



## KAPITEL 9 / CHAPTER 9<sup>9</sup>

### THERMOSTABILITY OF PDC: FACTORS AFFECTING THERMOSTABILITY AND WAYS TO IMPROVE IT

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#### Introduction

PDC (polycrystalline diamond compact) inserts are a highly sought-after product in the manufacturing of cutting tools for non-ferrous materials, mining, oil and gas drilling. Their outstanding properties, including high hardness, high thermal conductivity, high impact resistance and wear resistance, make them an invaluable addition to any production line.

The creation of diamond carbide inserts (PDC – polycrystalline diamond compact) marked a significant advancement in the improvement of diamond drilling tools. Today, they are the most important drilling tools for most geological formations in the exploration and drilling of oil and gas fields. The annual market for PDC tools exceeds 4.5 billion dollars [1]. This result was achieved due to the excellent properties of PDC inserts, including high hardness, thermal conductivity, impact resistance, and wear resistance. Drill bits equipped with PDC cutters have gained significant market traction in oil and gas drilling due to their long service life and ability to maintain high penetration rates.

#### 9.1. PDC plate technology and its disadvantages

Traditionally, PDC wafers are fabricated at pressures and temperatures of about 5.5 GPa and 1400°C.

The process of sintering of diamond grains during the production of ATP can be divided into 3 stages [2].

The first process is pressure creation in the apparatus, which occurs without heating of the reaction volume. During the application of pressure to the diamond-

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bearing layer, there is a notable reduction in its porosity. Consequently, if the porosity of the diamond briquette is 45% in a state of free filling, it will decrease to 19% after the effect of pressure. At this stage, the shrinkage process occurs due to the crushing, slipping, and packing of diamond grains.

The second stage of sintering is defined as the period of heating the reaction volume of the AHF from room temperature to the temperature at which the liquid phase is obtained. The duration of this non-isothermal period is dependent on the specific sintering technology in use. The shrinkage of the diamond layer of ATP at this stage of solid-phase sintering occurs primarily in accordance with the mechanisms of thermal activation of the grain packing process and the mechanism of plastic flow. The porosity of the diamond layer at the conclusion of this sintering stage is approximately 10%.

The third stage of sintering commences when the temperature of impregnation of the diamond layer with the liquid phase is reached. The duration of isothermal holding at this stage is also dependent on the specific sintering technology in use.

The impregnation process is initiated by the pressure differential between the porous substrate, which is subjected to uniform compression, and the pores of the diamond layer, where the pressure is approximately equal to atmospheric pressure.

As the melt penetrates the diamond layer, the liquid-phase sintering process begins. This involves further reduction of porosity and increase in the degree of plastic deformation of diamond grains. The final porosity of the diamond layer, calculated by the volume content of the binder phase filling the pore, is 4%.

The micro-X-ray spectral analysis data indicates that the bonding phase of the diamondiferous layer of the plate contains 65–70% (by mass) of Co and 30–35% W. This ratio of components is consistent with the composition of the Co-WC eutectic, as shown in the W-Co-Co system state diagram.

The conventional high-pressure, high-temperature (HPHT) PDC manufacturing technique has inherent weaknesses due to the unavoidable presence of metallic components that act as a bonding agent to bind the diamond grains in the PDC diamond layer.

Experimental results [3–9] have demonstrated that at temperatures above 650°C,



there is a significant decline in the physical and mechanical properties of the diamond layer. The reasons for this phenomenon are as follows:

1. At temperatures above 650 °C, diffusive interaction between diamond particles and cobalt occurs, resulting in the conversion of diamond back to graphite.
2. During rock drilling, a large amount of frictional heat is generated, the PDC material is subjected to high stresses in which the cutting edges of cobalt-bonded PDC are prone to micro-cracking, and diamond particles fall out/break when the stress exceeds the bonding strength of the diamond grains in the PDC cutters at a certain temperature. The reason for this can be attributed to the differences in the elastic modulus and coefficient of thermal expansion between the metallic cobalt bond and diamond, which can lead to a mismatch between the volume change of diamond and bond under high stress and high temperature conditions. This results in high stresses within the PDC material, leading to early failure.

Consequently, to minimise the impact of the metal component on the performance properties of PDC, particularly in terms of heat resistance, PDC and PCD manufacturers, with a particular focus on the drill bit industry, have concentrated their efforts on identifying methods to optimise the removal of the metal bond from the diamond layer.

The most promising avenues for the production of PDC with enhanced thermal stability are as follows. These methods involve either complete or partial leaching of cobalt from polycrystal by acid, or the addition of silicon to form silicon carbide (as a result of reaction with diamond particles). This acts as a bonding phase for diamond instead of cobalt, thereby improving the thermal stability of the material. The removal of cobalt or the low coefficient of thermal expansion of silicon carbide ensures the thermal stability of the materials obtained by such technologies up to temperatures above 1150 °C.



