Received: 25 July 2020 | Revised: 13 August 2020 | Accepted: 25 August 2020

DOI: 10.1002/ces2.10068

ORIGINAL ARTICLE

International Journal of Ceramic Engineering & Science

Sinterability of macrocrystalline and cryptocrystalline magnesite to refractory magnesia

Zongqi Guo[1] | **Ying Ma**[2] | **Michel Rigaud**[3]

[1]Yingkou Jindai Technologies, Jiachen Group, Yingkou, China

[2]RHI Magnesita (Dalian) Co., Ltd., Dalian, China

[3]Ecole Polytechnique, University of Montreal, Montreal, QC, Canada

Correspondence
Zongqi Guo, Yingkou Jindai Technologies, Jiachen Group, China.
Email: zguo.lemonde@outlook.com

Abstract

The purpose of this paper is to present the results of an investigation aiming at obtaining high quality sintered magnesia from two well-known Chinese magnesite. Two types of natural magnesite have been considered, one macrocrystalline, from Liaoning, with the grain size of 60-100 μm and one cryptocrystalline, from Tibet, with 2-4 μm grains. Calcining characteristics to transform the two magnesite to caustic magnesia have been studied at first. Subsequently, the calcining-sintering characteristics using a two- and a three-step process for both raw materials at different temperatures have been determined. A DTA–TGA study reveals that the minimum endothermic peak during the calcining step differs by 28°C (624 vs 652°C between the crypto- and macrocrystalline magnesite). It has also been observed that by using a two-step sintering process, it is possible to obtain a magnesia with a bulk density of 3.26 and 3.14 g/cm^3, respectively, for cryptocrystalline and macrocrystalline, while with a three-step process, it is possible to reach a bulk density of 3.48 g/cm^3, even at a temperature <1750°C.

KEYWORDS

densification, hydration, magnesia, microstructure, sinter/sintering

1 | INTRODUCTION

There are two major sources to produce sintered refractory magnesia over the world. One is to concentrate Mg^{2+} from seawater or natural brine and to obtain the sintered dense magnesia at normal temperature of 1600-1700°C after calcining the precipitated magnesium hydroxide.[1] The other is to calcine natural magnesite ($MgCO_3$) and to sinter the compacts of caustic calcined magnesia at extremely high temperature of 1900-2100°C, to obtain top-grade quality grains with more than 98% MgO in purity, 3.45 g/cm^3 and higher in bulk density, and with large grains crystals containing few pores, low boron oxide (B_2O_3 < 0.05%) and the correct CaO/SiO_2 molar ratio.[2]

During the last three decades, the sintered natural magnesia, from Liaoning area, has been one of the prevailing raw materials for worldwide refractory manufacturers. It is called as dead burnt magnesia (DBM97) with the bulk density of 3.26-3.30g/cm^3. With the increasing demand for higher purity-grade magnesia, it became necessary to make use of reverse flotation to remove SiO_2 carrying portion and to upgrade caustic magnesia to 98% MgO, calcined by either multi-hearth furnace or suspension calciner.

Recently, a magnesite reserve of ~200 million tons in Riwoqe county, Tibet, has been considered.[3,4] In this investigation, both types of magnesite, from Liaoning and Tibet, are studied to compare their main characteristics after calcining and sintering in a

two-step process and in a three-step process of calcining, hydrating, recalcining and sintering at various temperatures.

2 | EXPERIMENTAL PROCEDURE

The fracture morphology of both magnesite ores is shown in Figure 1. The ranges of grain sizes have been obtained using a ZEISS/EVO18 scanning electron microscope. The floated magnesite containing grains of 60-100 μm comes from the Haicheng-Dashiqiao district in Liaoning, and the Tibetan magnesite, with 2-4 μm grains, is located in a 3800 m-altitude deposit of Riwoqe County, Tibet. Generally, magnesite ore shows the dependent structural crystal, without pores and defects after perfect growth.

The purification was made to remove silicate-carrying portion by the reverse floatation, from crushed and milled magnesite, and so the floated macrocrystalline magnesite is received as powder. The cryptocrystalline magnesite lumps are also crushed and milled prior to various tests.

The chemical analyses of both magnesites have been determined by X-Ray Fluorescence, using a Bruker AXS/S4 PIONEER spectrometer and presented in Table 1.

