



Effect of TiO₂ on Melting and Crystallization Mechanism of Fused Magnesia

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Fused magnesia was prepared by electric arc furnace melting method using high purity brine magnesia as raw material. The melting and crystallization mechanism of fused magnesia containing 0.15, 0.25 and 0.35 wt % TiO₂ have been investigated. The bulk density, impurity content, crystal type and microstructure of product samples were characterized by Archimedes Method, ICP-AES, XRD, SEM, respectively. Results indicated that fused magnesia with purity of 99.472 wt %, bulk density of 3.569 g/cm³ and apparent porosity of 0.595 % could be obtained with addition of TiO₂ less than 0.25 wt %. It can promote impurities diffusion, MgO crystallization and structural densification. However, excess TiO₂ (> 0.35 wt %) over the solid solubility limit reacted with MgO to form magnesium titanate (Mg₂TiO₄), meanwhile the magnesia crystal was irregular and microstructure changed.

Keywords: TiO₂, Fused magnesia, Melting and crystallization, Solubility limit.

INTRODUCTION

Fused magnesia owns high crystallinity, large grain size, compact structure, good insulation resistance and excellent thermal conductivity and stability. Thus, it is widely used in metallurgical industry, special ceramics and glass industry as high-tech refractory materials. In recent years, high-purity fused MgO has played significant roles in the fields of HTS devices, high-precision optical thin film materials, high-temperature crucibles, semiconductor materials and aerospace science and technology. Unfortunately, the traditional production process introduced impurities inevitably by graphite anodes during the preparation of high-purity fused MgO. Its performance was far less than the demanding requirements of high-purity fused magnesia. Previously, researchers noticed that some artificial additives can lower the melting temperature of system, promote crystal growth and impurities purification for sintering magnesia production at above 1600-1500 °C. However, fused magnesia always is produced by electric arc furnace at about 3000 °C and the production process is totally different. Thus, we are dedicated to finding artificial additives to accelerate the process of impurities precipitation and study the melting and crystallization mechanism in molten pool. It would be helpful to improve the performance of high-purity fused MgO and then beneficial for practical production.

Many scholars¹⁻⁴ focused on studying on the influence of additives on sintering magnesia crystallization mechanism and then indicated that rare earth oxides, fluorides, TiO₂ and other

additives had positive impact on sintering magnesia to strengthen bulk density, grain size and purification. There exist two theories; one is the solid solution formed by additive and MgO; the other one is the grain boundary migration rate of periclase. Specifically, researches on effect of TiO₂ on sintering and grain growth kinetics of MgO from MgCl₂·6H₂O pointed out that TiO₂ solubilized in MgO was favorable to cation diffusion⁵. Also, the influence of Li₂O and ZrO₂ on sintering densification was determined by the mechanism of solid solution and high-temperature crystal transition, respectively. Han *et al.*⁶ added 2 wt % WO₃ in MgO at 1600 °C and found that the formation of low-melting compounds, such as MgWO₄, CaWO₄ and monticellite, was likely to increase the liquid volume during sintering process to enhance structure densification. Martinac *et al.*⁷ studied the effect of secondary crystalline phase on densification formed by Al₂O₃-MgO during the sintering, as well as the additives of SiO₂ and TiO₂. Martinac *et al.*⁷ considered that volume expansion and crack initiation caused by spinel (Al₂O₃-MgO) was unbeneficial for the bulk density and apparent porosity of sintering magnesia. The experimental data also confirmed that effectiveness of SiO₂ and TiO₂ were better than Al₂O₃ by generated forsterite and magnesium titanate, respectively. Especially, a tiny of TiO₂ could reduce sintering temperature effectively to accelerate grain growth and crystal boundary migration. In addition, Petric *et al.*⁸ stated that volatilization of B₂O₃ could be speeded up by added TiO₂ to form high-melting point of titanate, like CaTiO₃.

