Microwave sintering of Al_2O_3-TiC-TiN-Mo-Ni composite cermet

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Abstract

Processing route has been developed with the aim to sinter refractory Al_2O_3-TiC-TiN-Mo--Ni cermet. The influence of the sintering temperature and time on relative density, surface morphologies, composition and microstructure has been studied. Grain size of sintered materials has been calculated from the XRD pattern. Al_2O_3-TiC-TiN-Mo-Ni cermet with 99% relative density and grain size of 50 nm was successfully prepared at sintering temperature of 1400 °C and sintering time of 10 min. The used heating device had a high heating efficiency and simple structure. The developed process has shorter holding time and lower sintering temperature compared to the traditional processes.

K e y w o r d s: microwave sintering, nanometer grain size cermet, phase transition

1. Introduction

Sintering process is the key step to determine performance of products made from traditional powder metallurgy materials and cermets, which are the base of modern industry. Hot pressing (HP) in nitrogen atmosphere is the main technology for preparing cermet materials. In this technology, the powder is pressed into a disc at high temperature, and then cut into pieces. Another main technology is cold pressing (CP) in a mould and sintering in vacuum, at which the powder is pressed into required form at room temperature, and then sintered. Both technologies have some shortcomings. Firstly, ceramic materials made by CP have bigger grains what results in poor density; secondly, HP is a one-way compaction so the properties of products made by HP are anisotropic, although they have smaller grain size because they are exposed to high temperature for a shorter time than those made by CP. Therefore, HP can only be used to make simple shaped products. In recent years a new fast sintering technology, microwave sintering (MWS), has been developed thanks to advances in microwave research and application [1–5]. The microwave sintering, differently from traditional sintering process, has uniform heating, i.e., each part of the workpiece absorbs the microwave energy at the same time and increases its temperature with an approximately identical velocity. The body heating leads to shorter heating and holding time and smaller temperature difference between the inner and outer of the body. Ceramic materials prepared by MWS have super-small grain, higher density, higher strength and higher toughness.

There are many papers on microwave sintering process of oxide ceramic, but a few for the cermet because of its weak microwave absorbance ability [6–7]. The aim of this contribution is to study the microwave sintering process of an Al_2O_3-TiC-TiN-Mo-Ni cermet. An appropriate assisting heating unit was designed in order to improve the microwave absorbance after comparing effects of several assisting heating materials. The performance and microstructure were studied as functions of sintering time and temperature.

2. Experiment

2.1. Raw materials

The purity of α-Al_2O_3, TiC, TiN, Mo, Ni materials is higher than 99 %. Graphite powder, iron oxide black, chromic oxide powder, cobalt oxide powder, and manganese oxide powder are all analytically pure.

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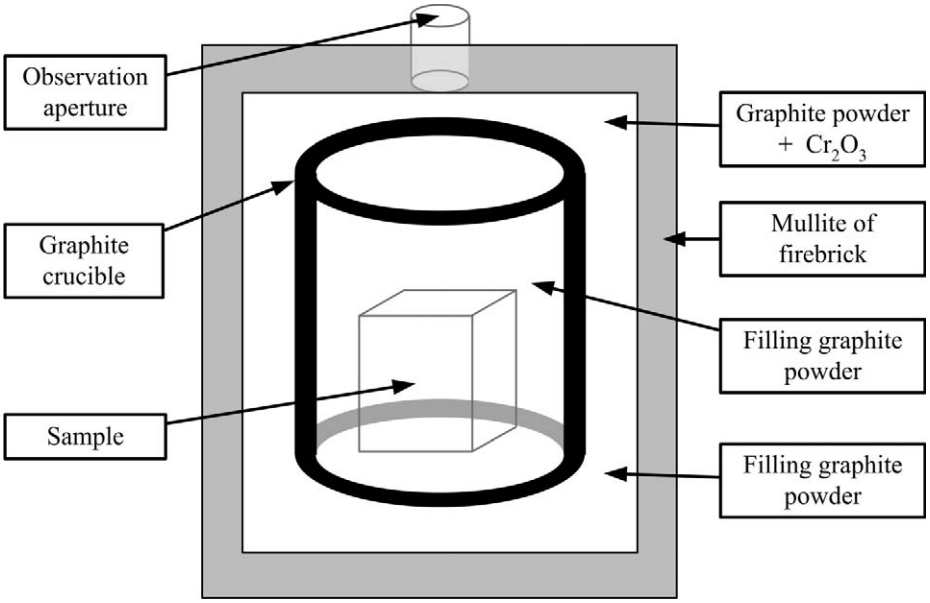

Fig. 1. Schematic of a home-made heat insulating device.

