Promising directions in studying and using polycrystalline diamond coating

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Abstract. The paper deals with the study of promising areas for obtaining and using thin diamond and carbon-containing coatings. The retrospective and current situation in distributing inventions protected by patents over the countries and companies and the role of Russian companies and scientific organizations in this process are analyzed. It is concluded that it is necessary to stimulate national applicants in order to maintain positive trends in patenting in the national market and abroad.

Introduction

Scientific and practical interest in diamond coatings in the world is due to the fact that this material is chemically inert, has high thermal conductivity, is transparent in a wide range of the spectrum, and is a good dielectric. Doped diamond is considered as a promising material for power and microelectronics [1]. High hardness and thermal conductivity, wear resistance, and chemical inertness are the key properties of diamond-based materials [2–4]. Therefore, polycrystalline diamond (PCD) films and composites can be used in heat sinks [5, 6], solid coatings of cutting tools and for applying a protective layer.

The formation of a specific structure of the PCD material, customized for the consumer, requires the use of accurate and flexible methods for diamond synthesis, and their application is determined by the level of technology development and market requirements.

One of the methods for producing diamond films is Chemical vapor deposition (CVD) technology, in which diamond deposition combines various physicochemical processes: dissociation of hydrogen and carbon-containing carrier with the formation of diamond precursor radicals, their transport to the surface, formation of diamond nucleation sites on the surface and their growth with the formation of a continuous polycrystalline diamond film with a thickness from units to hundreds of microns. Nucleation, formation, and growth of a diamond film in the CVD process is discussed in detail in [1, 2].

The first wear-resistant diamond coatings were obtained by chemical deposition at high temperatures of 950–1050°C from a vapor-gas medium in the mid-1980s [7]. For the first time, the CVD process was used for covering cutting tools by Sandvik Coromant (Sweden). This company has since made a number of major improvements to the original technology and is currently the holder of over 300 patents. The Kennametal Inc. (USA), known in Russia as a manufacturer of metal-cutting tools (in the 80s it was Kennametal Hertel AG (Germany)) is no less involved in research. The company has almost 8 thousand patents, and about 80 of them relate to diamond coatings.

For the Soviet Union and Russia, the CVD technology became available through the creation of joint ventures with these two companies. The Sandvik Coromant production, opened in the late 70s, has been successfully operating in Moscow and St. Petersburg until now. However, both at this and other national tool enterprises, the CVD installations use technologies based mainly on foreign developments.

The pronounced success of the first wear-resistant CVD coatings ensured their widespread in industry, but at the same time, significant limitations in the use of coated tools were revealed. The greatest problems are caused by insufficient adhesion of CVD coatings, as well as their negative impact on the mechanical properties of the substrate.

Nevertheless, now it can be stated that throughout the history of the development of functional coatings for cutting tools, the share of the CVD deposition method and its new varieties exceeds all other fundamentally different technologies that appeared later.

The second most applicable method for creating high-strength coatings is Physical Vapor Deposition (PVD). PVD coated tools appeared in the early 80s of the last century. The idea was first implemented in the Soviet Union, but its widespread industrial application by foreign companies proved to be more successful and extensive. The first PVD coatings were obtained in the form of a single layer of titanium nitride TiN with a thickness of 2–4 μm. The PVD-method improves the properties of those cutting tools, where the CVD technology is inefficient or useless [7]. At the same time, a thin layer of PVD coating cannot compete with more powerful CVD coatings with the total thickness of layers of up to 22–25 μm; therefore, to this day, it concedes to them the market share of replaceable non-regrindable plates.

Developers and manufacturers of high-tech products actively protect their rights to use the results of research activities. The patent portfolio, which includes the number of filed applications and supported patents for inventions and utility models, demonstrates the state and priority directions of company development and determines the technological sovereignty of the country [9].

This work is aimed at identification of the promising research and application areas for the polycrystalline diamond coatings based on the analysis of retrospective and current situation in distributing patents over the countries and companies and the role of Russian companies and scientific organizations in this process.

