

Effects of TiO₂ Addition on Kinetics of *In Situ* Spinel Formation and Properties of Alumina-Magnesia Refractory Castables

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Abstract

This work addresses the effects of TiO₂ addition on the kinetics of *in situ* spinel formation and the properties of alumina-magnesia refractory castables. The kinetics of the formation of spinel in alumina-magnesia refractory castables with TiO₂ addition (0–3 wt%) during firing at 1250–1450 °C for different times was investigated by means of XRD analysis. The reaction rate constant and apparent activation energy of spinel formation in castables calculated based on the Ginstling-Braunstein model varied with the firing temperature and TiO₂ addition. A comparison of the castables' properties including permanent linear changes, apparent porosity and strength was discussed. The results demonstrated that the *in situ* reactions and properties of the alumina-magnesia refractory castables depend on the combined effects of TiO₂.

Keywords: Castables, kinetic, spinel, reaction, properties

I. Introduction

Refractories are trans-scale multi-component and heterogeneous materials. One important development trend in refractories is the increase in unshaped monolithic refractories. Due to their excellent properties, such as high mechanical strength and corrosion resistance, alumina-magnesia refractory castables have been widely used in the wall and bottom impact pad of steel ladles¹. The performance of alumina-magnesia refractory castables was optimized with the introduction of novel aggregates^{2–4}. However, tailoring the microstructure and properties of castables with additives proved a low-cost alternative⁵. The formation of spinel as a consequence of the reaction between magnesia and alumina at high temperatures was associated with a volume expansion of 8 %⁶. The use of mineralization could increase strength, thermal shock resistance and other properties of refractories⁷. TiO₂ is one of the most effective multifunctional mineralizers as it can speed up spinel formation and promote the densification of castables⁸. In order to accurately control the properties of castables, the effects of TiO₂ on the *in situ* reactions in castables should be taken into account and quantitatively evaluated. Because of the limitation of thermodynamic equilibria based on phase diagrams for refractories⁹, the dynamic aspect had to be considered. However, the correlation between the mineralizer TiO₂ and phase evolution as well as properties of castables was very complex. Previous works focused on the changes in phase composition and properties of alumina-magnesia refractory castables with TiO₂ in the range from 0.5 to 2 wt% after calcining at elevated temperatures for 5 h^{8,10}. Spinel for-

mation was controlled by an inter-diffusion mechanism of ions¹¹, which also strongly depended on the reaction time. It was revealed that the densification rate of the magnesia-alumina system was increased with TiO₂ addition, which demonstrated that the kinetics of reaction sintering of compacted oxide mixture samples had been changed¹². But the kinetics of spinel formation in alumina-magnesia cement-bonded castables comprising multi-components (magnesia, tabular and calcined alumina) with a wide size distribution lacked research. In this study, the effects of TiO₂ addition (up to 3 wt%) on the kinetics of *in situ* spinel formation and the properties of alumina-magnesia refractory castables fired at 1250–1450 °C for different times were investigated.

II. Materials and Methods

Alumina-magnesia castables were prepared according to the compositions listed in Table 1. The added water content for vibrocasting was in the range of 4.5–4.7 wt%. All vibrocastables were cast, and then cured at 25 °C for 24 h with relative humidity of 100 %, followed by drying at 110 °C for 24 h. Samples were calcined at 1250–1450 °C for 30–300 min, respectively. The permanent linear change (PLC) was measured in compliance with GB/T 5988–2007. The apparent porosity of the castables was measured with the Archimedes technique. The cold modulus of rupture (CMOR) for castables was measured in a three-point bending test in accordance with GB/T 3001–2007. The phase composition of castables was analyzed by means of X-ray diffraction (XRD, Philips, X'pert Pro MPD, Netherlands). The degree of conversion of spinel was calculated based on the RIR method¹³. The microstructure of the fired castables was

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characterized with scanning electron microscopy (SEM, JEOL JSM-6610, Japan) and an energy-dispersive spectrometer (EDS, Bruker QUANTAX200–30, Germany).

Table 1: Composition of alumina-magnesia refractory castables.

