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Characterization and sinterability of chemically precipitated phosphate-bearing magnesia grains

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Abstract

Two brucite powders having different impurity levels and doped with 0.5 mol% P_2O_5 were coprecipitated from $MgCl_2$-rich solutions derived from natural magnesite rock. The precipitated powders were characterized for their chemical and mineralogical compositions, thermal analyses and particle size distribution as well as particle morphology. The effect of P_2O_5 as well as other impurities on densification, phase composition and microstructure of the dense-magnesia grains processed by two-stage firing process up to 1300–1550°C was discussed. Phase composition was qualitatively determined by XRD, whereas a SEM attached with an EDS unit was applied for investigating microstructure. The results reveal that dense periclase ceramics containing 93–96% MgO with variable degree of direct bonding could be obtained by firing the precipitated brucite pellets up to 1300–1550°C. Brucite doped with 0.5 mol% P_2O_5 has contributed in densification of magnesia grains in the presence of magnesia-rich calcium silicate, ferrite and phosphate liquid phase. As the impurity content increases, densification is accelerated and occurs as low as 1300°C with relative decrease in bulk density and degree of direct bonding.

Keywords: A. Sintering; Characterisation; Chemical precipitation; P_2O_5-doped magnesia

1. Introduction

Powder densification and characteristics of sintered ceramics are directly related to the quality of ceramic powder used in manufacturing process. Important properties of powders such as size distribution, agglomeration, purity and surface area can strongly affect their sinterability. The segregation of impurities during powder preparation is determental to subsequent ceramic performance [1].

Magnesia raw materials used in the production of basic refractories are obtained either by dead burning naturally occurring magnesites or by dead burning magnesia-bearing compounds recovered from Mg^{2+} containing solutions, e.g. sea water, brines, Mg-Nitrates, etc. It is now accepted that refractory products made from synthetic magnesia give superior performance, when compared with the best qualities of dead-burned natural magnesites [2–4].

Magnesia is generally prepared by a single or double-stage sintering process. Brucite [$Mg(OH)_2$] is conventionally used to produce lower grade magnesia [5,6]. Since sintering is enhanced by high temperature liquid phase (as a result of mineralizers adsorbed by the crystals), it is more difficult to obtain high density magnesia when purified raw materials are used. Therefore, a double-stage process, in which $Mg(OH)_2$ powder is calcined once at 800–900°C and then compacted before refiring, is used to produce high purity magnesia [7–12].

Several technological processes are known for the production of synthetic magnesia from different sources. Among these processes is the coprecipitation method, which is suitable for preparing homogeneous powder containing multicomponent compounds [12].

Kiyohi concluded that, the relative densities of pure MgO compacts with 0.5 mol% of P_2O_5 content attained 70–99% after sintering up to 1700°C for various times [12].

The purposes of the present research are to prepare magnesium-oxide powder with magnesium phosphate additions and to characterize this powder as well as to investigate the sinterability of the resulting powder at low temperatures.

