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Preparation of nano - coating powder $CaF_2@Al(OH)_3$ and its application in $Al_2O_3/Ti(C,N)$ self-lubricating ceramic tool materials



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ABSTRACT

Nano CaF_2 particles of different sizes were prepared by direct precipitation. The diameters of nano CaF_2 particles prepared in mixed solvent can reach 5–7 nm, and can be effectively dispersed. The surface of nano CaF_2 was modified and coated by heterogeneous nucleation method. A shell layer of $Al(OH)_3$ was coated on the surface of nano CaF_2 , and the structure and coating mechanism of the coated powder were analyzed. Under varying preparation conditions, the surface morphology of $CaF_2@Al(OH)_3$ was analyzed using TEM and SEM. The results showed that the coating powder showed good dispersion in mixed solvents, and the particle size of the composite powder was about 20 nm. Self-lubricating ceramic tool materials were prepared by adding coating particles to the $Al_2O_3/Ti(C,N)$ matrix. The coating powder shell and the matrix material melt during sintering, so that CaF_2 forms nanostructures in the particles. thereby improving the mechanical properties of the material. Cutting experiments show that the addition of coating particles can effectively reduce the temperature, cutting force and friction coefficient in the cutting process of the tool, thus improving the cutting performance of the tool material.

1. Introduction

Developing advanced tool materials suitable for dry cutting has become an important research direction in the field of high-speed dry cutting. Self-lubricating ceramic tool materials are prepared by introducing solid lubricant into the ceramic matrix, so that the tool provides anti-friction and anti-wear capabilities. This realizes an organic combination of ceramic tools and lubrication and is an effective way to improve the performance of dry cutting tools [1-3]. Common high temperature solid lubricants include CaF2 [4], h-BN [5], and MoS2 [6]. Adding micron-sized CaF₂ particles to ceramic materials allow for good self-lubricating abilities, which will effectively reduce the friction coefficient of ceramic tool materials in cutting processes and improve cutting conditions [7]. Calcium fluoride solid lubricant was added to Al₂O₃/TiC material to prepare self-lubricating ceramic tools. In the cutting process, the friction coefficient at the interface between the tool and the chip can be significantly reduced. CaF₂ forms a lubricating film on the tool-chip interface due to the action of cutting heat and acts as a lubricant in the machining process [8]. In addition, it was found that the friction coefficient decreases with the increase of calcium fluoride content, sliding speed and sliding load. Under high speed and high load, the wear surface will also form a lubricating layer, thus displaying the antifriction and wear resistance of self-lubricating materials under high speed and load [9]. Lu [10] prepared Y-TZP/MoS₂ composites with unique microstructures and good mechanical properties. The friction properties of the composites at room temperature were studied. The results show that the Y-TZP/MoS₂ composite exhibits good antifriction and wear resistance. With increasing MoS₂ volume fraction, the friction coefficient and wear rate of the composite decrease. The composites containing 50% MoS₂ have excellent antifriction and antiwear properties with friction coefficients and wear rates as low as 0.25 and $1.02\,\times\,10^{-6}m^3/Nm.$ However, due to the poor mechanical properties of solid lubricants, direct addition to the material will reduce the mechanical properties of the material. The higher the solid lubricant content, the lower the friction coefficient and mechanical properties of the self-lubricating material [11]. Particle surface modification can provide enhanced and uniform mixing of in different phases in the composite powder, effectively improving the material properties, and providing new chemical functionalities [12-16]. Therefore, by modifying the surface of the solid lubricant and then adding it to the material matrix, the mechanical properties of the material can be significantly improved. There are many methods for particle surface modification, such as the liquid method [17,18], gas method [19], and mechanochemical methods [20]. These methods have both advantages and disadvantages. Wu [21] synthesized h-BN@Ni powder with a coreshell structure by electroless plating. Compared with Al₂O₃/(W,Ti)C

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composites prepared by adding uncoated h-BN powder, $Al_2O_3/(W,Ti)C$ composites prepared by adding h-BN@Ni powder have significantly improved microstructures and mechanical properties. The dry sliding friction test shows that the composites mixed with h-BN@Ni have lower friction coefficients and higher wear resistance. Zhang [22] and Chen [23] et al. prepared alumina-coated solid lubricant composite powders by heterogeneous nucleation and added to the tool matrix. Mechanical property tests show that the microstructure, fracture toughness and bending strength of the material have been significantly improved. Cutting tests show that ceramic tools with coated powder have better antifriction performance and wear resistance than corresponding tools.

