Study on Hydrophobic Properties of Ceramic Materials based on Bionic Microstructure

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Abstract. This paper, hydrophobic porous ceramic materials with high porosity, high mechanical strength and high hydrophobic properties were prepared by preparing porous ceramic materials and modifying their surfaces. Superhydrophobic functional materials have broad application prospects in the fields of self-cleaning, anti-fouling, anti-corrosion, anti-fog, anti-icing, anti-bacteria, oil-water separation, etc. Although researchers have developed a variety of technical methods for constructing superhydrophobic surfaces, they are still subject to many restrictions in industrial production and practical applications. The main reason is that the hydrophobic properties of the surface are extremely unstable and the surface micro-nano rough structure is easy to It is damaged by external destructive effects (such as friction, knife scraping, corrosion, etc.), and then partially or completely loses super-hydrophobic properties. Generally speaking, reducing the surface free energy and increasing the surface micro roughness of ceramic materials are important ways to improve the surface hydrophobicity.

Keywords: Bionic Microstructure; Ceramic Materials; Hydrophobic Property.

1. Introduction

With the continuous progress of science and technology, people have higher and higher requirements for the performance of ceramic materials, making the development of ceramic materials with various special properties a new research focus [1]. Some biological "special functions" often inspire and enlighten humans. Through the research of some biological organisms, through continuous imitation, improvement and innovation, many high-performance tools and materials have been developed to solve many industrial production and daily life. Difficulties in [2]. Superhydrophobic coatings have excellent non adhesion and self-cleaning properties, and have broad application prospects in daily life, industrial production and even national defense and aviation fields [3]. Generally speaking, reducing the surface free energy and increasing the surface micro roughness of ceramic materials are important ways to improve the surface hydrophobicity of materials [4]. Porous ceramic material is an important structural material, which has the characteristics of uniform pore distribution, good chemical stability, high mechanical strength and easy regeneration. It is widely used in solid-gas separation, solid-liquid separation, gas-gas separation and so on [5]. Generally, there are two basic methods to construct superhydrophobic surface: one is to construct micro-rough structure on the surface of low surface energy substrate, the other is to further treat the surface with micro-nano structure with low surface energy [6].

2. The Theoretical Basis of Superhydrophobic Surfaces

The surface is the external region of the object when it exists alone. The molecules in the surface area of the material produce a force or potential energy which shrinks inward due to the unbalanced force, and the surface tension is applied to the liquid material. For the condensed system, Gibbs free enthalpy is approximately equal to Helmholtz free energy, so it is also called surface free energy [7]. Solid surface free energy is a physical quantity characterizing solid surface state, which is defined as: keeping thermodynamic parameters t, p and composition constant, the increment of Gibiss free energy is called surface free energy for every unit of surface area, which is called surface energy for short, and is recorded as σ, and its unit is j m-2. Since J = N • m, there is 1 j m-2 = 1n m-1, so the surface free energy is numerically equal to the surface tension [8].Generally speaking, the lower the surface energy of a solid, the less likely it is to be wetted by water. On the contrary, the easier it is to be

wetted. According to this property, solid surfaces can be divided into high free energy surfaces (such as metals, metal oxides, etc.) and low free energy surfaces (such as organic polymers, etc.) [9].

Interfacial tension is a kind of force produced by the difference between the molecular force in the interfacial region of two substances and that in each phase. When the liquid contacts with the solid, the interfacial tension σ_{SL} of the liquid-solid system and the surface tension σ_L of the liquid. The relationship between solid surface energy and solid surface energy σ_S is as follows:

$$\sigma_{SL} = \sigma_L + \sigma_S - 2\phi(\sigma_L\sigma_S)^{1/2} \quad (1)$$

ϕ is G00d and a parameter of Girifalco related to the matching of liquid-solid two-phase molecular interaction.

The wettability of the solid surface is given by the following formula:

$$\cos\theta = (\sigma_{SV} - \sigma_{SL})/\sigma_{LV} \quad (2)$$

σ_{SV}, σ_{SL} and σ_{LV} Are respectively the interfacial tension between solid - gas, solid - liquid and liquid – gas; θ Is the contact Angle of solid, liquid and gas at equilibrium.

σ_{SV}, σ_{SL} and σ_{LV} are the interfacial tension between solid-gas, solid-liquid and liquid-gas respectively; θ is the contact angle when the three phases of solid, liquid and gas are in equilibrium.