Raw materials	Content (wt%)				
	T0	T0.5	T1	T2	T3
Tabular alumina (≤ 6 mm) (Almatis)	61	61	61	60	60
Tabular alumina (≤ 200 mesh) (Almatis)	19	18.5	18	18	17
Reactive alumina (CL370) (Almatis)	7	7	7	7	7
Calcined magnesia (180 mesh)	6	6	6	6	6
Calcium aluminate cement (Secar71) (Kerneos)	6	6	6	6	6
Silicon fume (951U) (Elkem)	1	1	1	1	1
TiO ₂	0	0.5	1	2	3

III. Results and Discussion

As the formation of spinel from its constituent oxides was diffusion-controlled⁷, the function between the reaction

rate constant and time can be described with the Ginstling-Braunstein model¹⁴:

$$g(\alpha) = 1 - 2\alpha/3 - (1-\alpha)^{2/3} = kt$$

where a is the degree of conversion, and k is the reaction rate constant. The effects of the firing temperature and time on $g(a)$ of spinel in castables are shown in Fig. 1. It can be seen that the slope of the fitting curves based on the Ginstling-Braunstein model stands for the reaction rate constant increase with the addition of TiO₂ at 1250 °C. The reaction rate constant of the castables containing TiO₂ presented a significant difference to that of the reference composition fired at 1350 °C and 1450 °C. The maximum reaction rate constant was achieved in sample T2 after firing at 1450 °C.

The activation energy E of the reaction was calculated from the Arrhenius expression:

$$k = A \cdot \exp(-E/RT)$$

where A is the frequency factor and R is the gas constant. The logarithm of the reaction rate constant $\ln k$ for spinel is plotted against $1000/T$ in Fig. 2. The apparent activation energy of spinel formation in alumina-magnesia refractory castables derived from the Arrhenius equation was between 100.8 and 328.3 kJ/mol at the temperature range from 1250 to 1450 °C as listed in Table 2. It is worth noting that the relationship between the apparent activation energy of spinel formation and the amount of TiO₂ was not simply linear, which will be discussed in a later section.

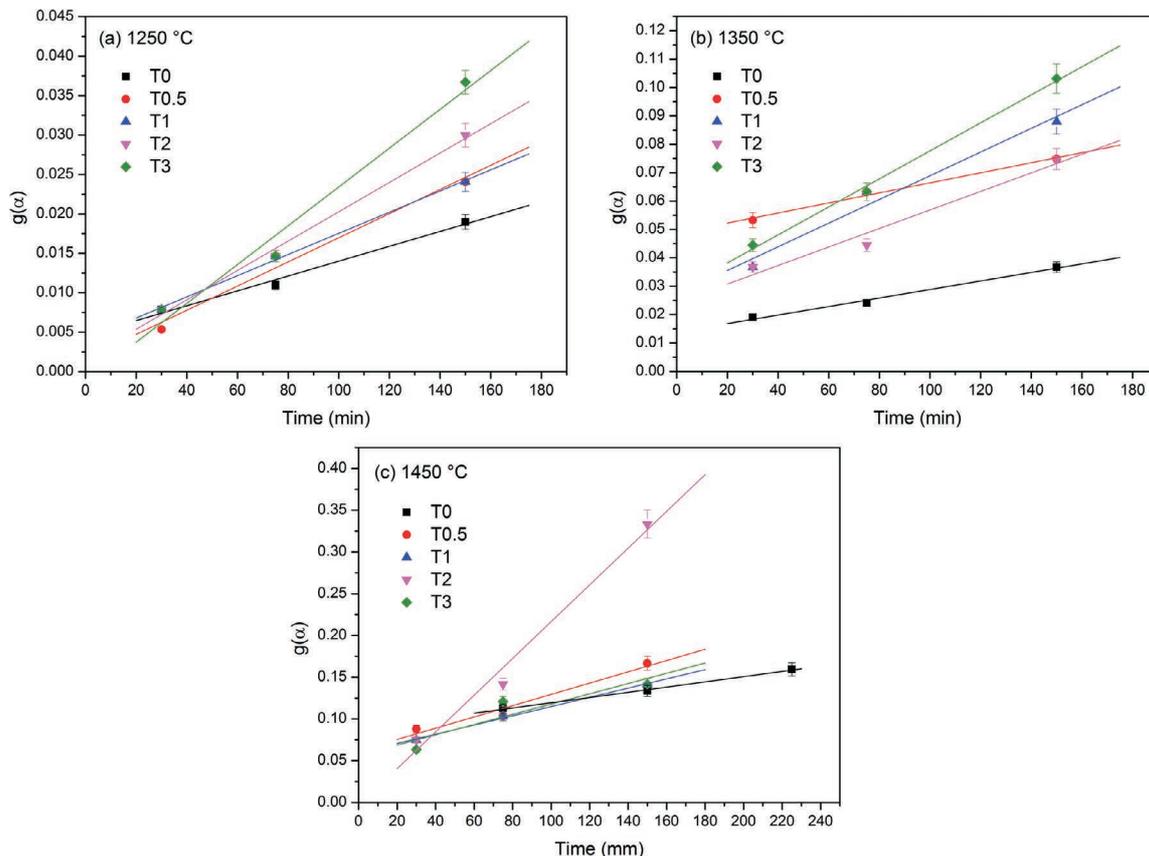


Fig. 1: $g(\alpha)$ of spinel in alumina-magnesia refractory castables after calcining at 1250 °C (a), 1350 °C (b) and 1450 °C (c).