It is well known that nano ceramic materials have many advantages. such as high toughness and strength [24]. The addition of nano-particles has a significant effect on the comprehensive mechanical properties of ceramic materials [25]. Niihara [26] and Nakahira [27] have studied ceramic nano-materials and have revealed that 5vol% silicon carbide nano-particles were dispersed into an Al₂O₃ matrix to increase the room temperature strength of ceramic materials from 350 MPa to 1.0 GPa. Yi et al. [28] prepared nano-scale CaF2 particles and added them to a the ceramic tool material to obtain high performance composite ceramic tool materials. The hardness, toughness and bending strength of the composite ceramic materials containing nano-sized CaF2 particles were significantly improved compared to conventional self-lubricating ceramics. However, the study found that there was aggregation and abnormal growth in the process of sintering. Synthesis, dispersion and particle surface modification of nano-particles is an important problem in the application of nano-technology [29-31]. Particle surface modification is also one of the important methods to modernize the application of nano-particles. Studies on the nucleation and growth mechanism of nano-particles in the preparation of particles and surface modification of particles have accelerated the development of related subjects and fields [32,33].

In this paper, nano-CaF₂ with different particle sizes were prepared by direct precipitation method. An Al(OH)₃ shell was coated on the surface of nano-CaF₂ particles by non-uniform nucleation methods to prepare composite particles with shell-core structures. CaF₂@Al₂O₃ composite particles can be obtained by appropriate heat treatment. This paper primarily mainly studies the influence of experimental parameters on the surface morphology and formation mechanism of the coating. Finally, the composite particles were added to the Al₂O₃/Ti (C,N) ceramic matrix as a solid lubricant to prepare self-lubricating ceramic tool materials with excellent performance.

2. Experimental procedure

2.1. Preparation of nano- CaF_2 particles

The reagents used in this experiment are shown in Table 1.

According to the volume ratio of 6:2:1, ethanol, benzene, and water are mixed to prepare a mixed solvent. A proper amount of NH_4F powder was weighted prepare a 0.22 mol/L NH_4F solution (A). To ensure sufficient reaction, ammonium fluoride was used in excess of 10% when preparing the solution. An appropriate amount of $Ca(NO_3)_2$ powder was added to prepare 0.1 mol/L $Ca(NO_3)_2$ solution (B). Solution A and the solution B were simultaneously poured into a pre-configured mixed solvent while being quickly and uniformly stirred. The chemical

Table 1

| Raw | materials | usea | m | une | test. | |
|-----|-----------|------|---|-----|-------|--|
| | | | | | | |

| Name | Specifications | Chemical formula |
|----------------------|-------------------|-----------------------------------|
| Xylene | analytically pure | C ₈ H ₁₀ |
| Calcium nitrate | analytically pure | Ca(NO ₃) ₂ |
| Ammonium fluoride | analytically pure | NH4F |
| Polyvinylpyrrolidone | analytically pure | PVP |

equation of the two reactions is as follows:

$$Ca(NO_3)_2 + 2NH_4F \rightarrow CaF_2\downarrow + 2NH_4(NO_3)$$
(1)

After the reaction was completed, the reaction product was centrifuged at a speed of 10000 r/min and washed four times alternately with deionized water and anhydrous ethanol. The centrifuged product is placed in a vacuum drying oven at 120 °C for 12 h to finally prepare nano CaF₂.

2.2. Preparation of Al(OH)₃-coated CaF₂ nanoparticles

The volume ratio of alcohol to benzene to water was 6:2:1 as a mixed solvent, and a proper amount of polyvinylpyrrolidone (PVP) was added as the dispersant. Using this as a solvent, 0.01 mol of nano-CaF₂ prepared in advance was added and fully ultrasonically stirred to prepare a diluted suspension of 0.1 mol/L. An Al(NO₃)₃·9H₂O solution with specified concentration was prepared and buffered with HAc (analytical purity) and NaAc (chemical purity) to control the pH value of the suspension. The suspension was placed in a DF-101S heat-collecting constant-temperature heating magnetic stirrer and stirred. After heating to 75 °C, slowly add dilute ammonia water dropwise, adjust the pH value of the suspension to 7.5, and keep the suspension warm for 1 h. The reaction product Al(OH)₃ was non-uniformly nucleated on the surface of nano CaF₂ to form a coating layer, and the reaction chemical equation is as follows:

$$Al^{3+} + 3NH_3H_2O \rightarrow Al(OH)_3\downarrow + 3NH^{4+}$$
⁽²⁾

The prepared $CaF_2@Al(OH)_3$ was centrifuged, cleaned and dried in a drying oven to obtain $CaF_2@Al(OH)_3$ coated powder. The coated nano-particles $CaF_2@AlO_3$ were obtained after sintering at 850 °C.