The MgO content in both raw materials is over 98%, with almost the same impurity levels of SiO_2, Al_2O_3, and CaO. But the trace content of Fe_2O_3 is significantly lower in the Tibetan magnesite than about 0.6% in Liaoning floated magnesite.

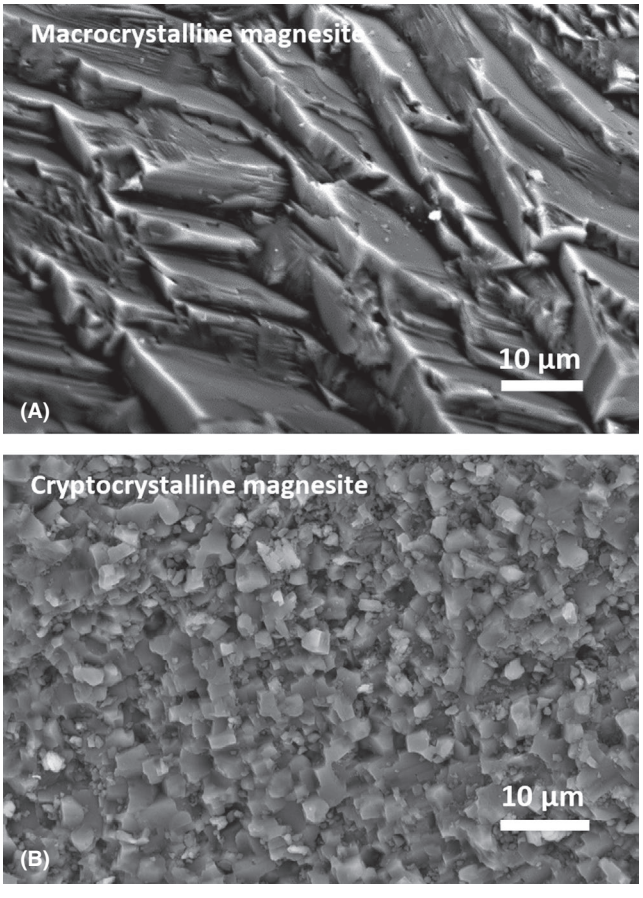

FIGURE 1 Fracture morphology of macrocrystalline and cryptocrystalline magnesite

The bulk density has been measured using mercury as an immersing media, according to GB/T 2999-2002 procedure. The decomposition temperature of 200-mesh magnesite powder is determined by thermo gravimetric analyzer (NETZSCH/DSC200F3). The particle size is measured by laser analyzer (Cilas/920L). Magnesium hydroxide is identified by X-ray diffraction (XRD) patterns (Rigaku/D-MAX 3B). Microstructural observation and the measurement of periclase crystal sizes are made by reflection optical microscopy (Nikon/Eclipse L150A), following the linear intercept procedure of ASTM E112-96(2006). The periclase crystal size is measured on the polishing section made of 60 grains of 3-5 mm in size, to match/record certain grids under microscope and then to calculate the average crystal size.

The activity of caustic calcined magnesia is tested by reacting with citric acid. The solution used at pH = 2.5 is obtained from the diluted citric acid of pH = 1.95 by adding distilled water. The caustic calcined magnesia of 2.0 g is put into 200 ml beaker, which is under magnetic mixer with the consistent temperature of 24°C. Turn on the mixer to 500 rpm and the second chronograph, and insert pH test stripscas in the solution immediately after 100 ml solution of citric acid is poured into the beaker. When pH value reaches 7.0, the number of the second is recorded by a counter to indicate the finished acid-base reaction. The activity is reflected by the second counting number of the reaction time between the caustic calcined magnesia and citric acid solution.

3 | RESULTS AND DISCUSSION

3.1 | The DTA-TGA variation

Differential thermal analysis (DTA) and thermo gravimetric analysis (TGA) patterns are shown in Figure 2 for

TABLE 1 The chemical analyses of Tibetan and Liaoning magnesite

Deposit origin	Tibet	Liaoning
Magnesite type	Cryptocrystalline	Macrocrystalline
Magnesite status received	Raw ore lump	Floated powder
Loss on ignition (1050°C)	50.81	51.68
Determination by XRF	(After loss on ignition)	
SiO_2	0.23	0.25
CaO	0.96	0.94
Fe_2O_3	0.03	0.59
Al_2O_3	0.02	0.04
MgO	98.75	98.18

