Study on Microwave Sintering Process and Surface Texture Characteristics of Ceramic Materials

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Abstract. The sintering process and properties of nano-cermet materials were studied by microwave sintering new technology. The results show that the microwave sintered \( \text{Al}_2\text{O}_3\)-TiC-Mo-Ni nano-ceramics can reach a relative density of 99.0% when kept at 1500 °C for 10 min; the sintering temperature is lowered, the sintering time is greatly shortened, and the grains are sintered before and after sintering. The diameters are 35 and 55 nm, respectively, with little change. At the same time, the paper discusses the surface texture formation and aesthetic characteristics of ceramic materials after sintering. The paper hopes to contribute to the art ceramics firing and decoration field.

1. Introduction
Microwave sintering is a new type of material densification sintering process, which uses microwave heating to sinter the material. Microwave sintering of materials began in the mid-1960s. Levinson and Tinga first proposed microwave sintering of ceramic materials. From the mid-1970s to the mid-1990s, microwave sintering technology was systematically studied at home and abroad, reflecting the microwave theory of different materials, device system optimization, dielectric parameters, numerical simulation and sintering process [1]; in the late 1990s, microwave sintering entered the industrialization stage, the United States, Canada, Germany, Japan and other developed countries began to produce ceramic products in small quantities. For example, the US Dennis Tool Company uses a microwave high-temperature continuous sintering equipment to sinter cemented carbide tool products; Canada Index Tool uses microwave sintering \( \text{Si}_3\text{N}_4 \) ceramic tools [2]. In 1988, China used microwaves for material sintering. At present, great progress has been made and it is gradually developing towards industrialization [3]. Microwave sintering technology is known as "the new generation of sintering technology in the 21st century" because of its outstanding advantages in the field of ceramic material preparation [4].

2. Traditional sintering and microwave sintering characteristics
Sintering is the most important and critical process in the final process of ceramic material preparation. Conventional sintering methods mainly include pressureless sintering, hot pressing sintering, hot isostatic pressing, etc. In recent years, some new sintering methods have been developed, such as atmospheric pressure sintering, microwave sintering, and discharge plasma sintering.
2.1. Traditional sintering technology
The pressureless sintering equipment is simple and easy to sinter complex shapes and large volume samples, and is the most basic sintering method. However, the high sintering temperature and long holding time required for sintering tend to cause abnormal growth of the crystal grains, which is not conducive to the improvement of mechanical properties. The long sintering cycle without pressure sintering causes excessive energy consumption and high production cost [5].

Hot-pressed sintering means that the ceramic green body is subjected to unidirectional external pressure while being heated, and the interaction of temperature and pressure promotes material migration, which is advantageous for densification of the green body. Compared with normal pressure sintering, the hot press sintering time is short, the temperature is low, the grain growth is suppressed, and the material properties are improved. However, hot press sintering can only produce articles with simple shapes, and the microstructure of the hot-pressed sintered material has anisotropy, resulting in anisotropic properties and limited use range [6].

Hot isostatic pressing is a process technology that integrates high temperature and high pressure. The high-pressure inert gas or nitrogen in the closed container is used as the pressure transmitting medium to make the powder evenly pressurized during the heating process and promote the compactness of the material. Chemical. Compared with non-pressure and hot-press sintering, hot isostatic pressing can lower the sintering temperature, and the prepared ceramic has high density, uniformity and excellent performance. However, hot isostatic pressing has high requirements on the material and technology of the jacket, and therefore is generally used for manufacturing a product having a simple shape and low production efficiency.

2.2. Microwave sintering
Microwave sintering is to use the dielectric loss of the ceramic material in the microwave electromagnetic field to heat the material to the sintering temperature to achieve sintering and densification. Microwave sintering is essentially different from traditional sintering: in traditional sintering, heat is diffused from the surface to the inside by radiation. When microwave sintering, the microwave energy absorbed by the material is converted into the kinetic energy and potential energy of the internal molecules of the material, so that the whole material is uniformly heated, and the internal temperature gradient of the material. The heating and sintering speed is very fast; under the action of microwave electromagnetic energy, the internal molecular or ion kinetic energy of the material increases, and the diffusion coefficient increases, so that low-temperature rapid sintering can be achieved, and the sintering can be completed after the crystal grains are too late to grow. Mechanical properties of ceramic materials. In addition, the microwave sintering process does not require heat conduction, no thermal inertia, the heat source can be instantly heated or instantaneously stopped, high efficiency and energy saving, short production cycle, large single furnace production volume and low single piece production cost.

