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Analysis of modern production of zirconium carbide

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Abstract. The analysis and systematization of information on the methods of zirconium carbide production are analyzed. It is shown that the basic method is carbothermal synthesis, which is realized in various options (furnace synthesis from traditional and highly dispersed batches, melting-crystallization, plasma heating, in the electrothermal fluidized bed). The SHS process, mechanosynthesis, plasmosynthesis, a vapor-gas phase plating method are considered.

1. Introduction

One of the most important tasks of modern materials science is obtaining materials for usage in extreme conditions – at high temperatures and voltages, under the influence of aggressive media, etc. In the solution of these problems the leading role belongs to the compounds of refractory metals with boron, carbon, nitrogen, silicon – borides, carbides, nitrides and silicides, which have heat resistance and high temperature strength, specific physical and chemical properties alongside with the high hardness and refractoriness. Among carbides of transition metals, zirconium carbide by combination of special properties is included in the leading group, combining such properties of practical importance as hardness, refractoriness, corrosion resistance in liquid, gas and metal environments, durability.

The purpose of this paper is to analyze information on the methods of zirconium carbide production. For the analysis more than 20 scientific articles and monographs published in the period from 1968 to the present were selected, a patent search was carried out.

2. Research and analysis of technological solutions in the zirconium carbide production

The analysis of scientific and technical literature shows that the basic method for the production of zirconium carbide is furnace carbothermic synthesis, which is realized in the following technological options [1-3]:

1) from dioxide and carbon char at a temperature of 2173 K, in the vacuum for 1.5 hours (industrial level);

2) from a highly dispersed charge (ZrO_2+C) obtained by the sol-gel method at a temperature of 1373 K in the vacuum (pressure 0.5 kPa) (laboratory level);

3) from zirconium dioxide and carbonaceous matter when the compacted batch is heated on a water-cooled copper substrate by the argon plasma jet to a temperature of 2770 K;

4) from zircon sand ($ZrO2$ + $SiO2$) and coal or carbonaceous waste during melting in the electric arc furnace and subsequent crystallization (industrial level);

5) from zirconium dioxide and carbonaceous matter (petroleum coke, low-ash carbonated coal of reksil) in the electrothermal fluidized bed at a temperature of 1673-2073 K.

In the first option the carbizided batch pellets are subjected to grinding and classification to obtain carbide powders within the size range from 3 to 63 µm. The second option provides zirconium carbide in the form of a micropowder with a particle size of 2-3 µm, the third – in the form of a nanopowder with a particle size of less than 100 nm.

The method of plasma heating did not receive industrial implementation. Melting in the electric arc furnace followed by melt crystallization is currently the only way of obtaining zirconium carbide when used in the materials for abrasive processing, spraying and surfacing, protective coatings. Industrial application for the production of zirconium carbide reactor with an electrothermal fluidized bed, characterized by the presence of a highly reactive medium – the microplasma formed during electrical discharges between fluidizable carbonaceous particles are not clear. The first variant of carbothermic synthesis of zirconium carbide, which in fact has a 60-year technological history, forms the basis of modern industrial technology for the production of its micropowders [1]. At the same time, reductive synthesis requires sufficiently high temperatures and technological vacuum, as well as mechanical dispersion of carbidization products, leading for superhard carbides to their substantial contamination due to the milling yield of grinding bodies and surface oxidation. Specification of the method feature creates significant technological difficulties and, apparently, hinder the wider use of zirconium carbide in modern materials science.

The method for the production of zirconium carbide by the self-propagating high-temperature synthesis (SHS process), comprising mixing zirconium powder of up to 50 µm in size and a carbonaceous substance of a size up to 1 µm, loading the prepared charge into the reactor, synthesis in the gaseous atmosphere, cooling, mechanical dispersion and classification of zirconium carbide powders, has not been widely used and is in limited demand for obtaining mainly preparative volumes for research purposes [2]. At the same time, this method can be very useful for SHS compaction of special-purpose structural elements containing zirconium carbide in their composition.