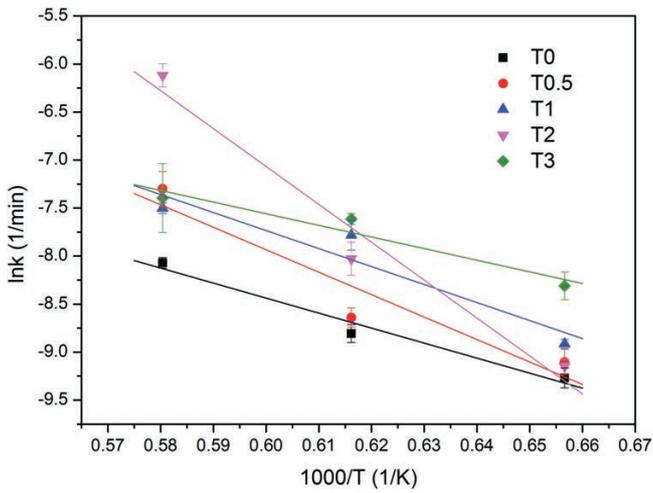


Fig. 2: Plots $\ln k$ vs. $1000/T$ for spinel in alumina-magnesia refractory castables.

There was no diffraction peak for the castable containing a Ti element such as TiO_2 and CaTiO_3 in the XRD patterns of the alumina-magnesia refractory castables after calcining at 1450°C for different times from 30 to 300 min as shown in Fig. 3, which indicates that TiO_2 as a mineralizer fully reacted with other components in the casta-

bles at high temperatures. The major phases in the fired castables were composed of corundum, spinel and CA_6 . The changes of the diffraction peak's position for spinel (311) and CA_6 (114) compared with the corundum (104) peak in castables fired at 1450°C are shown in Fig. 4. It was demonstrated that the solid-soluted content of these two phases depended on the TiO_2 addition. The spinel peaks shifted to a higher angle with increasing holding time, which represented more Al_2O_3 dissolved into the spinel. As the offset of the spinel peak for samples T0.5 and T1 was less than the reference sample T0, it was deduced that the dissolution of TiO_2 into spinel solid solution was more prominent in castables with 0.5 and 1 wt% TiO_2 . On the contrary, the peaks of CA_6 gradually shifted to a lower angle with TiO_2 addition, which was attributed to the solid solution of Ti and Mg atoms. It was evidenced that the dependence of the distribution of Ti element in spinel and CA_6 on the firing time as well as the temperature was governed by the TiO_2 addition. Moreover, the other major function of TiO_2 was the modification of sintering¹⁵. Therefore, the apparent activation energy of the spinel formation in alumina-magnesia refractory castables presented a non-monotonous change with the addition of TiO_2 .

