MICROWAVE SINTERING APPLIED TO CAC-BONDED ALUMINA-BASED CASTABLES CONTAINING ZnO

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ABSTRACT

Even though MgO-containing castables are broadly applied as commercial refractories, recent studies have pointed out that ZnO can also induce spinel-like phase formation in alumina-based compositions, giving rise to gahnite ($ZnAl_2O_4$). Compared to MgO, ZnO-containing castables present lower spinelization temperature, similar cold modulus of rupture and enhanced thermal shock damage resistance. Furthermore, the high microwave absorption of zincite arises the likelihood of applying microwave sintering to refractories comprising this oxide. In the present work, microwave and conventional sintering at several temperatures were applied to ZnO-containing alumina-based castables. Although a partial gahnite decomposition was detected by the microwave heated samples due to the reducing atmosphere induced by the oxidation of SiC microwave susceptors, higher densification, enhanced mechanical properties at room temperature, 26-times faster sintering procedure, and a rough-estimated 70%-lower energy consumption, were attained. Thus, if properly adjusted, the microwave technique could be applied to sinter some refractory compositions, potentially leading to environmental and performance enhancements.

1 INTRODUCTION

Never before in all human history such a massive number of people have been able to unrestrictedly access food, water, mobility and security, reaching a living standard unthinkable for individuals born just a few decades ago[1]. However, for different reasons, the same processes that led to an increase in the average quality of life also generated great inequalities in the distribution of resources. Although part of the population enjoys cutting-edge technologies such as 5G connection and high-speed transportation, another one still faces food restrictions, lack of basic sanitation and many other issues related to extreme poverty[2]. The most reliable way to measure

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such inequalities is by comparing the per capita energy consumption as any improvement in living conditions directly implies using a greater amount of energy[2]. In this sense, 2020 data indicate that about 40% of the population were living using no more energy than an average citizen from Germany or France in 1860[2, 3]. To provide minimal life quality to this part of the population, which is concentrated in developing countries, it will inevitably be required to increase their energy consumption by at least three-fold[1, 2]. In a world with finite natural resources and in which energy production fundamentally relies on the burning of fossil fuels, fulfilling this upcoming energy demand (47 % increase until 2050) ensuring environmental protection, is considered one of the greatest challenges of this century[3].

Accounting for close to 12 % of all energy consumed worldwide[1], special attention must be given to industrial processes that operate at high temperatures, such as the conventional sintering of ceramic materials. In this process, temperatures usually between 1000 and 2000 ºC are applied to compacted powder systems to induce the formation of ceramic bonds between the particles, thus, resulting in materials with lower porosity and improved mechanical properties[4]. Aiming at speeding up the sintering process and minimizing the energy consumed for it, different techniques have been developed in recent decades, such as microwave sintering[4]. However, to be effective, this sintering technique relies on the presence of phases capable of interacting with the microwave radiation, converting the electric and/or magnetic fields into an increase in thermal energy, or even directly enhancing the diffusion process of the sintering mechanisms. These aspects depend on the materials' dielectric and magnetic properties and is not the case of the most ceramic materials (*e.g.* Al_2O_3, MgO, and SiO_2)[5]. Therefore, although highly successful in lab conditions for specific compositions, scaling up this novel sintering process to massive production, as is the case of refractories, remains challenging[4, 5]. In fact, although microwave-dried castables were reported[6], no publications regarding using microwave for sintering refractories were found in the literature. Thus, adding microwave-absorbing compounds may foster using this sintering method to refractories and, in this sense, zincite (ZnO) is a promising candidate due to its suitable microwave absorption[7]. Notwithstanding the changes led to the castables' properties, recent studies[8] pointed out the feasibility of applying ZnO in alumina-based castables as these oxides react at intermediate temperatures (~ 800 ºC) forming a spinel-like phase with interesting properties (e.g. high refractoriness and low coefficient of thermal expansion)[8]. In this study, microwave sintered ZnO-containing alumina-based vibrated castables were produced at distinct temperatures and compared to their conventionally-fired counterparts.