The mechanical synthesis of zirconium carbide, which is usually realized in high-energy mills using zirconium-carbon batch, focused mainly on preparation of preparative amounts of carbide nanopowder of 5-200 nm size range for studying the features of its physicochemical properties in the nanostate and the justified search for new applications, during the last 20 years has not undergone any significant technological and hardware changes and upgrades and, according to its indicators, can still be attributed to laboratorial usage [4].

Plasma synthesis of zirconium carbide is the first attempt in its technological history to create an uninterrupted process. Technological fundamentals of plasma synthesis, laid down at the turn of the 70-80s of the last century, suggest the joint processing of $ZrCl_4$ and propane-butane technical mixture in the plasma flow of argon and hydrogen, quenching of products by plasma treatment and their trapping, non-reactor thermal treatment in the inert medium [5]. The method itself, the equipment and the hardware-technological scheme for its implementation were first mastered for the production of customized batches in the conditions of the Special Design and Technological Bureau of inorganic materials of the Academy of Sciences of Latvia, and then later and now for low-tonnage production in the conditions of the company “NEOMAT Co” (Latvia). The achieved indices allow the plasma synthesis to be considered as the most promising of the known methods for obtaining zirconium carbide in the nanostate state.

The method of obtaining zirconium carbide by precipitation from the vapor phase of $ZrCl_4+CH_4+H_2$ at a temperature of the order of 1573 K is focused mainly on the formation of carbide film coatings on substrate products and has no independent value in the total production of zirconium carbide [2, 3].

3. The research and analysis of the domestic and world market of zirconium carbide

Figure 1 presents information on the manufacturers of zirconium carbide, the technological options realized by them for its production and the main applications. Presented by the leading foreign manufacturers of nanopowders of metals and their compounds, scientific and technical information contains the following technological information about plasma processes for the production of zirconium carbide.

