Rare Metal Materials and Engineering
Volume 53, Issue 11, November 2024
Available online at www.rmme.ac.cn

Science Press

Cite this article as: Li Yi, Wang Jincheng, Ni Juan, et al. Modification of Paraffin Wax for Manufacturing Difficult-to-Form Green Compacts and Its Application in WC-Co Cemented Carbides[J]. Rare Metal Materials and Engineering, 2024, 53(11): 3064-3076. DOI: 10.12442/j.issn.1002-185X.20240163.

ARTICLE

Modification of Paraffin Wax for Manufacturing Difficult-to-Form Green Compacts and Its Application in WC-Co Cemented Carbides

Li Yi[1,2], **Wang Jincheng**[1], **Ni Juan**[2], **Shen Shaobo**[2]

[1] School of Materials Science and Engineering, Northwestern Polytechnical University, Xi'an 710072, China; [2] Jiangsu Taier Novel Material Co., Ltd, Suzhou 410075, China

Abstract: The production of deep well-shaped WC-Co cemented carbide blocks via industrial powder pressing remains a challenging technical problem, primarily due to the unsuitability of the forming agent. The forming agent paraffin wax was modified through four types of modifiers, including organic high-molecular-mass resins, plasticizers, surfactants and lubricants. The qualitative screening of resin types was explored and an orthogonal experiment involving the combination of these four paraffin wax modifiers was conducted to obtain an optimized quantitative ratio of modifiers. The results reveal that the insertion of the small molecule chain of resin into the interstitial spaces of paraffin wax crystals is likely a crucial factor for improving the compatibility between the resin and paraffin wax. Through orthogonal experiments, the optimized formulation for the forming agent is determined: 100 parts of 58# paraffin wax, 15 parts of EVA-2, 4 parts of DPHP, 4 parts of oleic acid amide and 2 parts of stearic acid. This optimized formulation is applied to industrial production at one Chinese company, and qualified deep well-shaped cemented carbide products are achieved, which contain 90wt% WC and 10wt% Co.

Key words: WC-Co cemented carbide; deep well-shaped products; forming agent; paraffin wax modifier; resin screening; modifier ratio optimization

The production of deep well-shaped tungsten carbide (WC)-cobalt (Co) cemented carbide blocks remains an extraordinarily challenging task in the realm of cemented carbide materials, which are composed of numerous protruding square-shaped cemented carbide platforms on the flat surface of WC-Co cemented carbide blocks. When viewed from the front, these small platforms resemble a multitude of deep wells. In industrial applications, deep well-shaped WC-Co blocks are used in rock drilling bits for excavation purposes and can also be employed in the military for manufacturing armor-piercing projectiles. The industrial manufacturing process for deep well-shaped WC-Co cemented carbide blocks by the paraffin wax-based forming agent consists of several critical steps. (1) Preparation of the forming agent A of cemented carbide. (2) Forming agent A dissolved in liquid industrial ethanol was mixed with the powders of WC and Co by ball-milling to create liquid mixture B. (3) Spraying granulation of liquid mixture B to produce granular material C. (4) Compression molding of granular material C into green compacts D using molds. (5) Sintering of green compacts D to produce the final WC-Co cemented carbide block products E.

In practical production, a significant technical challenge has been encountered with deep well-shaped products E. The sharp edges of the small square protrusions on these products are prone to breakage during the green compact compression and demolding processes. This problem has proven to be a formidable challenge for many enterprises and is typically addressed by selecting the suitable forming agents of the powders of cemented carbide WC and metallic Co.

Forming agents primarily serve for two purposes, i.e., they enhance the flowability of the granular material C in Step (3) to ensure particle bonding and maintain the shape of the green compacts D until they are heated and the binder is removed in Step (4).

Received date: March 21, 2024

Corresponding author: Wang Jincheng, Ph. D., Professor, School of Materials Science and Engineering, Northwestern Polytechnical University, Xi'an 710072, P. R. China, E-mail: jchwang@nwpu.edu.cn

Paraffin wax has low viscosity and is relatively hard and brittle, and lacks ductility. Obviously, paraffin wax alone cannot serve as the sole forming agent for WC-Co cemented carbide compaction, necessitating the addition of other modifiers to change the properties of paraffin wax.

Polymer resins, due to their longer polymer chains and certain proportions of branching, tend to exhibit physical entanglement and strong cohesion between polymer chains and branches, making them more cohesive than small-molecule paraffin wax. Therefore, adding an appropriate proportion of resin to paraffin wax can probably enhance the adhesive properties and tensile strength of the binder[1]. Additionally, resins have high purity, low ash content, and are easy to remove[2]. However, the choice of resin must consider its compatibility with wax and its effect on the viscosity of the system, flowability and its removal. Previous research has reported that the addition of terpene resin to wax can promote the compaction and compactness of green compacts, contributing to the improvement of the strength of sintered cemented carbide[3]. In summary, there is few research on the influence of resin types on the performance of wax binders for cemented carbide compaction to date. There is also no reported research on the mutual solubility and compatibility between resin and wax.

In industrial Step (3), when preparing a mixture of cemented carbide powder and paraffin wax by grinding, ethanol is commonly used as a solvent for wax. However, non-polar paraffin wax has poor dispersion and solubility in polar ethanol, resulting in an uneven distribution of wax in the mixture. This leads to the formation of wax-rich “hard granules” within the mixture, which is often evidenced by the “watermelon seed” phenomenon in fractured green compacts. To enhance the solubility of wax in ethanol, it is possible to consider adding surfactants that have both polar and non-polar groups. Additionally, the added surfactant may reduce the solid-liquid interfacial tension between non-polar wax and polar cemented carbide particles[1], thereby improving the wetting properties of wax binders on alloy powder particles and increasing the coverage of wax on the surface of alloy particles. It is reported that the addition of surfactants can effectively reduce the compaction height and improve green compact cracking[2–5].

In industrial Step (4), when pressing the granular wax material C, the friction between the granular wax material C and the mold sides is greater than that of rubber materials, resulting in a higher positive pressure applied by the wax material compared with rubber materials[6]. To address this problem, lubricants need to be added to the wax material. Lubricants commonly used in the powder metallurgy industry include oleic amide, erucic amide and ethylene bis-stearamide[2,7–10].

The addition of a certain amount of plasticizer to the wax-resin-modified binder has advantageous in unraveling the molecular chains of high-molecular-mass resin polymers, reducing the system viscosity and improving flowability[1]. It can also increase the flexibility of polymer molecules and enhance adhesive strength, elasticity, cold resistance and other properties. Overall, there is hardly systematic research on the influence of plasticizer types on the performance of wax binders for WC-Co cemented carbide to date.

Although previous researchers have proposed that high molecular mass polymers and surfactants can improve the performance of the paraffin wax-based forming agent, there are limited investigations on the effect of lubricants and plasticizers. Furthermore, prior studies have seldom examined the influence of combinations of these four wax modifiers on wax properties. Additionally, previous research on wax modifiers is predominantly qualitative and lacks quantitative results, whereas practical production requires precise quantification of modifier proportions. This research aimed to quantitatively study the proportions of these four modifiers through orthogonal experiments and utilized these quantitative results in actual production to verify their effectiveness.

1 Experiment

1.1 Experimental materials

The experimental materials used in this study included WC powder (Fsss 1.47 μm) and Co powder (Fsss 0.91 μm), which were supplied by Xiamen Jinle Special Alloy Co., Ltd. Other chemical reagents employed in the experiments are listed in Table 1[4, 11–12].