2 MATERIALS AND METHODS

The vibrated castables analysed in this work were produced as described in [8], with a packing distribution according to modified Andreasen's model (q = 0.26). Calcined and tabular alumina (CL370 and T60/T64, Almatis, Germany) were used as Al_2O_3 sources, whereas 11.4 wt% of ZnO (analytical grade, Basile Química, Brazil) was added to induce the formation of 23.1 vol% (25.7 wt%) of $ZnAl_2O_4$ after firing. The castables were bonded with 6 wt% of calcium aluminate cement (CAC, Secar 71, Imerys Aluminates, France) and dispersed using 0.2 wt% of a commercial surfactant (Castament FS60, BASF, Germany), as shown in Table 1(a). This dry mixture was first homogenized in rheometer equipment for 5 minutes, followed by the addition of 3.8 wt% of distilled water, giving rise to a castable with vibrated flow of 150% (according to ASTM C 1445). The fresh suspension was moulded into bars (25 mm x 25 mm x 150 mm), cured in a climatic chamber for 24 h under 50 ºC and 80 % of relative humidity, dried at 110 ºC for another 24 h, and calcined at 600 ºC for 5 h. The calcined samples were then sintered at different temperatures up to 1700 ºC using a conventional electric furnace (BF51314C, cavity capacity of 2.5 L, Lindberg/blue, USA) or microwave equipment (model MS6K, multimode cavity, 2.45GHz, useful cavity capacity of ~ 3 L, Cober Electronics, USA) with effective power (also referred to as non-reflected or forward power) up to 4 kW and silicon carbide as susceptors[7]. In the former case, a constant heating rate of 2 $ºCmin^{-1}$ and a dwell time of 5 h were applied, whereas for the latter, 50 $ºCmin^{-1}$ up to 1100 ºC and 20 $ºCmin^{-1}$ above it, and dwell time of 15 minutes, was used. These sintering conditions gave rise to the nomenclature system, depicted in Table 1(b). After the sintering step, all samples had their linear dimensional changes and mass loss assessed with a digital caliper and an analytical balance, respectively. Young's modulus was measured by the non-destructive sonic resonance technique (Scanelastic equipment, ATCP Physical engineering, Brazil). Cold modulus of rupture (CMOR) was carried out in MTS 810 equipment (MTS Systems, USA). Quantitative mineralogical content was estimated by applying Rietveld's refinement (Topas software, version 4.2, Bruker, USA) on the X ray diffraction patterns (D8 Focus, Bruker, Germany) obtained for grounded samples. Open porosity and density were evaluated by the immersion method based on Archimedes' principle and using kerosene as liquid media. Based on the samples' density and the theoretical density considering the quantitative phase content (XRD), the total porosity was estimated. For some selected sintering temperatures, the microstructure of the castable was evaluated by scanning electron microscopy (Inspect S50, FEI, USA) coupled with an energy dispersive X ray spectroscope (EDS). Additionally, thermodynamic calculations (FactSage 6.4, CRCT, Canada) were carried out to assess the phase evolution as a function of temperature and the oxygen partial pressure (pO_2).

Table 1: (a) Overall castable composition and (b), nomenclature used for the distinct sintering methods.

(a)

Raw material	(wt%)
TA<6 mm	77.6
CL370	5.0
CAC	6.0
ZnO	11.4

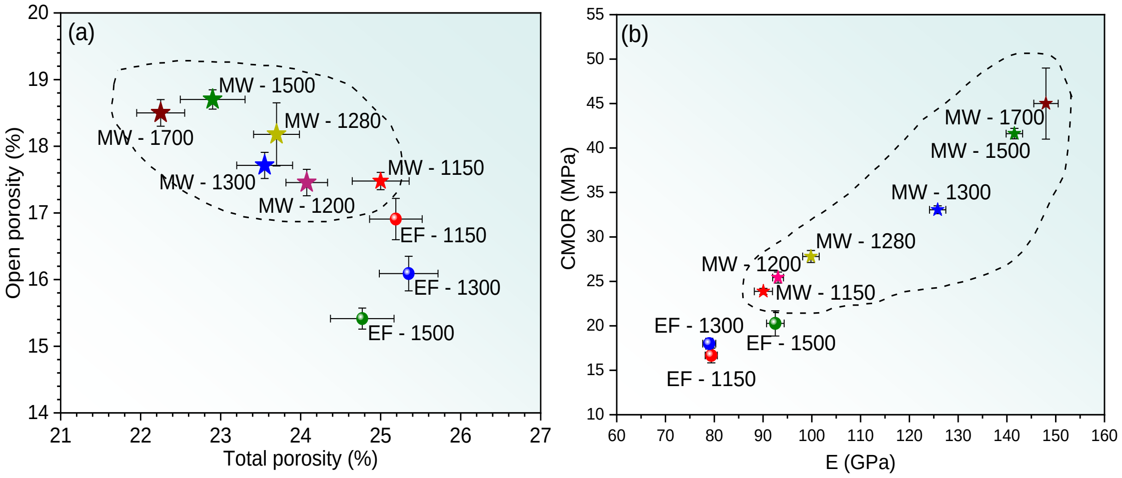
(b)