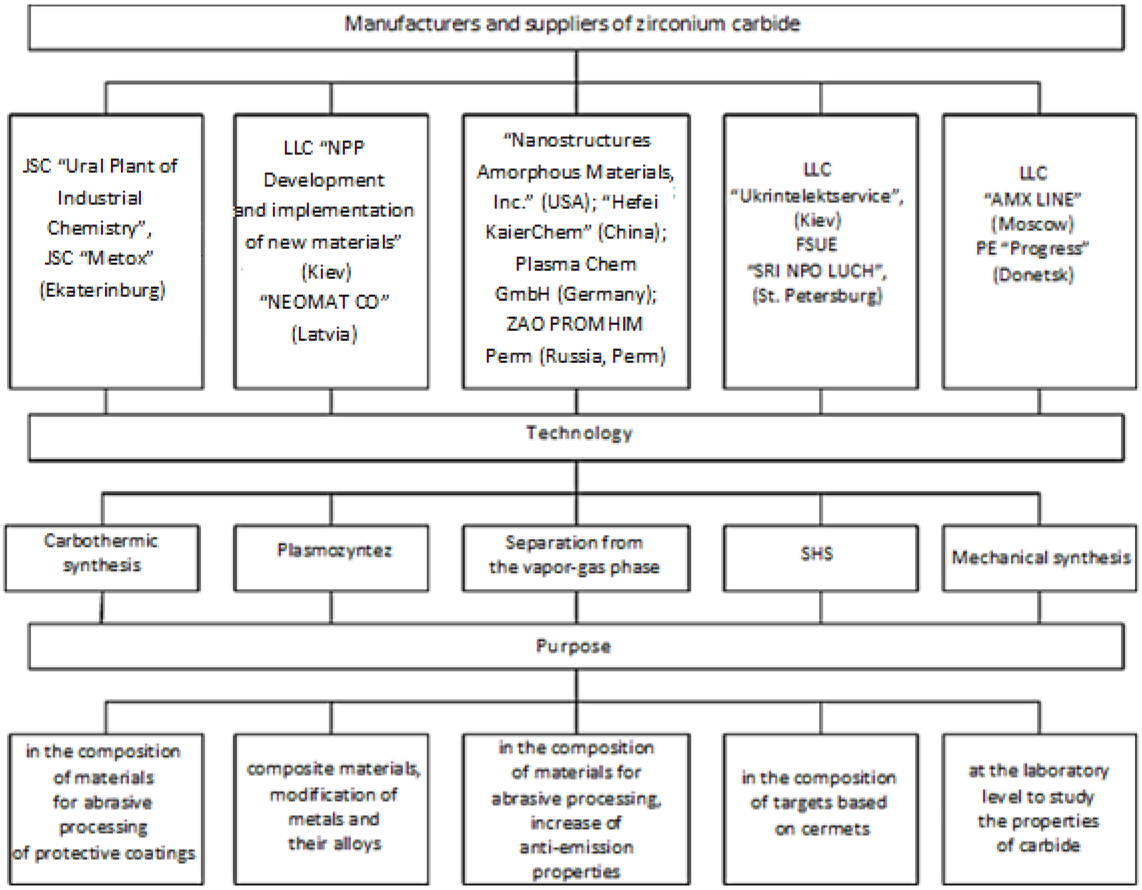

Figure 1. Information about the manufacturers of zirconium carbide, the technological options realized by them for its production and the main fields of application.

Among the most promising areas, the leading ones are occupied by the methods for obtaining zirconium carbide nanopowder in the plasma flow of argon and hydrogen (plasma synthesis), and the vapor-gas phase plating. Currently, the world's leading manufacturers of carbide are research and production companies – "Nanostructured & Amorphous Materials, Inc." (USA), "Hefei Kaier Nanotechnology & Development Ltd. Co" (China), "NEOMAT Co" (Latvia), "PlasmaChem GmbH" (Germany), which produce 97% of ZrC with a dimension of 10-60 nm in batches from 5 to 100g and several kilograms. To date, these manufacturers set the price range from $ 400 to $ 2 000/kg [6].

The market of CIS states is represented by several enterprises and laboratories of Ukraine: LLC "NPP Development and implementation of new materials" (Kiev), "Ukrintelektservice" LLC, (Kiev), "Progress" PE (Donetsk), which produce ZrC powder compliant with TU 6-09 -03-03-408-754. These specifications apply to the qualification of "pure" zirconium carbide, used in the composition of high-temperature alloys and in the composition of cathodes with a high work function of electrons.

The domestic market is mostly represented by small enterprises and laboratories that receive zirconium carbide by carbothermic method, plasma synthesis, mechanosynthesis, SHS, vapor-gas phase plating [7].

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The company "IPK YUMEKS" (Ufa) sells high-refractory ZrC in the form of a gray powder at a contract price. The Ural Industrial Chemistry Plant (UZPKh) produces and supplies zirconium carbide of the "Pur." classification. "UZPKh" JSC is a modern chemical enterprise of a full cycle, which products are in demand not only in the markets of Russia and the countries of customs union, but also in high-tech far-abroad countries: Japan, Australia, Canada, USA. The sale of products to the domestic market is carried out through the official Trading House – "RIVIERA" LLC, Moscow. "Alterhim" LLC (Dzerzhinsk) produces and supplies zirconium carbide of qualification "Pur.", corresponding to TU 6-09-03-408-75, in lots from 1 kg at wholesale and retail prices. "Redmetur" LLC (Ekaterinburg) is engaged in the supply of quality products from rare earth metals throughout the Russian Federation and 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 as fractionated powders 3-5, 40-60, 40-100 μm at the agreed price.

4. Conclusion

Zirconium carbide ZrC, studied and put into usage by the scientific school of the famous Russian material scientist Samsonov G.V. more than 50 years ago, is still in demand in the technology of various materials: metal-ceramic instrument and structural, refractory and abrasive, for the modification of coatings. Analysis of modern scientific and technical information reflects the tendency of the transition from zirconium carbide to coarse-grained to micro- and nanocrystalline, which is determined by the desire of scientists and technologists to achieve a qualitatively new level of performance properties of materials and coatings on its basis.

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