1.2 Manufacture of WC-Co cemented carbide

The modified wax binder thus obtained is mixed with WC-Co cemented carbide powder (90wt% WC+10wt% Co) to prepare the mixture through grinding. The modified wax binder accounted for 1.8wt% in the mixture. During the grinding process, cemented carbide steel balls were used as grinding media, with a ball-to-material ratio of 3.5: 1. The mass ratio of ethanol to the sum of cemented carbide and modified wax was 3:10, and the grinding time was 14 h. The slurry-like mixture was granulated by a spray granulator. Deep well-shaped WC-Co green compacts were produced in an industrial mold press, with a pressing rate of 11 pieces per minute. Sintering was mainly divided into three processes. The first process was degreasing at temperatures below 600 °C in H_2 atmosphere. The second process was pre-roasting, at a maximum temperature of about 1250 °C under vacuum. The third process was atmosphere sintering. The oven temperature was gradually raised from 1250 °C to a maximum temperature of about 1450 °C under vacuum, and it was held for 60 – 90 min in Ar atmosphere before gradual cooling to room temperature.

1.3 Materials characterization

Crystalline morphology of the modified paraffin wax samples after cooling was observed by polarized optical microscope (OM, Model 59XA, Shanghai Optical Instrument Factory). Thermal analysis was conducted by differential scanning calorimetry (DSC, Q20, TA Instruments, USA) and Thermo-gravimetry (TG, NETZSCH STA 449F3). The measurement of kinematic viscosity (v in mm²/s) followed the national standard GB/T 265-88[13] with a capillary viscometer.

Table 1 Chemical reagents and their properties

Reagent	Molecular formula	Dynamic viscosity/mPa·s	Solubility parameter/(J·mL^{-1})$^{1/2}$
58#PW	C_nH_{2n+2}	-	9.06[4]
SEBS-1	$(C_4H_6)_x(C_8H_8)_y$	2423.0	8.4[11]
SEBS-2	$(C_4H_6)_x(C_8H_8)_y$	410.7	-
EVA-1	$(C_2H_4)_x(C_4H_6O_2)_y$	35.46	8.68[12]
EVA-2	$(C_2H_4)_x(C_4H_6O_2)_y$	248.4	-
APAO-1	$(CH_2CHCH_3)_x(C_2H_4)_y$	31.0	-
APAO-2	$(CH_2CHCH_3)_x(C_2H_4)_y$	37.5	-
APP-1	$(CH_2CHCH_3)_n$	18.9	8.04[4]
APP-2	$(CH_2CHCH_3)_n$	147.5	-
Terpene-1	$(C_{10}H_{16})_n$	3.5	8.40[11]
Terpene-2	$(C_{10}H_{16})_n$	7.7	-
DPHP	$C_{28}H_{46}O_4$	-	-
Oleic acid amide	$CH_3(CH_2)_7CHCH(CH_2)_7CONH_2$	-	-
Stearic acid	$CH_3(CH_2)_{16}COOH$	-	-

Note: viscosities of modified paraffin waxes were measured at 80 °C with resin filling amount of 10% relative to paraffin wax and a shear rate of 3 s^{-1}

The dynamic viscosity (η) was calculated based on the formula: $\eta=v\rho$, where ρ in g/cm³ is the fluid density and η is measured in mPa·s. The dynamic rheological properties of the wax samples were tested by a rotational rheometer (RheoWin MARS 40, TA Instruments, USA). The rotational rheometer generates simple shear flow by rotating the fixtures and allows for rapid measurement of various rheological properties such as viscosity and elasticity[14]. The tensile strength of the wax was determined according to industry standard SH/T 0402-1992(2004)[15], and the wax tensile test specimen dimension is shown in Fig. 1. The needle penetration of the wax was measured following the national standard GBT 4985-2010[16]. The testing methods for residual carbon and ash content of wax sample followed national standards GB 268-87[17] and GB 508-85[18], respectively. The flowability of the granulated wax was measured by a Hall flow meter shown in national standard GB/T 1482-2010[19]. The size distribution of sprayed granules was obtained by the Nano-Measurer software. For the cemented carbide samples, the cylindrical end surfaces were polished by SiC sandpaper up to 2000 grit, followed by surface corrosion through alkaline potassium ferricyanide solution. Subsequently, the surface microstructure of the cemented carbide sintered samples was observed by scanning electron microscope (SEM, German ZEISS EVO-18). Phase analysis of the original sintered samples was conducted by X-ray diffractometer (XRD, Japanese Rigaku Smart Lab).

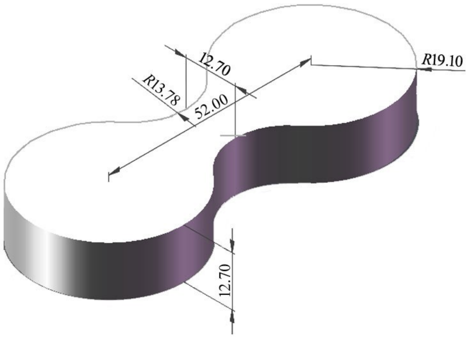

Fig.1 Paraffin wax specimen used for tensile strength test

2 Results and Discussion

2.1 Screening of resins

The solubility parameters can characterize the interactions between molecules. Generally, the closer the molecular chain structures of polymers, the closer their solubility parameter values, indicating better compatibility between them. To enhance the adhesion and tensile strength of the paraffin wax molding agent, five resins with parameters closely related to the solubility of paraffin wax were selected for paraffin wax modification: SEBS (styrene-ethylene/butylene-styrene block copolymer), EVA (ethylene-vinyl acetate copolymer), APAO (amorphous poly-alpha-olefin), APP (atactic polypropylene), and Terpene Resin (Table 1). The resin components were added to the modified paraffin wax with a relative concentration of 10wt%. Two different grades of each resin were employed, as shown in Table 1. Notably, Terpene-2 remains in liquid state at room temperature, while the remaining resins are in solid form under normal conditions. The forming agent of paraffin wax and resin was made by melting the mixture by heating.

2.1.1 Microstructure

To investigate the compatibility between the resins and the 58# paraffin wax matrix, the resin-modified paraffin wax samples were observed by polarized OM, as shown in Fig.2–4.

The 58# paraffin wax consists of long, leaf-like crystalline aggregates with tapered ends, with 50 μm in length and 5 μm in width, and is interwoven into a three-dimensional network with gaps (Fig.2a).

Fig.3a and Fig.3b depict the microstructures of two SEBS-modified paraffin waxes. The addition of SEBS can slightly

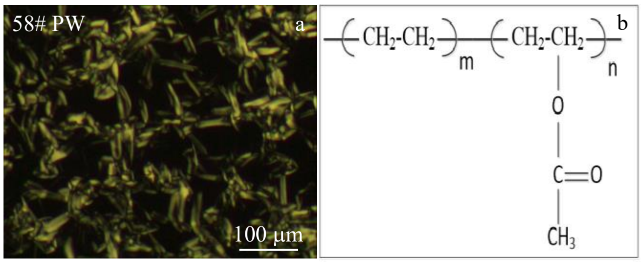

Fig.2 OM image of morphology of 58# paraffin wax (a) and structure of EVA resin (b)

reduce the size of the paraffin wax leaf-like crystals, indicating a partial dissolution and dispersion of paraffin wax in both SEBS types. SEBS, a block copolymer of styrene and butadiene (Table 1) [20–21], consists of separate styrene and butylene chains which are connected together, and the smaller butylene molecules might partially insert into the gaps within the paraffin wax crystals, resulting in compatibility between SEBS and paraffin wax.

Fig. 3c and Fig. 3d show the microstructures of two EVA-modified paraffin waxes. The addition of EVA significantly reduces the size of leaf-like crystals of the paraffin wax, particularly in the case of EVA-1, where the interface between EVA and paraffin wax almost disappears, indicating excellent compatibility between them. EVA is an ethylenevinyl acetate copolymer (Table 1) and consists of separate ethylene and vinyl acetate chains interconnected (Fig. 2b) [22], making it easier for the smaller ethylene chain segments to insert into the gaps within the paraffin wax crystals and resulting in good resin-paraffin wax compatibility. EVA-1 and EVA-2 have ethylene contents of 81wt% and 73wt%, respectively. Due to the higher ethylene content in EVA-1, a larger amount of ethylene is inserted into the paraffin wax crystals, thus providing better paraffin wax dispersion.