The sintering process and mechanical properties of some ceramic materials prepared by different sintering methods are shown in Table 1. The microwave sintering temperature is lower than the conventional sintering temperature by 100-300°C, the holding time is short (0-20 min), the sintering cycle is shortened by 50%-90% compared with the conventional sintering, and the grains of the microwave sintered material are finer and the mechanical properties are better. Therefore, microwave sintering is expected to be an effective means for preparing ultra-fine grain, high strength, high toughness, and high hardness ceramic tool materials. Using microwave thermal effects (rapid heating, volume heating) and non-thermal effects (promoting densification), high-performance ceramic tools with fine or ultra-fine grains and uniform microstructure are prepared on a technical level; from the production point of view, microwave energy is utilized. The high utilization rate and environmentally friendly characteristics enable the realization of large-scale production of ceramic tools with lower cost and less environmental pollution, creating greater economic value.


### Tab. 1 Comparison of Microwave Sintering Process and Mechanical Properties of Ceramic Materials

| Material        | Heating rate/°C·min⁻¹ | Holding time/min | Grain size/μm | Strength/Mpa | Toughness /MPa·m¹/² | Hardness/Gpa |
|-----------------|------------------------|------------------|---------------|--------------|----------------------|-------------|
| Al₂O₃/ZrO₂      | 200                    | 10               | 0.8           | -            | 6                    | 18          |
| Al₂O₃/TiO₂      | 100                    | 10               | -             | 362          | 3.64                 | 7.7         |
| Al₂O₃/TiC       | 50-60                  | 10               | -             | -            | 5.18                 | 21.2        |
| Al₂O₃/SiC       | 40                     | 20               | -             | -            | -                    | 14.8        |
| Ti (C, N)       | 25                     | 10               | -             | -            | -                    | 14.7        |

### 3. Sample preparation and test method

#### 3.1. Sample preparation

The purity of α- Al₂O₃, TiC, Mo and Ni powders in the test were all greater than 99.9%, and the ratio of the four components (mass fraction, %) was: 50α- Al₂O₃, 30TiC, 10Mo, 10Ni. High-purity graphite powder, chromium oxide, iron oxide, cobalt oxide and manganese oxide powder are all analytically pure. After being proportionated, the ball mill was placed in a rolling ball mill barrel, and acetone was used as a grinding medium. The ball milling time was 48 h, and then vacuum drying. A certain amount of the mixture is charged into the female cavity of the tableting machine, and the powder is pressurized by the pressure of 160-180 MPa through the male mold, and the pressure is maintained for 2 minutes. After the pressure is removed, the mold is removed and the blank is taken out for use.

The microwave oven for sintering is a modified household microwave oven. The working frequency of the microwave source is 2450MHz, the power is adjustable from 0 to 850W, and the temperature is measured by the ULTIMAX-20 optical pyrometer. The sintering temperature is 1400-2000 °C, and the heating rate is controlled by 5 to 7 minutes. The temperature is raised to the required sintering temperature, and the temperature is kept for 10 to 15 minutes. The microwave input is cut off and naturally cooled. Comparing the effects of various refractory materials and microwaves, as well as high temperature resistance and workability, a lightweight, porous mullite refractory brick was selected as the thermal insulation material. This material does not interact with microwaves and has good thermal insulation properties. It can withstand high temperatures above 1500 °C and has good processability. The high-purity graphite crucible is used for the sample, and since the sintering is performed at a high temperature, TiC, molybdenum, and nickel in the sample are easily oxidized, so that the powder is protected. High-purity graphite powder is used for burying powder, because graphite powder is both a strong microwave absorbing material and a good protective material. Part of the graphite powder is placed in the graphite crucible, then placed in a sample, and then pressed with graphite powder. The graphite crucible is placed in the heat-insulating refractory brick, and graphite powder is filled between the crucible and the heat-insulating material as a heat-assisting material, which also contributes to improving the uniformity of heating. The uppermost layer of the thermal insulation structure is filled with a small amount of chromium oxide and graphite mixed powder (volume ratio of 1:1), which can increase the heating rate and the sintering temperature (Fig. 1).
3.2. **Experimental methods**
Density is measured by the Archimedes method and converted to relative density (ratio of test density to theoretical density). The phase composition and grain size of the sample were measured by a DX-1000 X-ray diffractometer.

4. **Results and discussion**

4.1. **Effect of Microwave Sintering Process on Relative Density of Materials**
It can be seen from Fig. 2 and Fig. 3 that when the sintering temperature is above 1200 °C, the density of the sample increases rapidly with the increase of the sintering temperature, reaching a relative density of 99% at 1500 °C, and local melting occurs when the temperature exceeds 1600 °C. The relative density of the sample at the holding time of 10 min has reached 99%, and the relative density of the sample has not changed substantially. Therefore, the sintering temperature is 1500 °C and the holding time is 10 min.
4.2. **SEM analysis and grain size determination**

It can be seen from Fig. 4 that the sintered body is very dense and has no bubbles and pores. In the process of microwave sintering densification, the grain size of the sample is small, and the grain of the sintered product is fine and uniform, which is a prominent advantage of the microwave sintered ceramic material. It can also be seen from the figure that there are two distinct phases, which is consistent with the composition of the two interpenetrating skeletons described in [5]. One skeleton consists of Al₂O₃ grains and the other skeleton. It consists of carbide grains and binder metals. The content of Al₂O₃ and the content of carbides should ensure that each can form a continuous skeleton. This ceramic material maximizes the advantages of Al₂O₃ ceramics and TiC-Ni-Mo₂C alloys.