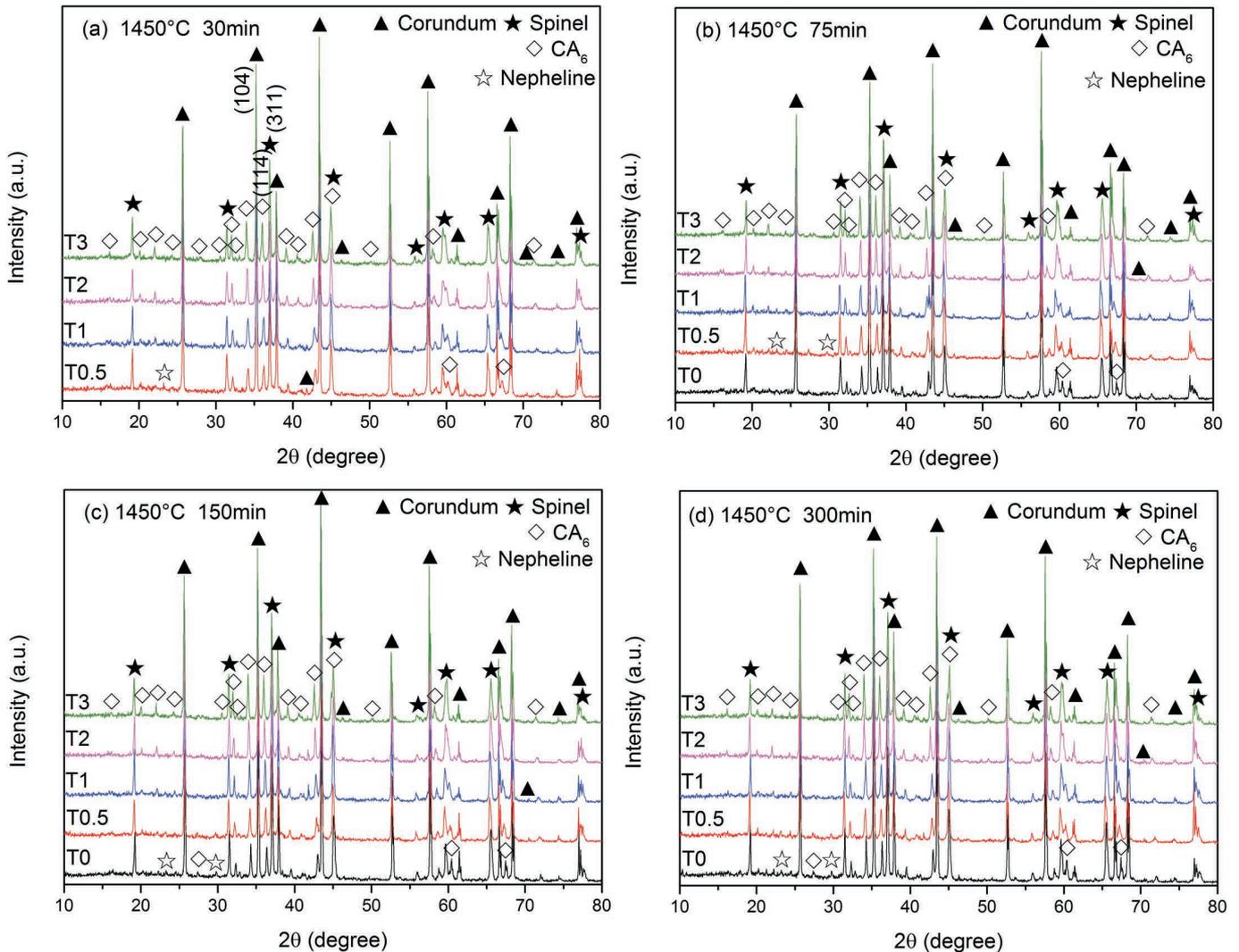


Fig. 3: XRD patterns of alumina-magnesia refractory castables after calcining at 1450°C : (a) 30 min, (b) 75 min, (c) 150 min and (d) 300 min.

Table 2: Apparent activation energy E_a of spinel in alumina-magnesia refractory castables with TiO_2 addition.

No.	E_a (kJ/mol)
T0	129.9 ± 11.0
T0.5	194.5 ± 31.0
T1	155.8 ± 24.1
T2	328.3 ± 30.6
T3	100.8 ± 13.3