The studies mentioned above are mainly focused on the effect of additives on sintering magnesia crystallization and mechanism rather than fused MgO crystallization process. It is rare to find the reports about analysis of the complicated process of fused MgO at 2850 °C or higher, needless to say, there are almost existed no research publication reporting the impact of TiO₂ on the performance of fused magnesia, like the purity, density, lattice parameter, crystal morphology, *etc.* This paper reports the densification behaviour and crystallization mechanism of fused MgO with additive of 0, 0.15, 0.25 and 0.35 wt % TiO₂ at extreme high temperature.

EXPERIMENTAL

The chemical composition of light burned brine magnesia was characterized by the X-ray diffraction. Table-1 revealed that the main impurities are CaO, SiO₂, Fe₂O₃ and Al₂O₃. The raw material with 0, 0.15, 0.25 and 0.35 wt % TiO₂ (AR-grade, purity > 99.0 wt %) was well mixed to be molten in three-phase electric arc furnace equipped with high-purity graphite anodes for more than 10 h and then cooled for 48 h in order to drop out impurities and promote grain growth. Finally, samples from crushed molten pool were classified manually in orders.

Standard liquid displacement method using Archimedes' principle helped to obtain the physical properties of bulk density and apparent porosity of these fused magnesia samples. Crystalline phases of samples were identified by a diffractometer (D/MAX 2550 VB/PC; Rigaku Corporation, Tokyo, Japan) with Cu K radiation source under operating conditions of 40 kV/100 mA. Impurity elements were analyzed by ICP-AES (ARCOS RAS12). Then, the microstructures of fused magnesia were observed by a scanning electron micro-scope (SEM; JEOL JSM-6360LV; JEOL Ltd., Tokyo, Japan). Also, Stereo Microscope (Discovery. V20, ZEISS) took the photos of fused magnesia crystals.

RESULTS AND DISCUSSION

Effect of TiO₂ on fused magnesia purity and densification: The raw material added with 0, 0.15, 0.25 and 0.35 wt % TiO₂ were fused in electric arc furnace for 10 h. Then, we sampled the MgO from different positions in the cooled molten pool to obtain the quantity of impurity element by using ICP-AES. The data were shown in Table-2 and Fig. 1. The result in Table-2 showed that the foreign matter had been strongly purified, especially the major elements: Ca, Si, Fe, Al. Compared with the purity of MgO showed in Table-1, indicated that a growing amount of TiO₂ had a strongly effect on improving the purity of fused MgO.

From Fig. 1, it is concluded that samples located in the center of molten pool owned the highest purity of MgO. With

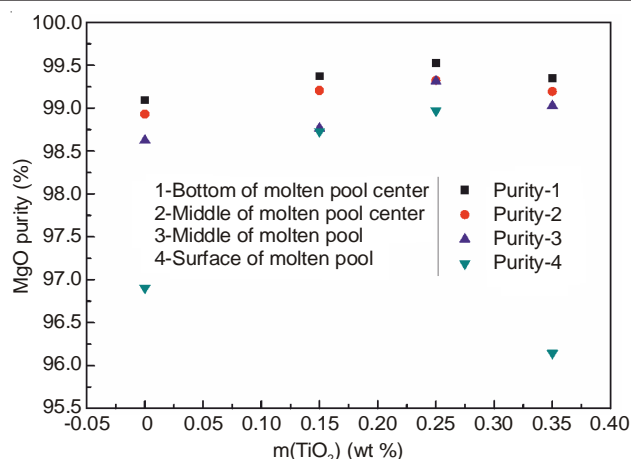


Fig. 1. Purity of molten pool with different addition of TiO₂

the addition of 0.25 wt % TiO₂, the purity of samples positioned in molten pool was outweighed the average. However, there would be a decreasing trend for MgO purity due to the content of TiO₂ added up to 0.35 wt %. Even so, its pureness was better than the raw material without TiO₂.

Fig. 2(a,d) presented the main impurities element, namely Ca, Si, Fe and Al. As shown, generally, the content of Ca and Si were relatively higher than other two. It was an inside-out trend that the impurity content of inner molten pool was lower than outer because of liquid impurity enrichment and precipitation to the surface and then sublimation at super-heat. In addition, for the same batch samples, with the rising content of TiO₂ added from 0 to 0.25 wt %, most of undesirable particles were expelled gradually. But, impurities would go up when TiO₂ reached its limit of removing impurities, the addition of 0.35 wt %.