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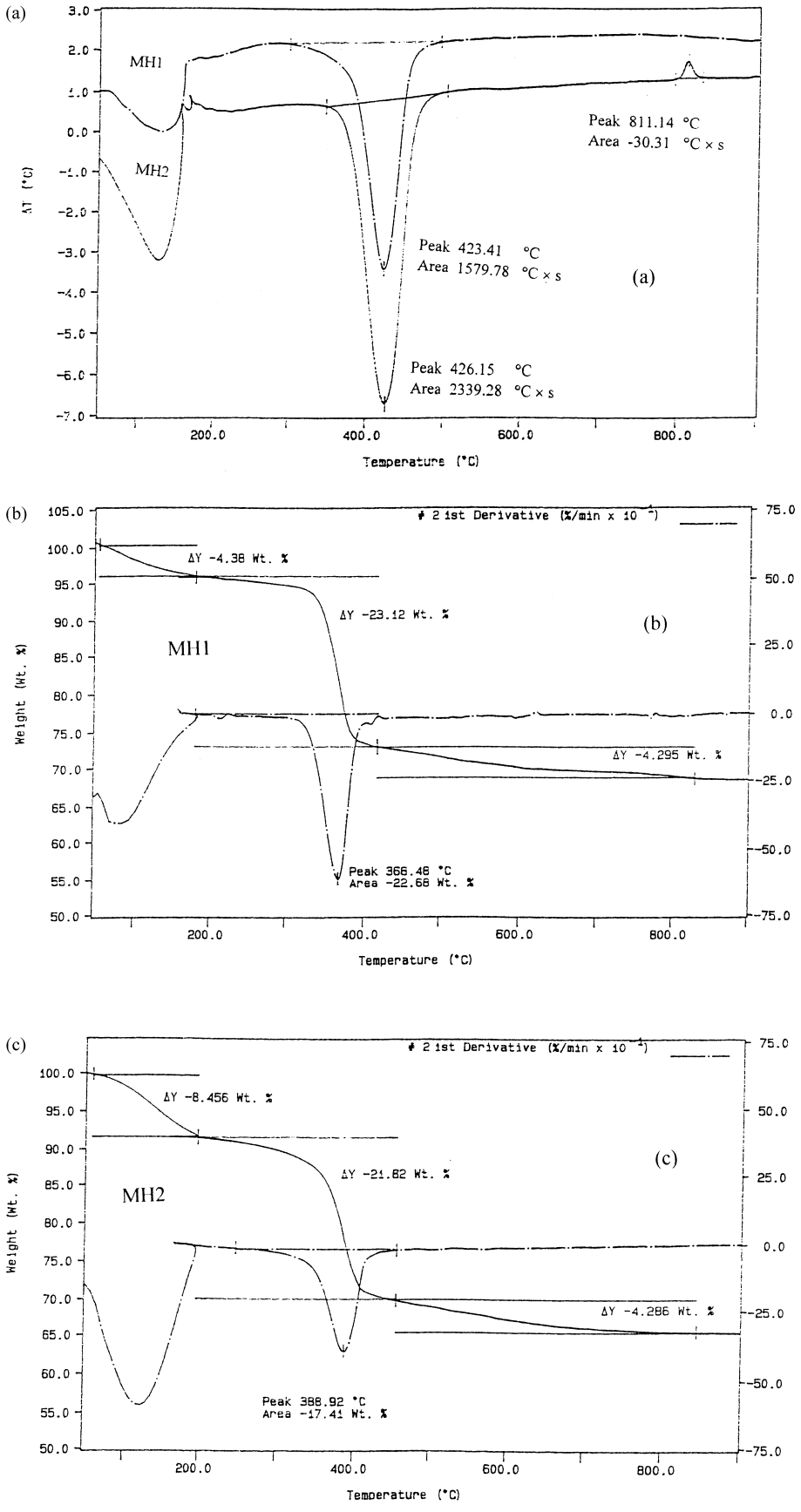

Fig. 1. DTA (a) and TG (b, c) curves of the co-precipitated MH1 and MH2 brucite powders.

2. Experimental procedure

Samples of MgO powder with 0.5 mol% of P_2O_5 were prepared by the coprecipitation technique. This manner is followed by pouring NH_3 solution into mixed solutions of $MgCl_2$ and H_3PO_4 [12,14]. Two $MgCl_2$ solutions were prepared from Egyptian raw magnesite containing some SiO_2, CaO and Fe_2O_3 as impurities. The first sample (MH1) was filtrated before adding NH_3 solution to separate the SiO_2 and Fe_2O_3 impurities, but the second one (MH2) was precipitated without separating the impurities in order to study its effect on sintering and properties of the precipitated MgO.

Chemical composition of the precipitated hydroxides and Egyptian natural magnesite as well as the produced magnesia powders were investigated using standard scheme of wet-chemical analysis [13].

Phase composition of the co-precipitated magnesium hydroxide was qualitatively determined using a Philips (PW 1710) Diffractometer using CuK_α radiation, while thermal analysis (DTA and TG) was examined by Netzsch simultaneous thermal analyzer attached with a computerized recording system.

Morphology and particle size distribution of the precipitated powders were examined by transmission electron microscope (TEM) type EM10, Zeiss Co., west Germany and FRITSCH, analy sette 22, Laser klasse 1, size analyzer, respectively.

The precipitated powder was firstly calcined at 1000°C for 1 h and then semi-dry pressed uniaxially at 60 Mpa. The pressed pellets were heated at a rate of 10°C min^{-1} in an electrical muffle furnace between 1200 and 1550°C.