## 9.2. Leaching of cobalt from diamond polycrystalline PDC layer

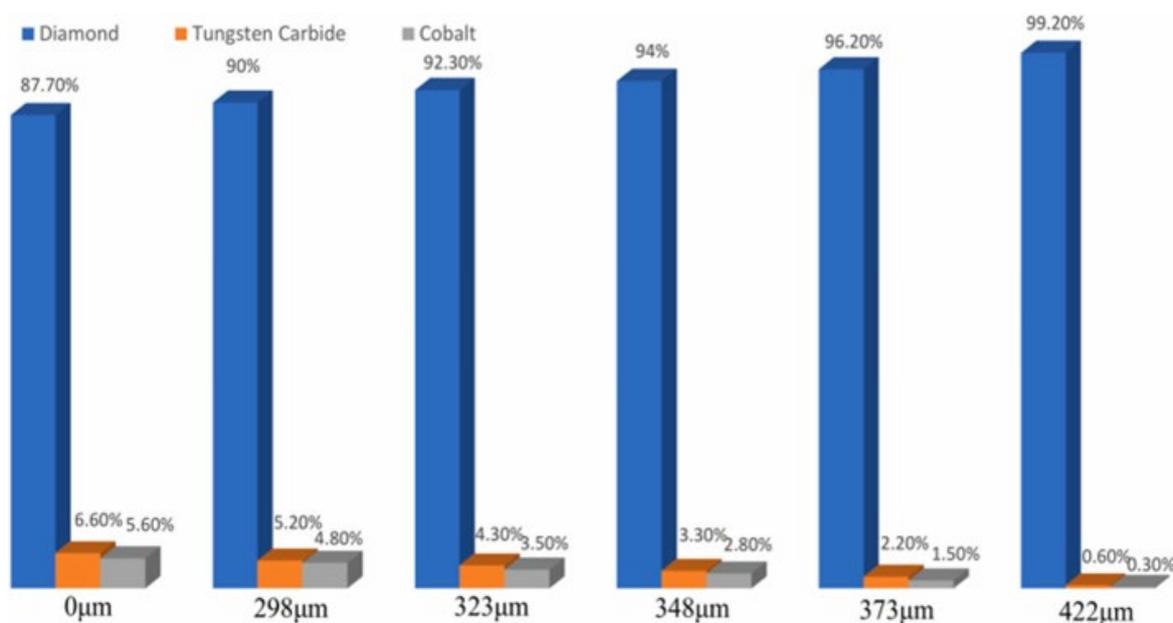
One of the first technologies developed to remove cobalt was its leaching from the diamond composite structure [10]. Drill bit manufacturers have established a guideline for PDC performance in high temperatures. Based on their experience, they have found that PDC can withstand temperatures up to 750 °C without issue. However, leaching can extend this limit to approximately 1200 °C.

In the most general sense, leaching is the transfer of one or more components of a solid material into solution, usually aqueous.

The process is comprised of three stages: the supply of reacting substances to the solid surface, the chemical reaction, and the removal of dissolved reaction products to the solution. In most cases, leaching occurs in the diffusion domain, with the first and third stages determining the process rate. However, a kinetic regime is also possible, in which the slowest stage is a chemical reaction, as well as a mixed diffusion-kinetic regime. The process can be accelerated by reducing the particle size of the material, increasing the temperature (especially in the kinetic mode), and in the diffusion region, by increasing the intensity of stirring. Leaching is carried out in a variety of ways, depending on the nature, composition, and condition of the material being treated. Leaching can be combined with mechanical, chemical, ultrasonic, and thermal influences on the material.

One advantage of using leaching technology to treat PDC is that it improves the thermal stability of PDC tools. This is achieved by reducing the tendency to graphitization at high temperatures and preventing accelerated cracking caused by thermal stresses. Conversely, the removal of the cobalt phase results in a reduction in the fracture toughness of PDC tools. Consequently, suppliers of PDC cutters frequently provide cobalt leaching services at varying depths, tailored to the specific functional application (Fig. 1).

Currently, the technology for removing cobalt from PDC typically employs an aggressive strong acid or a combination of strong acids as a cobalt removal reagent.