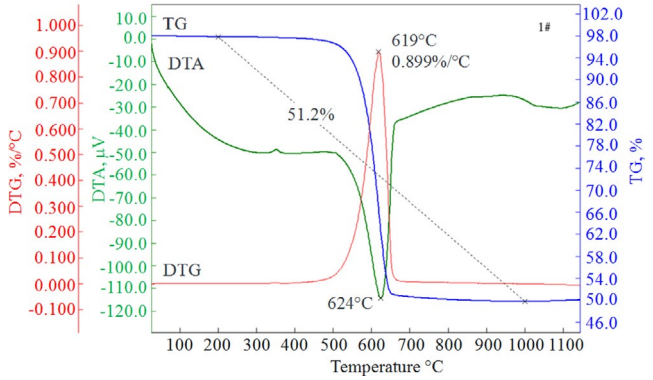

FIGURE 2 Differential thermal analysis (DTA) and thermo gravimetric analysis (TGA)patterns of cryptocrystalline magnesite

cryptocrystalline magnesite and in Figure 3 for macrocrystalline magnesite.

Cryptocrystalline magnesite starts to decompose at 510°C and finishes at 690°C, which is an endothermic reaction. The decomposition reaction takes place most dramatically at 624°C, which corresponds to the endothermic peak in Figure 2. Macrocrystalline magnesite decomposes at the temperatures between 512 and 712°C, with the endothermic peak at 652°C in Figure 3. Two types of magnesite have very similar characteristics of DTA–TGA variations, but the temperature of endothermic peak for cryptocrystalline magnesite is 28°C lower than that for macrocrystalline magnesite.

Thermal decomposition of magnesite is a solid-gas endothermic reaction to generate a solid phase MgO and a gaseous phase CO_2, in the following equation.

$$MgCO_3\,(s) \xrightarrow{\Delta} MgO\,(s) + CO_2\,(g)\,. \quad (1)$$

The weight loss ratio is 51.2% for cryptocrystalline magnesite and 53.8% for macrocrystalline magnesite. Comparing with theoretical value of magnesite decomposition of 52.19% calculated from the Equation (1), the thermal decomposition

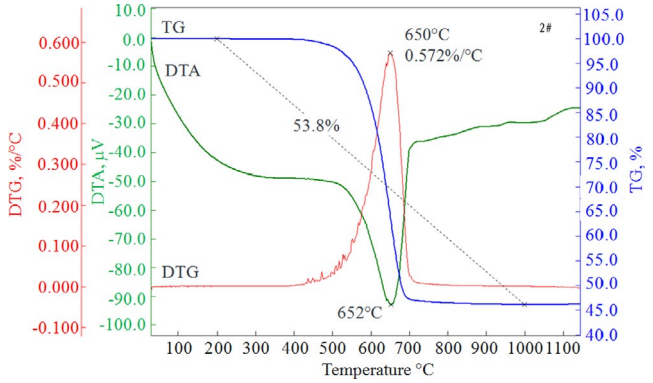

FIGURE 3 Differential thermal analysis (DTA) and thermo gravimetric analysis (TGA) patterns of macrocrystalline magnesite

is completed, generally. There is only one step of weight loss that is corresponding to one endothermic peak in both TG curves, which suggests that magnesite decomposition takes place in a one-step reaction.

3.2 | Influence of calcining temperatures on the activity of caustic magnesia

Both types of magnesite have been calcined at various temperatures between 600 and 1300°C, for 2 hours, respectively. After milling to $D_{50} = 10\mu m$, their activities have been determined according to the reaction time of calcined caustic magnesia (CCM) with citric acid, which is shown in Figure 4.

Since high activity of CCM results in short reaction time, the highest activity occurs at calcining temperature of 700°C for cryptocrystalline magnesite and 800°C for macrocrystalline magnesite. There is tardy acidic reaction of CCM from cryptocrystalline magnesite fired at the temperature lower than 650°C. The fast reaction occurs over 650°C, until 1300°C. However, CCM from macrocrystalline magnesite is inert to react with citric acid at the temperature lower than 700°C and higher than 1000°C. It is important to control calcining temperatures within the range between 750 and 900°C. Additionally, the activity is higher if CCM is ground to finer powder and the activity of CCM becomes important to enhance sinterability of CCM compacts.