When θ < 900, it is hydrophilic, θ > 90. It is hydrophobic. The surface with θ < 50 is called superhydrophilic surface, and the surface with θ > 1200 is called superhydrophobic surface.

2.1 Superhydrophobic Material Microstructure Surface

Based on the wetting model theory and the formation mechanism of superhydrophobic surface, the current preparation methods of superhydrophobic materials mainly have two basic ideas: one is to construct the rough structure on the low surface energy substrate, the other is to modify the rough surface with low surface energy [10]. With people's in-depth research on such materials, superhydrophobic surfaces have made great progress from theory to practice, and many preparation methods and processes have been proven effective. First, the wettability of surface materials is a prerequisite for determining hydrophilicity and hydrophobicity. Therefore, low surface energy substances are the most basic condition for hydrophobicity. Second, the fine surface structure is a key factor to significantly improve its hydrophobic properties [11]. From the point of view of contact angle, the surface group is the main factor that determines the hydrophobicity, and the morphology only enhances this effect. Considering that the wettability of polymer structure surface is anisotropic, the tetraprism array microstructure is taken as the analysis object. As shown in Figure 1, A, B and H are column width, column spacing and column height respectively.

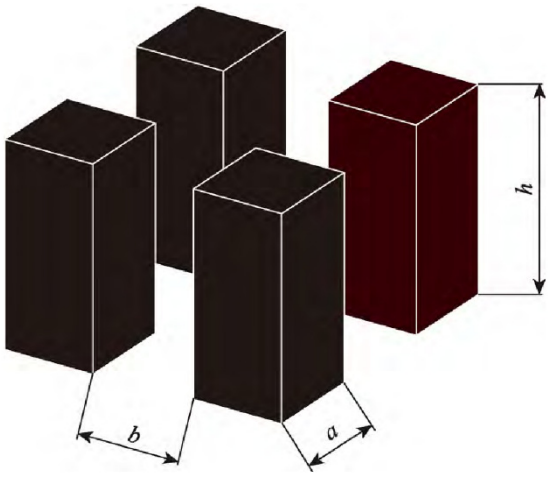


Figure 1. Micro-structure geometric model

In actual contact, the contact state of the droplet on the microstructure surface may not be the ideal Wenzel model and Cassie model, but is partially infiltrated into the microstructure to form a metastable composite contact, as shown in Figure 2.

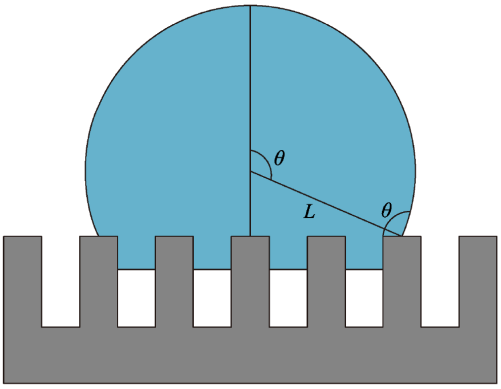


Figure 2. Metastable composite contact

Generally speaking, reducing the surface free energy of the material and increasing the micro-roughness of the material surface are important ways to improve the hydrophobicity of the material surface. Throughout the research results in recent years, there have been more studies on the surface hydrophobization of organic materials, and many practical technologies have been developed. However, as one of the three major engineering materials, ceramic materials have less research on the surface hydrophobization treatment. Reports are also relatively scattered [12]. Although domestic and foreign scholars have achieved certain results in the preparation of superhydrophobic coatings, there are still many problems, such as the preparation method is too cumbersome and complicated, and the comprehensiveness of the obtained coatings is difficult to meet the requirements of industrial applications. Therefore, it is necessary to strengthen the development and preparation of superhydrophobic coatings.