Methods and Results

To assess the development of the international patent market for carbon-containing coatings, the totality of patent documents in this subject area was analyzed for all countries with a search depth of 30 years. The databases of Rospatent https://rospatent.gov.ru/, the European Patent Office (EPO) https://ru.espacenet.com/, and Questel https://www.orbit.com/ were used. When analyzing data for the last 2 years, it should be noted that they are incomplete due to delays between the moment of filing an application and its publication. It can be concluded that the number of "fresh" patents exceeds greatly the number of outdated ones.

The level of practical application of technology can be determined by the patent literature. If fundamental and exploratory research is carried out, then the results are published in the open press. Applied research by scientific institutes and universities are beginning to be protected by patents. Industrial use of technology, improvement of its consumer qualities are protected by enterprise patents. Export potential is confirmed by international patents.

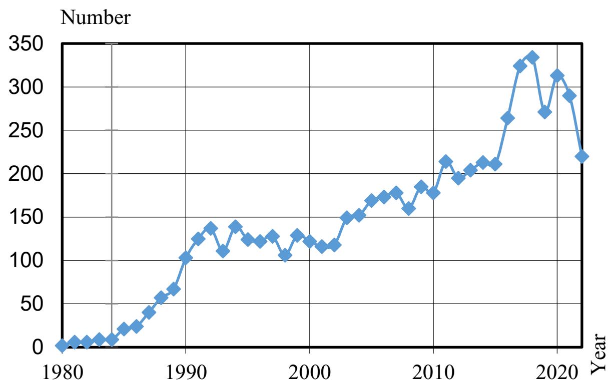

Fig. 1. Dynamics of patenting the diamond coatings. Plotted according to data of Questel https://www.orbit.com/. (© Questel)

In the field of diamond coatings, the active growth of patenting began precisely in the second half of the 80s of the last century. The number of annual patent publications is presented in Fig. 1. Let us note three phases of patenting dynamics: an accelerated growth in the number of patents since the mid-1980s, which lasted about 10 years, then approximately uniform distribution over the years, and a second wave of accelerated growth from about the second decade of the 21st century. An explanation of this dynamic will be given below.

Along with universities, industrial enterprises are the owners of inventions, and this confirms the practical orientation and relevance of these studies. According to Questel, there are 5 Chinese universities and 15 Japanese and American manufacturing companies among the first 20 organizations that hold the largest number of titles of protection, and we should note the absence of Russian residents (that is, Russian companies and universities are not included in the top 20 patent holders).

The following companies have the largest number of patent families: Smith international (208), Sumitomo electronic industries (194), Element six (134), Diamond innovation (112), Baker Hughes (109), US Synthetic (93), General electric (78), Henan diamond (72), Norris rods (61), and Element six abrasives (56).

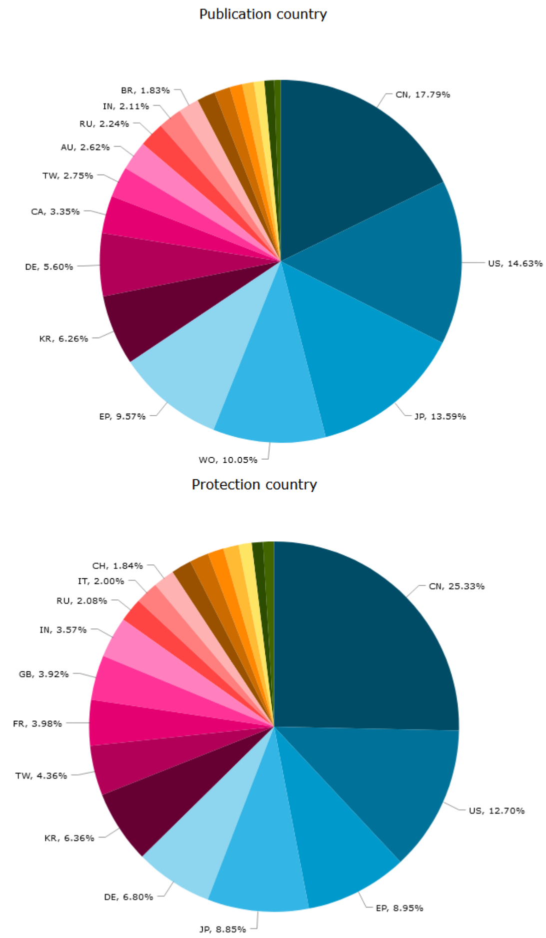

Fig. 2. Distribution of patent families in the field of diamond coatings by countries of protection and countries of residents Plotted according to data of Questel https://www.orbit.com/. (© Questel).

