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Application of zirconium carbide: assessment, determination of dominant trends and prospects

T I Alekseeva¹, G V Galevsky¹, V V Rudneva¹ and S G Galevsky²

¹Siberian State Industrial University, 42 Kirova street, Novokuznetsk, 654007, Russia

²St. Petersburg Mining University, V.O., 21 Line, 2, St. Petersburg, 199106, Russia

E-mail: kafcmet@sibsiu.ru

Abstract. The analysis and systematization of information on the application of zirconium carbide in modern technology: in the production of hard alloys and products from them, in technologies of anti-emission coatings, surface modification of powder materials. Prospective directions are indicated: a component in composite materials technologies, a modifying phase of galvanic metal matrix composite coatings, a functional component of wettable coatings for cathodes of alumina reduction cells.

1. Introduction

Priority directions of modern multidisciplinary engineering require materials capable of stable operation in the conditions of high temperatures (more than 1000 K), high loads, aggressive media. In this regard, the role and importance of synthetic refractory superhard compounds, carbides, borides, nitrides, oxides and their compositions, is constantly increasing. Among carbides of transition metals, zirconium carbide, by combination of special properties, is included in the leading group, uniquely combining such practically significant properties as hardness, refractoriness, corrosion resistance in liquid, gaseous media and metallic melts, wear resistance.

The earlier conducted analysis of available scientific and technological literature containing the study results of the properties and methods for the production of zirconium carbide confirms that the main ideas were formed in the 1960s and 1970s mainly by the efforts of the scientific school headed by Samsonov G.V., Corresponding Member of the Academy of Sciences of Ukraine, contain characteristics of properties and conditions for obtaining coarse-grained powders and compacted samples. The systemic studies of zirconium carbide in the nanocrystalline state were practically not carried out. Along with this in the scientific literature the information about the real applications of zirconium carbide in modern technology is extremely limited. In connection with this, the purpose of this paper is to analyze the most technologically and economically attractive areas of application of zirconium carbide and to predict new approaches to its use.

2. Application of zirconium carbide in modern technology: the actual state and forecast

In the technology of hard alloys, the choice of the carbide component, optimization of the structure of the metal bond, is described in detail in [1]. The increase in the level of performance properties is achieved by optimizing the structural state of the hard alloy. The main variable parameters are: the amount, dispersion, hardness, modulus of elasticity of the carbide phase, composition and mechanical properties of the metal binder, the thickness of the interlayer layer. The degree of dispersion of carbide powders obtained, as a rule, by carbothermic reduction or synthesis from elements, in most cases



amounts to several micrometers and rises to 0.3-1.0 microns during grinding-mixing operation of carbide charge. In the process of grinding the thin metallic structure of the carbide component undergoes significant changes, as evidenced by the observed usual increase in microconjugation and the degree of amorphization, the accumulation of linear and point defects, and defects such as grain boundaries. Such changes ensure the sintering of carbide mixtures in technologically acceptable conditions with the required set of properties.

According to the data of [1, 2] zirconium carbide is positively tested in the composition of the following hard alloys:

1) in the composition of hard alloys of the TTC group, usually containing up to 5-20% TaC, 3-15% TiC, 8-12% Co, the rest WC, instead of expensive TaC; alloys of this group are quite universal as they are used for processing both carbon steels and various cast irons;

2) in the composition of hard alloy WC-ZrC-Co of the TC group, which in its properties is practically equivalent to the WC-TiC-Co alloys;

3) in the composition of hard alloy of group THA SOT 30 (tungstenless hard alloys) on the carbonitride base – $(\text{Ti}_{0.95}\text{Zr}_{0.02}\text{Nb}_{0.10}\text{Ta}_{0.09})\text{C}_{0.53}\text{N}_{0.47}$; the alloy has $\delta 1000$ MPa, HRA 90 units, the average grain size of the carbonitride phase is 2-4 μm , the cutting resistance is 4 times higher than that of the alloy KNT 16;

4) in the composition of the hard alloy of group THA TiC-VC-ZrC-NbC-Ni-Mo (grade T and TP);

5) in the composition of carbidechrome hard alloys of the group KKhN10-40 $\text{Cr}_3\text{C}_2 - \text{Ni}$ (Ni + Co + Fe + Mo + Cu) for partial replacement of Cr_3C_2 ; the alloys have high hardness, scale resistance, resist to wear and corrosion in aggressive melts and liquids, have a low propensity for setting and magnetization and are used mainly for the manufacture of drawing-blocks, dies and mandrels for drawing ferrous and non-ferrous metals, molds and other wear-resistant parts.

Along with this, a rather cautious attitude of specialists to zirconium carbide as a component of various hard alloys should be noted, which, apparently, is due to the non-manufacturability of its production and poor wettability by melts of the iron group, which makes it difficult to select a binding metal.