Microstructural observations indicate decomposition reaction occurs from outer layer to inside, along cleavage plane of magnesite crystalline and with more cracks within grains. Rao's study proved that the particles of calcined magnesia powder are alike, somewhat smaller than those

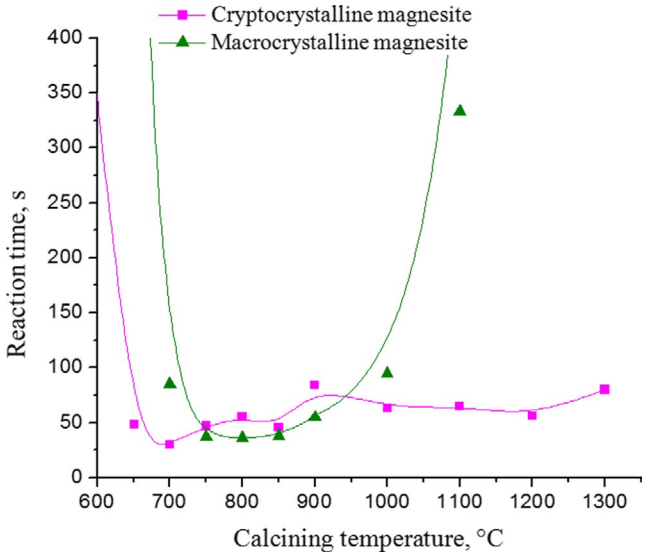

FIGURE 4 Reaction time of caustic magnesia calcined at various temperatures, with citric acid

of flotation-beneficiated magnesite particles in size, but their particle shapes look similarly rhombohedral.[5] It suggests the magnesite particles, after the liberation of carbon dioxide, remain the original shape to be the hard pseudomorphic particles or aggregates. Further calcination makes magnesia crystals get sintered within the pseudomorphic particles.[6] In the first phase, the crystals get rapid growth and the pseudomorphic aggregates get shrinkages to certain extend. Then, it is a sintering process governed by evaporation-condensation or surface diffusion mechanism. The growth of crystals is rapid at the beginning, but reduces to low speed. There is no significant shrinkage and change of the pseudomorphic aggregates, where the pores become large. Finally, the diffusion on crystal boundary starts working and the pseudomorphic aggregates shrink again. In the case of block magnesite ore, the volume of pseudomorphic aggregates contract, resulting in the decrease of coordination numbers and the specific surface area and sintering densification is impeded, showing slow densification process.[7] Additionally because of high strength, the aggregates are hardly to be disrupted under the ordinary compacting pressure.

Because of the pseudomorphic aggregates, it is not possible to sinter directly magnesia from magnesite in China, to an acceptable level of bulk density. The common industrial practice is to calcine magnesite firstly, to grind and compact, and finally to sinter at very high temperature.

3.3 | Sintered results, using both magnesites in a two-step process

Such a two-step process sintering is schematically summarized in Figure 5. It is proved that there is no significant influence of original size of magnesite ore (either small lump or powder) on CCM activity because the calcining process