**Fig. 1 – Histogram with different ingredients**

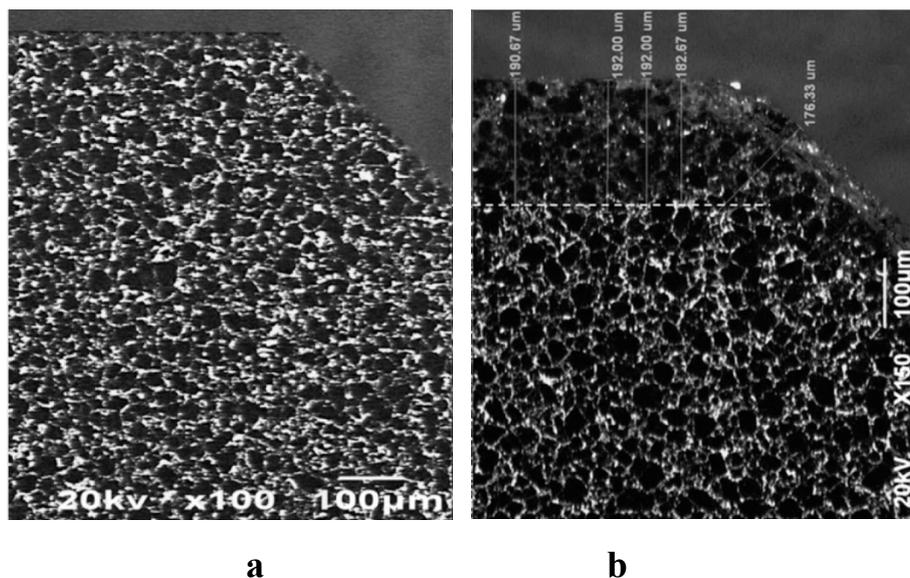
*A source: [1]*

The PDC is placed in a cobalt removal solvent and heated to a specific temperature under normal pressure. However, the cobalt removal efficiency is low, and the removal of cobalt takes a long period of time, which has a negative impact on the production capacity of PDC enterprises. Some strong acid reagents, particularly high concentrations of hydrofluoric acid and nitric acid, may cause severe corrosion and damage to the tanks in which they are stored or in which the leaching process takes place. Consequently, this technology represents a significant risk to the environment and the health and safety of workers.

In this regard, scientific research is being conducted globally to improve the classical method of cobalt leaching from the diamond layer of the PDC plate. One proposed solution is to use electrolysis to improve leaching efficiency [5]. This paper presents an example of the leaching process of PDC with a grain size of 10–30 µm and a cobalt metal phase content of 10–16 wt%, which are commonly used for rock drilling. In the PDC electrolysis process, a stainless steel or copper plate was utilized as the anode of the electrolytic apparatus. The electrolyte primarily consisted of cobalt chloride, ammonium chloride, and surfactant in a specific proportion by weight. It was determined that electrolyte temperature plays a significant role in regulating



electrolytic performance. At certain optimal temperatures (between 40 and 50 °C), electrolytic performance can be enhanced. Figure 2a presents a scanning electron microscope (SEM) photograph of the PDC section without the removed metal phase. The darkest phase is diamond, while the lighter phases are cobalt and/or tungsten carbide. Figure 2b presents the SEM image of the PDC section with an RMRD of approximately 190  $\mu\text{m}$ .



**Fig. 2. – SEM pictures of sections of PDC: a - without removed metal phase; b - with metal phase removal depth of approximately 190  $\mu\text{m}$**

*A source: [5]*

The data clearly shows a distinct separation between regions with and without removed metal. The boundary above represents the region where the residual metallic phase of cobalt is virtually absent. The authors conclude that electrolysis is an effective method for removing the internal residual metallic phase.

Additionally, it was determined that the W phase is effectively removed from the polycrystalline diamond layer in the acid bath, while the WC phase is retained in the diamond layer when using the electrolysis method. This indicates that the WC phase will not be removed by electrolysis. The data, according to the authors, indicate that the residual WC phase, as an integral substrate, plays an important role in improving the performance of PDCs. This is because it leaves relatively few pores in the



polycrystalline layer and does not affect the integrity of the substrate.

One of the improved leaching methods is the removal of cobalt from PDC wafers by chemical pressure deposition, as described in [9]. It is recommended that a mixed solvent of hydrochloric acid and a Lewis acid ( $\text{FeCl}_3$ ) be used in conjunction with the chemical pressure deposition method.

The concentration of hydrochloric acid in the cobalt removal reagent was 6 mol/L, and the concentration of the Lewis acid (ferric chloride) was 50 g/L, which was the optimal ratio of reagents for cobalt removal. The reaction temperature was 160°C, and the reaction pressure was controlled at 0.8 MPa, which were the optimal conditions for cobalt removal. After 72 hours of reaction time, the cobalt removal depth reached 0.580 mm, which met the requirement of 1.2 mm cobalt removal from PDC (cobalt removal depth > 0.5 mm).

A study demonstrated that at the same cobalt removal temperature (160°C) and cobalt removal time (72 h), the depth of cobalt removal by the chemical pressure deposition method for PDC was significantly greater than that of the conventional acid leaching method. The chemical pressure deposition method demonstrated superior wear resistance and impact strength of PDC after cobalt removal.

It is important to note the following fact. Currently, there is no single "standard" leaching technology. Instead, there is a range of technologies that meet different requirements for instrumental applications.