In coating technology the methods for the formation of effective high-reliability coatings of the following types are proposed:

- intermetallic anti-emission composition Pt_3Zr on the grids of powerful generator lamps [3]. The method for manufacturing an anti-ejection coating on mesh electrodes from molybdenum comprises forming a cataphoretic layer of carbide of zirconium with a thickness of the order of 10 μm ; its baking in a vacuum at a temperature of 1773 K; forming a cataphoretic platinum layer; baking at a temperature of 1273-1573 K. In the composite coating obtained in this way, the anti-emission layer is platinum, and zirconium carbide acts as a diffuse barrier between the platinum and the core of the grid;

- abrasive composition of ZrC on particles of diamond powders [4]. On the particles of diamond abrasive produced by the company "Element Six", the coating from zirconium carbide is performed by the chemical vapor deposition. The fraction of zirconium carbide layer with a diamond particle size of 40 μm is 0.77%. The ZrC layer has a thickness of the order of 1 μm . During the X-ray structural analysis the diamond, ZrC, Zr were found in the composition of particles. Diamond powders with a carbide coating are widely used for the manufacture of cutting, grinding and drilling tools;

- corrosion-resistant composition Zr-ZrC on ceramic powders. Zirconium carbide is used when depositing metallic zirconium coating on ceramic powder materials [5]. The use of ZrC is conditioned by the need to increase the corrosion resistance of ceramic powder.

In the technology of superhard materials the application of nanocrystalline nitrides, carboronitrides, carbides, boronitrides of transition metals of IV-Va groups and their compositions with metallic powders as components and initiating additives in the sintering of materials based on boron nitride and diamond has been introduced on an industrial scale, which will allow a number of advantages to be obtained [6]:

- to reduce the processing time of the charge at high pressure and high temperature up to 30-60 s due to the high surface activity of the powders and thus increase the productivity and service life of high-pressure apparatuses;
- to increase the yield of suitable products to 75-80% due to the high activating ability of powders, reducing sensitivity of process to the accuracy of holding the pressure and temperature;
- to increase the hardness of compacts and their wear resistance when processing high-strength steels and alloys with HRC > 60 by reducing the powder content in the charge to 1-3% without reducing the efficiency of the process.
- to reduce the size of boron nitride crystals in compacts, which increases the strength and wear resistance of the cutting tool by changing the nature of its wear;
- to create new composite superhard materials containing up to 30% or more of nanodispersed components characterized by increased toughness, chemical inertness with respect to the treated surfaces, modified electrophysical properties.

The use of nanocrystalline borides and carbides CrB_2 , Cr_3C_2 , TiC , SiC as modifying additives ensuring the production of high-density coatings with a high complex of physical and mechanical properties through the formation of a fine-grained structure with low porosity has been introduced into the technology of galvanic composite metal-matrix coatings in the processes of nickel plating, galvanizing, chromium plating. The combination of a nanocrystalline state with a direct-formed complex of properties inherent in nanoborides and nanocarbides ensures the stable achievement of a number of positive effects when using them as a modifying electrodeposited metal phase matrix [7, 8]. The low concentration of nanopowder in the electrolyte simplifies the operation of galvanic baths and reduces the loss of nanopowder due to the removal of electrolyte with parts. The presence of nanopowder in the electrolyte improves its productivity due to the increase in the upper limit of cathode current density. Testing of titanium diboride nanopowder instead of nanodiamonds in the process of obtaining protective galvanic coatings of different tools shows that with comparable characteristics and service life of a hardened tool, the following technological and economic advantages are achieved when replacing nanodiamonds: the technology of preparation of electrolyte suspension is simplified and accelerated, the deposition rate of the coating increases by 2.5 times, the corrosion resistance of coatings increases by 1.5 times, the cost of 1 m³ electrolyte-suspension decreases by 4 times. When replacing 1 kg of nanodiamonds with nanopowder titanium diboride, the economic efficiency is 105 thousand rubles. Economic efficiency is determined for the cost of nanopowders of titanium diboride 500, diamonds \$ 2 000.

A considerable amount of research devoted to the technology of aluminum production by electrolysis of fluoride cryolite-alumina melt has been carried out and many technical suggestions have been made to increase the service life of the cathode of aluminum cell by protecting it with a coating wetted by aluminum. Such coating should be chemically inert to aluminum and electrolyte melts, hard, high-electroconductive, wear-resistant, well wetted with aluminum. As a part of the functional basis of such coating, borides and carbides of titanium and zirconium can be used. The results and technical solutions described in the literature propose so far only the use of titanium diboride. Taking into consideration the mentioned above facts, it can be assumed that further improvement of the cells design and technical and economic parameters of electrolytic aluminum production process can be associated with the expansion of the range of materials used and their availability due to development of efficient production technologies that reduce their real value to less than \$ 100/ kg [9].

3. Conclusion

The conducted analysis of the scientific and technical literature demonstrates the positive technological testing of zirconium carbide with standard granulometry in the composition of hard alloys, anti-emission, abrasive and corrosion-resistant coatings, which makes it possible to predict such areas of its effective application in the nanostate as the production of polycrystalline superhard materials and products thereof, the electrodeposition of composite metal coatings in electroplating, the formation of protective wettable coatings of cell cathodes in the metallurgy of aluminum.

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