2.3. Preparation of self-lubrication ceramic tools

The materials required for preparing the self-lubricating ceramic tools are shown in Table 2.

Weigh the raw materials in proportion respectively. Through mixing ball milling, vacuum drying and filling into the graphite mold. Al₂O₃/Ti (C,N)/CaF₂@Al(OH)₃ self-lubricating ceramic tool materials with shell-core structures were prepared by vacuum hot pressing sintering. The specific sintering parameters are: sintering temperature of 1650 °C, heating rate of 20 °C/min, holding time of 15min, and hot pressing pressure of 30 MPa.

2.4. Testing and characterization methods of materials

The particle size and dispersion of the prepared CaF₂ nanoparticles were observed by transmission electron microscopy (TEM). The morphology and dispersion of Al(OH)₃-coated CaF₂ particles were observed by thermal field emission scanning electron microscope (SEM). The phase composition of nano CaF₂ and the coated powders was analyzed by X-ray diffractometer (XRD). The obtained ceramic was observed by high resolution transmission electron microscope (HRTEM). The ceramic tool materials were processed into a spline with a surface roughness of less than 0.1 μ m and a size of 3 mm \times 4 mm \times 20 mm. Vickers hardness and fracture toughness of the materials were measured by an indentation method. The indentation load was 196 N and

| Table 2 | | | | |
|---------------------------|-----------|-------------|---------|--------|
| Materials for preparation | of self - | lubricating | ceramic | tools. |

| Name | Chemical formula | Size (nm) | Ratio (%) |
|-----------------------|---------------------------------------|-----------|-----------|
| Alumina | Al ₂ O ₃ | 200 | 67.30 |
| Titanium carbonitride | Ti(CN) | 80 | 22.20 |
| Magnesium oxide | MgO | 1000 | 0.5 |
| Coated powder | CaF ₂ @Al(OH) ₃ | 10–30 | 10 |



Fig. 1. Nano CaF₂ particles prepared in different solvents: (a) the pure water, (b) the volume of C_2H_5OH and H_2O ratio of 1:1, (c) the volume of C_2H_5OH , C_8H_{10} and H_2O ratio of 6:2:1.

the holding time was 15 s. The bending strength of materials was measured by a three-point bending method. The displacement loading speed was 0.5 mm/min, and the span was 20 mm.

2.5. Cutting test

The model of the machine tool used in the cutting test is CDE6140A. The model of the tool shank is Kena GSSN R/L 2525M12-MN7. The cutting temperature in the cutting process was measured by infrared thermal imager (FLAR-A320). The Kistler-9129A dynamometer was used to measure the cutting force during cutting. The selected cutting workpiece material is 40Cr hardened steel, which has wide application and high hardness and strength.

3. Results and discussion

3.1. Characterization of nano-CaF₂ particles

Fig. 1 shows the TEM detection results of CaF₂ particles prepared in different reaction solutions. In Fig. 1(a), CaF₂ prepared in pure water solution has a significantly uneven particle size. It also has a particle size greater than 100 nm, which is due to the formation of a large number of calcium fluoride particles together. From Fig. 1(b), it was found that adding a certain amount of ethanol to the solution can significantly reduce the particle size of CaF₂, with an average particle size of 30-50 nm. As the particle size of nano-powder decreases, the particles have noticeable agglomeration. This is primarily because the particle size of the nano-powder decreases leading to larger specific surface area and higher surface energy of the particles. Nanoparticles show stronger small size effect and surface effect, thus showing more obvious agglomeration. In Fig. 1(c), it can be seen that by using a mixed solvent composed of ethanol, water and xylene in a ratio of 6:2:1 as a reaction solution, nanoparticles having a smaller particle size can be prepared. The average particle size of CaF₂ produced by the reaction can reach 5-10 nm, and shows good dispersibility.

Fig. 2 is an XRD pattern of CaF_2 powder prepared under different conditions. Only the characteristic peak of CaF_2 exists in the figure, and



Fig. 2. XRD patterns of CaF_2 precipitates prepared: (a) the pure water, (b) the volume of C_2H_5OH , C_8H_{10} and H_2O ratio of 6: 2:1.

no other impurity phases are generated. Characteristic peak analysis shows that the main phase belongs to cubic perovskite type with good crystallinity. Moreover, it can be seen from Fig. 2(b) that the diffraction peak of CaF_2 prepared in the composite solvent is obviously widened. According to the Scherrer formula [15], the average grain size of CaF_2 prepared with aqueous solution as the reaction medium is 52 nm (Fig. 1(a)), while the average grain size of CaF_2 prepared in a compound solvent is about 8 nm (Fig. 1(c)). This is consistent with the results observed by TEM.