One of the avenues being explored is the deep leaching method. The essence of the method is as follows: First, a diamond polycrystal with a metal bond is sintered. Subsequently, the leaching procedure is carried out by immersing the polycrystal in acid in order to maximize the removal of the bond. It is important to note that this method has certain limitations. Some metals are sealed in closed pores where liquids cannot enter and remain.

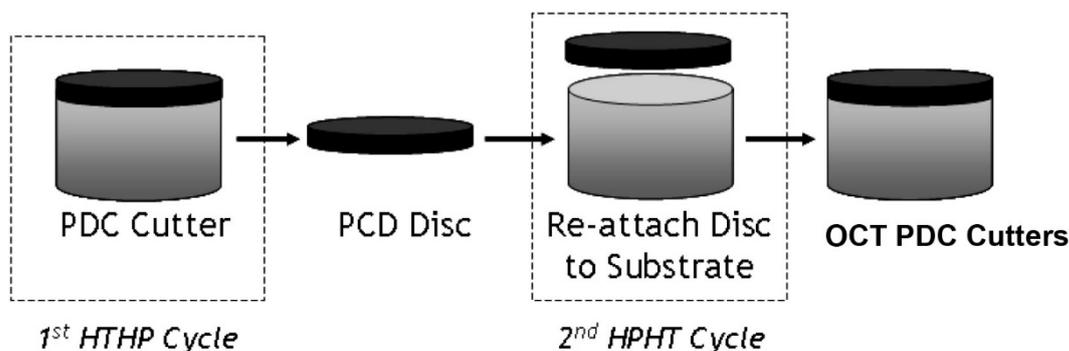
Leached diamond polycrystal is thermally stable in an inert or reducing atmosphere up to 1200 °C. However, it should be noted that it degrades at 875 °C in the presence of oxygen. Increased thermal stability of a polycrystal comes at a price. A thermally stable polycrystalline diamond polycrystal cannot be integrally bonded to



a carbide substrate, as is the case with standard PDC sintering technology. Furthermore, the diamond polycrystal's strength is reduced following leaching due to its open structure, which is designed to facilitate complete leaching. The requisite thickness for structural strength precludes effective self-sharpening action. Consequently, the high strength and the advantage of non-separable bonding of the diamond layer and the carbide substrate are foregone in order to achieve increased heat resistance.

Without a carbide substrate, heat-resistant diamond polycrystals are limited by their small size and must be placed in a matrix like natural diamonds. Furthermore, the lack of cobalt in the structure results in polycrystals being poorly wetted by brazing alloys, necessitating mechanical holding.

New approaches to obtain thermostable PDC are currently being developed, including the technology called ONYX Cutter Technology (OCT) [13]. This technology enables the production of PDC with high abrasion resistance. The production process is a two-stage technology that uses high pressure and temperature (HPHT) (Fig. 3).



**Fig. 3. – Steps to manufacture OCT cutters**

*A source: [13]*

The first step involves fabricating a polycrystalline diamond disk (PCD) using conventional high-pressure high-temperature (HPHT) sintering parameters. The diamond disk is then treated in acid to remove any residual metal.

The disk is then reassembled with the WC substrate and subjected to a modified



HTHP process that differs from the first.

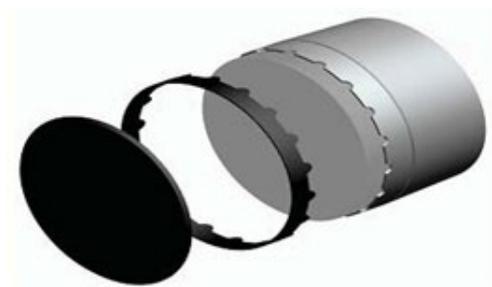
The second step involves re-sintering the PCD synthetic diamond plate onto a new carbide substrate using a modified HTHP sintering process, which is different from the first step.

This method offers several advantages over the traditional one-step process.

1. The PCD disk is subjected to an additional process to reduce residual stresses. In the second process, controlled infiltration of cobalt material is injected back into the intergranular region of the diamond, creating less residual stress than the conventional one-step PDC wafer fabrication process.

2. The two-step HTHP process enhances the strength of the PCD microstructure.

A new generation of thermostable PDC cutters has also been proposed [14], which builds upon the existing thermostable structures by complementing the planar leached layer with a non-planar diamond-solid interface (Fig. 4).



**Fig. 4. – New generation Thermo Stable PDC Cutters**

*A source: [14]*

As illustrated, the proposed design of thermostable PDCs features a leached layer across the wafer surface, complemented by a "ring" of leached material around their periphery.

