It is an introduction phase with a wide region of homogeneity, which ranges from 38.4 to 50 % carbon, which corresponds to the formula $ZrC_{0.62}$ and $ZrC_{1.0}$, respectively.

Physical properties. Zirconium carbide is a gray powder. It has a cubic face-centered lattice of the NaCl type, space group Fm3m, with a period a = 0.4693 nm.

- Electrical resistivity 50 μOhm·cm;
- The coefficient of linear thermal expansion $7.01 \cdot 10^{-6}$ 1/K (25-1000 °C);
- Microhardness 28.44 GPa;
- Modulus of elasticity 412 GPa[7].

Chemical properties. Zirconium carbide is a chemically stable compound to sulfuric, hydrochloric, phosphoric, perchloric, oxalic acids and mixtures of sulfuric and phosphoric, sulfuric and oxalic acid at room temperature. It is insoluble in 10% and 20% sodium hydroxide solutions. It is soluble in boiling sulfuric, nitric, perchloric acids. It is highly soluble in mixtures of hydrochloric and nitric, mixtures of sulfuric and nitric, nitric and hydrofluoric acids. Zirconium carbide reacts with oxygen to form ZrO_2 , starting at 700 °C. Zirconium carbonitrides are formed in the presence of nitrogen at high temperatures [3].

Application. The high melting point and small cross section for neutron capture of zirconium carbide allows it to be used as a protective coating on graphite matrices in fuel rods containing uranium and thorium carbides. The zirconium carbide coating deposited by the CVD process on uranium dioxide is used as a diffusion barrier from the reaction products of the half-life of nuclear fuel. ZrC-UC composite is used in thermoelectric generators. Zirconium carbide is also used as an abrasive material for polishing metals[4]. Zirconium carbide is used in hard alloys, targets, welding consumables, cermets, electronics, metallurgy, mechanical engineering, textile industry, aviation, etc.

2.1. Zirconium carbide production

The modern production of zirconium carbide is based on the carbothermic method, which is implemented in several technological options and is used for obtaining zirconium carbide when used as part of materials for abrasive processing, spraying and surfacing, protective coatings. However, the strategically important nanocrystalline segment of the zirconium carbide market is fully provided by foreign suppliers, including companies such as Nanostructured Amorphous Materials, Inc. (USA), «Hefei Kaier Nanotechnology Development Ltd. Co» (China), «NEOMAT Co» (Latvia), «PlasmaChem GmbH» (Germany). It determines the development of Russian zirconium carbide nanotechnology. These companies produce 97% ZrC with a dimension of 10-60 nm in batches from 5-100 g to several kilograms. To date, these manufacturers have established a price range from 400 to 2000 US dollars/kg [10].

The neighboring countries market is represented by several enterprises and laboratories in Ukraine: LLC NPP Development and Implementation of New Materials LLC (Kiev), Ukrintellectservis LLC (Kiev), Progress PE (Donetsk), which produce ZrC powder that complies with TU 6-09 -03-03-408-754[11].

The national market is represented by small enterprises and laboratories that receive zirconium carbide in the carbothermic manner, plasmosynthesis, mechanosynthesis, SHS, and vapor deposition.

IPM UMEX Company (Ufa) sells highly refractory ZrC in the form of a gray powder at an agreed price. The Ural Plant of Industrial Chemistry (USPH) produces and supplies zirconium carbide grades of the “Ch” classification. JSC "UZPH" is a modern full-cycle chemical enterprise, whose products are in demand not only in the markets of Russia and Custom Union’s countries, but also in high-tech countries of the far abroad: Japan, Australia, Canada, and the USA. Products are sold to the national market through the official Trading House - RIVIERA LLC, Moscow.

Alterkhim LLC (Dzerzhinsk) manufactures and supplies qualification grade Zirconium carbide, corresponding to TU 6-09-03-408-75, in batches of 1 kg at wholesale and retail prices [12]. Redmetural LLC (Ekaterinburg) supplies quality rare-earth metal products throughout the Russian Federation and the CIS countries. The main products are metals (molybdenum Mo, niobium Nb, tantalum Ta and magnesium), carbides (TaC, NbC, VC, TiC, ZrC, Cr_3C_2, Mo_2C), etc. Zirconium carbide is supplied in the form of fractionated powders 3-5, 40-60, 40-100 microns at the contracted price[8].

2.2. ZrC synthesis methods

1) Mechanosynthesis.

Mechanosynthesis is the high-frequency high-speed processing of charge powder material in high-energy planetary, ball and vibration mills. The particles of the mixture are subjected to mechanical action with the force necessary for brittle fracture and plastic deformation [10]. Solid particles are subjected to first elastic and then plastic deformation as a result of efforts from grinding media impact until the stress exceeds the tensile strength of the material in any section. Granules are often formed, which are fragile particles coated with plastic material. In the process of mechanosynthesis, the particle size decreases, the contact area increases, surface oxide films are destroyed and surface impurities are removed, defects in the crystal structure accumulate, which leads to an increase in the chemical activity of the reaction mixtures.