Fig.4a and Fig.4b display the microstructures of two APAO-modified paraffin waxes. The addition of APAO results in minimal changes in the size of the paraffin wax leaf-like crystals, indicating poor dispersion of both types of APAO in the paraffin wax. APAO is a copolymer of polypropylene and polyethylene (Table 1) [23], and both components are polymerized into a single large molecule, making it too bulky to insert into the gaps within the paraffin wax crystals and leading to low compatibility between APAO and paraffin wax.

Fig.4c and Fig.4d illustrate the microstructures of two APP-modified paraffin waxes. The addition of APP-1 slightly reduces the length and width of the paraffin wax leaf-like crystals, while APP-2 has almost no effect on the crystal size, indicating a slight dissolution and dispersion of both types of APP in paraffin wax. APP is an atactic polypropylene copolymer (Table 1) with randomly distributed methyl side chains on the main chain, resulting in a large molecular size[24], making it difficult to insert into the gaps within the paraffin wax crystals and leading to poor compatibility between APP and paraffin wax.

Fig. 4e and Fig. 4f present the microstructures of two Terpene-modified paraffin waxes. The addition of solid Terpene-1 increases the length and width of the leaf-like crystals of paraffin wax by nearly 50% and reduces the gaps between the crystals, possibly because solid Terpene-1 causes agglomeration of the paraffin wax leaf-like crystals. The addition of liquid Terpene-2 also increases the length and width of the paraffin wax leaf-like crystals and significantly expands the gaps between them. This is attributed to more pronounced agglomeration of the paraffin wax leaf-like crystals due to the mixing of liquid Terpene-2, settling to the

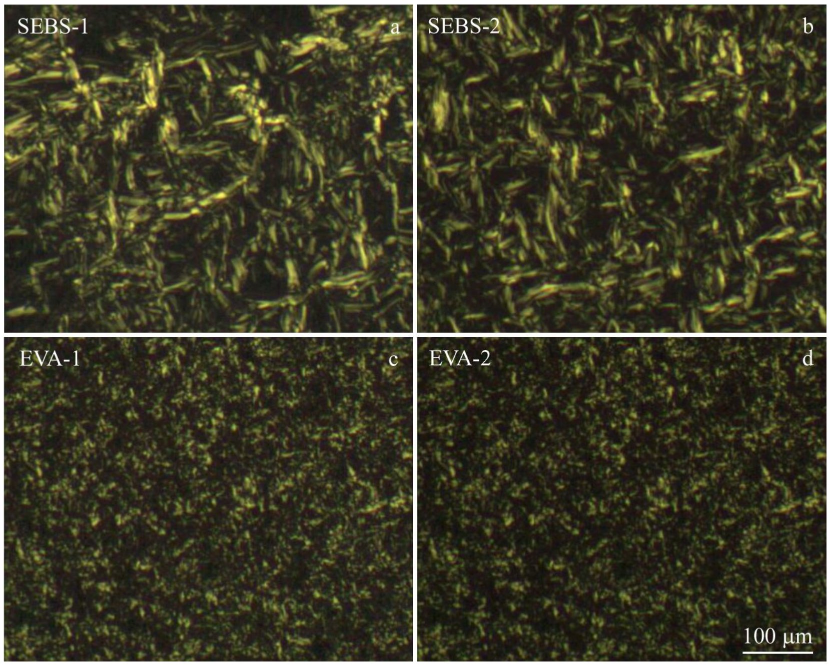

Fig.3 OM images of microstructure of resin-modified paraffin waxes: (a) SEBS-1, (b) SEBS-2, (c) EVA-1, and (d) EVA-2

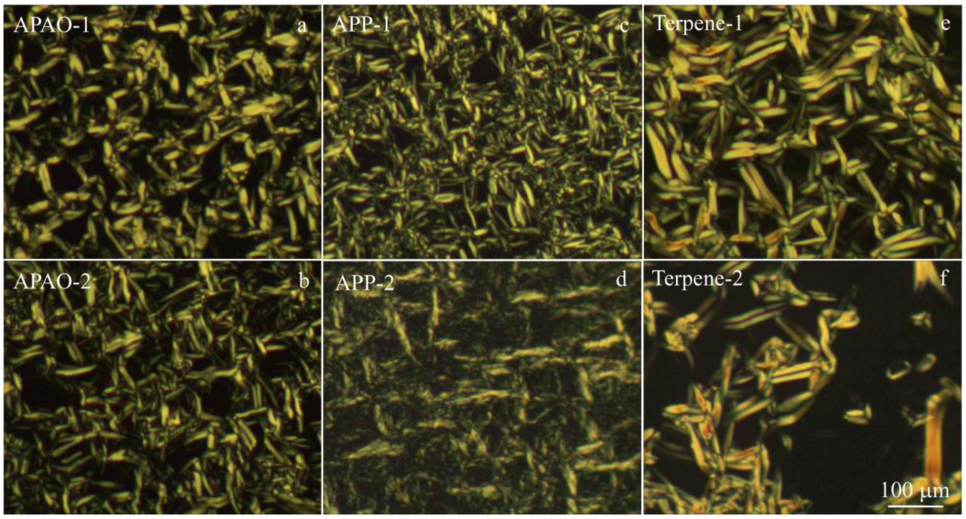

Fig.4 OM images of microstructure of resin-modified paraffin waxes: (a) APAO-1, (b) APAO-2, (c) APP-1, (d) APP-2, (e) Terpene-1, and (f) Terpene-2

lower portion during sampling for microscope analysis, which was performed after pronounced agglomeration and focused on the lower-density portion of the upper layer solution, resulting in larger gaps between the crystals. Terpene resins are linear polymers formed by the polymerization of α-pinene or β-pinene (Table 1)[25]. α-pinene or β-pinene consists of 6-membered ring with multiple side chains, forming a three-dimensional large molecule with 10 carbons. The large size of α-pinene or β-pinene molecules makes it difficult to insert into the gaps within the paraffin wax crystals, leading to poor compatibility between Terpene and paraffin wax. Additionally, the pinene chains may entangle with paraffin wax straight-chain molecules, increasing the size and mass of the paraffin wax crystals and causing them to agglomerate under gravity.

In summary, the compatibility enhancement between the resins and paraffin wax may be attributed to the insertion of small molecules of the resins into the gaps within the paraffin wax crystals. Block copolymers with small ethylene segments are more likely to dissolve and to disperse within the paraffin wax, leading to good compatibility.

2.1.2 Tensile strength

Paraffin wax is primarily a mixture of straight-chain alkanes, and its structure is similar to that of polyolefins. The addition of polymers affects the tensile strength of paraffin wax.

The tensile strength of the 58# paraffin wax, which serves as the matrix material for the molding agent, is approximately 600 kPa, and the effect of resin addition on the tensile strength of paraffin wax is depicted in Fig.5a.

When 5wt% SEBS-1 and SEBS-2 are added in the paraffin wax, the modified paraffin wax achieves the maximum tensile strength of 1970 and 1827 kPa, respectively (Fig.5a). SEBS is a styrene-butylene block copolymer, and its molecular structure consists of high-molecular-mass and rigid styrene segments along with softer small-molecule butylene segments[20–21]. SEBS-1 has a higher viscosity than SEBS-2 (Table 1), indicating a higher content of the rigid styrene segments in SEBS-1. Since a small amount of butylene segments can carry the styrene segments and insert into the gaps within the paraffin wax crystals, SEBS-1 has a more pronounced effect on improving the tensile strength of paraffin wax.