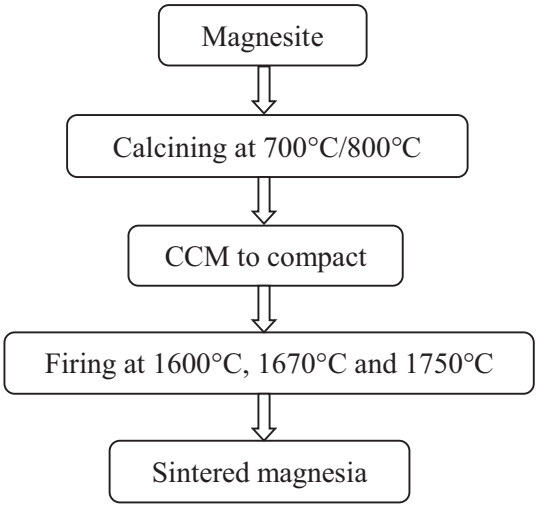

FIGURE 5 Two-step process sintering

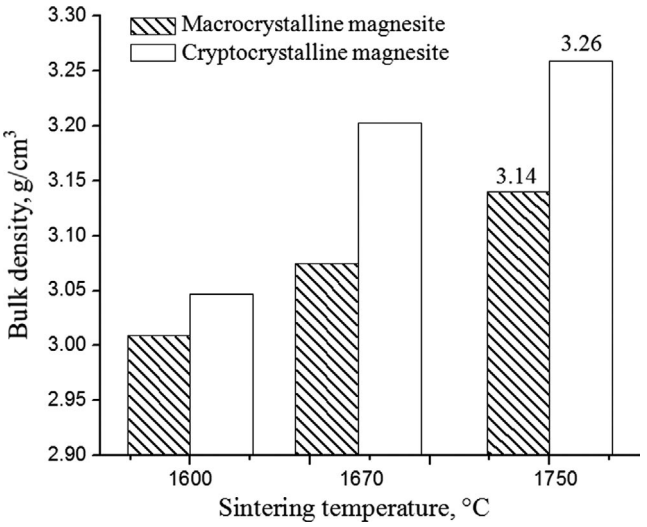

FIGURE 6 Bulk density as a function of sintering temperature

is driven by the decomposition of magnesite to release most portion of CO_2.

Macrocrystalline magnesite has been calcined at 800°C and cryptocrystalline magnesite at 700°C for 2 hours. After being crushed and milled for 24 hours to have the particle size of D_{50} = 10μm, both types of CCM are pressed under 100 MPa to prepare compacts of 25 × 25 × 125 mm bars. After being dried at 120°C for 12 hours, the compacts are fired at 1600, 1670, and 1750°C for 6 hours, respectively, being available burning temperatures in tunnel kilns.

As expected, the bulk density of the compacts after sintering increases significantly with temperatures, as shown in Figure 6. It reaches a maximum of only 3.14 and 3.26 g/cm^3 at 1750°C for macro- and cryptocrystalline samples, respectively. The periclase crystal sizes follow the same trend.

3.4 | Sintered results, using both magnesites, in a three-step process

The three-step process sintering is schematically illustrated in Figure 7.

After same calcination in Section 3.3, the calcined magnesia is ground with water for 24 hours. The resulting solution is heated at 80-90°C for 3 hours to make magnesia hydrated and dried at 200°C for 12 hours. It is then ground again for 5-6 hours to obtain brucite $Mg(OH)_2$ powder, with D_{50} = 4.43 μm for the floated magnesia and D_{50} = 4.06 μm for Tibetan magnesia. Both types of brucite $Mg(OH)_2$ powder are calcined at 500, 600, 700, 800, 900, and 1000°C for 1 hour, respectively, and then milled to active CCM powder (D_{50} = ~12 μm). The active MgO powder is pressed under the pressure of 180 MPa to make the cylinders of ϕ36 mm in diameter and 50 mm in height. After dried at 110°C,

the cylinders are fired at 1670 and 1750°C for 6 hours in tunnel kiln.

The XRD patterns for the two respective hydrated powders obtained prior to the second calcining step are shown in Figure 8, where the hydration degrees of only most active CCM are determined after macrocrystalline magnesite is calcined at 800°C and cryptocrystalline magnesite at 700°C. It is possible to acquire a content of about 89% brucite $Mg(OH)_2$ and to remain ~11% periclase MgO from cryptocrystalline CCM against ~95% and ~5% from macrocrystalline CCM.

After re-calcination and sintering, the bulk density of the sintered magnesia obtained after sintering at either 1670 or 1750°C does vary with the recalcining temperature variations, as clearly shown in Figure 9.

All those results show the potential benefit to use a 3-step process rather than 2-step process, in other words, to sinter the calcining caustic magnesia derived from a transformed $Mg(OH)_2$ mix rather than directly from the magnesite source, in order to obtain sintered magnesia with a bulk density of 3.48 g/cm^3. Such results are in line with previous studies, confirming the observations made by Ref [8–10], that is either first to grind CCM obtained from $Mg(OH)_2$ rather than $MgCO_3$, then to produce higher bulk density after sintering