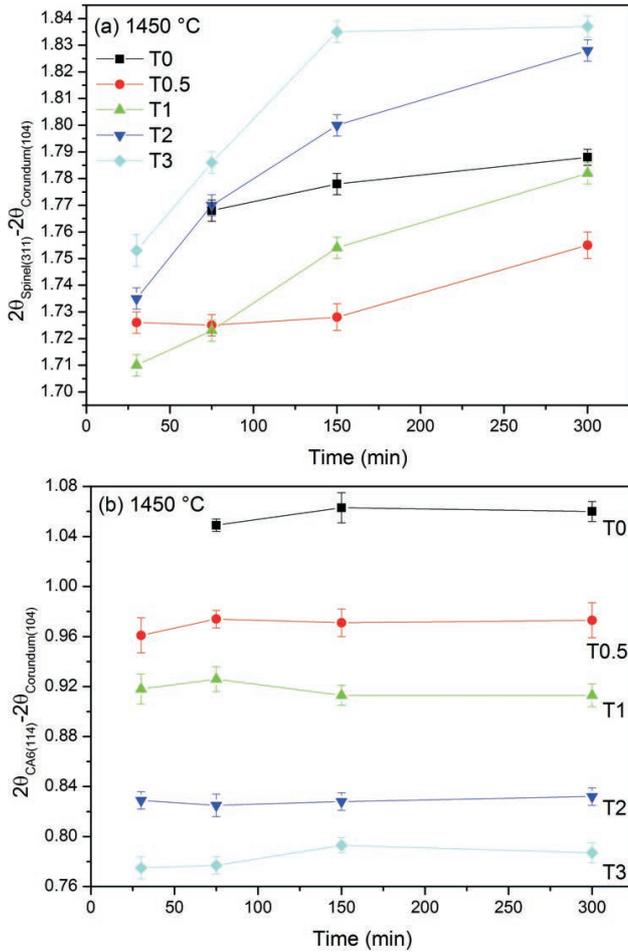


Fig. 4: The position shift of the diffraction peaks for spinel in alumina-magnesia refractory castables after calcining at 1450 °C: (a) spinel and (b) Ca_6

Controlling the expansion behavior of alumina-magnesia castables was essential to maintain the integrity of the component during use. Fig. 5 presents permanent linear changes of castables after calcining at 1250–1450 °C. The expansion of castables with 0.5 wt% of TiO_2 addition was slightly greater than that of the referenced castable T0. In general, the expansion of sample T1 achieved the highest value at 1250 and 1350 °C except for 300 min. In contrast, the expansion of sample T2 was basically less than that of sample T1. Especially castables containing 2 wt% (holding time ≥ 75 min) and 3 wt% TiO_2 presented a certain amount of shrinkage after firing at 1450 °C. The shrinkage of sintering could completely counterbalance the expansion derived from *in situ* reactions when more TiO_2 was added.

Thus, the expansion behavior of alumina-magnesia castables depended not only on the phase formation but also the sintering.

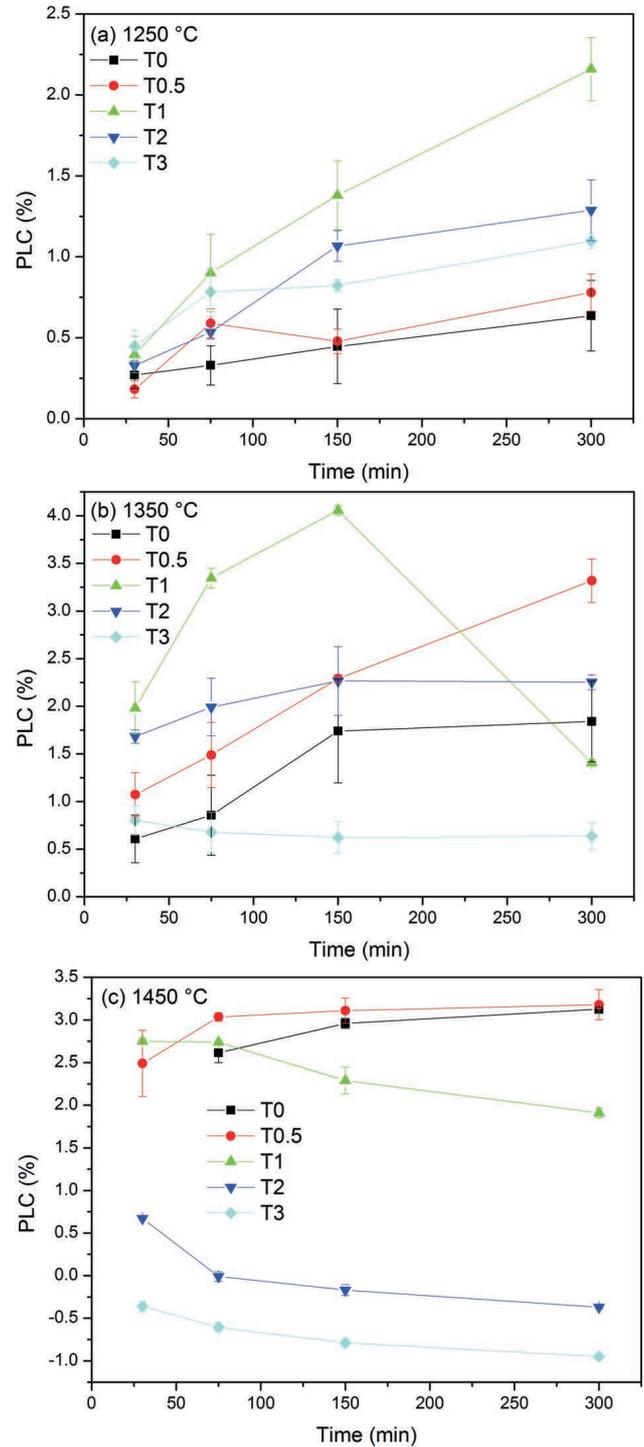


Fig. 5: Permanent linear changes of alumina-magnesia refractory castables after calcining at 1250 °C (a), 1350 °C (b) and 1450 °C (c).

