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REPORT ON THE SINTERING AND PROPERTIES OF MgO and MgO-5%TiC

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1. INTRODUCTION

MgO is a ceramic material with many potential applications owing to its high melting point (2620°C ¹), high resistivity ($>10^{14}$ ¹), and good corrosion resistance ². MgO has only one structure type at all temperatures up to the melting point. Above 1600°C it is completely ductile, which can also be used to advantage. Another very important advantage regarding MgO is its affordability and availability. There are vast, well-distributed resources of magnesite in the world and there are even more abundant resources of dolomite which are cheaper to obtain than magnesite. MgO is also extracted directly from sea water ².

The main disadvantage of this material is its low fracture toughness ($2-3 \text{ MPam}^{1/2}$ ³) and strength (flexural strength about 100 MPa ¹). Limited effort has been devoted on the development of MgO based composites so far. Ikuma et al. ³ incorporated ZrO_2 particles into a MgO matrix, resulting in toughness values of $3.7 \text{ MPam}^{1/2}$. Niihara ⁴ developed nanophase composites including MgO-SiC with fracture toughness and strength values 2-4 times that of MgO alone. Tamari ⁵ produced hot pressed MgO-SiC composites and achieved a fracture toughness of about $5 \text{ MPam}^{1/2}$ with 30 vol% SiC. Higher strength values were also reported for composites with 30-50 vol% SiC particles.

The present study attempts to illuminate some of the untouched areas with regard to rapid rate sintering of MgO and MgO-TiC composites, as well as to the resultant mechanical properties.

II. EXPERIMENTAL

II.1. Preconsolidation Processing

The starting materials were 99.5% pure MgO^* (MgO_p), technical grade MgO^{**} (MgO_{Tg}) containing 98% MgO , 0.8% CaO , 0.35% SiO_2 , 0.2% Fe_2O_3 , 0.15% Al_2O_3 , and 0.4% other impurities, and 99.5% pure TiC^{***} . Average Fisher particle sizes given by the manufacturers were 0.28 μm , 5.00 μm , and 1.56 μm , respectively. MgO -5vol% TiC (MgO -5 TiC) mixtures were prepared by ball milling in methanol for 5 hours. Mixed slurries were partially dried on a hot plate while stirring. Further drying was achieved in a furnace at 100-200°C for 10-15 min. This method prevented segregation of the different phases. Dried cakes were crushed and ground using an alumina pestle and mortar. The powders were screened using a 175 mesh sieve. MgO -5 TiC powders prepared with the above method as well as MgO_p and MgO_{Tg} powders were dry pressed at 19 MPa. Graphite foil was used to prevent sticking of pure MgO -containing powders to the top and bottom of the steel mold during cold pressing.

Slips of each composition were prepared for slip casting by mechanical stirring of the constituents at high speed using a 3-speed household mixer. Since MgO reacts with water, alcohol is recommended for its slip casting⁶. Ethanol was used with MgO_p while methanol was found to provide better dispersion of MgO_{Tg} . In the case of MgO_p and MgO_p -5 TiC powders, a solid-to-liquid ratio of 80% was used. On the other hand, a solid-to-liquid ratio of 150% was possible in the case of MgO_{Tg} and MgO_{Tg} -5 TiC powders, probably due to the larger particle size, and thus, a smaller surface area that needed to be wet. Preliminary experiments with slip casting of alcohol-based slurries indicated that cracking occurs due to high drying rates. Therefore, drying rates were reduced by covering

* - M-1017, Cerac, Inc., Milwaukee, WI

** - MagChem 35, Martin Marietta Specialties, Inc., Hunt Valley, MD

*** - T-1227, Cerac, Inc., Milwaukee, WI

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the molds. This allowed drying of 30 mm diameter by 10 mm thick samples in about 36 hours. Slow drying totally eliminated the cracking problem.

Both cold pressed and slip cast MgO_p -containing bodies had lower green densities compared to MgO_{16} -containing bodies; 29% theoretical density (TD) vs 32-35%TD in the case of cold pressed samples and 20% vs 25%TD in the case of slip cast samples.

Rods 6 mm in diameter and 20 mm in length were prepared for plasma sintering experiments. W filaments were inserted from one end of these rods.

II.2. Sintering

II.2.1. Conventional Sintering

For conventional sintering studies, slip cast and cold pressed discs were put on alumina plates. The sintering schedule consisted of a 2-3 h heat-up regime, a 4 h hold time at 1600°C, and furnace cooling. All samples were sintered in air.