Densfication parameters of the fired samples were determined by means of bulk density and apparent porosity according to the Egyptian Standard No. 1859 (1990). Microstructure of the dense samples was investigated using a computerized SEM of the type Philips XL 30. This microscope was attached with an EDS unit for microanalysis.

Table 1
Chemical analysis data of raw magnesite and precipitated magnesium hydroxides

Oxides wt.%	Raw magnesite	MH1	MH2
SiO_2	0.89	0.45	1.60
Al_2O_3	0.37	0.31	0.45
CaO	1.35	1.40	1.50
MgO	45.51	62.90	61.50
P_2O_5	–	nd[a]	nd[a]
Fe_2O_3	0.40	0.35	1.03
I.L.	51.42	32.64	31.89

[a] Not determined.

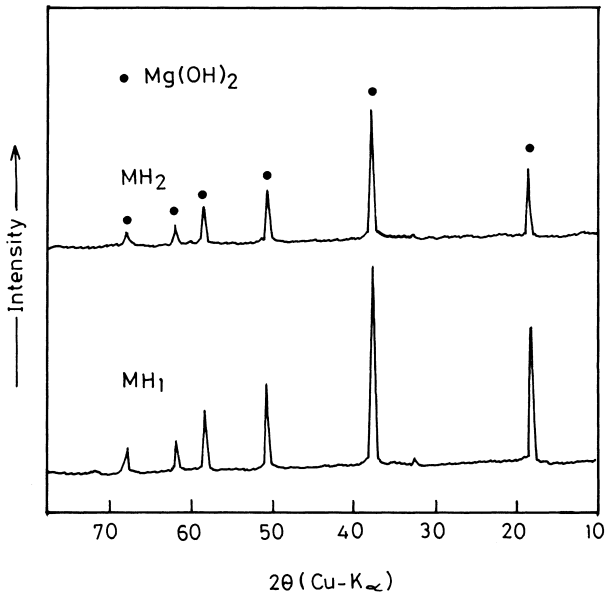

Fig. 2. XRD patterns of the co-precipitated MH1 and MH2 brucite powders.

3. Results and discussion

3.1. Identification of the precipitated hydroxides

The chemical analysis results of raw magnesite and precipitated magnesium hydroxides are shown in Table 1. The former contains about 93.80% MgO on calcined basis and the rest is SiO_2, Al_2O_3, CaO and Fe_2O_3 (6.19%). On the other side, the two precipitated magnesium hydroxides MH1 and MH2 contain 96.16 and 93.07% MgO, respectivty after omitting ignition-loss. MH2 contains higher amounts of SiO_2 and sesquioxides (R_2O_3) than that in MH1 due to separation of acid-insoluble impurities by filtration in case of the latter.

Fig. 1a, b, c exhibits the DTA and TG thermograms of the two coprecipitated magnesium hydroxides MH1 and MH2. They show an intense endothermic peak at about 423 and 426°C, with a loss of weight of 23 and 22 wt.%, respectively, due to the dehydration of

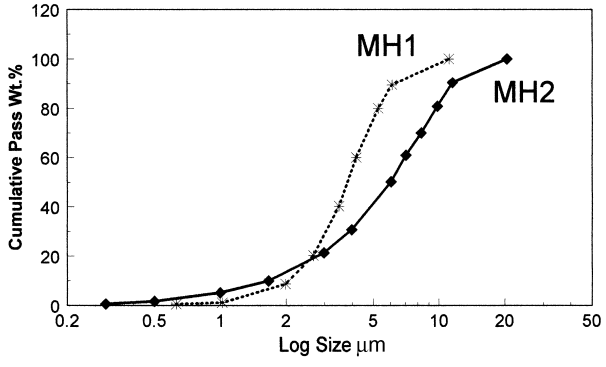

Fig. 3. Particle size distribution of the co-precipitated MH1 and MH2 brucite powders.

$Mg(OH)_2$. Also, another broad endothermic peak is observed in the two samples at about 130°C, due to adsorbed water releasing with a loss of weight of 4.4 and 8.4 wt.%, respectively. A very small exothermic peak at 810°C in MH2 was also appeared due some structural reorganization to form silicate phases namely, forsterite ($2MgO.SiO_2$).