The variation of the apparent porosity for castables containing TiO_2 with the calcining temperature and time presented a similar trend as the PLC as shown in Fig. 6. The greater expansion of the castables resulted in higher porosity. The apparent porosity of castables with 2 wt% and 3 wt% after firing at 1450 °C was reduced dramatically, which was possibly related to the phase evolution in castables.

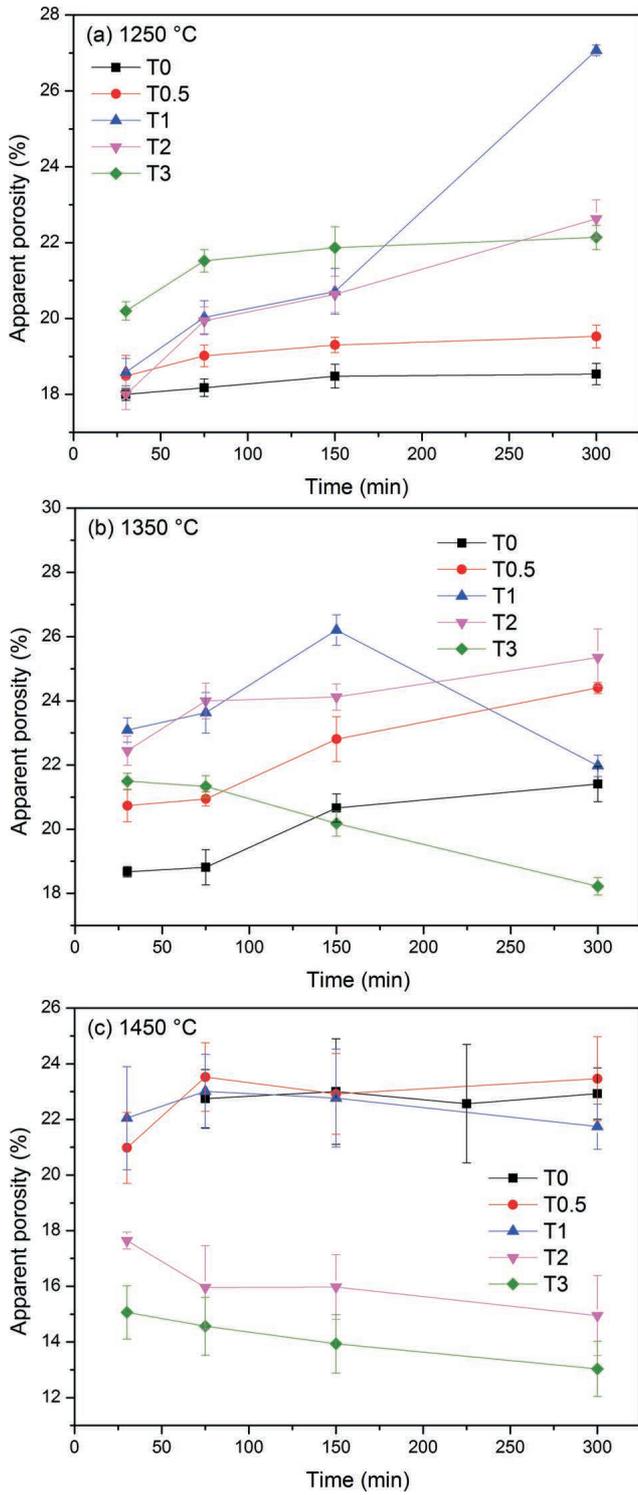


Fig. 6: Apparent porosity of alumina-magnesia refractory castables after calcining at 1250 °C (a), 1350 °C (b) and 1450 °C (c).

In Fig. 7, the significant difference in strength for castables containing TiO₂ at room temperature is presented. The cold modulus of rupture for castables with TiO₂ addition after firing at 1250 °C was less than that for the referenced castables as a result of their high apparent porosity. Because the bonding between different phases was enhanced by the formation of spinel and CA₆ solid solution in castables containing TiO₂, the contribution of the bonding to the strength of the castables became more dominant at higher temperatures.