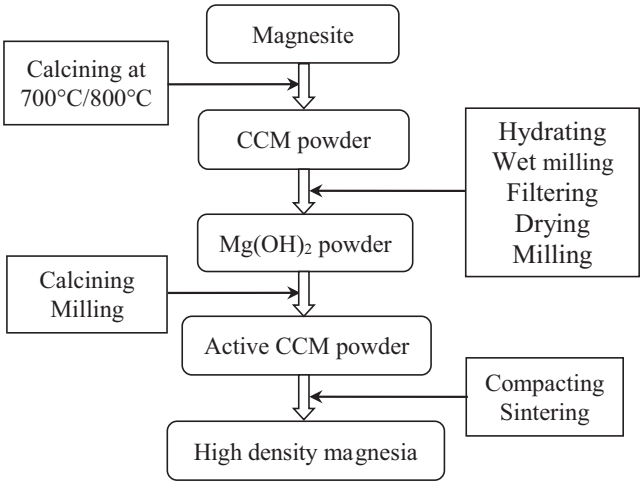

FIGURE 7 Three-step process sintering

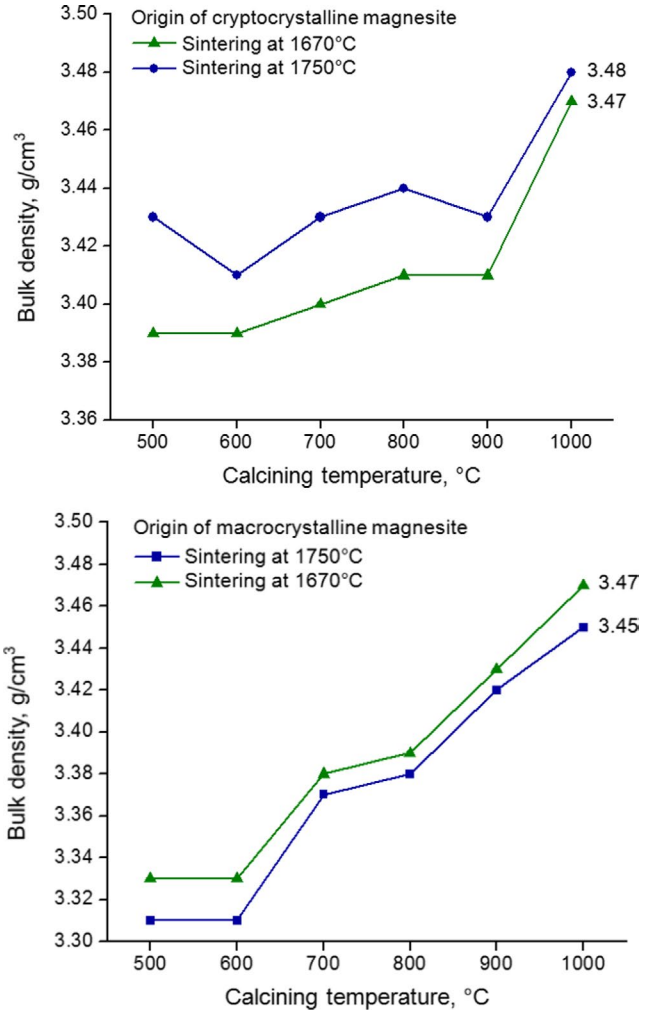

FIGURE 9 Bulk density after sintering at either 1670 or 1750°C, as a function of the calcining temperature to obtain an active calcined caustic magnesia powder

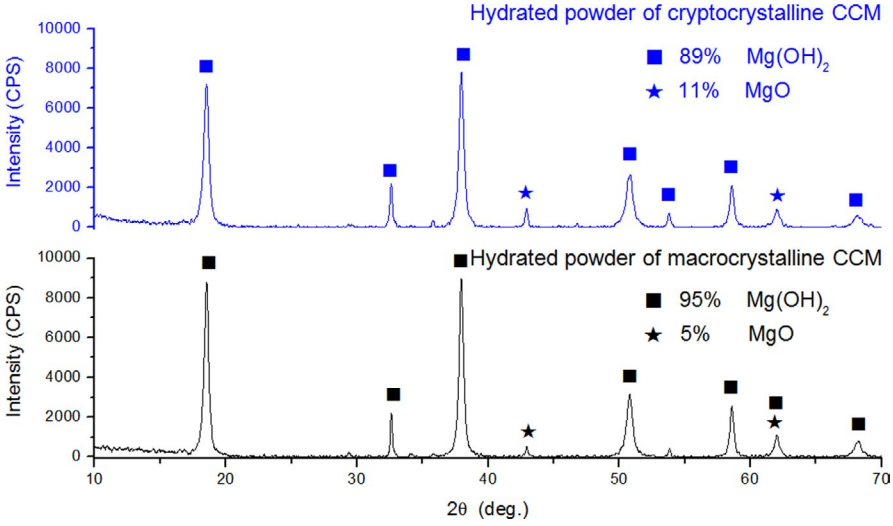

FIGURE 8 XRD patterns of hydrated powders

TABLE 2 Average crystal size of three-step sintered magnesia, μm

Magnesite type and sintering temperature		Calcining temperature of $Mg(OH)_2$ powder, °C					
		500	600	700	800	900	1000
Macrocrystalline	1670°C	58	63	64	64	75	78
	1750°C	61	67	73	80	85	98
Cryptocrystalline	1670°C	88	92	94	96	106	115
	1750°C	92	94	105	107	110	117