Fig. 3 shows the bulk density and apparent porosity of fused magnesia. The data obtained from Archimedes' principle indicated that few quantities of TiO₂ additives favorably influence the density of fused MgO samples. The bulk density of samples increased to 3.57 g/cm³ with the increasing content of TiO₂ from 0 to 0.25 wt %, thus samples mixed with TiO₂ were denser than the undoped ones, also were more less porosity (minimum 0.60 %). However, the density began to decrease when added more than 0.25 wt % TiO₂, even lower than the original one. Since MgO and TiO₂ are face-centered-cubic ionic crystals with a total grid effect and also Mg²⁺ and Ti⁴⁺ radius are close to each other. During the melt crystallization process, Ti⁴⁺ would occupy the lattice sites where Mg²⁺ really positioned. Additionally, one Ti⁴⁺ icon with four positive charges would replace two Mg²⁺ icons with two positive charges in order to obtain electric neutrality. Thereby, large numbers of vacancies have been born eventually and this rule would

TABLE-1
XRF ANALYSIS RESULT FOR MgO RAW MATERIAL

	MgO	CaO	SiO ₂	Fe ₂ O ₃	Al ₂ O ₃	SO ₃	TiO ₂	Cl	Na ₂ O	K ₂ O	B ₂ O ₃	Cr ₂ O ₃
wt %	97.630	0.540	0.338	0.051	1.260	0.004	0.070	0.011	0.062	0.010	0.006	0.002

TABLE-2
ICP-AES ANALYSIS RESULT FOR MOLTEN POOL CENTER FUSED MAGNESIA WITH ADDITION OF 0.25 wt % TiO₂

	MgO	CaO	SiO ₂	Fe ₂ O ₃	Al ₂ O ₃	SO ₃	TiO ₂	Cl	Na ₂ O	K ₂ O	B ₂ O ₃	Cr ₂ O ₃
wt %	99.472	0.245	0.145	0.022	0.064	—	0.052	—	—	—	—	—