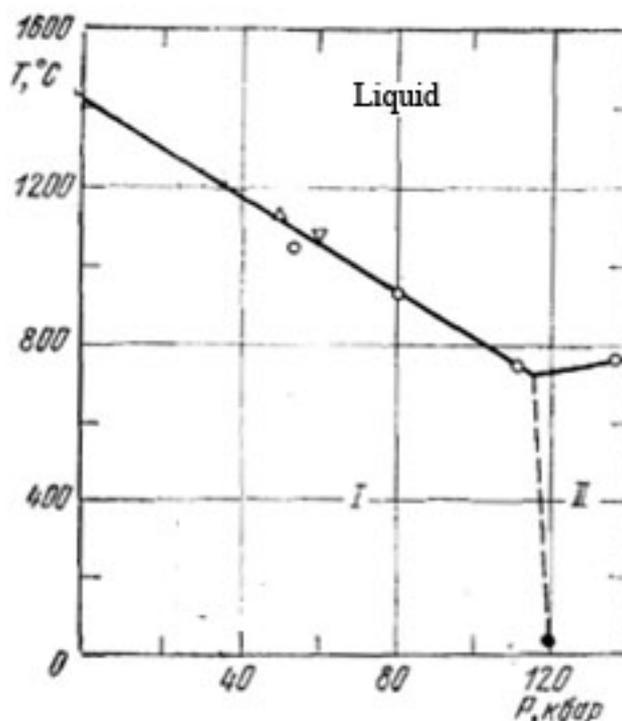
The incorporation of additional thermostable material in the cutting edge area of the PDC further delays the onset of wear compared to first-generation thermostable PDCs. During the wear of the cutting edge, a "double-edge" cutting structure is formed. This increases productivity as both edges are able to cut the rock. The crescent-shaped cutting edge provides additional support and complements the cutting edge seen in first-generation thermostable cutters. This enhances the cutter's overall rigidity and resistance to cutter back movement and axial shock loads.



### 9.3. Technology for obtaining thermostable PDCs based on silicon impregnation of diamond powder

As previously stated, the PDC sintering technology, which includes silicon impregnation of diamond powder, also contributes to the reduction of the metal component (cobalt) content in the diamond composite. During the sintering process, PDC serves as a binder. The selection of this particular binder is based on the following considerations:

1. The melting point of silicon decreases with increasing pressure, which provides a lower impregnation temperature that can minimize graphitization of diamond. This is illustrated in Figure 5.



**Fig. 5. – Pressure dependence of silicon melting temperature**

*A source: [15]*

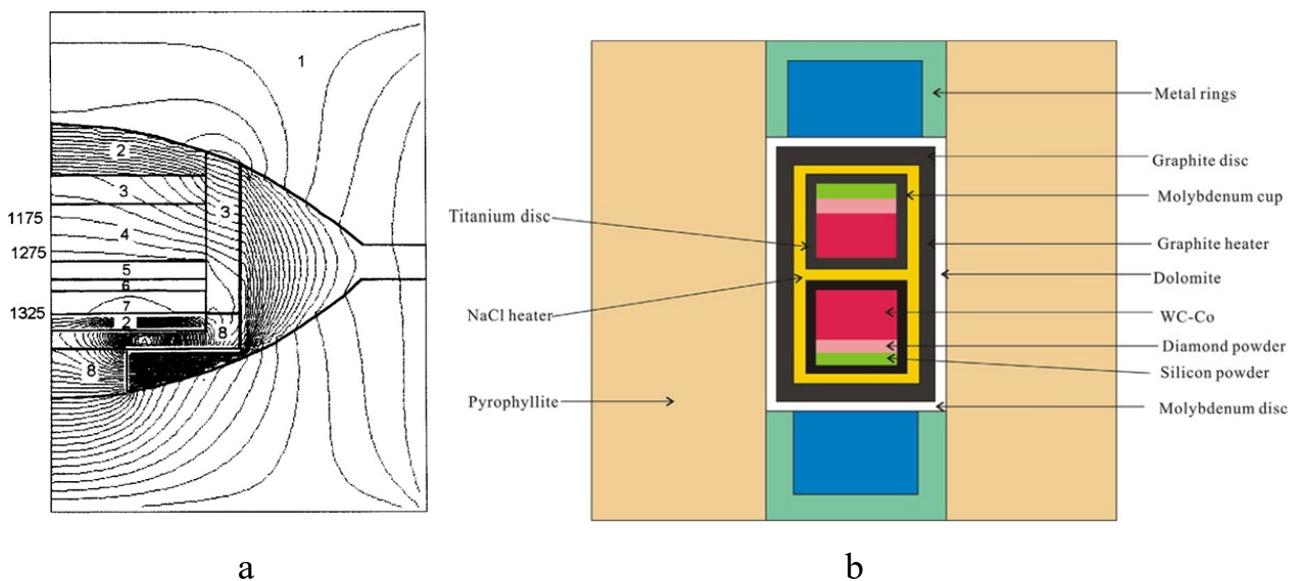
2. As a result of the chemical reaction between diamond and silicon, a new phase (SiC) is formed that consolidates the diamond particles into a bulk composite. The structural similarity between the reaction product (SiC) and diamond provides a strong bond.