in the range of 1670 to 1750°C. Yu[11] found that the H_2O involved during the decomposition of magnesium hydroxide was partially dissolved in MgO to generate many divacancies. It could be understood that no CO_3^{2-} group residuum confinement and the dissolved H_2O are very helpful to sintering in CCM of magnesium hydroxide.

Combined with the average crystal sizes listed in Table 2, it is clear to see that higher calcining temperatures are beneficial to crystal growth and sintering densification, particularly for cryptocrystalline magnesite. In both cases of cryptocrystalline and macrocrystalline magnesite, it is essential to calcine magnesium hydroxide at 1000°C to densify sintered magnesia over 3.45 g/cm^3, which can be achieved either at 1670 C or 1750°C. Whatever the calcining temperature is, the better sintering temperature is 1670°C for macrocrystalline magnesite, whereas it is 1750°C for cryptocrystalline magnesite. It is very valuable to sinter magnesia at relatively low temperatures and with large temperature range for industrial process. Again by three-step sintering process, it is proven that it is more susceptible to sinter cryptocrystalline magnesite.

After calcining, hydrating, recalcining, and sintering, microstructures of high-purity, dense magnesia are shown in Figure 10. The periclase crystals are well grown, showing approximately hexagonal shapes. There are lots of small pores, particularly along the boundary of periclase crystals, in 1670°C sintered magnesia of macrocrystalline magnesite (Figure 10A). They become larger after sintered at 1750°C. The pores and defects are much smaller and less in sintered magnesia of cryptocrystalline magnesite (Figure 10B). The formation of interstitial phases depends on CaO/SiO_2 ratio along the route from $2MgO{\cdot}SiO_2$ to $2CaO{\cdot}SiO_2$ in the MgO–CaO–SiO_2 system. In the sintered magnesia with the high purity of >98% MgO and the high density of >3.45 g/cm^3, the CaO/SiO_2 ratio, that is much larger than 2.2, must result in the formation of dicalcium silicate as the interstitial phase, which is difficult to be detected in fine boundary shown in Figure 10.