Table 1. Chemical composition of the raw material

Composition	α-Al_2O_3	TiC	TiN	Mo	Ni
Content [wt.%]	35	35	10	8	12

2.2. Composition, mixing and pressing of discs

Mixture was homogeneously mixed in a ball mill with acetone and grinding medium for 48 hours, and then vacuum dried. The mixture was embedded into the female mould cavity of a tablet-pressing machine. The power mixture was pressed at 160–180 MPa for 2 minutes. The average grain size of pressed green bodies was, according to the XRD measurements, about 35 nm. The chemical composition of the raw material is in Table 1.

2.3. Microwave sintering

The pressed green bodies were sintered in a home-renovated furnace. The microwave frequency was 2450 MHz and its power was adjustable from 0 to 850 W. Sintering temperature was between 1200 ℃ and 1600 ℃ and it was measured by a leucoscope. At first, the temperature was increased from the room temperature to the specific sintering temperature, during 5–7 minutes, then hold at this for 10–15 minutes; after this, the microwave input was stopped and the samples were naturally cooled down in the furnace. Highly purified graphite powder was used as a protective medium in order to protect from oxidation of TiC, TiN, Mo, and Ni.

2.4. Testing of sintered samples

Densities were determined by using Archimedes' method and converted into relative densities. X-ray diffraction (XRD) patterns were measured by a Y-4Q X-ray diffractometer manufactured by Dandong Fangyuan Instrument LLC, China, using Cu Kα radiation. Scanning velocity was 0.03 degree per second. Then the structure and phase composition were determined. From the XRD patterns the average grain size has also been calculated using Scherer's equation in the software platform of MDI Jade 5.0. The surface morphology was recorded using Scanning Electron Microscope (SEM) (Model S-450, Hitachi, Japan).

3. Results and discussion

3.1. Selection of heat insulating materials and design of heat insulating device

Selection of heat insulating materials and design of heat insulating device have a great importance for stable, uniform, efficient heating and holding temperature. Selected heat insulating materials have an excellent resistance at elevated temperatures, performance at holding temperature, ability to be used repetitively, a good penetrance of microwave to ensure high microwave energy absorbance of sintered materials.

A heat-insulating device is constituted of, as illustrated Fig. 1, an outer layer of resistant brick, and an inner layer of graphite crucible. The powder mix was filled in the crucible. After the interaction,

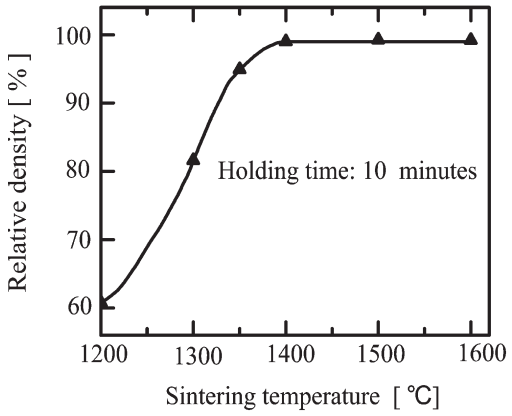

Fig. 2. Relative density dependence on the sintering temperature after 10 minutes of holding time.

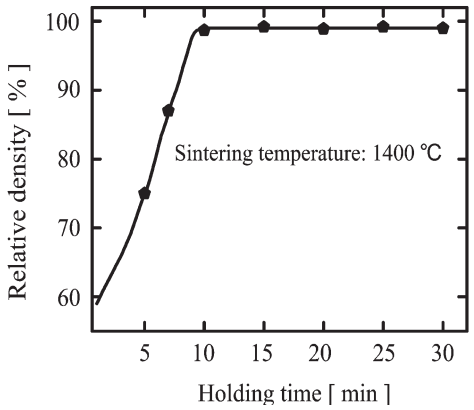

Fig. 3. Dependence of the relative density on the holding time at the sintering temperature 1400 ℃.

the microwave intensities, the high temperature resistance and processing ability were compared in several resistant bricks. A lightweight, porous Mullite firebrick was used as the outmost layer, which could hardly interact with microwave, and is able to resist at temperatures higher than 1500 ℃, can be easily processed, and is excellently holding the achieved temperature.

In order to improve performance of heat insulating device, several methods were used. Firstly, highly pure graphite powder was put on the bottom of the crucible and the powder mix was put on it. Then the powder mix was covered with a powder containing high amount of graphite and compacted. These measures could keep TiC, TiN, Mo and Ni from oxidation during high temperature sintering, because graphite has both an intense absorbance of microwave and excellent protection ability. Secondly, the high purity graphite powder was filled in the space between the graphite crucible and the firebrick, which can support the heating up and improve the temperature uniformity. Thirdly, one 5–6 cm layer of a specific mixture of graphite powder and Cr_2O_3 were put on the upmost surface of graphite powder in the inner of heat insulating device, which can accelerate the temperature rise and increase the sintering temperature.