3. The high melting point of SiC (>2200 °C) makes the obtained composites suitable for high temperature applications.

The primary benefit of the silicon impregnation method is that the liquid phase fills the open pores in the diamond skeleton. One key limitation of this process is that it is essential to maintain the pores open throughout the liquid phase impregnation process. Otherwise, the so-called self-stopping process can limit or even completely block the flow of binder, which would have a detrimental effect on the entire sintering process.

In PDC sintering, a counter-impregnation method of silicon and cobalt melt impregnation of diamond micropowder is employed.

Depending on the PDC manufacturing technology, both asymmetrical and symmetrical high-pressure cell assembly schemes are employed (Fig. 6).



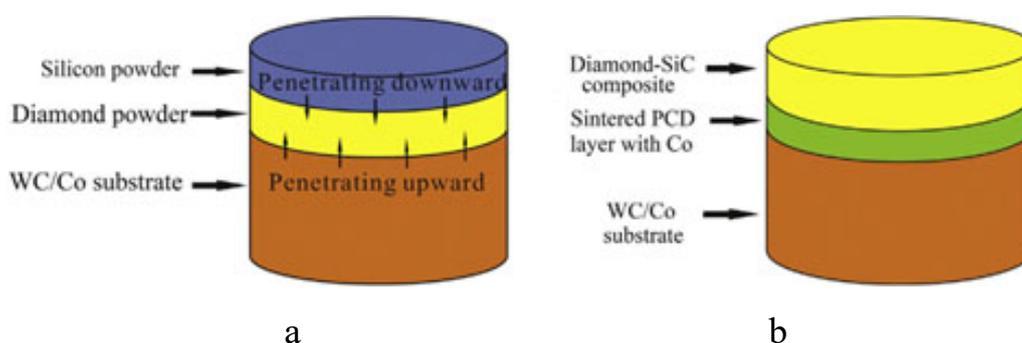
**Fig. 6. – Schematic diagram of the cell assembly used in the high-pressure and high temperature experiments: a – asymmetrical circuit [16] (1 – block-unit, 2 – heat insulators, 3 – heating elements, 4 – carbide substrate, 5 – diamond powder, 6 – silicon disk, 7 – electrical insulator, 8 – current leads); b – symmetrical circuit [17]**

The reaction volume is provided as follows: A layer of silicon powder is applied to the diamond powder. During the sintering process at high pressure and temperature,



the top silicon layer penetrates into the diamond layer to form a diamond-SiC composite. This composite has a higher thermal stability than that of polycrystalline diamond obtained by conventional sintering. Conversely, the diamond-SiC composite layer will be formed as an intermediate layer involving cobalt from the substrate, which will penetrate upwardly into the diamond layer.

Please refer to Fig. 7 for a schematic of the resulting PDC structure.



**Fig. 7. – Schematic of newly-designed structure for the HPHT sintering of PDC, showing the dynamic process of HPHT sintering for the Si, diamond and WC/Co substrate (a) and the well-sintered three-layered PDC (b). Note: the top layer is diamond–SiC composites**

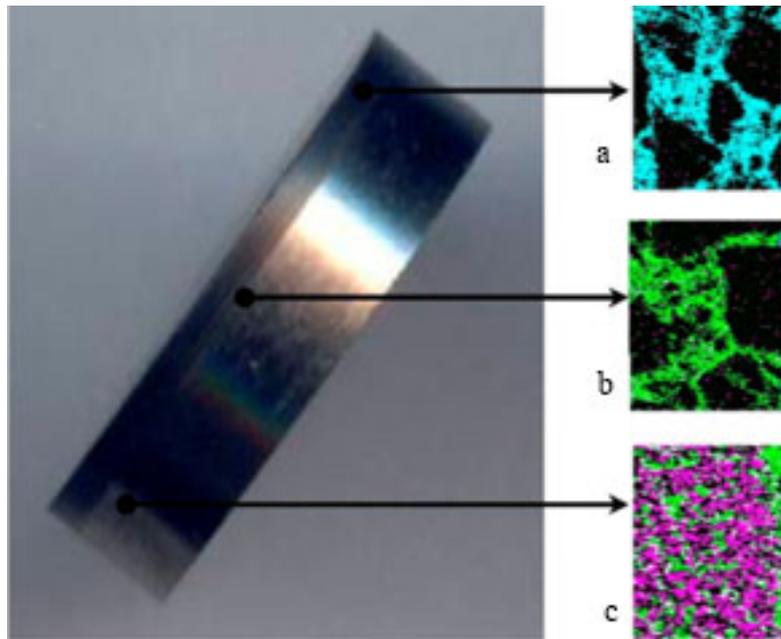
*A source: [17]*

Figure 8 below illustrates a micrograph of a general view of a heat-resistant PDC, which is a three-layer composite material. The top layer is the result of the sintering process, which is the consolidation of the diamond–SiC composite.