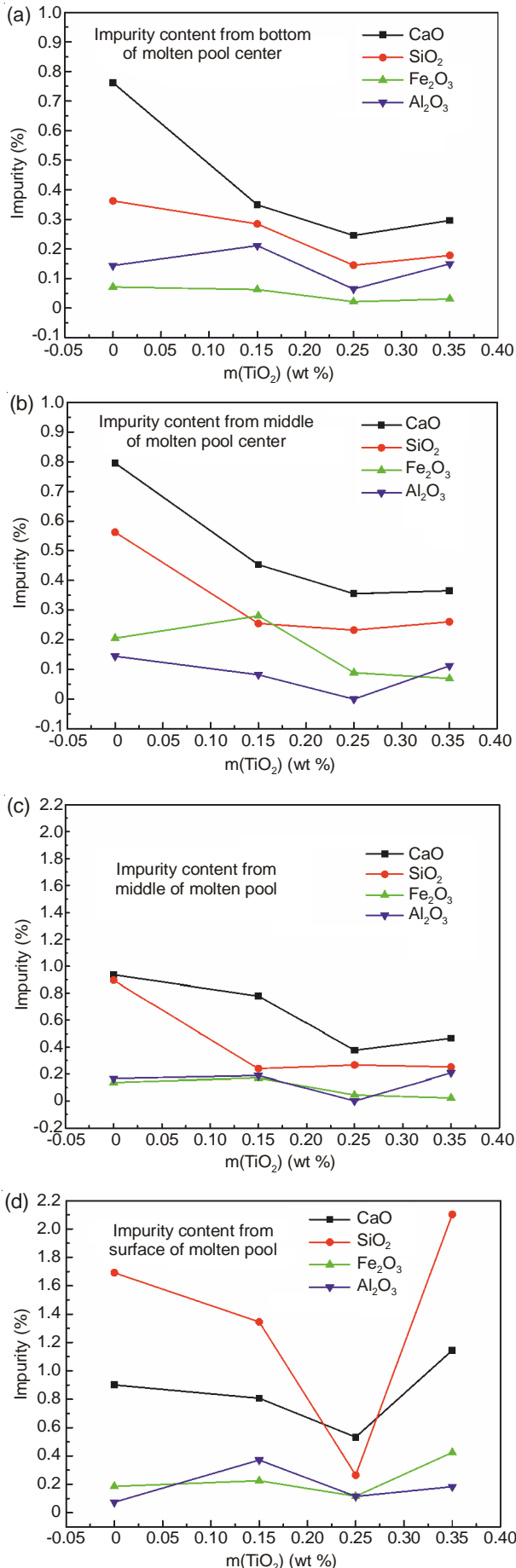


Fig. 2. Main impurity of molten pool with different addition of TiO₂

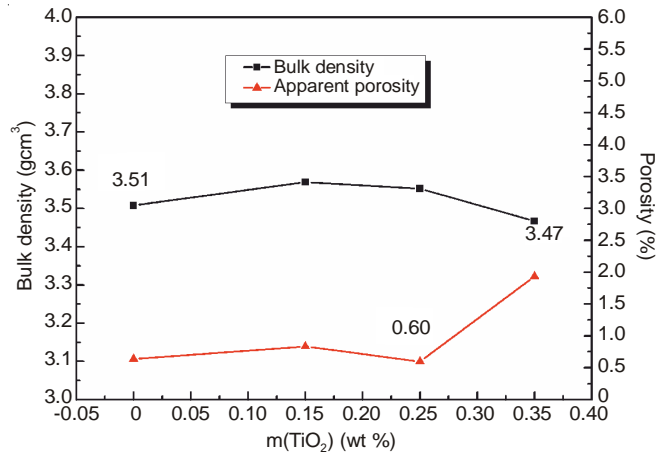
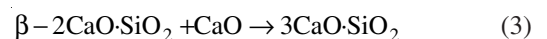


Fig. 3. Bulk density and apparent porosity of fused magnesia with different addition

activate the damage of crystal lattice integrity, thus it led to the reduction of volume density.

Researchers⁹ claimed that solid solution developed by MgO and additives must be the factor influencing magnesia melting mechanism. Therefore, in the course of fused magnesia melting, MgO grew gradually into periclase phase. At the same time, the main impurities, like CaO, SiO₂, Fe₂O₃, Al₂O₃, would solid solution into an adjacent periclase or react with other foreign matters. For an instance, the silicates compound reacted by CaO and SiO₂ resided in the periclase grain boundaries. Due to the high heating, in the whole system, alkaline CaO would react with acidic SiO₂ preferentially. So, in general, the ratio of Ca/Si was a fundamental measurement criterion of fused magnesia performance¹⁰. The higher Ca/Si ratio was, the more CaO and SiO₂ formed high-melting-point silicates on the boundaries of MgO grain, thus, the better of fused magnesia stability and densification would probably be acquired.

In the melting pool, with the temperature rising up, the reaction occurred¹¹ between CaO and SiO₂ as eqns. 1 and 2¹¹. When it was higher than 1200 °C, xCaO·MgO·2SiO₂ would disappear gradually while β-2CaO·SiO₂ generated little by little. In fact, only the temperature should be high enough that the equation 3 could happen. In consideration of the extreme heating environment of the molten pool, obviously, 3CaO·SiO₂ existed dominantly. But, when it came to the cooling stage, the reaction 3 would work reversely. At the same time, the bulk density happened to decrease because of 2CaO·SiO₂ crystal transition led to volume expansion. In addition, the density of CaO (3.32 g/cm³) is less than MgO (3.50-3.90 g/cm³). So, it could be conclude that the more content of CaO in the system, the poor performance of fused MgO bulk density would have.