These data demonstrate the high patent activity of foreign companies in diamond coatings, and patent holders seek to protect their developments in the markets of other countries, primarily in such countries as China, the USA, Korea, Japan, Taiwan, and also in European countries. This is due to the fact that the development of industrial technologies and the main production of items that use carbon-containing coatings are concentrated in these countries.

The distribution of patent families in the field of diamond coatings by protection countries and resident countries is presented in Fig. 2. At that, the number of patents protected in China (25.3%) exceeds the number of applications by Chinese residents (17.79%), which indicates that international companies organize production in China. For the United States, on the contrary, the number of applications filed by US residents (14.63%) is more than the number of patented decisions in the United States (12.7%), which indicates that the United States is transferring production from its country to other territories. The share of Russian residents is noticeable: a little over 2 percent and is almost the same in both diagrams.

Based on the patent search, four main areas of application of polycrystalline diamond coatings were identified (Table 1).

Table 1. The main application areas of polycrystalline diamond coatings.

No.	Area	The main properties that determine the use of diamond coatings in the given area
1	Tool production	high hardness and wear resistance; high impact strength; high thermal stability; low friction coefficient
2	Production ofprotectivecoatings.	high wear resistance; high impact strength; high corrosion resistance and chemical inertness; optical transparency
3	Production of electronic components	high temperature resistance; low coefficient of thermal expansion; high thermal conductivity; chemical inertness; dielectric properties
4	Use in optical devices (including lasers)	high wear resistance; high temperature resistance; low coefficient of thermal expansion; optical transparency; dielectric properties

An analysis of available literature and patent data allows us to conclude that the main areas of application of polycrystalline diamond coatings in the world are primarily associated with electronic components, use in optical devices, including lasers, with the production of tools and protective coatings.

As for the actual development of the method for depositing diamond coatings, then, as it was noted at the beginning, in the dynamics of patent decisions after a significant increase in the 80s (Fig. 1), an almost constant number of new decisions was observed until the second half of the zero years, then accelerated growth, associated with new areas of research, began: the development of combined materials, automation, and nanotechnology.

As an example of the explosive growth of scientific results, we can note the dynamics in the number of decisions for graphene coatings (Fig. 3) in the last decade.

The potential of graphene as a protective layer is due to its unique physical and chemical properties. Graphene has exceptional thermal and chemical stability in an inert environment; it is stable at high temperatures exceeding 1500 °C. In addition, graphene has high optical transparency (~2.3% absorption per layer) in the visible region, high electrical and thermal conductivity, which minimizes the effect of coatings on the properties of materials. The thickness of graphene coatings is 0.34 nm per layer, which is also significantly less than the thickness of all existing protective layers. Theoretical studies show that graphene is almost impermeable to gas [8].

In addition to being an independent barrier layer, the graphene coating can be considered as an intermediate layer in complex protective coatings; the combination of the graphene layer with various metal and ceramic layers opens up a wide range of possibilities for creating new materials highly resistant to hydrogen embrittlement.

Graphene is associated with diamond coatings primarily because it is a modification of carbon; it is also used to form strong coatings, including together with polycrystalline diamonds [9].