The intermediate layer's structure is identical to that of the diamond-containing layer of standard PDCs.

The mass of silicon is calculated based on the possibility of liquid silicon completely filling the porous space of diamond micro powder under high pressure conditions.

PDC sintering is carried out in a high-pressure apparatus at a pressure of 5.5–7.7 GPa and a temperature of 1500–2000 °C.

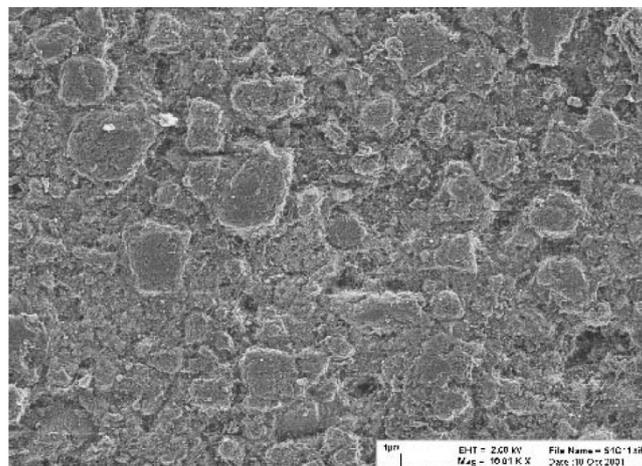


**Fig 8 – Microphotographic image of the general view of the heat-resistant PDC: a – diamond – SiC composite structure; b - structure of the diamond–Co transition layer c – hard alloy structure [4].**

*A source: [4]*

The sintering process involves the formation of the heat-resistant diamond-containing layer at a temperature of 1470–1770 K, followed by a rise in temperature to 2070-2170 K. At this point, the layer is connected to the substrate due to the penetration of cobalt to a depth of the order of the size of diamond grains in the heat-resistant layer.

This process enables the creation of a porous diamond-containing layer with an interpenetrating diamond and silicon carbide framework structure (Fig. 9).



**Fig. 9 – SEM images of composites diamond-SiC**

*A source: [18]*



The structure and properties of the material are primarily influenced by the regularities of the processes of silicon impregnation of diamond powder and carbide formation. These processes, in turn, depend on the p, T-parameters of sintering and the grain size of the diamond powder.

X-ray data demonstrate that the composites contain no residual silicon phase that has not reacted with diamond. The composites have a typical structure of interpenetrating diamond and silicon carbide frameworks that form a high-density material.

The strength of the diamond-containing layer bonded to the carbide substrate is dependent on the characteristics of the transition layer in the contact zone. This is of significant importance for both product performance and manufacturing technology. It is essential to achieve a high yield of high-quality samples while reducing the probability of the diamond layer detaching from the substrate.

By studying the construction of the contact zone using electron scanning microscopy and micro-X-ray spectral analysis methods, we can conclude that when using the method of obtaining two-layer wafers using silicon, a very thin intermediate layer is formed, which provides a strong connection between the PDC components – the heat-resistant diamond-containing layer and the carbide substrate.

The impregnation of diamond powder with silicon melt occurs at high speed in a non-isothermal regime and is completed by the formation of silicon carbide in the temperature range of 1470–1770 K as a result of a chemical reaction with diamond. At the same time, a dense PDC structure is formed, which effectively prevents the migration of cobalt from the carbide. After thermobaric action at 8 GPa and a temperature range of 2070–2170 K for 60 seconds, cobalt was found in a thin layer with diamond in the transition zone of PDC samples. The width of this layer did not exceed 40  $\mu\text{m}$ , which is consistent with the maximum size of the original diamond grain (ASM 40/28).

The maximum cobalt content at the interface is significantly higher than that of the solid alloy (by a factor of 2). This effect is the result of the process of directed heat and mass transfer, which is realized by using special equipment of the high-pressure



cell. This equipment allows for an intensive heating of the sample from the outer end surfaces.

The accumulation of cobalt in the transition layer has clear advantages. It not only acts as a bonding agent, but also makes this layer more ductile and capable of relaxing external stresses.

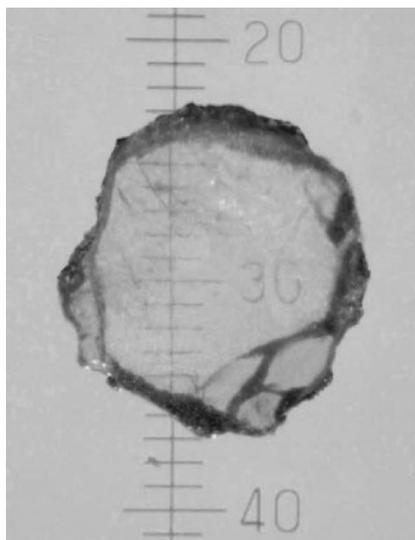
The diamond-containing layer is distinguished by the complete absence of cobalt in the structure and the presence of only silicon in the carbide composition.