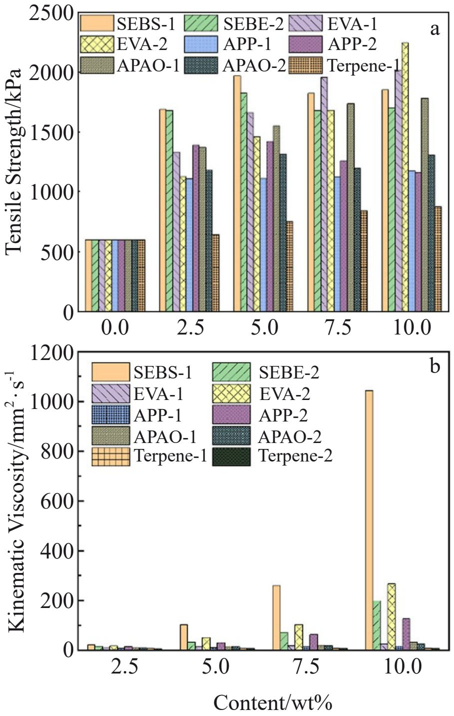

Fig.5 Effect of modifier content on tensile strength (a) and kinematic viscosity (b) of modified paraffin waxes

When 10wt% EVA-1 and EVA-2 are added in the paraffin wax, the modified paraffin wax achieves the maximum tensile strength of 2013 and 2246 kPa, respectively (Fig.5a). EVA is a block copolymer of ethylene and vinyl acetate, and its molecular structure consists of rigid vinyl acetate segments and softer ethylene segments[22]. The tensile strength of vinyl acetate segments is greater than that of ethylene segments. The rigid vinyl acetate content in EVA-1 and EVA-2 is 19wt% and 27wt%, respectively, so the dynamic viscosity of EVA-2 is much larger than that of EVA-1 (Table 1). The higher content of rigid vinyl acetate segments in EVA-2 contributes to the biggest tensile strength of modified paraffin wax.

When 10wt% and 5wt% APAO-1 and APAO-2 are added in the paraffin wax, the modified paraffin wax achieves maximum tensile strength of 1784 kPa and 1316 kPa, respectively (Fig. 5a). APAO is a copolymer of rigid polypropylene chains and soft polyethylene chains (Table 1) [23]. APAO-1 has lower viscosity than APAO-2 (Table 1), indicating a higher content of soft small-molecule ethylene chains. This makes it easier for APAO-1 to insert into the gaps within the paraffin wax crystals, resulting in a greater increase in tensile strength.

When 10wt% and 5wt% APP-1 and APP-2 are added in the paraffin wax, the modified paraffin wax achieves the maximum tensile strength of 1178 kPa and 1421 kPa, respectively (Fig. 5a). APP is a copolymer of rigid polypropylene chains (Table 1) [24]. APP-1 has significantly lower viscosity than APP-2 (Table 1), implying a lower content of polypropylene chains in APP-1. This results in a smaller number of polypropylene chains from APP-1 which has inserted into the gaps within the paraffin wax crystals, thus leading to a smaller increase in tensile strength.

When 10wt% Terpene resins are added in the paraffin wax, the modified paraffin wax achieves the maximum tensile strength of 878 kPa (Fig. 5a). Terpene resins are linear polymers formed by the polymerization of α-pinene or β-pinene from pine resin (Table 1)[25]. α-pinene or β-pinene molecules are very large in size and cannot easily insert into the gaps within the paraffin wax crystals, resulting in a minimal contribution to the tensile strength of paraffin wax.

In conclusion, the contribution of resins to the tensile strength of paraffin wax follows the order: EVA>SEBS>APAO >APP>Terpene, and the contribution may be proportional to the amount of resin inserted into the gaps within the paraffin wax crystals. Additionally, the rigid large-molecule chains in the resin appear to have a more significant effect on increasing the tensile strength of paraffin wax compared with softer small-molecule chains. Therefore, the mechanism of the influence of block copolymer resins on the tensile strength of paraffin wax involves two aspects: firstly, the small-molecule chains from the resin must insert into the gaps within the paraffin wax crystals; secondly, the presence of rigid large-molecule chains in the resin enhances the tensile strength of paraffin wax.

2.1.3 Viscosity

Kinematic viscosity (mm^2/s) is a measure of the resistance during the flow of the modified paraffin wax under gravity, while dynamic viscosity (Pa·s) is a measure of its own viscosity. Kinematic viscosity can be calculated by dynamic viscosity/ρ, where ρ is the density (kg/m^3). Therefore, under the melting condition at 80 °C, when 10wt% resin is added to the 58# paraffin wax liquid, the dynamic viscosity of the modified paraffin wax measured at a very low shear rate (3 s^{-1}) essentially reflects the dynamic viscosity of the resin itself, as shown in Table 1. From this, it can be observed that the dynamic viscosity of the resins follows the order: SEBS-1> SEBS-2>EVA-2>APP-2>APAO-2>EVA-1>APAO-1>APP-1> Terpene-2>Terpene-1. The dynamic viscosity of pure paraffin wax is much lower, only 2 mPa·s.

The kinematic viscosities of paraffin wax modified with different contents of resin are presented in Fig. 5b. The kinematic viscosity of resin-modified paraffin wax increases significantly with the increase in resin content. When the resin content is 10wt%, the kinematic viscosity of resin-modified paraffin wax follows the order: SEBS-1>EVA-2>SEBS-2>APP-2> APAO-1>APAO-2>EVA-1>APP-1>Terpene-1>Terpene-2. In general, the greater the dynamic viscosity of the resin, the higher the kinematic viscosity of the paraffin wax after resin modification. However, there are some exceptions, such as APAO-1. The higher kinematic viscosity of modified paraffin wax liquid indicates poorer flowability. When it is mixed with cemented carbide powder and melted modified paraffin wax liquid for granulation, the paraffin wax liquid may not fully mix and wet the alloy powder, resulting in poor flowability of the granules and difficulties in filling the mold. Therefore, the kinematic viscosity of the modified paraffin wax should not be too high.

2.1.4 Carbon residue and ash

The residual carbon is an indication of the left carbon content after removing the paraffin wax-based organic forming agent by heating. Table 2 lists the residual carbon and ash content for 58# paraffin wax and the paraffin waxes modified by different resins, and the resin content in all the modified paraffin waxes is 10wt%. The residual carbon of 58# paraffin wax is 0.007wt%. Both types of EVA resin-modified paraffin waxes also have a residual carbon content of 0.007wt%, indicating that EVA does not affect the carbon content. The residual carbon values for APP-1, APP-2, APAO-1, APAO-2, Terpene-2, and SEBS-2 resin-modified paraffin

Table 2 Residual carbon and ash content of paraffin wax modified with different resins (wt%)

Resin	Residual carbon	Ash
58#PW	0.007	0.0027
SEBS-1	0.016	0.0070
SEBS-2	0.012	0.0050
EVA-1	0.007	0.0040
EVA-2	0.007	0.0030
APAO-1	0.011	0.0040
APAO-2	0.010	0.0067
APP-1	0.009	0.0047
APP-2	0.009	0.0035
Terpene-1	0.023	0.0070
Terpene-2	0.011	0.0030

waxes are 0.009wt%, 0.009wt%, 0.011wt%, 0.010wt%, 0.011wt%, and 0.012wt%, respectively, which are slightly higher than that of the paraffin wax. SEBS-1- and Terpene-1-modified paraffin waxes have the residual carbon values of 0.016wt% and 0.023wt%, respectively. Therefore, the addition of SEBS-1 or Terpene-1 significantly increases the residual carbon content of the paraffin wax-based forming agent.