The mixture of graphite powder and Cr_2O_3 was selected as a supporting heating material after making a comparison of several materials. Using the mixture of graphite powder and MnO_2, the temperature can reach 1200 ℃ or more after 2–3 minutes, but after that, the temperature goes up only slowly. For the mixture of graphite powder with Fe_3O_4, the temperature can reach 1000 ℃ during 10–15 minutes only, which is too slow. However, for the mixture of graphite powder and Cr_2O_3, the temperature can reach 1400 ℃ in 5 minutes. Therefore, the mixture of graphite powder and Cr_2O_3 was used as the supporting heating material with the volume ratio of 1 : 1.

3.2. Relative densities

Similarly as in the traditional sintering process, relative densities of ceramic materials were determined mainly by the sintering temperature and holding time of the microwave sintering process. Figure 2 shows the dependence of relative densities on the sintering temperature at a constant holding time of 10 minutes. Figure 3 shows the dependence of relative densities on the holding time at a constant sintering temperature of 1400 ℃.

Relative densities quickly increase with increasing the sintering temperature from 1100 ℃ to 1400 ℃ as it is shown in Fig. 2. When the sintering temperature was below 1100 ℃ the proof sample was hardly densified. For the sintering temperature 1400 ℃ the relative density reaches 99 %, and it changes little with further increasing. However, a local fusion of the sample was observed when the sintering temperature was higher than 1500 ℃.

Relative densities increase with the increasing of holding time, but they reach the maximum of 99 % after 10 minutes, but with further extending the holding time they varied only slightly.

Based on the above results, a compact cermet with relative density higher than 99 % was successfully sintered at 1400 ℃ for 10 minutes.

3.3. SEM analysis and grain size measurement

Figure 4 shows the SEM photo of an Al_2O_3-TiC--TiN-Mo-Ni cermet sintered at 1400 ℃ for 10 minutes. Figure 4 shows that the sintered body is very dense, without pores. Two phases can be clearly detected on the SEM, these were also reported by other researchers who described that the structure of this material was composed of two frameworks interlocking each other [8]. One skeleton consisted of Al_2O_3 grains and the

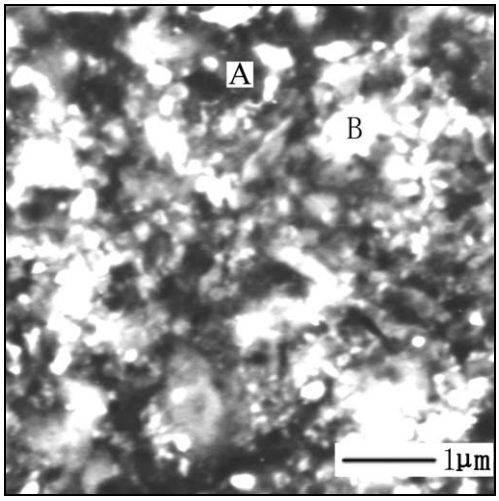

Fig. 4. SEM micrograph of an Al_2O_3-TiC-TiN-Mo-Ni cermet sintered at 1400°C for 10 minutes: A – Al_2O_3, B – carbonized grain with adhesive metal.

other was composed of carbide grains and bonding metal.

The content of Al_2O_3 and of carbonized material should guarantee the formation of respective frames. This kind of ceramic material has maximum performance advantages of both Al_2O_3 ceramics and TiCN--Ni-Mo_2C alloy. The content of Al_2O_3 should meet the need to form its framework, so should carbide. The Al_2O_3-TiC-TiN-Mo-Ni cermet has absolutely main merits of both Al_2O_3 ceramics performance and that of TiCN-Ni-Mo_2C alloy.

Average grain size of the sintered body was determined by using Scherrer's formula to deal with peaks of XRD pattern in MDI Jade analysis platform. The Scherrer's formula is as follows:

$$d = \frac{K \cdot \lambda}{FW(S) \cdot \cos\theta}, \tag{1}$$

where d is the grain size, K is a constant and is equal approximately to one, λ is the X-ray wavelength and is equal to 1.54178 Å, θ is the diffraction angle corresponding to the peak in XRD pattern, and *FW(S)* is the net full width half maximum of XRD peak.

FW(S) is calculated by

$$FW(S) = FWHM - FW(I), \tag{2}$$

where *FWHM* is full width half maximum of measured XRD peak of sintered body and *FW(I)* is full width half maximum resulted from X-ray Diffractometer itself.