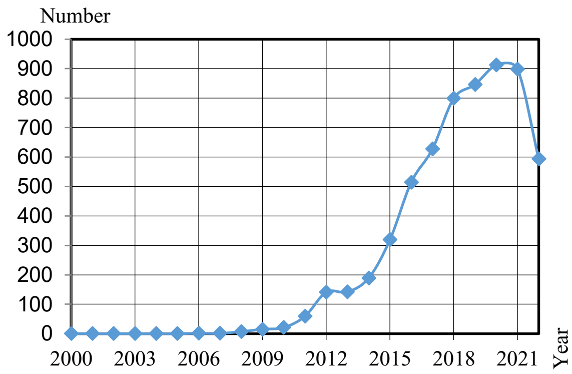

Fig. 3. Patenting dynamics for graphene coatings by years Plotted according to data of Questel https://www.orbit.com/. (© Questel).

According to Fig. 4, as in the case of diamond coatings, the production of graphene tools will be organized mainly in China, and the share of Chinese companies is overwhelming. The significant market shares belong to the USA, Korea, Japan, the European Union, and, separately, Germany.

For instance, in the patent application "Graphene Based Phobic Coating on Carbon" by Akhan Semiconductor Inc. (USA), application number

US2023126873A1, a method for manufacturing a graphene layer on a non-graphene carbon layer is disclosed, including the steps of cleaning and seeding the substrate, deposition of crystalline diamond on the substrate, deposition of an aluminum layer on crystalline diamond, where the aluminum layer exceeds 5 nm and is less than 50 nm; and treating the surface of the aluminum layer with an ion beam, resulting in a graphene layer, formed on crystalline diamond.

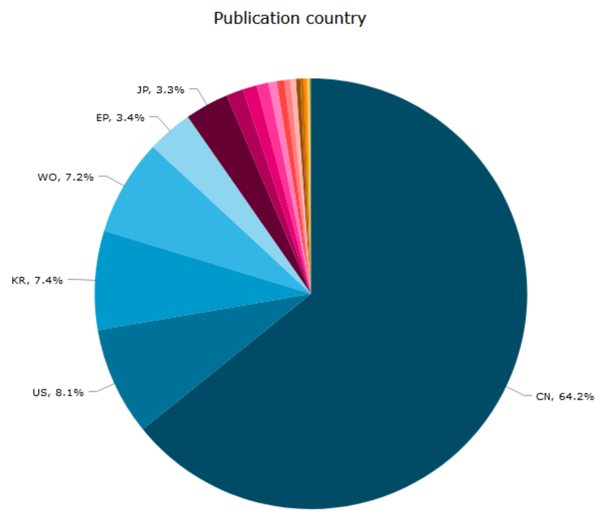

Fig. 4. Distribution of patent families in the field of graphene coatings by resident countries. Plotted according to data of Questel https://www.orbit.com/. (© Questel).

And this applies to almost the entire intellectual property market. The USA possesses not only the world currency, but also the maximum number of patents (3 million) protected in more than 100 countries. The income from royalties is half a percent of GDP (the highest income in the world). China caught up with the US in the number of patents in 2021: also, about 3 million (in 2010, these figures were 190 thousand and 1455 thousand, respectively), but it lags behind in IP revenue. For comparison, in Russia in 2010 there were only 130 thousand patents, a number comparable to China, and in 2021, it was 170 thousand. Ownership of IP rights determines the economy competitiveness [10].

As an example of introducing nanotechnology and composite materials, we can cite the latest Sandvik Coromant patents, publication number WO2023066840 (A1), the title "Coated Cutting Tool", related to a nanolayered coating containing alternating sets of the first and second layers, while the average thicknesses of the sublayer set in the first and second layers differ from each other. The nano-layered coating exhibits increased edge toughness and improved resistance to flank wear and comb cracks.

We can also cite patents of the same company related to combined materials. Application US2023093032 protects a coated cutting tool for metalworking with carbide, cermet, ceramic, steel or rapid steel substrate and covered with a wear resistant coating. The coating includes a layer of Ti1-xAlxCyNz, some amount of MeCaNb is present on the Ti1-xAlxCyNz layer. The share of MeCaNb covers from 5 to 28% of the Ti1-xAlxCyNz layer. Application WO2022268660A1 relates to a tool containing a superhard part with polycrystalline diamond (PCD) or cubic boron nitride (cBN), a sintered compact bonded to a cemented carbide substrate, and a maraging steel part, where the cemented carbide substrate and part of maraging steel are joined by soldering. The tool provides a strong brazed joint and uniform hardness of the steel item.