XRD patterns (Fig. 2) of MH1 and MH2 were identical to that of brucite ($Mg(OH)_2$). MH2 showed a low degree of crystallinity than MH1 due to its higher amount of impurities.

Fig. 4. Transmission electron micrographs of of the co-precipitated MH1 and MH2 brucite powders.

The particle size distribution of the two magnesium hydroxide powders are shown in Fig. 3. It is found that MH1 sample has maximum particle size of 10 μm, with about 90% finer than 5 μm particle size, but MH2 has a maximum particle size of 20 μm, with about 90% finer than 10 μm particle size. MH2 is coarser than MH1 due to its higher amount of impurities as SiO_2 and Fe_2O_3. Fig. 4 shows the morphology of MH1 and MH2 as investigated by TEM. It appears that the particles of the two hydroxides are spherical.

3.2. Properties of the densified bodies

Fig. 5 illustrates the densification parameters of periclase sintered bodies P1 and P2 after firing MH1 and MH2 for 1 h up to 1550°C, respectively. It is evident that the addition of 0.5 mol% of P_2O_5 in presence of SiO_2 and Fe_2O_3 as impurities in MH2 leads to stimulation of its densification by liquid phase at lower temperatures as indicated by its higher bulk density and lower apparent porosity, respectively. On raising temperature from 1300 to 1550°C, the density generally decreased in P2 and increased in P1, with a maximum at 1450°C. It decreases again with increasing temperature up to 1550°C.

In a previous study [15], it is concluded that by firing brucite doped with limited amount of impurity oxides, namely SiO_2, Al_2O_3 Fe_2O_3 and CaO ($\leqslant$2.0 mass%) up to 1700°C, bulk diffusion of periclase is enhanced due to vacancy formation mechanism [16–18]. But the undoped

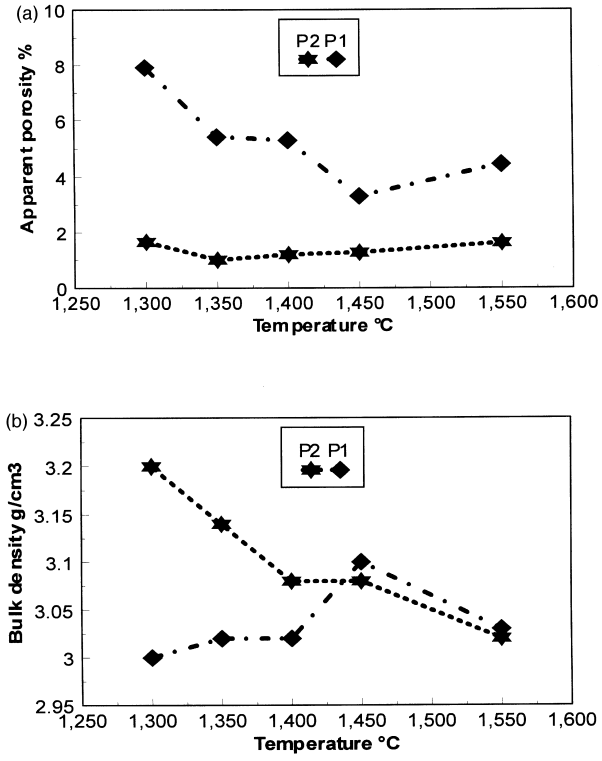

Fig. 5. Bulk density and apparent porosity of P1 and P2 magnesia ceramics after firing up to 1550°C.

periclase grains show higher linear shrinkage values with a lower bulk density, which are generally characteristic for bulk diffusion of pure oxides [9]. Such grains need higher temperature, i.e. more energy to achieve the final sintering stage.

Other grains processed from undoped natural magnesite fired up to 1700°C, also exhibited maximum bulk density of 3.40 g/cm^3 and a minimum apparent porosity as well as linear shrinkage of 0.3 and 19.4%, respectively. This could be attributed to its higher content of calcium and/or magnesium silicate and alumino-ferrite phases, the total of which amounts ≈6.4 mass%. This led to the development of limited amount of liquid phase up to 1700°C, which contributes well in the densification process [7–11].