Firing Method	Maximum temperature	Nomenclature
Electric furnace	1150 ºC	EF-1150
	1300 ºC	EF-1300
	1500 ºC	EF-1500
Microwave	1150 ºC	MW-1150
	1200 ºC	MW-1200
	1280 ºC	MW-1280
	1300 ºC	MW-1300
	1500 ºC	MW-1500
	1700 ºC	MW-1700

3 RESULTS AND DISCUSSION

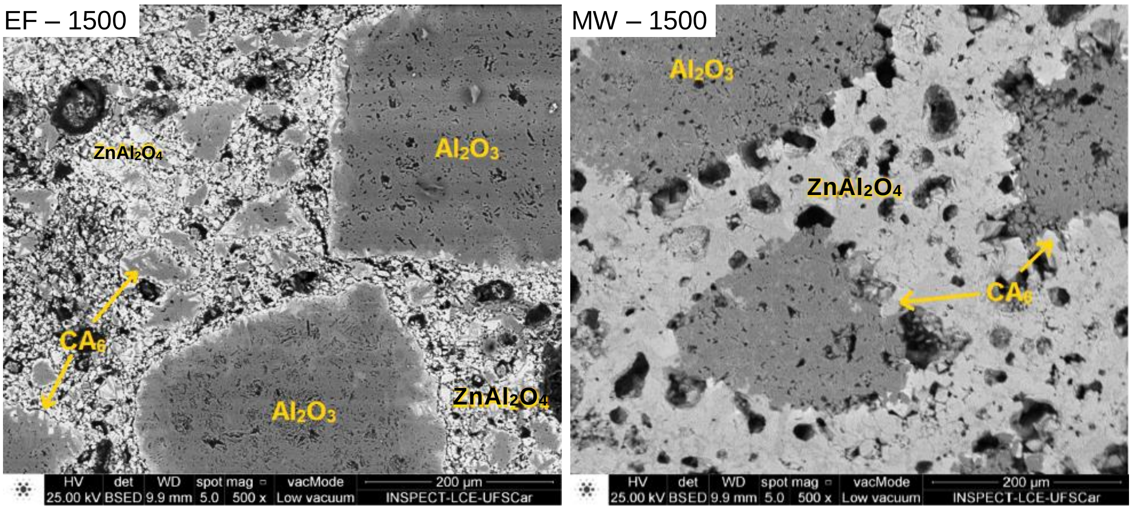
Aiming at addressing the effect of the sintering method on the microstructure of the castable, the total and apparent porosity were measured and are depicted in Figure 1(a). For conventional firing, it could be seen that the increase in temperature resulted in a decrease in both open and total porosity, especially in the former. Additionally, a clear trend between total and apparent porosity could be attested, in which the lower the total porosity, the lower the apparent porosity. This behavior is expected for the traditional sintering model as the densification process will usually act similarly on open and closed pores located among the particles (pores within the grains require higher energy to be eliminated), reducing their amount[5]. As higher heating rates favored the densification process rather than grain coarsening, a more pronounced reduction in both types of pores was expected for the microwave sintering[5]. Nevertheless, for these samples, the increment in the sintering temperature led to a significant total porosity decrease, as expected, but with an apparent porosity increase. Therefore, although more effective to densify the castable, in this system the microwave heating technique also induced a higher number of open pores. Although this aspect will be addressed ahead, it is worth highlighting that this additional apparent porosity is not necessarily detrimental to the castables' properties, acting differently depending on the size and homogeneity of the pores along with the microstructure. On one hand, if they are small and well dispersed, these open pores can induce toughening mechanisms by branching the cracks and/or increasing the crack tip curvature radius, which will lead to enhanced fracture energy. On the other hand, if coarse and randomly located, this apparent porosity will act as critical defects and paths for slag infiltration, reducing the mechanical and corrosion resistance[9]. To evaluate the impact of each sintering condition on the mechanical properties of the castable, Youngs' modulus (E) and cold modulus of rupture (CMOR) were carried out and are presented in Figure 1(b).