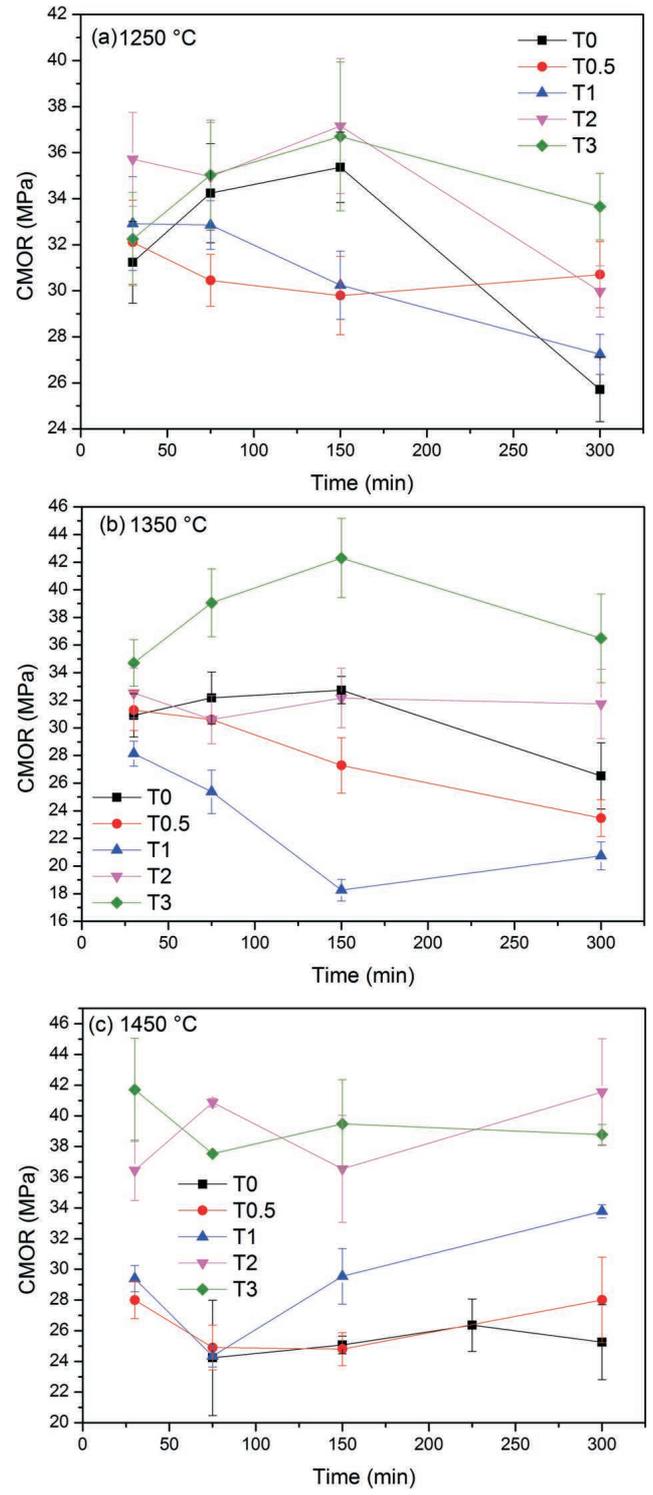


Fig. 7: Cold modulus of rupture (CMOR) of alumina-magnesia refractory castables after calcining at 1250 °C (a), 1350 °C (b) and 1450 °C (c).

Figs. 8(a)-(e) show SEM images of alumina-magnesia refractory castables after calcining at 1450 °C for 5 h. It can be observed that there were coarse CA₆ platelets in the castables without TiO₂ (Fig. 8(a)). The addition of 0.5–2 wt% TiO₂ resulted in much finer CA₆ grains (Fig. 8(b)-(d)). The spinel and CA₆ in the matrix of the castables were bonded tightly in the case of TiO₂ addition up to 3 wt%. Both spinel and CA₆ are not even recognizable from Fig. 8(e).