However, when TiO₂ was added into the molten pool, with the help of powerful heat, it was the priority for TiO₂ to diffuse and enrich around adjacent CaO and react with it. This explanation could consist of several parts. Firstly, CaO and MgO own the same NaCl-type crystal structure, but compared with Mg²⁺ radius (0.078 nm), Ca²⁺ radius (0.108 nm) is larger,

while the crystal lattice energy of CaO (34.8×10^5 J/mol) is smaller than MgO (39.2×10^5 J/mol) yet. Then, the bond strength of Ca-O (1.33×10^5 J/mol) is also lower than Mg-O (1.55×10^5 J/mol). In conclusion, at the same heating temperature, the energy requirement of solid solution or reaction between TiO₂ and CaO can be satisfied more easily. Thus, the additive of TiO₂ in the molten pool can reduce the quantity of free calcium oxide to drop down the possibility of C₂S compound accordingly and minimize the negative effect of crystal transition on volume. Furthermore, CaTiO₃ (m.p. 1901 °C) maybe appear because of the reaction between CaO and surplus TiO₂. It also contributed the liquid phase among the periclase grains at elevated temperatures to promote the impurity diffusion, which further improved the purity of fused magnesia, bulk density and porosity reduction.

Effect of TiO₂ on fused magnesia crystalline phase: It is easy to get 3000 °C by using three-phase electric arc furnace. So, impurities can hardly exist in the bottom of molten pool center. The experimental samples came from the middle layer of pool and characterized by X-ray diffraction shown in Fig. 4.

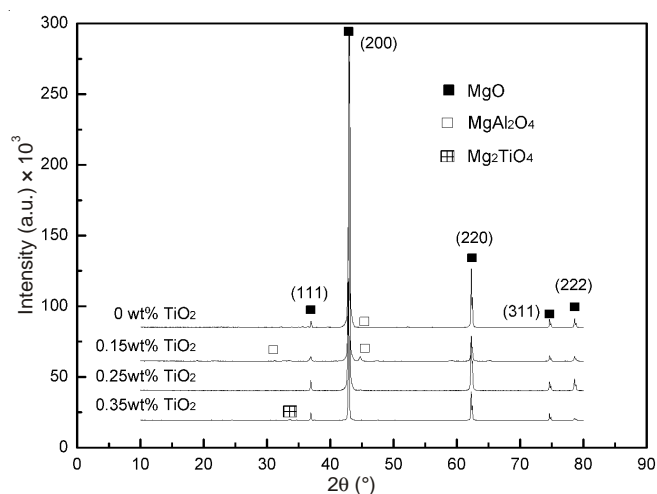
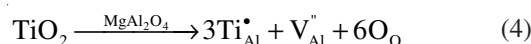


Fig. 4. XRD pattern of fused magnesia in middle of molten pool with different addition of TiO₂

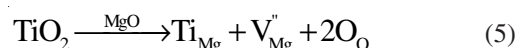
The main crystalline phase can be easily identified as periclase from the high and sharp characteristic peaks, which indicated that the samples owned a perfect degree of crystallinity and completed crystal structure. Yet, according to XRD pattern, some other mineral phases can be detected from the samples without additive of TiO₂. When added 0.15 wt % TiO₂, some little secondary crystalline phase, the spinel (MgAl₂O₄) appeared. With 0.25 wt % TiO₂, there were hardly any various mineral phases peak positions. Mg₂TiO₄ appeared when the amount of TiO₂ reached to 0.35 wt %.

It can be noticed that in the Fig. 2(b), the content of Al element rocked up suddenly when samples doped with 0.15

wt % TiO₂. Correspondingly, the XRD pattern indicated the characteristic peaks of spinel at the same addition. The reason was likely that on account of TiO₂ preferential enrichment to CaO in the melting process, Al₂O₃ reacted with MgO to be high-melting-point MgAl₂O₄ staying on the boundaries of periclase. So, the occurrence of spinel could be reasonable. If the number of dopant continued to increase to 0.25 wt %, on one hand, the excess additive could further form a new solid, containing both TiO₂ and MgAl₂O₄, namely, the eqn. 4



On the other hand, the Ti⁴⁺ began to integrate into MgO crystal, the formation process was carried out as eqn. 5.