Figure 1: (a) Open and total porosity, and (b) elastic modulus and cold modulus of rupture for conventional (EF) and microwave (MW) sintered castables.



Analyzing these results, one can see a clear relationship between E and CMOR for both sintering techniques, which is related to the brittleness of the ceramic material. Additionally, although increasing the sintering temperature resulted in enhanced mechanical properties for conventional and microwave sintered samples, this effect was much more pronounced for the latter. Although further information on pores sizes distribution (*e.g.* using mercury porosimetry) would be required for assessing their real impact on mechanical properties, comparing Figure 1(a) and Figure 1(b) shows that the total porosity plays a major role on the mechanical strength. Conversely, the apparent porosity presented no correlation with E and CMOR, indicating that the open pores are most likely small and well distributed, not acting as critical defects. Therefore, the pronounced densification led by the microwave sintering resulted in stronger (higher E and CMOR) samples, which is attributed to the higher heating rate and enhanced ion diffusion induced by this sintering technique[5]. Note that the samples sintered by microwave radiation at 1150 ºC for 15 minutes presented equivalent strength to those conventionally-fired at 1500 ºC for 5 hours. Moreover, the microwave heated at 1500 ºC ones presented E-values 100 % higher than their conventional-fired counterpart. Thus, while the conventional sintering (1500 ºC) last 17.5 h to complete the firing schedule, the microwave technique (1150 ºC) requires less than 40 minutes to produce castables with similar E and CMOR, which is twenty-six-times faster. Regarding the energetic aspect, in a rough estimation of the energy consumption, the mean power used for each furnace equipment to sinter two bar samples was estimated as 3 kW and 0.4 kW for microwave and electric heating, respectively. Multiplying these values by the time required to sinter the distinct bars (17.5h and 40 minutes), one can see that the conventional sintering demanded 3.5 kWh per sample, whereas the microwave consumed 1 kWh per sample. Even though this is a rough estimation, as just the mean power consumption was measured, it shows that despite the higher power demanded by the microwave equipment, the faster sintering schedule resulted in significant energy savings (~ 70 %). This can be explained by the fact that for conventional heating, the air inside the furnace and the refractories around the electrical resistances absorb considerable amounts of energy, whereas for the microwave heating, only the susceptors and the sample itself will absorb the energy, leading to a process with higher energy efficiency. Although these are eye-catching features, it is worth noticing that higher E and CMOR are just two of several other key properties that must be fulfilled by the refractory material. Depending of the application, further analyses are required to assess the feasibility of applying such sintering technique to the fabrication of refractories. Going forward in these characterizations, the microstructural changes resulted by the distinct sintering methods were evaluated by SEM of samples thermally treated at 1500 ºC. The images can be seen in Figure 2.

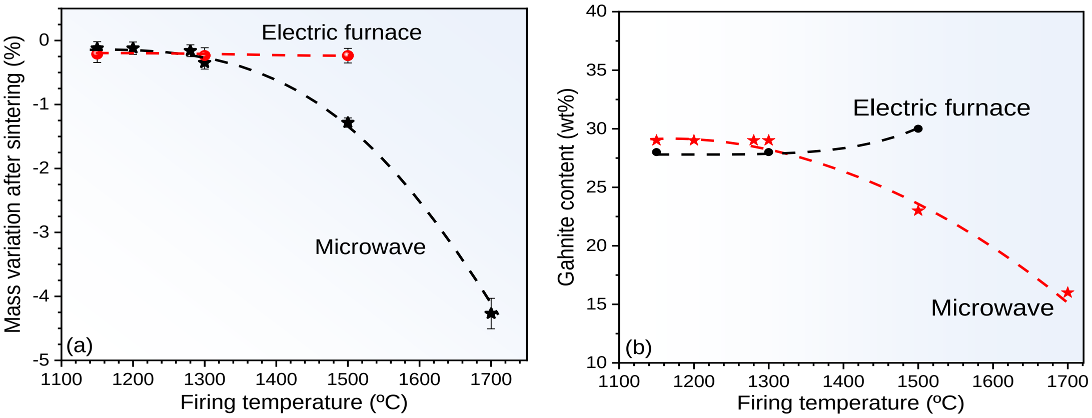
Figure 2: Microstructure of samples fired at 1500 ºC in a conventional electric furnace (EF – 1500) for 5 h or microwave equipment (MW -1500) for 15 minutes.