3.2. Effect of different technical parameters on the preparation of $Al(OH)_3$ -coated CaF_2 nanoparticles

(1) The influence of Al^{3+} concentration



Fig. 3. HRTEM images of nano coated powder produced at different Al³⁺ concentration: (a) 0.1 mol/L (b) 0.3 mol/L (c) 0.5 mol/L.

As shown in Fig. 3(b), a lattice stripe representing CaF_2 can be observed and judged to be nano CaF₂. According to the lattice fringes, it can be judged that the particle size of CaF₂ is about 10 nm. When the concentration of Al^{3+} is 0.3 mol/L, a layer of amorphous Al(OH)₃ is uniformly coated on the surface of CaF₂ particles, and the thickness of the coating material is 5-10 nm. As shown in Fig. 3(a), when the concentration of Al^{3+} in the solution is 0.1 mol/L, no Al(OH)₃ coating is observed on the surface of most CaF2 particles. This is because under alkaline conditions, if the concentration of Al³⁺ is too low, the driving force for the reaction between Al³⁺ and OH⁻ will be insufficient. However, when the concentration of Al^{3+} is 0.5 mol/L, as shown in Fig. 3(c), a large amount of amorphous substance exists between nano the CaF_2 particles. This is because the concentration of Al^{3+} in the solution is higher than the critical concentration of non-uniform nucleation, and Al^{3+} and OH^{-} and a large amount of uniform nucleation occurs in a short time. At the same time, due to poor diffusion conditions, this will cause a large number of coated CaF₂ particles to much larger particle.

Fig. 4 is a TEM image of the coated powder agglomerate growth. When the concentration of CaF_2 in the liquid environment is increased, a large number of CaF_2 particles will gather to form larger particles. These agglomerated CaF_2 particles will be uniformly coated by Al (OH)₃. It can be seen from Fig. 4(a) that the nano-CaF₂ inside the

coating exhibits a certain aggregation phenomenon. The size of these agglomerated CaF_2 particles can be as large as 100 nm, at which time the coated powder has a relatively good dispersion effect.

(2) The influence of titration speed of dilute ammonia aqueous solution

When the titration rate is 2 mL/min, the coating reaction proceeds slowly, and the generated aluminum hydroxide is uniformly coated on the surface of CaF₂ (Fig. 5(a)). As shown in Fig. 5(b), when the ammonia titration rate was 4 mL/min, a layer of ultrafine amorphous substance can be found around the nano CaF₂ particles. However, since the titration speed is too fast and the chemical reaction is robust, the local saturation is too high in the solution. Amorphous Al(OH)₃ grows fast, resulting in uneven coating. In addition, more Al(OH)₃ exists in the form of direct precipitation. Therefore, accelerating the titration speed of ammonia water will lead to poor coating effect of particles.

(3) Influence of pH

The pH value of the solution has an important influence on the morphology and structure of aluminum hydroxide. It was found that Al $(OH)_3$ exists in an amorphous state when the pH value is lower than 4. As pH increases, Al $(OH)_3$ will gradually change from the amorphous



Fig. 4. TEM images of agglomeration growth of coat powder: (a) excess CaF₂ Concentrations (b) a partially enlarged view of Fig. (a).



Fig. 5. TEM photos of CaF₂@Al(OH)₃ nano-composite particles with different titration rates: (a) 2 mL/min (b) 4 mL/min.



Fig. 6. TEM images of CaF₂@Al(OH)₃ nanocomposite particles prepared at different pH: (a) 6.5, (b) 7.5 and (c) 8.

state to the crystalline state. As shown in Fig. 6(a), when the pH value is 6.5, no obvious $Al(OH)_3$ is found on the surface of the nanoparticles. As the pH rises to 7.5, it can be seen that a layer of obvious $Al(OH)_3$ appears around CaF_2 (as shown in Fig. 6(b)). However, when the pH value further increases, the thickness of the coating increases. And the particles are connected by $Al(OH)_3$ to form larger particles, which will adversely affect the dispersion of coated particles (as shown in Fig. 6(b)). This is primarily due to the increasing number of OH⁻ groups to Al^{3+} as the pH of the solution increases. A significant amount of Al (OH)₃ heterogeneous nucleation growth also occurred.