At present, the industrial requirements for residual carbon and ash content after the removal of paraffin forming agents are less than 0.05wt% and 0.005wt%, respectively[26]. The average level of the residual carbon in industrial cemented carbide production in China is 0.03wt%. Thus, the additions of all the above resins do not exceed the industrial level.

2.1.5 Choice of resin

Based on the comprehensive analysis of the effect of resins type on the paraffin wax matrix, the performance of the mentioned resins is summarized in Table 3, where “×” indicates that the resin performs poorly in that specific parameter. Terpene-2, EVA-1 and APAO-1 show poor compatibility with 58# paraffin wax. Terpene resin and APP have less improvement effect on the tensile strength of the paraffin wax matrix. SEBS, EVA-1, APP-2 and other resins significantly increase the kinematic viscosity of 58# paraffin wax, which is undesirable. Terpene-1- and SEBS-modified paraffin waxes have higher residual carbon and ash contents, and APAO-2-modified paraffin wax has higher ash content.

In addition, EVA-2 resin exhibits good compatibility with 58# paraffin wax and significantly enhances the strength of the paraffin wax matrix. Among the resins, the 10wt% EVA-2 resin-modified paraffin wax shows low residual carbon and low ash content compared with paraffin wax modified by other resin components, which is very important in controlling the stable carbon content and thus stable quality of the sintered cemented carbide. It is also reported that EVA has good adhesion to metal surfaces[25]. Based on the above analysis, EVA-2 is thus selected as the resin added to the paraffin wax-based forming agent.

2.2 Screening of other modifiers

Although the addition of EVA-2 resin has increased the tensile strength of the wax, it also increases the dynamic viscosity, resulting in reduced flowability, which adversely affects the wetting of cemented carbide particles during the ball-milling and spraying granulation process. Furthermore, the long chains of the resin tend to intertwine, resulting in a higher torque produced by the resin-modified wax during the ball-milling and granulation process compared with pure wax. To address these two problems, it is considered to add plasticizers to the resin-modified wax. Plasticizers can insert into gaps between the long chains of the resin, facilitating the untying of molecular chains and thus reducing their dynamic viscosity. To compare the effect of different environmentally friendly plasticizers on the performance of resin-modified wax, Di (2-propylheptyl) phthalate (DPHP) and Tri- (2-ethylhexyl) trimellitate (TOTM) were selected and added separately to the EVA-2-modified wax. Through systematic research, it is found that DPHP performs better, with specific details to be reported elsewhere.

Table 3 Summary of the characteristics of different resins

Resin	Compatibility	Tensile strength	Viscosity	Residual carbon	Ash
SEBS-1			×	×	×
SEBS-2			×	×	
EVA-1	×		×		
EVA-2					
APAO-1	×				
APAO-2					×
APP-1		×			
APP-2		×	×		
Terpene-1		×		×	×
Terpene-2	×	×			

For the modification of wax with surfactants, stearic acid (SA), nonylphenol polyoxyethylene ether (TX-10), sorbitan monostearate (S-60), polyoxyethylene sorbitan monostearate (Tween-60), and fatty alcohol polyoxyethylene ether (AEO-3) are chosen as the surfactants, each of which is added at a concentration of 5wt%. Through systematic research, it is found that SA performs better, with specific details to be reported elsewhere.

Previous studies have reported that microcrystalline wax has a strong viscosity, causing excessive adhesion between the green compacts and the mold, which can lead to problems during demolding due to sticking. The addition of oleic acid amide to the wax binder as a lubricant has been found to effectively reduce the adhesion between the green compacts and the mold[3], which is particularly important for the preparation of complex-shaped green compacts such as deep well-shaped ones. The melting point of ethylene bis-stearamide is 144–146 °C, which significantly differs from the melting point of the wax matrix. Upon heating, it dissolves in the wax and can be precipitated from the wax matrix during the subsequent cooling and solidification process, exhibiting poor compatibility with wax. In contrast, oleic acid amide (OAA) and erucicamide (EA) both have melting points below 80 °C and do not exhibit the precipitation phenomenon described above. Therefore, OAA and EA are selected as lubricant modifiers for the wax, with a lubricant concentration of 5wt%. Through systematic research, it is found that OAA performs better, with specific details to be reported elsewhere.

Briefly speaking, DPHP, SA and OAA are selected as plasticizer, surfactant and lubricant, respectively. Overall, EVA-2, DPHP, SA and OAA are selected as the four types of modifiers for the paraffin wax-based forming agent.

2.3 Orthogonal experiments

Some orthogonal experiments were performed in this work to quantitatively determine the mass ratios of these four modifiers in the forming agent.

The evaluation parameters used in the orthogonal experiment include five aspects: the physicochemical properties of the forming agent, thermal mass loss behavior of the forming agent, apparent density of the mixed powder, green compact density and sintered product performance. The physicochemical properties of the forming agent include density, penetration, cloud point, tensile strength, dynamic viscosity, residual carbon and ash content. It is required that the residual carbon and ash content should be less than 0.05wt% and 0.005wt% in industry, respectively[26].

Based on the preliminary experiments, the suitable proportions for EVA-2, DPHP, SA, and OAA are found to be 10wt%, 2wt%, 5wt% and 5wt%, respectively. With this information, nine orthogonal experiments are designed, as shown in Table 4.

2.3.1 Physical and chemical properties

For the modified forming agents of wax used in the nine orthogonal experiments, the residual carbons and ash contents (Table 5) meet the industrial requirements and do not exceed the average industrial level mentioned previously, which is crucial for ensuring stable quality of produced cemented carbide. There are no specific requirements for density, penetration and freezing point of the modified paraffin wax (Table 5). The greater the penetration, the softer the paraffin wax.

Aimed for higher tensile strength, the optimal combination of factors is 15 parts of EVA-2, 3 parts of DPHP, 6 parts of SA and 2 parts of OAA. For obtaining low kinematic viscosity, the optimal combination of factors is 5 parts of EVA-2, 2 parts of DPHP, 6 parts of SA and 2 parts of OAA. Therefore, it is evident that relying solely on the tensile strength and kinematic viscosity cannot lead to a consistent formulation for the forming agent, and other criteria need to

Table 4 Orthogonal experiments design about tensile strength, kinematic viscosity and pyrolysis residue

Sample No.	EVA-2	DPHP	OAA	SA	Tensile strentgh/kPa	Kinematic viscosity/mm^2·s^{-1}	Pyrolysis residue/%
1	5	2	2	2	1497	12.31	0.30
2	5	3	4	4	1509	12.04	0.72
3	5	4	6	6	1418	12.08	0.18
4	10	2	4	6	1526	20.80	0.35
5	10	3	6	2	1542	21.56	0.19
6	10	4	2	4	1448	21.37	0.23
7	15	2	6	4	1587	37.03	0.34
8	15	3	2	6	1666	36.56	0.22
9	15	4	4	2	1532	39.65	0.18
Mean 1 (tensile strength)	1474	1537	1537	1524	-	-	-
Mean 2 (tensile strength)	1505	1572	1522	1515	-	-	-
Mean 3 (tensile strength)	1595	1466	1515	1537	-	-	-
Extreme-difference (tensile strength)	120	106	21	22	-	-	-
Mean 1 (viscosity)	12	23.4	23	24.5	-	-	-
Mean 2 (viscosity)	21	23.41	24	23.4	-	-	-
Mean 3 (viscosity)	38	24.4	23.6	23.1	-	-	-
Extreme-difference (viscosity)	26	0.987	0.75	1.36	-	-	-
Mean 1 (pyrolysis)	0.40	0.33	0.25	0.22	-	-	-
Mean 2 (pyrolysis)	0.26	0.38	0.42	0.43	-	-	-
Mean 3 (pyrolysis)	0.25	0.20	0.24	0.25	-	-	-
Extreme-difference (pyrolysis)	0.15	0.18	0.18	0.21	-	-	-

Table 5 Physical and chemical properties of nine modified paraffin waxes

Sample No.	Density/g·mL^{-1}	Needle penetration (25 °C, 1/10 mm)	Freezing point/°C	Residual carbon/wt%	Ash/wt%
1	0.92	16.2	54	0.0078	0.0025
2	0.92	18.7	56	0.0078	0.0024
3	0.92	20.4	55	0.0088	0.0022
4	0.93	16.1	53	0.0087	0.0022
5	0.92	18.4	55	0.0078	0.0020
6	0.93	17.2	54	0.0070	0.0020
7	0.92	16.0	54	0.0100	0.0018
8	0.93	16.2	55	0.0060	0.0029
9	0.92	20.8	55	0.0090	0.0033

be considered.