EF – 1500

MW – 1500

Looking at the images, one can see that hibonite (CA_6) and gahnite ($ZnAl_2O_4$) were formed at the matrix and interface of the alumina aggregates in both microstructures, as expected. Nevertheless, the conventionally sintered sample showed lower matrix densification. In tune with previously reported works[8], this behavior can be assigned to the pronounced Kirkendall effect (due to the faster diffusion rate of ZnO in alumina) induced by gahnite formation that led to grain detachment. Regarding the microwave sintering, the enhanced densification process has overlapped this phenomenon, resulting in a denser matrix with pores homogeneously dispersed. These types of microstructures are in accordance with the porosity results presented in Figure 1(a), in which the microwave sintering was more effective to reduce total porosity, but induced the formation of a higher number of open pores. However, as the mechanism that led to this open porosity increase during the microwave sintering remains unclear, calcined samples had their mass loss analyzed as shown in Figure 3(a). At temperatures in the range of 1100 ºC up to 1500 ºC no appreciable mass loss was detected for conventionally fired samples, which is assigned to the lack of organic or hydrated phases, as they were decomposed in the calcining process. However, the mass loss faced by microwave heated samples stood out. The firing at 1500 ºC and 1700 ºC in the microwave equipment resulted in a mass decrease of 1.3 wt% and 4.3 wt, respectively. Aiming at understanding the causes of these mass losses, quantitative XRD analyses were conducted. Although all phases were quantified, Figure 3(b) shows only the gahnite content.

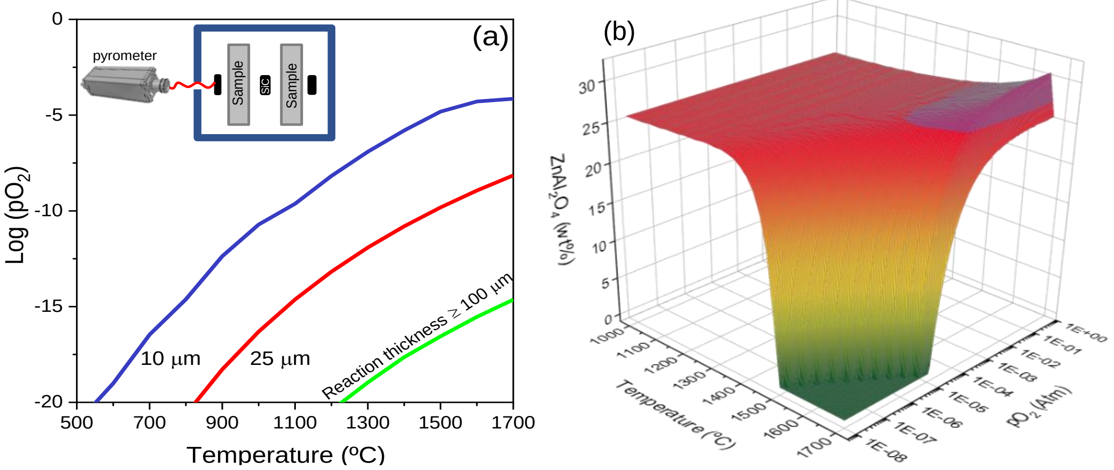
Figure 3: (a) Mass variation after firing; (b) $ZnAl_2O_4$ (gahnite) content measured by quantitative XRD.



Conversely to the conventionally firing, in which gahnite was stable at all analyzed temperatures, the microwave heating led to partial gahnite decomposition at 1500 ºC and 1700 ºC. Moreover, as no other Zn-containing phase was detected and the reduction in $ZnAl_2O_4$ content took place along with alumina content increase, gahnite decomposition could have happened by the volatilization of Zn, that is withdrawn from the spinel structure as gaseous zinc, leaving corundum behind. The zinc removal from spinel structure is largely studied in the literature, especially applied to zinc recovery from the blast furnace dust, which presented up to 5 wt% of zinc ferrite ($ZnFe_2O_4$) and gahnite ($ZnAl_2O_4$) in its composition[10]. Nevertheless, in this system, zinc volatilization just takes place close to 1300 ºC at reducing atmospheres[10]. Although neither the electric furnace nor the microwave equipment had a controlled atmosphere, the latter presented susceptors made out of silicon carbide, which could be oxidized at high temperature leading to a reducing environment inside the microwave chamber. To evaluate this hypothesis, thermodynamical simulations were carried out considering the total volume of the microwave cavity (~ 3 L) and the dimensions of each silicon carbide piece (25 mm x 25 mm x 150 mm). A 2-D schematic representation is presented in Figure 4 (a), in which the location of bar samples, SiC susceptors and the pyrometer equipment can be seen. Additionally, the furnace was assumed to be a closed system and, as not all SiC would be available for reaction due to kinetics effects, distinct thicknesses of oxidative reaction zone (10 µm, 25 µm, ≥ 100 µm) were considered [also depicted in Figure 4(a)] to evaluate their effect on pO_2