Usually a mixture of zirconium and carbon is subjected to grinding in a ball mill. The formation of carbide occurs after 4-12 hours of grinding. The size of the powders after 48 hours of grinding is about 7 ± 1 nm [8].

2) Precipitation of zirconium carbide from the vapor-gas phase.

The method consists in the interaction of gaseous carbon and volatile zirconium compounds.

Deposition occurs on the surface of a tungsten filament, heated to a temperature of 1700-2400 °C. Carrying out the process at high temperature (about 2400 °C) allows obtaining a single-crystal precipitate. Hydrogen contributes to the development of the reaction and significantly reduces the synthesis temperature in some cases.

3) Plasmosynthesis.

The starting material was zirconia powder with a content of the main substance of at least 99.3%. A technical propane-butane mixture is used as a carbon-containing reagent, and nitrogen of a special frequency (N2 = 99.99%) is used as a plasma-forming gas. The synthesis process occurs in the reactor in the presence of a hydrocarbon and in a high-temperature stream of nitrogen, depending on the carbon: oxide ratio, an oxygen-containing product of complex chemical and phase composition is formed [10].

4) Self-propagating high temperature synthesis.

In contrast to traditional technologies for producing such materials using powder metallurgy, the method of self-propagating high-temperature synthesis has several advantages, among which: the possibility of synthesizing high-temperature ceramic materials with high service characteristics and high chemical purity. This method will make it possible to reproducibly produce high-quality high-temperature ceramics based on borides and silicides Zr and Mo [6].

The technological scheme for obtaining SHS product powders includes the following operations: mixing pre-prepared powders, loading into the reactor, supplying reaction gas, synthesis, grinding and sieving of the product. A feature of the synthesis process is the possibility of a reaction in a narrow zone moving along a compressed sample due to heat transfer after local reaction initiation.

5) Carbothermic synthesis.

The studied scientific and technical literature provides information about 5 technological options for implementing this method described below.

Furnace carbothermal reduction of zirconia uses a compact charge. This method is the most effective and economical. The reduction of zirconia with carbon (graphite) produces technically pure zirconium carbide on an industrial scale. Mixtures of zirconium dioxide and carbon (graphite) in amounts corresponding to the complete synthesis reaction are mixed in a mixer, rubbed through a sieve, pressed into tablets at a pressure of 98.1–196.2 Pa, placed in an oven and heated to the required temperature. The reaction mixture is carburized in one or more stages in a resistance electric furnace or in gas furnaces. After unloading from the furnace, carbide is crushed and classified according to the size of granules [5].

The reduction of zirconium dioxide is expediently carried out in a vacuum, which excludes the possibility of nitriding, shifts the reaction equilibrium and allows it to be carried out at lower temperatures. In vacuum, a higher content of bound carbon in the carbide is also achieved [2].

ZrC synthesis by reduction of zirconia by melting in an electric arc furnace. The technological option is the fusion of zircon sand containing 67% ZrO_2 with carbon material in an electric arc furnace. As a part of the reducing agent, waste of graphite products (crucibles, electrodes, etc.) is usually used.

ZrC synthesis due to carbothermal reduction of zirconium dioxide by heating the plasma of a densified charge. Zirconium carbide, practically free of oxygen impurities, was obtained by reducing zirconium dioxide with carbon under conditions of heating the charge with a plasma stream of argon.

ZrC synthesis due to carbothermic reduction of zirconia in an electrothermal fluidized bed. In the works, a method for producing zirconium carbide by reducing dioxide in an electrothermal fluidized bed reactor was studied. The process is carried out in a vertical graphite reactor with ETKS at temperatures of 1673 - 2073 K. The initial raw material for producing zirconium carbide is ZrO_2 powder crushed to a size of 0.1 - 0.4 mm and a carbon reducing agent in the form of petroleum coke [1].

3. Conclusion

The analysis of the current state of production and use of zirconium carbide has been carried out. It has been confirmed that zirconium carbide has a unique combination of practically significant properties, it is multifunctional and is able to work as part of composite materials and coatings under extreme conditions. It has been established that the carbothermic method is the basis of the modern production of zirconium carbide. The strategically important nanocrystalline market segment is fully provided by foreign suppliers such as Nanostructured Amorphous Materials, Inc. (USA), «Hefei Kaier Nanotechnology Development Ltd. Co»(China), «NEOMAT Co»(Latvia), «PlasmaChem GmbH»(Germany), which necessitates the development of Russian nanotechnology of zirconium carbide.

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