3.3. Analysis of CaF₂@Al(OH)₃ by SEM and XRD

Fig. 7(a) is an SEM image of CaF₂@Al(OH)₃ coated powders. From the figure, it can be found that the average particle size of the coated particles is 20–30 nm, which provides a good dispersion effect. Fig. 7(b₁) is an XRD pattern of CaF₂@Al(OH)₃ coated powders. Obvious characteristic peaks of CaF₂ and NH₄(NO₃) can be observed in the figure. NH₄(NO₃) is an impurity phase and can be removed by hightemperature calcination. Because aluminum hydroxide is amorphous, it cannot show characteristic peaks on XRD patterns. CaF₂@Al(OH)₃ powders were heated to 850 °C in a muffle furnace and kept warm for 2 h. NH₄(NO)₃ will fully decompose during heating. Al(OH)₃ was dehydrated during heating to form Al_2O_3 . Finally, $CaF_2@Al_2O_3$ coated powders were prepared (The XRD pattern is shown in Fig. 7(b₂)).

It is generally believed that the growth mechanism of nanoparticles is controlled by Ostwald-ripening (OR) [18] and Oriented-attachment (OA) [19]. The Aggregative Growth theory [20,21] that large particles can be formed by direct fusion between nanoparticles (as shown in Fig. $8(a_2)$). In the process of preparing CaF₂ particles coated with Al (OH)3 by heterogeneous nucleation, we can control the nucleation potential barrier between homogeneous nucleation and heterogeneous nucleation, so that single particle coating can be achieved. However, When the Al³⁺ concentration and pH value in the solution environment are too low, although the nucleation process occurring at this time belongs to heterogeneous nucleation, the particle surface cannot form a complete coating (as shown in Fig. $8(b_1)$). When the Al³⁺ and pH value in the liquid phase environment are too high, a large amount of homogeneous nucleation will occur in the solution, thus generating a large amount of Al(OH)3, which will lead to contact and fusion between different nano-CaF₂ particle coatings (as shown in Fig. $8(b_3)$).

3.4. $Al_2O_3/Ti(C,N)$ ceramic tools with $CaF_2@Al_2O_3$ powders

As shown in Fig. 9, The diameter of nano CaF_2 particles in Al_2O_3 /Ti (C,N) ceramic tools is less than 10 nm, and they maintain relatively



Fig. 7. SEM micrograph and XRD pattern: (a) CaF₂@Al(OH)₃ powders (b₁) CaF₂@Al(OH)₃ powders (b₂) CaF₂@Al₂O₃ powders.

good dispersibility. CaF₂ has a melting point of 1430 °C (when the material size reaches the nanometer scale, the melting point will be lower). However, when the sintering temperature of the material reaches 1650 °C, there is no obvious melting loss and agglomeration of CaF₂ nanoparticles. This shows that the coating design prevents agglomeration and loss of nanoparticles during hot pressing and sintering. During the sintering process, the alumina coating on the CaF₂ surface and the matrix material will be integrated. However, CaF₂ is completely coated in alumina ceramic matrix to form an in-crystal structure.

Under certain sintering conditions, self-lubricating ceramic tool

materials with direct addition of 10 vol% CaF_2 and addition of 10 vol% $CaF_2@Al_2O_3$ were simultaneously prepared. The test results of the mechanical properties are shown in Table 3. The comprehensive mechanical properties of ceramic materials coated with powder are better than those of materials directly coated with solid lubricant. This is because the mechanical properties of lubricants are poor and directly adding them to ceramic materials will lead to a significant reduction in material properties. However, the mechanical properties of lubricants can be improved by coating a layer of compact shell on its surface, thus enhancing the performance of self-lubricating materials.



Fig. 8. Theoretical sketch of the nucleation and growth of nanoparticles and the modification of the surface coating.