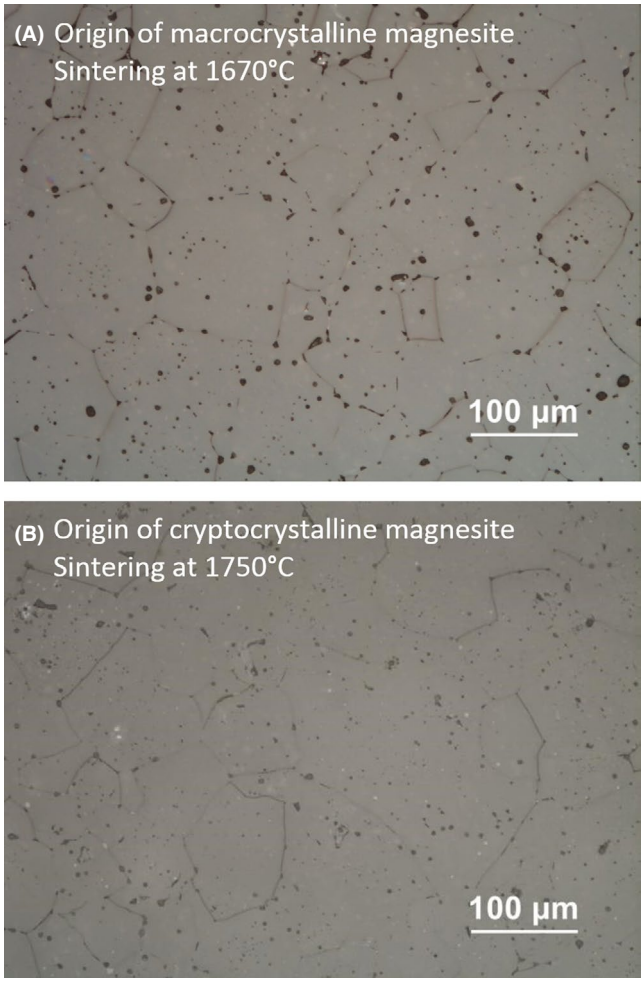

FIGURE 10 Microstructures of high-purity, dense sintered magnesia

4 | CONCLUSIONS

1. Based on the same grain size of the powder and same amount used in the DTA-TGA tests, the cryptocrystalline magnesite starts decomposition at 510°C, and finishes at 690°C, with the endothermic peak of 624°C. The macrocrystalline magnesite exhibits the endothermic reaction for decomposition at the temperatures between 512 and 712°C, being most drastic at 652°C as the endothermic peak.
2. Significant differences of activity for the caustic magnesia obtained by calcining at different temperatures exist. The highest activity occurs at 700°C for the cryptocrystalline magnesite and at 800°C for the macrocrystalline one.
3. With a two-step sintering process, the highest bulk density of magnesia attainable is 3.26 g/cm^3 from the cryptocrystalline magnesite and only 3.14 g/cm^3 from the macrocrystalline magnesite.

4. With a three-step sintering process, the highest bulk density obtainable is 3.48 g/cm^3, starting with a cryptocrystalline Tibetan magnesite, after sintering at 1750°C while it only reach 3.47 g/cm^3, starting with a macrocrystalline Liaoning magnesite and sintering at 1670°C.
5. In order to reach such performance it is essential to recalcine the magnesium hydroxide powder at 1000°C for both types, after due milling and compacting prior to sintering.

ORCID

Zongqi Guo https://orcid.org/0000-0002-5321-2133

REFERENCES

1. Bhatti AS, Dollimore D, Dyer A. Magnesia from seawater: a review. Clay Miner. 1984;19(5):865–75.
2. Rong ZH, Liang XY, Feng SC. Development of the technology for producing high-quality magnesia from Haichengmagnesite, China. *Proceedings of International Symposium on Refractories*; 1988 Nov 15–18; Hangzhou, China. p. 179–88.
3. He ZY, Ma LT, Liu BK. Crystallographic characterization and thermal decomposition behavior of high purity microcrystalline magnesite. Proceedings of UNITECR2011; 2011 Oct 30-Nov 2; Kyoto, Japan. p. 2-B2-16.
4. Feng RT, Liu BK, Tian XL. Research and application of microcrystalline magnesite in Tibet, China. Proceedings of UNITECR2019; 2019 Oct 13–16; Yokohama, Japan. p. 15-B-15.
5. Rao DS, Geng XM, Xu XW. Characters and sintering of magnesite in the south of Liaoning province. Proceedings of International Symposium on Refractories; 1988 Nov 15–18; Hangzhou, China. p. 217–23.
6. Li N, Chen RR. Kinetics of sintering and grain growth of MgO during calcination of magnesite. J Chin Ceram Soc. 1989;17(1):64–8.
7. Zhou BY, Li ZJ, Wu F. Periclase particles densification behavior at early stage of block magnesite sintering. Trans Mater Heat Treat. 2015;36(5):1–4.
8. Kim MG, Dahmen U, Searcy AW. Structural transformations in the decomposition of $Mg(OH)_2$ and $MgCO_3$. J Am Ceram Soc. 1987;70(3):146–54.
9. Yu JK, Ma PC, Li H, Yuan L. Preparation of high-density magnesia from natural magnesite. Proceedings of UNITECR2011; 2011 Oct 30-Nov 2; Kyoto, Japan. p. 31-E-10.
10. Livey DT, Wanklyn BM, Hewitt M, Murray P. The properties of MgO powders prepared by the decomposition of $Mg(OH)_2$. Trans Br Ceram Soc. 1957;56(5):217–36.
11. Yu GC. The divacancies in MgO —— II. the solid solution (MgO, H_2O). J Chin Ceram Soc. 1978;6(4):251–5.

How to cite this article: Guo Z, Ma Y, Rigaud M. Sinterability of macrocrystalline and cryptocrystalline magnesite to refractory magnesia. *Int J Ceramic Eng Sci*. 2020;2:303–309. https://doi.org/10.1002/ces2.10068