II.2.2. Plasma Sintering

Rods were suspended from one end via W-filaments along the central axis of two concentric steel cylinders. Plasma sintering was carried out using the hollow-cathode discharge (HCD) assembly depicted in Fig.1. Upon reaching a 300 mTorr vacuum, the plasma is generated by applying a 600-700 V DC voltage between the anode and cathode. Samples at the center of the cylinders (anode and cathode) are heated by atom bombardment and the hot plasma. The sample temperature was measured by an infrared pyrometer*. Sintering was conducted in air plasmas at 1200-1300°C, which was the highest temperature attainable in the system. Two samples per composition were sintered with a hold time of 4 minutes at the peak temperature.

* - Mikron M90, Mikron Instrument Co., Inc., Wyckoff, NJ

II.2.3. Microwave Sintering

A 2.45 GHz microwave source was used for sintering. Each sample was individually sintered in low density ZrO_2 insulation in air. Sample temperatures were measured using a fiber optic thermometer *. Sintering was done at 1500-1600°C for 5 minutes in air.

III. RESULTS

III.1. Sintering of MgO and MgO-5TiC

The consolidation behavior was analyzed by comparing the relative density of each sample after completion of sintering runs. Table I shows the final relative densities achieved by three different sintering methods. Relative densities of plasma-sintered samples are very low due to the low sintering temperatures and relatively slow sintering kinetics of MgO. Microwave-sintered samples attained higher relative densities compared to plasma-sintered samples, but lower densities than those obtained by conventional sintering. The lower relative densities of microwave-sintered materials are possibly due to the much shorter sintering times compared to conventional sintering (5 min vs 240 min, respectively). In the case of MgO-TiC composites, low bulk densities were achieved by microwave processing. The reason for low densities is the internal porosity caused by a gaseous reaction product. The pores formed a spongy structure in the composites and resulted in low relative densities. However, the exterior of the samples sintered to a much higher density probably due to easier exit of the gaseous reaction product. X-ray analysis of the composite indicated that Mg_2TiO_4 formed during sintering of all MgO-TiC composites. This suggests that the gaseous reaction product was CO or CO_2 .

The results illustrated in Table I indicate that MgO_{16} and MgO_{16} -5TiC samples are easier to sinter than MgO_p and MgO_p -5TiC

* - Accufiber Model 100, Multichannel Optical Fiber Thermometer, Accufiber, Inc., Beaverton, OR

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samples. The reason for improved sinterability of MgO_{16} -based samples is probably a higher contribution of liquid phase sintering to overall consolidation, due to the presence of impurities such as SiO_2 , Fe_2O_3 , and Al_2O_3 . Liquid phase sintering has previously been shown to improve the sintering of MgO ⁷.

Comparison of the relative densities of conventionally sintered samples in Table I indicates that MgO -5TiC composites attained higher relative densities than did monolithic MgO . This is an interesting result since second phase particles are generally known to decrease the sinterability of a parent material, such as in the case of TiC, SiC, or B_4C particles in Al_2O_3 ⁸. In fact, plasma sintering results also show that TiC limits the sinterability of MgO when sintering is done in vacuum, where TiC does not react with MgO . Table I shows that the addition of 5 vol% TiC limited the sinterability of MgO significantly in all cases. Hence, these results suggest that TiC (or Ti, since C is lost by the reaction) acts as a sintering aid in MgO when sintering is done in air. One possibility that comes into mind is liquid phase sintering by the phase Mg_2TiO_4 . However, this phase has a melting point of 1740°C ⁹ and since the highest sintering temperature was 1600°C , liquid phase sintering due to the new phase does not apply to the present case.

Comparison of the sintered relative densities of slip cast and cold pressed samples of same composition show that pressed samples reached to higher fractional densities than slip cast samples. This difference is most likely due to the higher green densities of cold pressed samples. It is generally accepted that higher powder compact densities lead to higher sintered densities. Higher particle packing densities and smaller average pore sizes lead to a higher average curvature in the neck regions between particles. Therefore, the average driving force for sintering is higher ¹⁰.

Overall, the results suggest that rapid rate, short-term sintering does not bear any advantage over conventional sintering since MgO powders, unlike, for example, Al_2O_3 ¹¹, have sluggish sintering kinetics.

III.2. Microstructure

Microstructures of fracture surfaces are shown in figs.2 through 7. In general, these micrographs support our discussion given in the previous section. Comparison of fig.2(a) and (b) indicates that the porosity in pressed and sintered MgO_{TG} decreased significantly by the addition of 5 vol%TiC. A similar result is found in the case of slip cast and cold pressed plus sintered MgO_p (Figs.3 and 4). It is also seen that grain growth accompanies decreased porosity.