Fig. 9. HRTEM images of self-lubrication ceramic tools.

| Table 3 | |
|------------|------------------------------|
| Mechanical | properties of ceramic tools. |

| I I I I I I I I I I I I I I I I I I I | | | | |
|--|--------------|---------------------|----------|--|
| Material | Flexural | Fracture toughness/ | Hardness | |
| | strength/MPa | MPa·m $^{1/2}$ | /GPa | |
| $\begin{array}{l} Al_2O_3/\text{Ti}(\text{C},\text{N})/10\text{vol}\%\text{CaF}_2\\ Al_2O_3/\text{Ti}(\text{C},\text{N})/10\text{vol}\\ \%\text{CaF}_2@\text{Al}(\text{OH})_3 \end{array}$ | 432 | 5.79 | 17.91 | |
| | 471 | 6.50 | 18.58 | |

3.5. Analysis of cutting performance of self-lubricating ceramic tool materials

(1) Effect of Adding CaF₂@Al₂O₃ on Cutting Temperature

In order to ensure the accuracy of the experimental results, the cutting tool is selected to measure the temperature after the stable cutting 40Cr reaches 500 m depth of cut $a_p = 0.2$ mm, feed rate f = 0.102 mm/r, the results are shown in Figs. 10 and 11. The test results show that ceramic cutting tools with coated solid lubricant have obviously lower cutting temperature at two different cutting speeds, which proves that the addition of coated powder can effectively reduce the cutting temperature of the cutting tools. When the cutting speed is 100 m/min, the cutting temperature of ceramic tools with coated nanosolid lubricants is reduced by 29% compared to traditional tools. When the cutting speed is 200 m/min, the cutting temperature of the tool is reduced by 31%. This is because the introduction of nano solid lubricant effectively reduces the friction coefficient and changes the friction environment in the cutting process. The solid lubricant separated out from the cutting surface of the cutter is dragged by the cutting chips to form a film, which is more beneficial to the dispersion of cutting temperature.

(2) Effect of adding CaF₂@Al₂O₃ on cutting force and friction coefficient

Under the cutting conditions: depth of cut $a_p = 0.2$ mm, feed rate f = 0.102 mm/r, and cutting speed of 200 m/min, the average measurement results of three cutting forces for the two tools during cutting are shown inFig. 12.

According to the main cutting force Fz and radial force Fy measured in the cutting process, the friction coefficient of the tool rake surface can be calculated, as shown in formula (4.1):

$$\mu = \tan(\gamma_0 + \arctan(\frac{F_y}{F_z})$$
(4.1)

Compared with the cutter materials without lubricant, the three cutting forces of ceramic cutter materials with coated solid lubricant are obviously reduced. Through formula calculation, it is found that the friction coefficient of $Al_2O_3/Ti(C,N)$ ceramic tool is 0.485, and that of $Al_2O_3/Ti(C,N)/CaF_2@Al_2O_3$ ceramic tool is 0.39. This is mainly due to the introduction of $CaF_2@Al_2O_3$, which effectively improves the friction environment between the tool and the workpiece in the cutting process, thus reducing the friction coefficient and cutting temperature.

4. Conclusions

- 1. Nano-CaF₂ particles of different sizes were prepared by direct precipitation. The diameters of nano-CaF₂ particles prepared in mixed solvent were less than 10 nm and showed good dispersibility.
- 2. Al(OH)₃ was coated on the surface of nano-CaF₂ by heterogeneous nucleation. When the pH value was 7.5, the Al³⁺ concentration was 0.03 mol/L and the titration speed was 2 mL/min, and the nano-particles showed good coating ability. Through HRTEM imaging, the core size of the coated particles is less than 10 nm, and the thickness of the Al(OH)₃ coating is about 5–10 nm. Al(OH)₃ will be dehydrated by high temperature heating to obtain Al₂O₃-coated CaF₂ composite powders.
- The self-lubricating ceramic tool materials were prepared by adding coated particles to the Al₂O₃/Ti(C,N) matrix. During the sintering process, the Al₂O₃ coating on the CaF₂ surface and the matrix



Fig. 10. Comparison of cutting temperatures of cutting tools at cutting speed of 100 m/min: (a)Al₂O₃/Ti(C,N), (b)Al₂O₃/Ti(C,N)/CaF₂@Al₂O₃



Fig. 11. Comparison of cutting temperatures of cutting tools at cutting speed of 200 m/min: (a)Al₂O₃/Ti(C,N), (b)Al₂O₃/Ti(C,N)/CaF₂@Al₂O₃



Fig. 12. Comparison of cutting forces of different cutting tools.

material will be bonded together. So that CaF_2 is completely coated in the alumina ceramic matrix to form an inner crystal structure.

4. Through the analysis of cutting performance, it is found that the addition of $CaF_2@Al_2O_3$ can effectively reduce the temperature, cutting force and friction coefficient in the cutting process of the tool, thus improving the cutting performance of the tool material.

Declaration of competing interest

We declare that we have no conflict of interest.