2.3.2 Pyrolysis residue

In the DSC experiment (Fig. 6), the forming agent starts to thermally decompose at around 200 °C, which is caused by the removal of paraffin wax, and the decomposition process is completed at around 375 °C, which is caused by the removal of the four modifiers. The residual mass after these two processes is called pyrolysis residue, which is caused by the high temperature polymerization of organic macromolecules in the modified paraffin wax that cannot be volatilized and removed. According to the extreme-difference analysis, the significant influence of each factor on pyrolysis residue of the modified wax is as follows: SA>OAA=DPHP>EVA-2 (Table 4). Aimed for low pyrolysis residue, the optimal combination of factors is 15 parts of EVA-2, 4 parts of DPHP, 2 parts of SA and 6 parts of OAA (Table 4).

2.3.3 Apparent density and green compact density

A higher apparent density indicates better flowability of the mixed powder, making it easier to shape during compression. The extreme-difference analysis of the test data for the apparent density is shown in Table 6. It indicates that the significant influence of each factor on the apparent density of the mixed powder is as follows: OAA>EVA-2>SA>DPHP. Therefore, to increase the apparent density of the mixed powder, the lubricant oleic acid amide should be the primary consideration, while the plasticizer DPHP has the least effect on the apparent density. It is worth noting that although oleic acid amide has the least effect on the physicochemical properties of the modified wax, such as tensile strength and dynamic viscosity, it significantly affects the apparent density of the mixed powder.

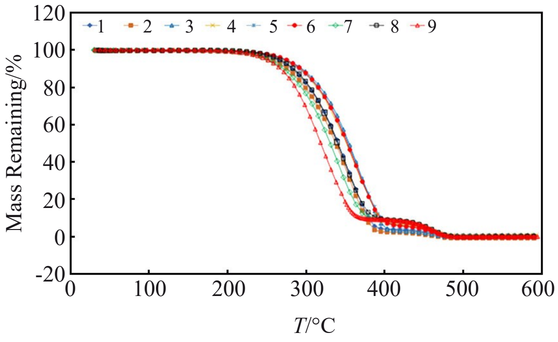

Fig.6 DSC heating curves of nine types of modified paraffin waxes listed in Table 4

The influence mechanism of the lubricant oleic acid amide on the apparent density of the mixed powder is as follows. Within a certain range of addition, oleic acid amid, as a lubricant, forms a lubricating film on the surface of the alloy powder, reducing friction between the powder particles, enhancing the flowability of the mixed powder, and thereby increasing its apparent density. However, with the further increase in oleic acid amid content, the lubricating film gradually thickens, and the increase in adhesion between particle surfaces counteracts the decrease in friction between particles[27], slightly reducing the flowability of the mixed powder and causing the decrease in apparent density, as shown in Table 6.

Aimed for a high apparent density of the mixed powder, the optimal combination of factors is 4 parts of OAA, 15 parts of EVA-2, 6 parts of SA and 2 parts of DPHP.

A higher green density results in better mechanical properties of the green compacts. The extreme-difference analysis of the green compact density is shown in Table 6. It indicates that the significant influence of each factor on green compact density is as follows: OAA>DPHP>EVA-2>SA.

Table 6 Orthogonal experiment of apparent density and green compact density

Sample No.	EVA-2	DPHP	OAA	SA	Apparent density/g·cm^{-3}	Green compact density/g·cm^{-3}
1	5	2	2	2	2.83	7.03
2	5	3	4	4	3.02	7.15
3	5	4	6	6	2.95	7.06
4	10	2	4	6	3.08	7.34
5	10	3	6	2	2.97	7.21
6	10	4	2	4	2.83	6.94
7	15	2	6	4	2.98	7.21
8	15	3	2	6	2.87	7.18
9	15	4	4	2	3.06	7.19
Mean 1 (apparent density)	2.93	2.96	2.84	2.95	-	-
Mean 2 (apparent density)	2.96	2.95	3.05	2.94	-	-
Mean 3 (apparent density)	2.97	2.95	2.97	2.97	-	-
Extreme-difference (apparent density)	0.04	0.01	0.21	0.02	-	-
Mean 1 (green compact density)	7.08	7.19	7.05	7.14	-	-
Mean 2 (green compact density)	7.16	7.18	7.23	7.10	-	-
Mean 3 (green compact density)	7.19	7.06	7.16	7.19	-	-
Extreme-difference (green compact density)	0.11	0.13	0.18	0.09	-	-

Similar to apparent density, the lubricant oleic acid amide is the dominant factor, affecting the green compact density. Aimed for a high green compact density of the mixed powder, the optimal combination of factors is 4 parts of OAA, 15 parts of EVA-2, 6 parts of SA and 2 parts of DPHP, which is exactly the same as that of apparent density.

2.3.4 Optimized formula of forming agent

In the formulation design of the forming agent, apparent density and green compact density are crucial test criteria, and the goal is to achieve the highest possible green compact density. Additionally, an excessive amount of stearic acid results in porous and less dense green compact originating from the reaction between stearic acid and metallic cobalt, leading to a reduction in green compact strength. Moreover, stearic acid can cause corrosion in the sintering equipment, so the amount of stearic acid should be minimized.

According to Table 7, it can be observed that a higher quantity of EVA-2 is advantageous for increasing apparent density and green compact density, reducing thermal decomposition residue, and lowering dynamic viscosity. However, it has a detrimental effect on tensile strength. Therefore, EVA-2 is selected with a quantity of 15 parts.

Among the nine samples, it is found that Sample 9, with 15 parts of EVA-2 and the lowest amount of SA (2 parts), exhibits a green compact density of 7.19 (g/cm^3), which is the third highest among the nine samples. At this point, the tensile strength of modified paraffin wax is 1532 kPa, also ranking as the third highest among the nine samples.

Table 7 Dosage of four modifiers relative to paraffin wax under optimized performance conditions (wt%)

Optimized condition	EVA-2	DPHP	OAA	SA
Apparent density& green compact density	15	3	2	6
Tensile strength	5	2	2	6
Pyrolysis residue	15	4	6	2
Kinematic viscosity	15	2	4	6

Based on this, the optimized formulation for the forming agent is Sample 9 (Table 4), with 100 parts of #58 paraffin wax, 15 parts of EVA-2, 4 parts of DPHP, 4 parts of OAA and 2 parts of SA. This formulation of modified paraffin wax is used in the subsequent industrial production of WC-Co cemented carbide with a deep well-shape.

2.4 Preparation of deep well-shaped WC-Co cemented carbide

2.4.1 Spraying granules

The spray granules made from both original paraffin wax and resin-modified paraffin wax are abbreviated as O-granules and M-granules and presented in Fig. 7a and Fig. 7b, respectively. Basically, both granules are spherical.