Another important observation from fracture surfaces is the change in fracture modes. In the case of monolithic MgO , the fracture mode is predominantly intergranular, as seen in figs.2(a), 3(a), and 4(a). On the other hand, in the case of MgO -TiC composites, a significant portion of fracture occurred in the transgranular mode, as suggested by faceted grains in figs.2(b), 3(b), and 4(b). Even in the composites with considerable porosity this behavior is evident. The change of the fracture mode from intergranular to transgranular may be due to the increased grain size as suggested elsewhere¹².

Figures 5 and 6 show the microstructures of microwave sintered samples. Microwave sintered MgO_p has a fine grain size (about 3 μm) and little porosity (Fig.5(a)). The average particle size of microwave sintered MgO_p is larger than that of MgO_p (about 7 μm grain size). This difference is probably due to the higher sintering temperature used for these samples (1600°C vs 1500°C, respectively). The interior of MgO_p -5TiC composite has a spongy structure caused by the gaseous reaction of MgO and TiC. This structure is shown in fig.5(b). The microstructure of microwave sintered MgO_{TG} -5TiC is significantly coarser than that of MgO_{TG} (roughly 15 μm grain size).

Although the bulk of plasma sintered MgO had a low relative density, its exterior was sintered to quite high densities as suggested by the micrograph shown in Fig.7. The average grain size is very small (1-2 μm) indicating that no grain growth occurred during the short term, low temperature sintering. This suggests

that longer sintering times may produce higher densities by the plasma sintering process.

III.3. Mechanical Properties

The mechanical properties of monolithic MgO and MgO-5TiC composites fabricated by various techniques are shown in Table II. Overall, hardness values improved with increasing relative densities, as expected. For example, the hardness of MgO_p increased from 1.3 to 3.4 GPa when its relative density was increased from 78.8% to 87.7% TD by the application of cold pressing instead of slip casting. Similarly, the hardness of MgO_p-5TiC was raised from 2.1 to 4.0 GPa with a density increase from 81.3% to 91.7%. The average hardness of MgO_p increased from 3.4 to 4.0 GPa and that of MgO₇₆ increased from 2.6 to 4.0 GPa with the addition of 5 vol% TiC. This increase may be explained by the improvement in the fractional densities.

The hardness of microwave-sintered MgO₇₆-5TiC is quite high when its relative density is taken into account. This discrepancy is due to the fact that the tabulated density comes from the bulk sample. The hardness values were determined from the outer region which had a much higher relative density than the sponge-like interior.

The fracture toughness of MgO was raised by TiC additions in the case of conventionally sintered samples, which were the only samples where a useful number of tests was possible. The fracture toughness of slip cast and sintered MgO_p remained essentially constant but that of MgO₇₆ increased from 2.1 to 2.7 MPam^{1/2} with TiC additions (Table II). Similarly, the fracture toughness of pressed and sintered MgO₇₆ increased from 2.2 to 2.9 MPam^{1/2} with 5 vol% TiC addition.

These results show that the mechanical properties of MgO can be improved by small additions of TiC. Additions of larger amounts of TiC to MgO (50 vol%) resulted in extreme reaction and porosity in an air-sintered sample. Therefore, high amounts of TiC additions to MgO are not advisable.

IV. CONCLUSIONS

The following conclusions have been found from the present study: 1) Sintering of technical grade MgO yields higher fractional densities compared to research grade (relatively pure) MgO sintered under the same conditions. The higher densities can be attributed to a larger contribution of liquid phase sintering in the former powder, where a high fraction of liquid phase formers are present. 2) TiC reacts with MgO when sintering of MgO-TiC composites is employed in air. This reaction yields Mg_2TiO_4 and CO or CO_2 gas. The gaseous reaction products produce macropores during rapid heating (microwave sintering) or when the amount of TiC is high (e.g. 50vol%) during conventional sintering. 3) The reaction between MgO and TiC can be suppressed in vacuum according to plasma sintering results. This indicates that the reaction between MgO and TiC is promoted by air sintering. 4) Plasma sintering of MgO at relatively low temperatures (1300°C) and short times does not produce satisfactory results. TiC particles decrease the sinterability of MgO during vacuum (plasma) sintering. 5) 5 vol% TiC additions increase the sinterability of MgO during conventional air sintering. The mechanism of this improvement is not clear. Larger (50 vol%) additions decrease sinterability due to severe reaction leading to macropores formed by the gaseous reaction product. 6) Microwave sintering of MgO has been shown to be possible by indirect microwave heating for the first time to the authors' best knowledge. The sintering conditions need to be further optimized for maximum densification. 7) The mechanical properties of MgO have been improved by the addition of small amounts of TiC to the starting powders. This improvement is probably due to increased fractional densities.