As for the methods for obtaining diamond coatings, the number of patents dealt with the CVD method began to grow steadily from the mid-80s, since the invention of this method (Fig. 5), but then reached a constant level. With the development of nanotechnology, the PVD has become more widely used, and decisions in the PVD area demonstrate the growth.

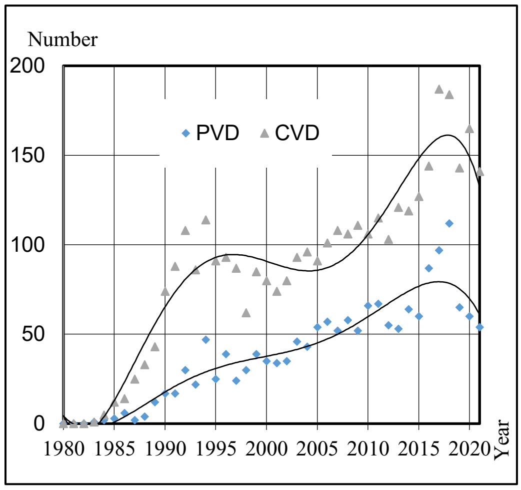

Fig. 5. Patenting dynamics for making diamond coatings by CVD and PVD methods. Plotted according to data of Questelhttps://www.orbit.com/.(© Questel).

For instance, in application "PVD device and method for preparing superhard nanocomposite coating and layer structure" of NanjingNahu New Material Tech Co Ltd. (China), application number CN202010792172A, priority 2020-08-08, the PVD method is used to obtain a superhard nanocomposite coating, which is a multilayer diamond film.

As for Russian applicants, according to the Rospatent search system, since 1991, only about 200 inventions and utility models related to diamond coatings have been registered in our country. Among these applications, 174 are from Russian applicants, 27 are from foreign companies. There are currently 69 patents, and only three of them are the patents of foreign residents (Table 2). ComadurSa (Switzerland), Gen Electric (USA), and Univ Newcastle (England) remained on the Russian market.

Table 2. Valid patents of foreign residents in Russia.

Patent No.	Prioritydate	Title	Patent holder
2769154	28.03.2022	Method for cutting boules of crystals with diamond wire	Comadur Sa (Switzerland)
2738696	15.12.2020	Oil and gas well pump components	GenElectric (USA)

		and methods for coating such components	
2656476	05.06.2018	Method for separating clusters of diamond particles	Univ Newcastle (England)

Most likely this is due to the joint production of these instruments in Russia. The Gen Electric maintains energy facilities in Russia, in particular, gas turbines; Comadur Sa is a Swiss company that specializes in processing of hard alloys, ceramics, precious stones; and Lydia Siller and Yury Butenko, our departed scientists, wrote a patent to the University of Newcastle.

What are the trends in Russia in the study and application of diamond coatings? The small number of patents and their short lifespan suggests that national production in Russia is still insignificant, and foreign companies do not consider our country as an acquirer of their technologies. On the other hand, our scientific research in this area is at a high level, which is confirmed by the level of publications and interest of foreign companies in Russian patents. For example, back in 2009, a patent for nanodiamond and a method of its production was obtained in Russia, No. 2348580. According to the invention, nanodiamond, which is not a purely carbon material, was created; its elemental composition in percent by weight is as follows: carbon of 90.2-98,0; hydrogen of 0.1-5.0; nitrogen of 1.5-3.0; oxygen of 0.1-4.5, and carbon itself is available in the product simultaneously in several modifications, and only one of them corresponds to the structure of diamond. The resulting nanodiamond allows it to be used as a nanoscale component of highly efficient composite materials, in the form of additives that improve the performance properties of structures (wear resistance and strength).

In 2012, the rights to this invention were transferred to Karbodeon Ltd. (Finland) for the entire duration of the patent.