![Fig. 3 Relationship between holding time and relative density](image)

The grain size of the microwave sintered samples was measured by MDI Jade 5.0 analysis software and calculated by Scherrer's formula [6]. The average grain size before sintering is 35 nm, and 55 nm after sintering. It can be seen that the grain change of the sample before and after microwave sintering is very small, so that highly densified fine or ultrafine grain ceramic materials can be prepared by microwave sintering.

4.3. **Phase analysis**

It can be seen from Fig. 5 that molybdenum is present in the sample as Mo₂C, which is mainly to replace the titanium atom in the TiC lattice at the sintering temperature, form a (Ti-Mo) C solid solution on the surface of the TiC particle, and reduce the pure TiC particles. The contact between them avoids the growth of TiC grains. Through the phase analysis, it can be found that there is no oxide in the phase, which indicates that the sintering protection is successful. At 1500 °C, the highly oxidizable TiC, molybdenum and nickel are not oxidized, so the designed thermal insulation device and the choice of protection measures is feasible.
In the ceramic sintering process, the growth of crystal grains is inevitably accompanied. Therefore, how to control the growth of the nanoparticles during the sintering process to maintain the original characteristics is a difficult problem in the preparation of nano-block ceramic materials. There are two main factors leading to grain growth. One is the sintering temperature, the grain size increases significantly with the increase of sintering temperature, and the second is increased with the increase of holding time. Therefore, the current conventional sintering process is difficult to ensure the characteristics of the nano ceramic material. Only by preparing a fine-grained sintered body, the material can have high strength, high hardness and high toughness at the same time, and microwave sintering is an effective means for preparing nano materials.

5. Ceramic texture formation and characteristics

5.1. Material texture
The texture organization shown by the natural properties of pottery and porcelain. The formation is mainly controlled by raw materials, process manufacturing, especially the subjective and objective factors in the burning, such as the mineral composition, chemical composition, particle composition, colorant and physical indicators of the glaze layer, furnace atmosphere, temperature curve and cooling rate. The ceramic glaze is calcined at high temperature through kiln fire. The internal structure is not only dense, impervious to water, but also resistant to acid and alkali. The surface also produces various colors and transparent, opaque, crystallization, crack, kiln and other visual effects.

5.2. Fabrication texture
Textured tissue produced by human action. The production process is mainly controlled by the producer, and the producer intentionally acts on the surface of the product to form a texture structure, such as scoring, kneading, slap, extrusion, stamping, polishing, carving, under glazing, glaze. On the decoration and so on. In terms of fabric texture, the plasticity, thixotropy and combination of clay and the impressibility of the glaze directly record the producer's perception of formal skills and life experiences.

5.3. Artistic use
The change of the ceramic material is not only the change of the plasticity, but also the different texture effects due to the difference in color, the size of the soil particles and the thickness of the texture are different. The texture effect of ceramics, which is not simply attached to the surface of the
body, serves the form, and its texture itself has a unique decorative interest. There are many methods of treatment, such as patterning the regular stripes on the plane blank, and then sticking the strips with different lengths to produce a texture contrast, which makes the texture-based plane shape more decorative. Another example is the color of the ceramic material itself, that is, the inherent color of the soil, which itself has a decorative feeling, giving a simple, dignified visual effect. The new era requires us to use new means of expression to reflect real life. The new modern living environment also provides us with rich creative qualities. In recent years, many of our peers have explored new themes, new techniques, and new techniques. Many useful attempts have been made to create a variety of texture effects that have never been imagined before, enriching the connotation of ceramic culture.

6. Conclusion
(1) The cermet is sintered in a modified domestic microwave oven and a self-made auxiliary heat preservation device, and the sintered body having a relative density of 99.0% can be obtained by holding at 1500 ° C for 10 minutes, which can greatly shorten the sintering time, thereby achieving high efficiency and energy saving. (2) The micro-sintered cermet has little change in grain size before and after sintering, and the sintered body is uniform and dense, which provides an important process for preparing nano-materials. (3) Ceramic texture is derived from material texture and production texture, and has certain artistic value in art decoration. New techniques can add more texture effects.

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