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Appendix A. Supplementary data

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References

- C.H. Xu, G.Y. Wu, G.C. Xiao, et al., Al₂O₃/(W,Ti)C/CaF₂ multi-component graded self-lubricating ceramic cutting tool material, Int. J. Refract. Metals Hard Mater. 45 (2014) 125–129, https://doi.org/10.1016/j.jirmhm.2014.04.006.
- [2] C.H. Xu, G.Y. Wu, G.C. Xiao, et al., Al₂O₃/(W,Ti)C/CaF₂ multi-component graded self-lubricating ceramic cutting tool material, Int. J. Refract. Metals Hard Mater. 45 (2014) 125–129, https://doi.org/10.1016/j.ijrmhm.2014.04.006.
- [3] Zhaoqiang Chen, et al., Mechanical properties and microstructure of Al₂O₃/TiC based self-lubricating ceramic tool with CaF₂@Al(HO)₃, Int. J. Refract. Metals Hard Mater. 75 (2018) 50–55, https://doi.org/10.1016/j.ijrmhm.2018.04.001.
- [4] A. Piasecki, M. Kulka, M. Kotkowiak, Wear resistance improvement of 100CrMnSi6-4 bearing steel by laser boriding using CaF₂ self-lubricating addition, Tribol. Int. (2016), https://doi.org/10.1016/j.triboint.2016.01.028 S0301679X16000402.
- [5] Y. Zhao, K. Feng, C. Yao, et al., Microstructure and tribological properties of laser cladded self-lubricating nickel-base composite coatings containing nano-Cu and h-BN solid lubricants, Surf. Coating. Technol. 359 (2019) 485–494, https://doi.org/ 10.1016/j.surfcoat.2018.12.017.
- [6] H. Torres, T. Vuchkov, M. Rodríguez Ripoll, et al., Tribological behaviour of MoS₂based self-lubricating laser cladding for use in high temperature applications, Tribol. Int. 126 (2018) 153–165, https://doi.org/10.1016/j.triboint.2018.05.015.
- [7] G.Y. Wu, C.H. Xu, Y.L. Zhang, et al., Development of Al₂O₃/TiC/CaF₂ graded selflubricating ceramic cutting tool materials, Mater. Sci. Forum 723 (2012) 258–263 https://doi.org/10.4028/www.scientific.net/MSF.723.258.
- [8] D. Jianxin, C. Tongkun, Y. Xuefeng, et al., Self-lubrication of sintered ceramic tools with CaF₂ additions in dry cutting, Int. J. Mach. Tool Manufact. 46 (9) (2006) 957–963, https://doi.org/10.1016/j.ijmachtools.2005.07.047.
- [9] C.T. Kun, D.J. Xin, Friction and wear behavior of self-lubricating ceramic composite, Tribology 25 (6) (2005) 564–568.
- [10] L.J. Jun, L.H. Xun, Lanzhou, Tribological properties of self-lubricating ceramic composite Y-TZP/MoS₂, Tribology 23 (6) (2003) 490–494.
- [11] X.Q. Qi, X.P. Zhang, Mechanical and friction-wear properties of MoS2 Al-matrix self-lubricating, Adv. Mater. Res. 304 (2011) 6–11 https://doi.org/10.4028/www. scientific.net/AMR.304.6.
- [12] D. Vollath, D.V. Szabó, Coated nanoparticles: a new way to improved nanocomposites, J. Nanoparticle Res. 1 (2) (1999) 235–242, https://doi.org/10.1023/ A:1010060701507.
- [13] C. Shuwei, Z. Yue, Z. Dahai, et al., Effect of surface nano-modification on the antioxidation properties of Si₃N₄, ceramics, J. Alloys Compd. 766 (2018) 678–685, https://doi.org/10.1016/j.jallcom.2018.06.363.
- [14] Y. Lv, J. Fan, Y. Han, et al., The influence of modification route on the properties of W-0.3 wt%Y₂O₃ powder and alloy prepared by nano-in-situ composite method, J. Alloys Compd. 774 (2019) 1140–1150, https://doi.org/10.1016/j.jallcom.2018.09. 163.
- [15] Z.W. Wang, T.J. Wang, Z.W. Wang, et al., Organic modification of nano-SiO₂ particles in supercritical CO₂, J. Supercrit. Fluids 37 (1) (2006) 125–130, https://doi. org/10.1016/j.supflu.2005.06.011.
- [16] W. Chuang, J. Geng-Sheng, P. Lei, et al., Influences of surface modification of nanosilica by silane coupling agents on the thermal and frictional properties of cyanate ester resin, Results Phys. (2018), https://doi.org/10.1016/j.rinp.2018.03.056 S2211379717325329.
- [17] R.Z. CsŐGŐ, M. Nacken, M. Sameti, et al., Modified silica particles for gene delivery, Mater. Sci. Eng. C 23 (1–2) (2003) 93–97, https://doi.org/10.1016/S0928-4931(02)00238-2.
- [18] Wang, H. Zhang, W.U. Xiao-Hong, et al., A study on photophysical behavior of silica gel nano-particles modified by organic molecule in different mediums, Hua Hsueh Hsueh Pao 61 (12) (2003) 1921–1925.
- [19] Y.E. Kim, S.G. Kim, H.J. Shin, et al., Vapor-phase surface modification of submicron particles, Powder Technol. 139 (1) (2004) 81–88, https://doi.org/10.1016/j. powtec.2003.10.011.
- [20] W. Wu, S.C. Lu, Mechano-chemical surface modification of calcium carbonate particles by polymer grafting, Powder Technol. 137 (1–2) (2003) 41–48, https:// doi.org/10.1016/j.powtec.2003.08.029.
- [21] G. Wu, C. Xu, G. Xiao, et al., An advanced self-lubricating ceramic composite with the addition of core-shell structured h-BN@Ni powders, Int. J. Refract. Metals Hard