This volume-expansion solid solution reaction would bring adverse impact on bulk density, which echoed to the slight density changes in Fig. 3. Sarkar and Bannerjee¹² explored effect of addition of TiO₂ on reaction sintered MgO-Al₂O₃ spinels and figured out that the variation of bulk density had been changed with addition of 2 wt % of TiO₂ due to dissolution of Ti and exsolution of Al in spinel. It was believed that created vacancies and lattice distortion had the capability to accelerate the impurities precipitation, grain boundary movement and crystal growth. Therefore, the exotic particles could be purified, reflecting no impurity peaks in XRD pattern. As for the hypothesis of solid solution reaction, it could be testified by the variation of diffraction angle and lattice spacing in Table-3.

Table-3 verified the Ti⁴⁺ ions integrated into MgO crystal. More specifically, with the increase of the mixed amount of TiO₂, each diffraction peak positions of MgO were inclining to shift to small angle with the increasing of lattices spacing. Additionally, Ti⁴⁺ ions' radius is greater than Mg²⁺. Thereby, the solid solution between TiO₂ and MgO could be confirmed well, which led to lattice expansion, generating vacancies, lattice distortion, *etc.* Gao *et al.*¹³ studied the solution behaviour of TiO₂ in Al₂O₃-ZrO₂ fused material. They thought that although Ti⁴⁺ could be replaced by Al³⁺ to form substitutional solid solution. Comparatively speaking, Ti⁴⁺ tends to enter into the crystal structure of MgO, ZrO₂ and CaO in order.

Cai *et al.*¹⁴ reported the solid phase reaction mechanism of MgO doped with TiO₂. This reaction kinetics and crystalline phase detected by XRD spectrum proved that Mg₂TiO₄ was the most stable phase MgO-TiO₂ system, but its solid solution was limited. Bardhan and McNally¹⁵ studied the presence form of titanium ions in periclase phase, believed that with high temperature, Ti³⁺ was able to solid into MgO crystal lattice easily, but as the temperature decreased, Ti³⁺ was desolvated gradually. This was very detrimental to the performance of magnesia, because Ti⁴⁺ might form Mg₂TiO₄ to locate at periclase grains boundary stably. Also, Lee *et al.*³ claimed that

TABLE-3
XRD DIFFRACTION PEAK POSITION AND LATTICE SPACING OF FUSED MAGNESIA WITH DIFFERENT ADDITION OF TiO₂

TiO ₂ (wt %)	2θ (111)(°)	d ₁₁₁ (Å)	2θ (200) (°)	d ₂₀₀ (Å)	2θ (222) (°)	d ₂₂₂ (Å)
0	36.9440	2.4311	42.9410	2.1045	78.6380	1.2156
0.15	36.9390	2.4314	42.9220	2.1054	78.6000	1.2161
0.25	36.9020	2.4338	42.8990	2.1064	78.5800	1.2164
0.35	36.8610	2.4364	42.8610	2.1082	78.5590	1.2167

the solid solubility limit was TiO₂ > 0.3 wt %. Beyond that range, it could not produce MgO-TiO₂ continuous solid solution. Thus, Mg₂TiO₄ phase appeared in the Fig. 4 when the doped amount of TiO₂ exceeded 0.35 wt %. It might exceed the limitation of TiO₂ solubility in MgO.

Effect of TiO₂ on fused magnesia microstructure:

Fig. 5(a-d) present the SEM images of samples from middle layer of molten pool with different amounts of TiO₂. As Fig. 5(a) shown, fused MgO crystal without TiO₂ had visible grain structure which was perfectly intact and cubic. By comparison, the crystal structure of fused magnesia added TiO₂ due to the immigration of Ti⁴⁺ made MgO crystal lattice distorted and lattice constant changed. Its appearance became irregular and accompanied by impurities phase which was exhibited clearly in the Fig. 5(b). When Ti⁴⁺ merged into the MgO lattice, it could promote molten matter diffusion and structure densification and then resulted in bulk density rise and porosity reduction, meanwhile. As Fig. 5(c) indicated, the tight joint between the MgO particles had a certain crystal deformation when the addition amount exceeded the solubility limit TiO₂ in MgO. Then the reaction between TiO₂ and MgO produce low melting mineral salts at high temperature. Most of them volatilized with lots of pores and gaps left between the periclase grain boundaries as shown in Fig. 5(d).