One of the key benefits of PDC wafers produced using this technology is their high thermal resistance. This enables them to withstand high temperatures without compromising their properties. The high thermal resistance of the composite is attributed to the high thermal compatibility of the phases, which is enabled by the proximity of the coefficients of thermal expansion, the absence of phase transitions in silicon carbide during heating, the difficulty of graphitization of the diamond phase due to the high density of the composite, and the almost complete absence of metals—carbon solvents in it (there are only fine inclusions of the solvent alloy, which is used for the synthesis of the initial diamond powder).

Wear resistance tests have demonstrated that after 10 minutes of heating the plates to 850 and 1000 °C, the wear surface remains virtually unchanged.

#### **9.4. Technology of obtaining polycrystalline diamond compact materials without the use of metal bonds and solvents**

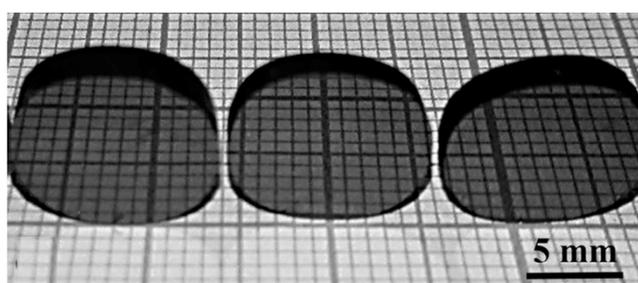
The development of high-pressure techniques has enabled us to significantly expand the achievable pressure range, resulting in the creation of high-pressure apparatuses capable of generating pressures up to 65 GPa in their reaction volumes. The apparatus was used to obtain ultrasolid polycrystalline diamond by direct transition from ultrapure graphite (Fig. 10). Experiments were conducted at the following process parameters: pressure: 12–25 GPa; temperature: 2300–2500 °C [20].



**Fig. 10 – Sintered polycrystalline diamond synthesized by direct conversion of graphite. Optical microscopic image of a sample of the synthesized diamond (about 0,1 mm in diameter and 0,3 mm thick)**

*A source: [20]*

Further enhancements to the high-pressure apparatus have enabled the development of a technology for producing catalyst-free polycrystalline polycrystalline diamond compact materials (CFPDC) up to 1 cm (Fig. 11) [21].



**Fig. 11 – Optical photo of end-polished samples of micro-grained polycrystalline diamond**

*A source: [21]*

CFPDC samples were fabricated at a pressure of 16 GPa and a temperature of 2300°C.

The development of a two-stage loading device that is directly integrated into the first cubic high-pressure apparatus has made it possible to obtain specimens of this



size. This eliminates the intermediate conversion process of single-axis loading, which was previously required. Three-axis loading offers a significant improvement in load transfer efficiency compared to single-axis pressing technology.

The field tests of the obtained polycrystals demonstrated record results in terms of wear resistance and thermal stability for PDC cutters used for drilling in the oil and gas industry.

The new material has been demonstrated to exhibit exceptionally high wear resistance, exceeding 300% that of the most advanced commercial PDC materials currently utilized in the industry. Furthermore, the material demonstrates the highest thermal stability and oxidation resistance up to a temperature of 1200 °C. The exceptional combination of the highest hardness, highest wear resistance, and highest thermal stability of the new CFPDC material is expected to play an important role in scientific research and in industries such as oil and gas exploration, drilling, and cutting materials.

## **Summary and conclusions**

Polycrystalline diamond (PD) is a material with a number of highly desirable properties, including high hardness and wear resistance, low friction, high thermal conductivity, high corrosion resistance, and low electrical conductivity. As a result, PD plays a leading role in the selection of tools used in the oil and gas industry. PDC cutters are the primary and essential components of PDC drill bits for cutting a variety of formations. However, drilling very hard and highly abrasive formations represents a significant challenge for current PDC drill bits. The current technology is limited by the necessity of using metal catalysts to bond the diamond grains that make up PDC cutters in conventional high-pressure, high-temperature (HPHT) manufacturing.

Consequently, PDC manufacturers, particularly those in the drill bit industry, have concentrated their efforts on identifying methods to minimise the necessity for metal bonding in the diamond layer.



The most promising avenues for the development of PDC with enhanced thermal stability are as follows. This fabrication method involves leaching cobalt from polycrystalline material using acid, or adding silicon to form silicon carbide (as a result of a reaction with diamond particles). This acts as a bonding phase for diamond instead of cobalt.

The development of catalyst-free PDC cutters could have a transformative impact on the drill bit landscape, paving the way for the realization of the goal of "One Pass to Full Depth" in drilling technology.