V. SUGGESTIONS FOR FUTURE STUDY

In order to prevent unwanted reactions, second phase particles compatible with MgO should be carefully selected. Data in MgO-metal

nitride, carbide, and boride systems are very limited but valuable. Such systems should be systematically studied to understand their chemical, physical, and mechanical behavior. Second phase additions should be oxidation resistant if the composite is considered for high temperature applications in oxidizing atmospheres.

The reaction of TiC and MgO can be suppressed by vacuum consolidation according to the present study. Hot pressing in vacuum or inert atmosphere might be an ideal way of producing MgO-TiC composites and analyze their mechanical properties.

Microwave sintering of MgO should also be studied further. Emphasis should be given to increasing the sintering temperatures and times which may improve the sintered densities. An interesting study would be the microwave sintering of MgO-ZrO₂ composites, since ZrO₂ is more easily coupled with microwaves¹³ and the composite has been shown to have good mechanical properties³.

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**Table I. Fractional Densities of MgO and MgO-5TiC
Fabricated by Different Methods**

Fabrication Method	Material	% Theoretical Density
plasma sintering/ 1300°C/ 4 min/ vacuum	MgO _p	65.6
	MgO _p -5TiC	41.8
	MgO _{TG}	69.8
	MgO _{TG} -5TiC	48.0
slip casting/ conventional sintering/ 1600°C/ 240 min/ air	MgO _p	78.8
	MgO _p -5TiC	81.3
	MgO _{TG}	87.5
	MgO _{TG} -5TiC	90.7
cold pressing/ conventional sintering/ 1600°C/ 240 min/ air	MgO _p	87.7
	MgO _p -5TiC	91.7
	MgO _{TG}	86.2
	MgO _{TG} -5TiC	92.5
cold pressing/ microwave sintering/ 1500-1600°C/ 5 min/ air	MgO _p	77.4
	MgO _p -5TiC	71.8
	MgO _{TG}	84.0
	MgO _{TG} -5TiC	77.3

**Table II. Mechanical Properties of MgO and MgO-5TiC
Fabricated by Different Methods**

Fabrication Method	Material	% Theoretical Density	HV (GPa)	K _{Ic} (MPa m ^{1/2})	Number of Samples
plasma sintering/ 1300°C/ 4 min/ vacuum	MgO _p	65.6	N/A	N/A	N/A
	MgO _p -5TiC	41.8	0.3	N/A	N/A
	MgO _{TG}	69.8	2.3	N/A	N/A
	MgO _{TG} -5TiC	48.0	1.0	N/A	N/A
die casting/ conventional sintering/ 1600°C/ 240 min/ air	MgO _p	78.8	1.3	2.3	3
	MgO _p -5TiC	81.3	2.1	2.1	3
	MgO _{TG}	87.5	2.1	2.1	7
	MgO _{TG} -5TiC	90.7	2.9	2.7	6
cold pressing/ conventional sintering/ 1600°C/ 240 min/ air	MgO _p	87.7	3.4	N/A	N/A
	MgO _p -5TiC	91.7	4.0	2.6	2
	MgO _{TG}	86.2	2.6	2.2	6
	MgO _{TG} -5TiC	92.5	4.0	2.9	4
cold pressing/ microwave sintering/ 1500-1600°C/ 5 min/ air	MgO _p	77.4	1.5	1.2	4
	MgO _p -5TiC	71.8	2.3	N/A	N/A
	MgO _{TG}	84.0	2.2	2.0	4
	MgO _{TG} -5TiC	77.3	3.2	1.7	1

Fig.1. HCD plasma sintering set-up

Fig.2. SEM micrograph of pressed and sintered a) MgO_{16} and

Fig.3. SEM micrograph of slip-cast and sintered a) MgO_p and

Fig.4. SEM micrograph of pressed and sintered a) MgO_p and

Fig.5. SEM micrograph of microwave sintered a) MgO_p and

Fig.6. SEM micrograph of microwave sintered a) MgO_{16} and

Fig.7. SEM micrograph of plasma sintered MgO₁₆

The following equipment are required for future work on the sintering and properties of MgO and MgO-TiC,

- DTA and control panel: To analyze the reaction(s) between MgO and TiC
- Dilatometer: To study the sintering kinetics of MgO and MgO-TiC compacts
- Lindberg furnace: To sinter MgO and MgO-TiC ceramics
- Clousing lathe: To shape green and sintered ceramic bodies
- Control panel for hydraulic press: To control the necessary cold-pressing parameters during static powder compaction.

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