3. Hydrophobicity of Ceramic Materials

3.1 Ceramic Material

In recent years, hydrophobic ceramic materials have attracted widespread attention because of their wide application prospects in industrial and agricultural production, national defense construction and people's daily life [13]. Texturing of ceramic materials means that the grains are preferentially oriented and arranged under the action of an external gradient field (mechanical force field, magnetic field or temperature field, etc.). Texturing can make the properties of materials anisotropic, thus significantly improving their properties in a certain direction [14]. Because texturing can not only make ceramics have the excellent mechanical properties of polycrystalline materials, but also make them have the characteristics of anisotropic physical properties of single crystal materials, so it is an important way to improve the performance limit of materials. There are three main methods to realize the texture of ceramic materials, of which the first two have been used to prepare textured ceramic materials. Strong magnetic field induction method, hot forging method, template grain growth method. The wettability is a very important physical and chemical property of the solid surface. It refers to the spreading ability of the liquid on the solid surface. The contact angle is usually used to characterize the wettability of the material surface. When the static contact angle between the surface of the material and water is greater than 90°, it indicates that it is hydrophobic, and when the contact angle is greater than 150° and the rolling angle is less than 10°, it is super-hydrophobic. The hydrophobicity of the coating surface is related to its surface chemical composition and structure, and the lower surface energy substances on the surface, the better hydrophobicity [15]. In the preparation of porous ceramic materials, 60% ~ 65% alumina is mixed with 34% ~ 40% high

temperature binder, and 1% ~ 5% Arabic gum is added. Table 1 shows the formula of high temperature binder, and composite mineralizer can replace part of high temperature binder.

Table 1. The formula of high temperature adhesive

Suzhou soil	Feldspar	Talc
42~47	42~47	8~12

In the natural superhydrophobic biological surface, there are lotus leaf surface composed of micro-mastoid and fibrous nano-structure, butterfly surface with scaly structure and shark skin surface, etc. The distribution of these structures is regular, but irregular. Traditional ceramic engineering materials have irreconcilable contradictions in strength and toughness. The structural characteristics of biomimetic organisms under macro/micro/nano-scale conditions are called structural bionic technology. Nature provides us with a large number of novel research objects, such as shell structure, porous structure, membrane-fin structure and so on. An effective method for strengthening and toughening ceramics is to obtain ceramics with the characteristics of rod crystals and plate crystals in the microstructure. When crack propagation encounters this kind of interlocking structure of bar crystals and slab crystals, the cracks are more likely to deflect, branch or bridge, which can improve the fracture toughness of the material. The surface roughness of the coating has a direct relationship with the microstructure, and the roughness of the coating also has a direct effect on the friction coefficient [16]. The hardness of coating is related to the coating material, microstructure and phase structure. The higher the porosity of the coating, the lower the microhardness, these factors also have an important influence on the bonding strength of the coating. The microhardness and bonding strength of the two coatings are shown in Table 2:

Table 2. Mechanical Properties of coating

Samples	Coatings	Micro-hardbess $HV_{0.1}$	Adhesive sterngth/MPa
Coating 1	AT	562	7
	PFA/AT	74	
Coating 2	AT	583	15
	PFA/AT	110	

3.2 Surface of Material

The lower the surface free energy is, the stronger the hydrophobicity is. The methods for preparing rough surfaces include doping method, template method, etching method, sol-gel (SOL - gel) method, vapor deposition method, and hydrophobic surface composed of nano silicon and TiO2. In addition to the above methods, there are many technical means to build superhydrophobic surfaces, such as microemulsion, phase separation and so on. However, most of the data study the functional indexes of the prepared superhydrophobic materials, but the data reports on their durability are relatively few. Because the micro-nano structure of superhydrophobic surface is easily damaged by friction, knife scraping and corrosion, resulting in the loss of microstructure and low surface energy substances, and the decline of hydrophobic properties, it is particularly important to improve and optimize the preparation process based on the existing preparation methods [17]. The adsorption capacity of porous ceramics for water vapor is significantly reduced after surface modification. This is because the non-polar methyl groups on the surface of the porous material after surface modification are not infiltrated with water, which reduces the adsorption of the material and water. The surface-modified porous ceramic is immediately adsorbed by the surface of the pores when it encounters water, and the porous ceramic is wetted. A self-cleaning surface generally refers to a functional surface that can

automatically fall off or be degraded by natural external forces such as gravity, rain, wind, or solar energy. When the static contact angle of the material surface reaches 150° or more, the superhydrophobic surface can achieve the effect of rolling self-cleaning only when the rolling angle is less than 10° [18]. The microstructure of superhydrophobic surface plays an important role in maintaining the stability of hydrophobicity after mechanical loading. Sol gel method (SOL - gel) was used. Sol-gel coating technology was to react with water in some solvents by using easily hydrolyzed metal alkoxides or inorganic salts. After hydrolysis and condensation, sol was coated on the surface of the metal and then dried and heat treated to form the coating.

In the following figure, in 1805, British scholar ThomsonYoung assumed an ideal solid surface and according to the basic laws of thermodynamics, obtained the functional relationship between solid-liquid-gas interfacial tension and contact angle, namely the famous Young's equation.