The minimum, maximum and mean particle sizes are 30, 230 and 120 μm, respectively, for O-granules (Fig.7c), and 60, 280 and 130 μm, respectively, for M-granules (Fig.7d). Thus, the particle size of M-granules is larger than that of O-granules. The paraffin wax modification can significantly improve the formability of spray granules. The apparent density of O-granules and M-granules is 3.08 and 3.13 g/cm^3, respectively (Table 8). The flowability of O-granules and M-granules is 36.7 s/50 g and 28.5 s/50 g, respectively (Table 8). Paraffin wax modification can notably enhance the flowability and apparent density of the sprayed granules.

2.4.2 Green compacts and sintered parts

In many Chinese companies, non-modified paraffin wax is used to produce spray granules, resulting in the inability to press qualified green compacts of deep well-shaped WC-Co

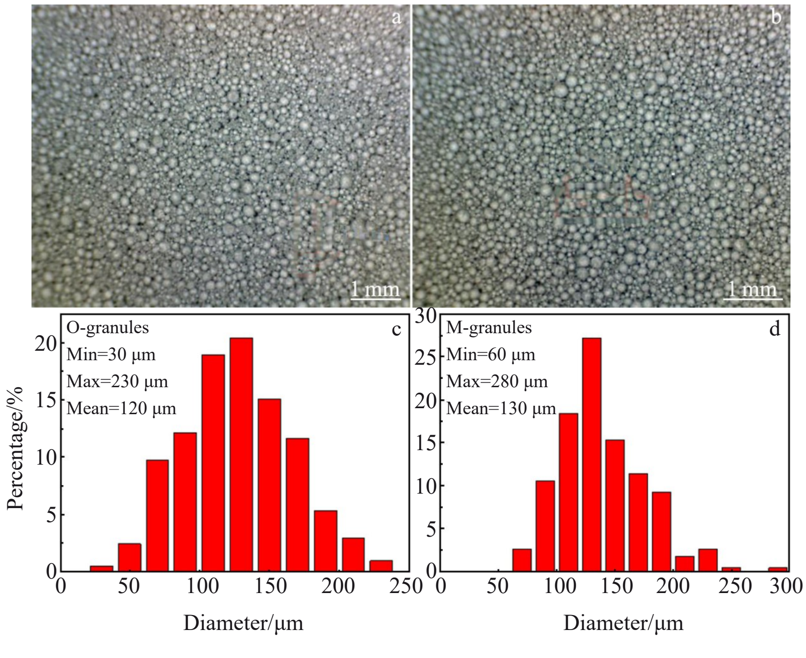

Fig.7 Appearances (a–b) and size distributions (c–d) of sprayed granules made from O-granules (a, c) and M-granules (b, d)

Table 8 Properties of industrial spraying granules

Spraying granule	Apparent density/g·mL^{-1}	Flowability/s·(50 g)$^{-1}$
O-granule	3.08	36.7
M-granule	3.13	28.5

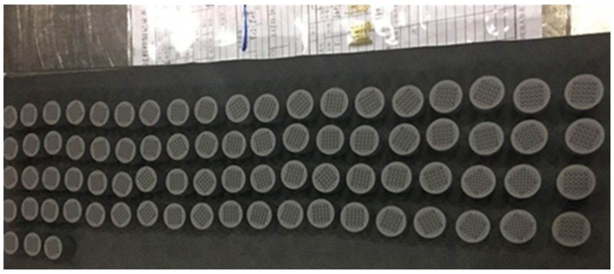

Fig.8 Green compacts produced by the forming agent of modified paraffin waxes

cemented carbides. The main problem is the sticking of the deep well-shaped protrusions, which prevents proper formation. However, one Chinese company used the modified paraffin wax developed in this work to manufacture spray granules and then press them into the qualified green compacts of deep well-shaped WC-Co cemented carbides (Fig. 8). That company can produce 11 qualified green compacts per minute, meeting production requirements.

The sintered piece obtained from the green compacts is shown in Fig. 9a. It features numerous deep well-shaped protrusions, with a height of 0.98 mm and a square top surface with 1.10 mm in side length. The sintered piece has a height of 15.62 mm, diameter of 21.14 mm, mass of 76.10 g and density of 14.52 g/cm^3. Both hardness and bending strength of the deep well-shaped cemented carbides are measured and the average values are 88.3 HRA and 3529 MPa, respectively. All these values meet the product specifications. XRD analysis indicates that this cemented carbide contains only WC (PDF No. 73-471) and Co (PDF No. 15-806) phases (Fig.9b), which is a normal cemented carbide with the two phases.

OM (Fig. 9c) and SEM (Fig. 9d) images show that the interior of the sintered piece consists of many rectangular WC-Co cemented carbide grains, with approximate dimensions of 2 μm in length and 1 μm in width. There is approximately a 0.5 μm gap between these grains. EDS results of the end

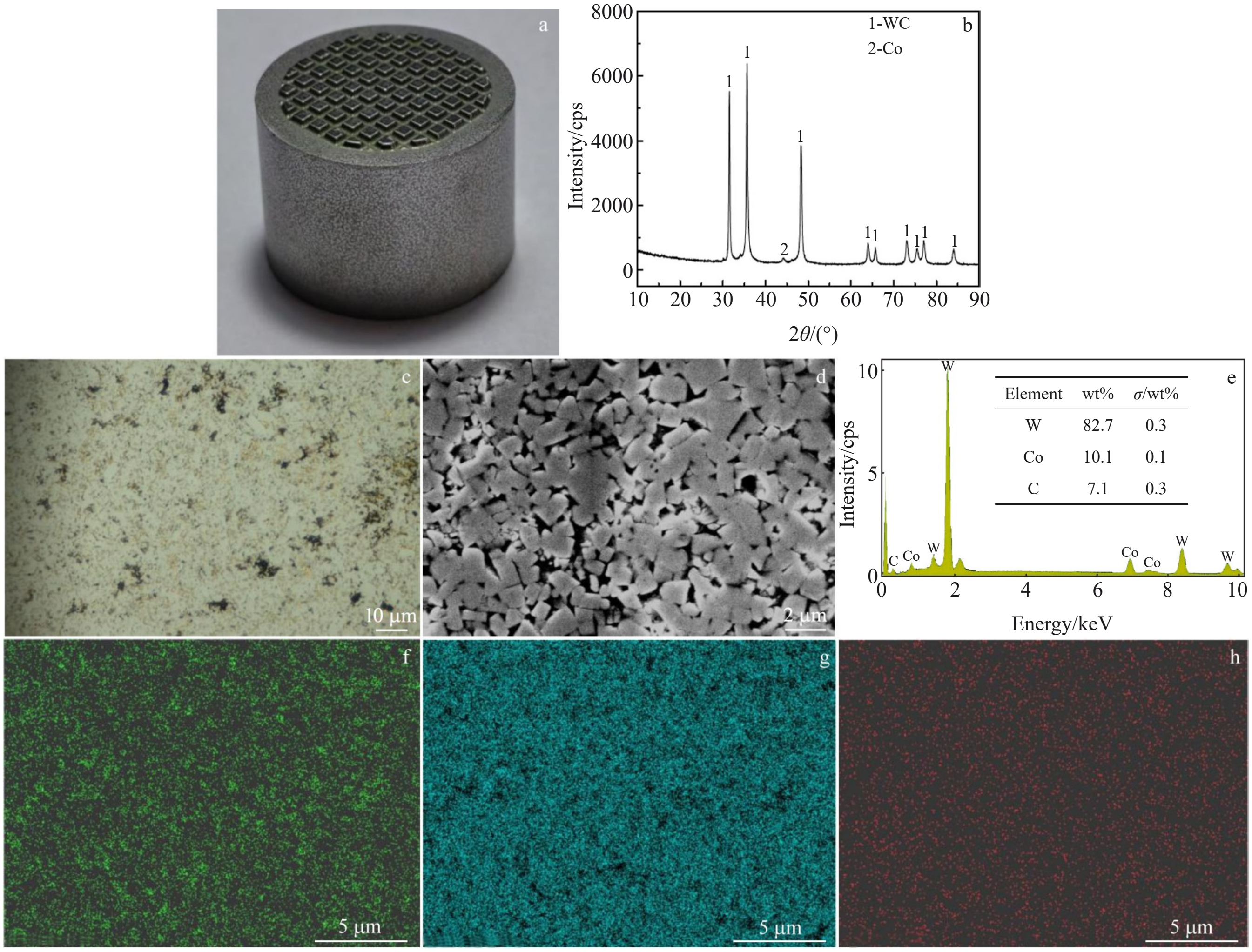

Fig.9 Appearance (a), XRD pattern (b), OM image (c), SEM image (d), EDS analysis result (e) and EDS mappings of element Co (f), W (g) and C (h) of surface of deep well-shaped WC-Co alloy block made in industry