In the second half of the 2010s, foreign companies left the Russian market of diamond coatings, which did not see the need to maintain their Russian patents in force.

On the other hand, in the last few years there has been an increase in publications and patent applications in the field of diamond coatings from Russian universities and, fortunately, from industrial companies.

Russian residents should more intensively protect their rights to intellectual property. For example, in 2023, the Alkom company (Ufa) began to produce the first national polycrystalline diamond cutters with improved characteristics for drilling wells with difficult geological conditions; until now, such cutters have been imported*. But at the same time, the company is the holder of only two patents of 2011 and 2015, and has not filed an application for protecting its new technology with Rospatent. Such an attitude to one's patent portfolio may entail unjustified risks associated with the registration of rights to similar objects by another applicant.

Meanwhile, the high scientific and technical level of national research carried out at our research institutes and universities is confirmed by high citation of open publications of authors and a significant number of patents confirming the novelty of inventions.

As an example of correspondence of Russian research to the world level, we can cite the patents in the field of diamond coatings and graphene films using nanotechnologies and composite materials.

For instance, these are invention "Microwave plasma reactor for obtaining a homogeneous nanocrystalline diamond film" GPI RAS, patent No. 2644216, application of 2016 and invention "Method for obtaining a composite metal-diamond coating on the surface of a medical device, a dispersed system for deposition of a metal-diamond coating and a method for its production", patent holders - individuals, application of 2020.

Separately, we should note the patents of Kutateladze Institute of Thermophysics SB RAS. The advantage of the inventions of IT SB RAS on gas-jet deposition of coatings RU 214891 U1, RU 2788258 C1, RU 2653036 C2, RU 2403317 C2 is the creation of a device and a method for gas-jet deposition of diamond films, which ensure a high deposition rate and a high quality of diamond films. This scheme allows initial surface treatment with atomic hydrogen (creation of nucleation sites) and immediate deposition without substrate removal into the atmosphere and interaction of the treated surface with undesirable components. To do this, only hydrogen is first supplied (without carbon-containing gas), it is activated by a microwave discharge, and the surface of the substrate is treated with atomic hydrogen, which is chemically active and has a high temperature.

The device allows a deposition rate of up to 100 μm/h and production of high-quality diamond coatings with nano- and micro-sized crystals. The quality of the resulting diamond coatings allows them to be used as a heat-conducting electrically insulating base for placing microelectronic devices in order to intensify their cooling.

Conclusions

Research in the field of developing methods for creating carbon-containing polycrystalline diamond and graphene coatings has been intensively performed since the 80s of the last century in developed countries and China. In the last decade, there has been an intensive growth of patentable decisions related to nanotechnologies, composite materials, process automation, including a new impetus received by the PVD method for obtaining diamond coatings.

These technologies are focused on specific applications in a wide range of fields: microelectronics, medicine, instrumentation, cutting tools, etc. The most

*https://expert.ru/expert/2023/19/importozamescheniye-reztsy-dlya-bureniya-skvazhin/

promising areas of research on polycrystalline diamond coatings at the moment are the production of electronic components, tools and protective coatings, as well as their use in optical devices, including lasers.

At the same time, the application field of diamond coatings is much wider than the above areas, therefore, a change in the structure of promising areas is not ruled out.

In the market of intellectual property for diamond coatings, the main rightholders are companies from China, the USA, Japan, and Korea. In the field of graphene coatings Chinese universities and companies occupy more than three quarters of the market.

On the one hand, there are very few patents in this field in Russia, and the territory of protection is only Russia, and patents are not maintained in force for a long time. But on the one hand, the high level of scientific research in this field is conditioned historically and proved by the quality of publications; on the other hand, the withdrawal of foreign companies from the national diamond coating market created new prospects for patenting by Russian universities and industrial companies. In this regard it is necessary to stimulate national applicants to keep the positive trend. We should also protect our intellectual property in competing countries and countries that are consumers of our products.

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Link to project information:
http://www.itp.nsc.ru/structura/ctt/fp/grant_ctt.html

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