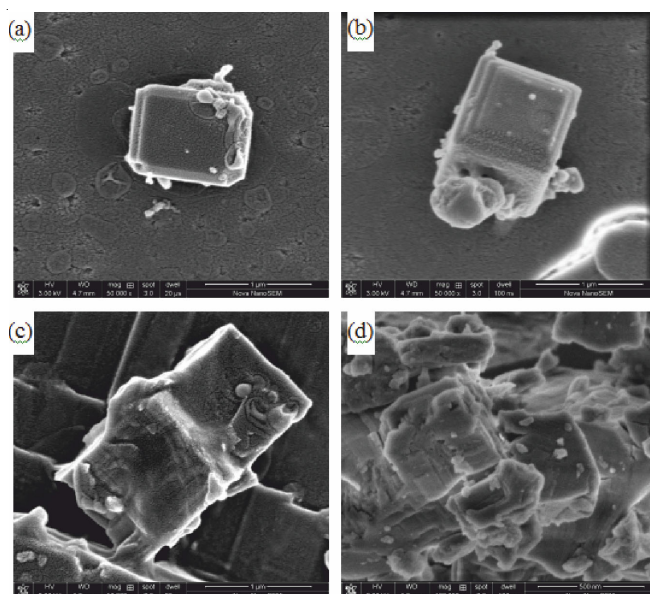


Fig. 5. Surface SEM images of fused magnesia with different addition of TiO₂. (a) 0 wt % TiO₂; (b) 0.15 wt % TiO₂; (c) 0.25 wt % TiO₂; (d) 0.35 wt % TiO₂

Fig. 6(a, b) showed the macroscopic morphology of fused magnesia crystalline particles sampled from centre of molten pool, with the aid of stereo zoom microscope for magnification of 10 times. Fused magnesia particles undoped TiO₂ were shaped basically as a cube, but opaque with poor appearance and covered with numerous pores and defects. Also, the particle size was relatively small, just about 2 mm. Nevertheless, the grains of fused magnesia crystal added TiO₂ were greatly grown and completely developed. The size of transparent fused MgO crystal was about 5 mm.

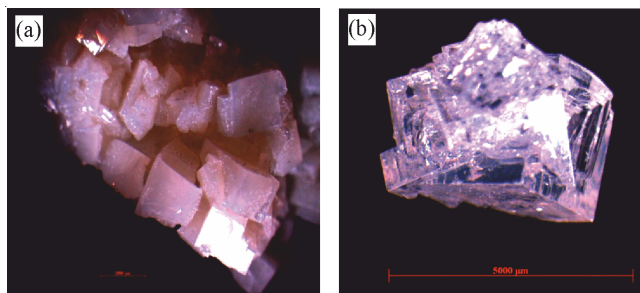


Fig. 6. Stereo microscope images of fused magnesia with different addition of TiO₂. (a) 0 wt % TiO₂; (b) 0.25 wt % TiO₂

Conclusion

Fused magnesia samples from the center of the molten pool owned the highest MgO purity. The increasing amount of TiO₂ helped to improve the purity and bulk density of fused magnesia. It could be acquired the best bulk density of 3.57 g/cm³ and minimum apparent porosity of 0.60 % when TiO₂ addition came to 0.25 wt %. While the doped quantity of TiO₂ reached 0.15 wt %, samples were mainly consisted of continuous periclase phase and few spinel phase (MgAl₂O₄). When added more than 0.25 wt % of TiO₂, fused MgO crystal would be associated with Mg₂TiO₄ phases. Therefore, the addition of TiO₂ should be under control strictly. Exceeding its solubility limit in MgO to form solid solution would generate other impurity phase which affected the performance of fused magnesia adversely. Fused magnesia grains added TiO₂ were tightly bound to each other. As Ti⁴⁺ got into MgO lattice, it probably activated lattice distortion, vacancies and crystal defects to change the appearance of microstructure.

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