surface of the cemented carbide cylinder indicate that metal Co content is approximately 10wt% (Fig. 9e), meeting the product specification. The carbon content is 7.1wt% (Fig. 9e), which is higher than the theoretical C content of 6.12wt%. σ in Fig. 9e represents the standard deviation (wt%) of element content. Considering the high Co content (10wt%) in the alloy, the carbon content width of the two-phase zone might be large, so this carbon content may also be a normal value. In addition, the EDS analysis results of C element have a larger error compared with that of other elements such as Co, so this larger C content may also be caused by EDS analysis errors. The distribution of the three elements Co, W and C is shown in Fig. 9f−9h, respectively. The three elements are uniformly distributed inside the cemented carbide, which is beneficial for achieving good mechanical properties of the cemented carbide.

The linear shrinkage coefficient of the green compacts during pressing is also determined, and the formula for calculating the linear shrinkage coefficient is as follows:

$$K = \sqrt[3]{V_1/V} \tag{2}$$

where K represents the linear shrinkage coefficient, V_1 the volume of the pressed green compact and V the volume of the sintered product. It is determined that the linear shrinkage coefficient (K) for the sintered deep well-shaped WC-Co cemented carbide (Fig. 9a) is 1.253, which meets the product specifications.

3 Conclusions

1) Using non-modified paraffin wax to produce spray granules cannot obtain qualified green compacts for deep well-shaped WC-Co cemented carbides, while using the optimized modified paraffin wax for spray granules can do.

2) Paraffin wax modification significantly improves the flowability and apparent density of spray granules of paraffin wax.

3) The possible reason for the improved compatibility between resin and paraffin wax is the insertion of small resin molecule chains into the paraffin wax crystal gaps.

4) Considering the compatibility, tensile strength, viscosity, residual carbon and ash content of resin-modified paraffin wax, EVA-2 performs the best among all the selected resins.

5) The optimized formulation for the forming agent is: 100 parts of #58 paraffin wax, 15 parts of EVA-2, 4 parts of DPHP, 4 parts of OAA and 2 parts of SA.

References

1 Hsu K C, Lin C C, Lo G M. *Canadian Metallurgical Quarterly*[J], 1996, 35: 181
2 Chen Shuanglin, Fu Kun, Zhou Jianhua. *Pneumatic Tools for Rock Drilling Machinery*[J], 2013, 1: 46 (in Chinese)
3 Tang Kai, Yan Jie, Huang Xin. *Cemented Carbide*[J], 2008, 25: 28 (in Chinese)
4 Zaky M T, Soliman F S, Farag A S. *Journal of Materials Processing Technology*[J], 2009, 209: 5981
5 Zheng Guoliang, Zheng Chen. *Rare Metals and Cemented Carbides*[J], 1992, 2: 39 (in Chinese)
6 Qu Xuanhui, Gao Jianxiang, Qin Mingli *et al*. *International Journal of Refractory Metals & Hard Materials*[J], 2005, 23: 273
7 Peng Yida, Dai Yongchuan, Zhao Dezhi *et al*. *Journal of Liaoning Shihua University*[J], 2018, 38: 13 (in Chinese)
8 Liu Shuhong. *Investigation of TiH2 Powder Injection Molding*[D]. Changsha: Hunan University, 2009 (in Chinese)
9 Zhou Zhuyi. *Chinese Patent, CN109175352A*[P], 2019
10 Zhou Jian. *Chinese Patent, CN105176636A*[P], 2015
11 Li Yuheng, Liu Xuemei, Liu Chao *et al*. *Rare Metal Materials and Engineering*[J], 2021, 50(6): 2169 (in Chinese)
12 Shi Kaihua, Zhou Kechao, Li Zhiyou *et al*. *Rare Metal Materials and Engineering*[J], 2016, 45(12): 3149 (in Chinese)
13 GB/T 265-1988[S]. 1988 (in Chinese)
14 Wang Biqiong, Cheng Shibing, Zhang Piaoling. *Guangdong Chemical Industry*[J], 2013, 40(5): 39 (in Chinese)
15 SH/T 0402-1992[S]. 1992 (in Chinese)
16 GB/T 4985-2010[S]. 2010 (in Chinese)
17 GB/T 268-1987[S]. 1987 (in Chinese)
18 GB/T 508-1985[S]. 1985 (in Chinese)
19 GB/T 1482-2010[S]. 2010 (in Chinese)
20 Chu Junfeng, Li Hongxia, Zhang Liqun. *New Chemical Materials*[J], 2023, 51(8): 124 (in Chinese)
21 Li Jing, Li Conghui, Wang Fanghui. *Membrane Science and Technology*[J], 2023, 43(2): 95 (in Chinese)
22 Wang Hongxue, Zhao Suyuan, Ba Xuduo. *Chemistry and Adhesion*[J], 1998, 5: 110 (in Chinese)
23 Li Yanyan, He Xuelian, Liu Boping. *Journal of East China University of Science and Technology, Natural Science Edition*[J], 2016, 42(1): 35 (in Chinese)
24 Peng Zhigang, Qi Zhigang, Cao Huilian *et al*. *China Rubber/Plastics Technology and Equipment*[J], 2015, 41(6): 42 (in Chinese)
25 Pan Liang, Gao Jian, Zhou Xianmin *et al*. *Automobile Technology & Material*[J], 2022(6): 47 (in Chinese)
26 NB/SH/T 0888-2014[S]. 2014
27 Lin Tao, Guo Shiju, Li Mingyi *et al*. *Powder Metallurgy Technology*[J], 2000, 18(1): 8 (in Chinese)

难成形生坯用石蜡的改性及其在WC-Co硬质合金中的应用

李　毅[1,2]，王锦程[1]，倪　娟[2]，沈少波[2]
(1. 西北工业大学 材料学院，陕西 西安 710072)
(2. 江苏泰尔新材料股份有限公司，江苏 苏州 410075)

摘　要：工业模压生产深井字形WC-Co硬质合金块是一个难以解决的技术难题，主要是所用石蜡基成形剂不合适造成的。采用有机高分子树脂、增塑剂、表面活性剂和润滑剂这4种改性剂对成形剂石蜡做了改性，研究了树脂种类的定性筛选和4种石蜡改性剂组合的正交实验，以得到改性剂的优化定量比例。结果表明，树脂中小分子插入石蜡支晶间隙可能是树脂和石蜡相容性提高的一个重要原因。通过正交实验，确定了成型剂的最佳配方为：100份58#石蜡、15份EVA-2、4份DPHP、4份油酸酰胺和2份硬脂酸。该优化配方在一家中国公司的工业生产中得到了应用，生产出了质量合格的深井形状硬质合金产品，其中WC质量分数为90%，Co质量分数为10%。

关键词：WC-Co硬质合金；深井字形产品；成形剂；石蜡改性剂；树脂筛选；改性剂比例优化

作者简介：李　毅，男，1964年生，博士生，西北工业大学材料学院，陕西 西安 710072，E-mail：wwwlee@chinawaxes.com