Mater. 72 (2018) 276-285, https://doi.org/10.1016/j.ijrmhm.2017.12.038.

- [22] Wenliang Zhang, et al., Al₂O₃-coated h-BN composite powders and as-prepared Si₃N₄-based self-lubricating ceramic cutting tool material, Int. J. Refract. Metals Hard Mater. 71 (2018) 1–7, https://doi.org/10.1016/j.ijrmhm.2017.10.018.
- [23] H. Chen, C. Xu, G. Xiao, et al., Synthesis of (h-BN)/SiO₂ core-shell powder for improved self-lubricating ceramic composites, Ceram. Int. 42 (4) (2016) 5504–5511, https://doi.org/10.1016/j.ceramint.2015.12.102.
- [24] A. Mukhopadhyay, D. Chakravarty, B. Basu, Spark plasma-sintered WC-ZrO₂-Co nanocomposites with high fracture toughness and strength, J. Am. Ceram. Soc. 93 (6) (2010) 1754–1763, https://doi.org/10.1111/j.1551-2916.2010.03685.x.
- [25] M.Y. Tian, E.W. Shi, W.Z. Zhong, et al., Nano ceramics and nano ceramic powders, J. Inorg. Mater. 13 (2) (1998) 129–137.
- [26] K. Niihara, A. Nakahira, Particulate Strengthened Oxide Ceramics- Nanocomposites, (1990).
- [27] N. Koichi, New design concept of structural ceramics-ceramics nanocomposites, J. Ceram. Soc. Jpn. 99 (3) (1991) 974–982.
- [28] M. Yi, C. Xu, Z. Chen, et al., Effect of nanosized CaF₂ on mechanical properties of

selflubricating ceramic material, J. Chin. Ceram. Soc. 42 (9) (2014) 1127–1133, https://doi.org/10.7521/j.issn.04545648.2014.09.08.

- [29] C.D. De Souza, B.R. Nogueira, M.E.C.M. Rostelato, Review of the methodologies used in the synthesis gold nanoparticles by chemical reduction, J. Alloys Compd. (2019), https://doi.org/10.1016/j.jallcom.2019.05.153.
- [30] S. Ko, C. Huh, Use of nanoparticles for oil production applications, J. Petrol. Sci. Eng. (2018), https://doi.org/10.1016/j.petrol.2018.09.051.
- [31] S. Kango, S. Kalia, A. Celli, et al., Surface modification of inorganic nanoparticles for development of organic-inorganic nanocomposites—a review, Prog. Polym. Sci. 38 (8) (2013) 1232–1261, https://doi.org/10.1016/j.progpolymsci.2013.02.003.
- [32] E.E. Finney, R.G. Finke, Nanocluster nucleation and growth kinetic and mechanistic studies: a review emphasizing transition-metal nanoclusters, J. Colloid Interface Sci. 317 (2) (2008) 351–374, https://doi.org/10.1016/j.jcis.2007.05.092.
- [33] J. Belloni, J.L. Marignier, M. Mostafavi, Mechanisms of metal nanoparticles nucleation and growth studied by Radiolysis, Radiat. Phys. Chem. (2018), https://doi. org/10.1016/j.radphyschem.2018.08.001.