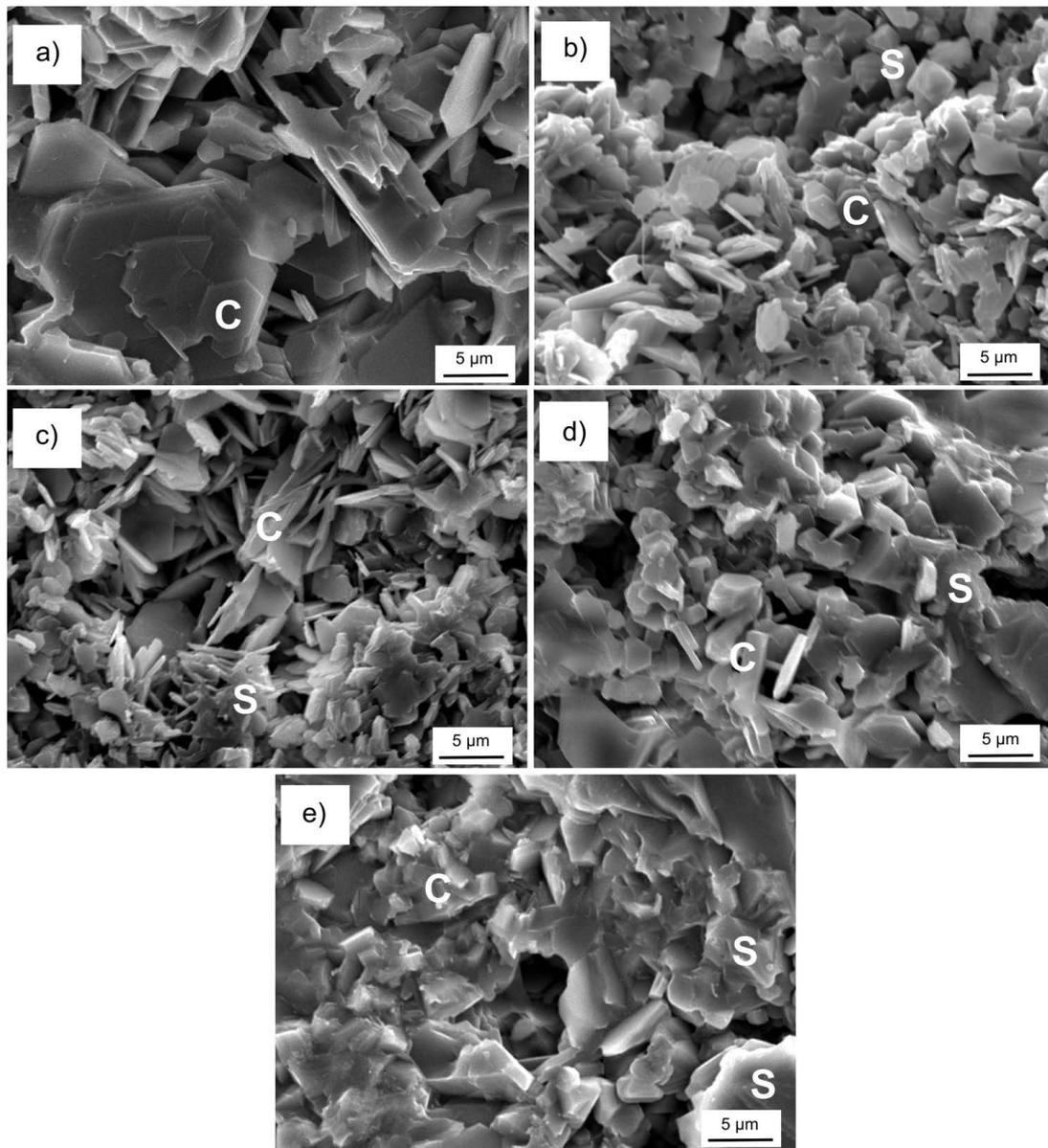


Fig. 8: SEM images of alumina-magnesia refractory castables after calcining at 1450 °C for 5 h: (a) T0, (b) T0.5, (c) T1, (d) T2 and (e) T3 (C-CA₆ and S-spinel).

IV. Conclusions

The effects of the addition of TiO₂ on the kinetics of *in situ* spinel formation and the properties of alumina-magnesia refractory castables were investigated. The reaction rate constant of the spinel formation depended on the addition of TiO₂ as well as the firing temperature. The apparent activation energy of the spinel formation presented a non-monotonous change with TiO₂ addition as a consequence of the variation of Ti distribution in the spinel and CA₆. A small amount of added TiO₂ (0.5–2 %) resulted in higher expansion and apparent porosity of castables after firing at 1250 and 1350 °C. Castables with higher TiO₂ content (2–3 %) fired at 1450 °C presented a certain amount of shrinkage, and possessed lower porosity as well as higher strength. Moreover, the comprehensive effects of TiO₂ as a mineralizer need to be considered for the design of engineered castables.

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