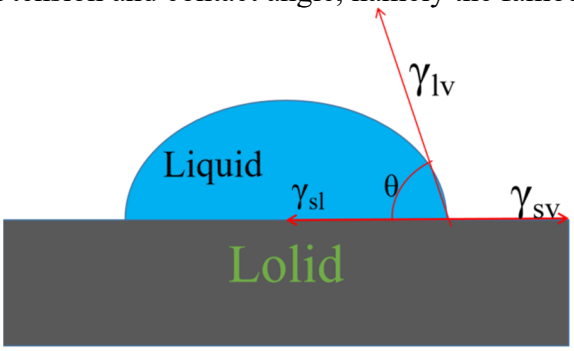


Figure 3. Ideal plane model, interfacial tension and contact angle constructed by young's equation

Based on the Young's equation, the following conclusions can be drawn: as long as the composition of the solid surface changes, its surface energy will change, and the contact angle of the droplet on the surface will also change.

3.3 The Hydrophobic Surface is Composed of Nano Si and TiO_2

Nakajima et al. used ultrasonic method to mix aluminum acetylacetonate (and titanium acetylacetonate), then coated the mixture on heat-resistant glass sheet at a speed of 1500 r/min, and heated at 500℃ for 20s, thus obtaining a transparent bionic super-hydrophobic nano-TiO_2 surface with self-cleaning function. They sublimated aluminum acetylacetonate at 193℃ to prepare a rough surface, and then chemically modified it with fluoroalkyl siloxane to obtain a transparent bionic superhydrophobic surface. The static contact angle between water and it is 152.5±1.6. Experiments have found that the hydrophobicity of this film decreases with the decrease of its surface roughness. When the average roughness of the film is 33nm, the film does not have superhydrophobicity, and its contact angle with water droplets is only 120.3°. Dongpeng uses liquid nano-silicon material to coat ceramic products such as glazed tiles with special coating technology, which is treated at a certain temperature to obtain ceramic products with nano-scale film layer, which has good anti-pollution performance, is not easy to adhere to water droplets and oil droplets, and is very easy to clean. In recent years, an ultra-clean and bright antifouling technology for polished tiles has appeared in a certain market. It uses nano-composite materials to repeatedly and evenly polish the surface of the polished tiles, thereby forming a special layer on the surface of the polished ceramic tiles. The nano-level protective layer with protective function and stable structure can not only improve the anti-fouling performance of polished tiles, but also greatly enhance the glossiness of the surface of the tiles.

4. Conclusion

In recent years, hydrophobic ceramic materials have attracted people's attention because of its broad application prospects in industrial and agricultural production, national defense construction and people's daily life. The glass treated by various ceramic hydrophobic technology can be made

into self-cleaning glass, which can be used as the windshield of automobile, aircraft, spacecraft, etc. it can not only reduce the pollution of dust and other pollutants in the air, but also keep it dry in high humidity environment or rainy days, which can greatly improve people's sight and improve the driving safety. In this paper, the thermal shock properties of ZrB2 based ultra-high temperature ceramic materials are optimized by using the bionic principle of structure and morphology in biomechanics. Biomimetic thermal shock coatings were prepared by sol-gel technology and heterogeneous growth technology. The poor thermal shock performance of ZrB2 ceramic matrix composites limits its service in extreme environments such as high temperature. Traditional methods of toughening or increasing thermal conductivity can only improve its mechanical stability in large temperature gradient and high temperature environment, but still cannot meet the requirements of human spacecraft for ultra-high temperature ceramic materials. Therefore, new methods must be found to improve the mechanical stability and thermal shock properties of ZrB2 ceramic matrix composites. Bionics principle provides a new research method and solution for us to solve the problems of ceramic material mechanics and thermal shock. At present, super-hydrophobic surfaces are subject to certain restrictions in terms of efficient and stable preparation or specific applications. Artificially prepared super-hydrophobic surfaces have problems such as low strength, poor durability, and difficulty in mass preparation. The main factors affecting surface wettability include the chemical composition and micro-rough structure of the material surface. Under normal circumstances, only changing the chemical composition of the surface of the material to reduce its surface energy cannot fully realize the superhydrophobic function. The surface roughness, friction coefficient and surface energy of the coating together affect its superhydrophobicity, that is, the greater the surface roughness, the lower the surface energy and friction coefficient, the better the superhydrophobicity.

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