The average grain size is 50 nm, which was calculated by SEARCH/MATCH function provided by MDI Jade 5.0. This indicates that the grain sizes did not increase markedly after sintering. So highly dense ceramic materials with small, or super-small grain can be prepared by microwave sintering.

3.4. Phase analysis

Based on the XRD patterns, phases of the sintered body were analysed by the MDI Jade 5.0 analysis platform. Figure 5 shows phases of a sample sintered at

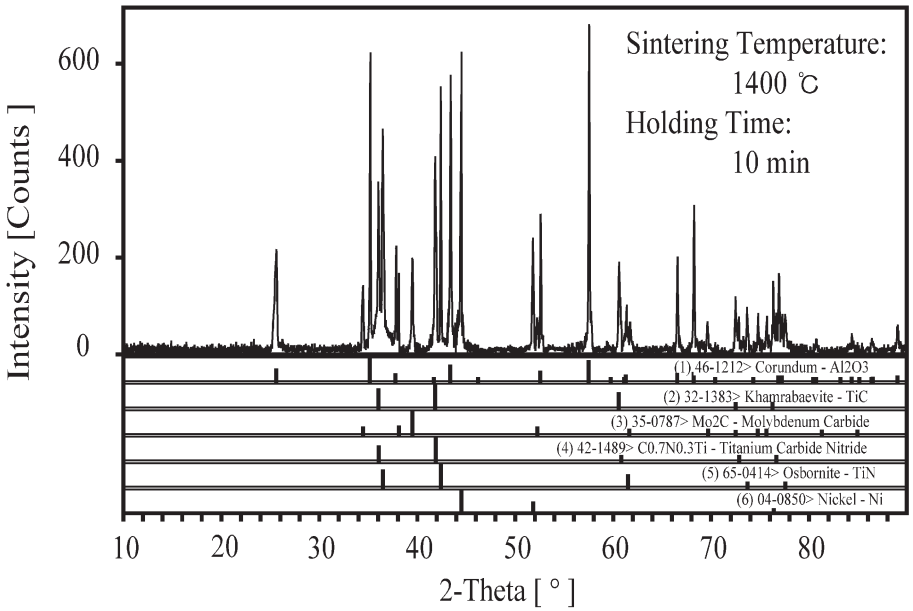

Fig. 5. X-ray diffraction pattern of an Al_2O_3-TiC-TiN-Mo-Ni cermet sintered at the sintering temperature of 1400°C for 10 minutes and the results of phase analysis.

1400 ℃ for 10 minutes. The results show that (1) in the sintered body Mo exists in the form of Mo_2C, which may result from substituting Mo atoms for Ti atoms in TiC crystal lattice. This substitution also causes formation of the (Ti-Mo)C solid solution in the surface of TiC grains, which restrains the growth of TiC grains; (2) The TiN content in sintered body varies with increasing the sintering temperature. Below 1200 ℃ the TiN content is almost constant, but from 1200 ℃ to 1400 ℃ it decreases with increasing temperature; (3) At high temperature TiN and TiC will react to form a TiCN solid solution because both TiN and TiC are structures of cubic system and can exist in the non-stoichiometric form of nitride or carbide. The performance of the TiC_xN_y solid solution is related to the sum of x and y. In general, this sum should be equal to or approach one. If the sum is less than one, free Ti atoms and Ni atoms may form a fragile Ni_3Ti phase because of shortage of carbon atoms, or nitrogen atoms, or both. This will decrease the cermet performance, moreover, the content of carbon or nitrogen will affect the composition and size of the hard phase in sintered body and cause unstable performance. Figure 5 shows that the $TiC_{0.7}N_{0.3}$ phase was gained at optimized sintered conditions; (4) Oxides were not present there in the sintered body, although the sintering temperature was up to 1500 ℃. This proves that the protective methods are effective. Heat insulating device in this contribution can be applied for sintering of oxidizing materials.

4. Conclusion

Microwave sintering technology has been developed with the aim to prepare refractory, poor microwave-absorbent Al_2O_3-TiC-TiN-Mo-Ni cermet using specific heat insulating device. Relative density and composition have been determined by the sintering temperature and holding time. With increasing temperature or/and time the relative density increases and reaches up to an almost constant value 1400 ℃/10 min. An Al_2O_3-TiC-TiN-Mo-Ni cermet with 99% relative density was successfully prepared using the optimized sintering conditions. The prepared cermet is dense and homogeneous with the grain size of 50 nm, which is only a little higher compared to the grain size of the materials before sintering. Such a low grains growth is a consequence of the formation of TiCN solid solution and the microwave heating process used.

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