Even for a narrow reaction zone (10 µm), pO_2 close to 10^{-5} atm were attained at high temperatures (> 1300 ºC). Although experimental measurements of the pO_2 are required to validate the simulated results, it can be inferred that the SiC oxidation will lead to a reducing atmosphere inside the microwave chamber during sintering. However, how the temperature and the pO_2 will affect the zinc volatilization in the analyzed composition was still unclear. Thus, the thermodynamical approach was applied again to track down the gahnite content as a function of these two parameters, as presented in Figure 4 (b). At atmospheric conditions (pO_2=0.2 atm), no gahnite decomposition was detected up to 1700 ºC. In fact, for $pO_2 > 10^{-3}$ atm, an increase in $ZnAl_2O_4$ content can be seen at temperatures above 1400 ºC (purple region), which is assigned to the dissolution of the alumina in the gahnite structure, increasing their content by the formation of a solid solution (non-stoichiometric spinel compound), as previously reported in the literature[8]. Furthermore, this behaviour is in tune with the quantitative XRD of conventionally-fired compositions, presented in Figure 3 (b). However, this trend changes when a more reducing atmosphere is applied. For $pO_2 < 10^{-3}$ atm, the increase in temperature led to $ZnAl_2O_4$ decomposition due to zinc volatilization.

Figure 4: (a) pO_2 inside the microwave chamber as a function of temperature and thickness of SiC oxidative reaction zone; and (b) gahnite content as a function of temperature and pO_2.



A likely alternative to overcome this issue rely on replacing silicon carbide susceptors with oxide materials[7]. However, to be effective, such oxide needs to (i) have a high capacity to interact with the microwave radiation to dissipate heat; (ii) withstand high temperatures without melting or reacting; and (iii) present a well-established profile of emissivity vs. temperature, as the pyrometer measurements depend on this property to be reliable. Some promising alternatives are been evaluated and the results will be reported in a forthcoming paper. Therefore, although other key aspects must be addressed to assess the feasibility of applying the microwave heating method to ZnO-containing castables, interesting features such as higher densified microstructure with open pores remaining homogeneously scattered in the matrix, enhanced mechanical properties at room temperature (E and CMOR), 26-times faster sintering performance, and a roughly-estimated 70%-lower energy consumption, were already attained. Thus, if properly adjusted, the microwave radiation could be applied to sintering some refractory compositions, optimizing their firing step.

4 CONCLUSIONS

The feasibility of applying microwave sintering to ZnO-containing alumina-based castables bonded with CAC was assessed up to 1700 ºC with a dwell time of 15 minutes. To enable comparisons, conventionally-fired samples were produced in an electric furnace after sintering for 5h at selected temperatures. Due to the higher heating rate and enhanced ion mobility led by the microwave technique, denser (lower total porosity) and stronger (higher E and CMOR) samples were produced in a 26-times faster and 70% less energetic sintering procedure. The microwave sintered technique also induces an increase of open porosity that, as shown by SEM micrographs, was relatively small and homogeneously scattered along with the matrix of the castable, which could positively impact thermomechanical properties. Although these worthwhile features, mass loss and quantitative XRD indicated zinc volatilization for samples microwave heated above 1300 ºC, which was just expected for reducing atmosphere. Thermodynamic simulations pointed out that the SiC pieces used as microwave susceptors may have induced a low oxygen partial pressure due to its oxidation, explaining the zinc volatilization, which could be avoided by using alternative oxide-based susceptors. Therefore, even though some parameters must be optimized, the present work highlights that the microwave radiation could be applied to sinter some refractory compositions, leading to environmental, productivity and performance enhancements.

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