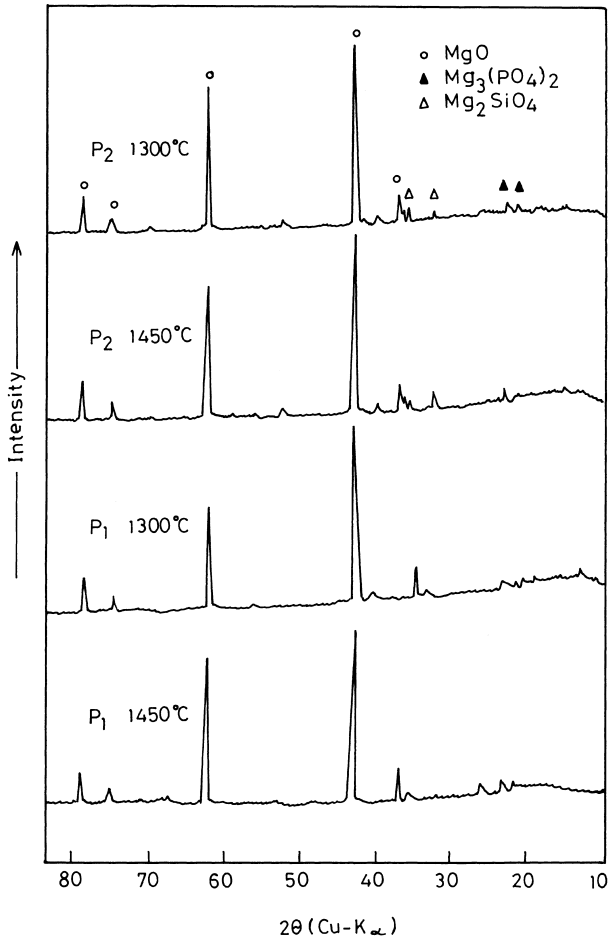

Fig. 6. XRD patterns of P1 and P2 magnesia ceramics after firing at 1300 and 1450°C.

Itatani et al. also studied the effect of phosphate addition to pure magnesia on its sintering process. It was found that the relative density and bending strength are increased as the temperature rises. This phenomena can be interpreted as reinforcement of bonding between grains due to reduction of pores and sintering in the presence of liquid phase developed within MgO–P_2O_5 system [12].

In the present work, the presence of P_2O_5 and other impurity oxides namely, SiO_2, CaO and Fe_2O_3 leads to enhance of densification process by the developed liquid phase. In P2 bulk density decreases from 3.20 g/cm^3 at 1300°C to 3.02 g/cm^3 at 1550°C. This is due to an increase in pore size which may result from the partial decomposition of $Mg_3(PO_4)_2$ [12] at earlier stage in presence of calcium andor magnesium silicate and ferrite-rich liquid phases. Meanwhile, P1 grains show an increase in bulk density from 3.0 g/cm^3 at 1300°C to 3.10 g/cm^3 at 1450°C. This is attributed to the presence of lower amount of impurity oxides which results in delaying the decomposition of $Mg_3(PO_4)_2$ to higher temperature i.e. 1450°C. At 1550°C, the bulk density is decreased again due to decomposition of $Mg_3(PO_4)_2$ at this temperature.

The XRD patterns of P1 and P2 ceramics are shown in Fig. 6. The two samples show XRD lines of a well crystalline periclase phase at all firing temperatures, beside some lines of magnesium phosphate [$Mg_3(PO_4)_2$]. P2 grains exhibit some weak lines belonging to a forsterite solid solution phase (M_2S) due to the relatively higher amount of SiO_2 in P2 than in P1. These results confirm the results obtained from thermal analysis Fig. 1.

SEM photomicrographs obtained for dense P1 and P2 grains fired at 1300 and 1450°C at two magnifications are shown in Fig. 7a–d). It is evident the most dense periclase sintered bodies i.e. P1 fired up to 1450°C and P2 fired at 1300°C have different degrees of periclase direct-bonded network with inter- and intra-granular

Table 2
Point analysis of P1 and P2 ceramic samples fired at different temperatures

Oxides	P1				P2			
	1300°C		1450°C		1300°C		1450°C	
	Point (1)	Point (2)	Point (1)	Point (2)	Point (1)	Point (2)	Point (1)	Point (2)
MgO	96.66	75.11	97.91	82.95	95.43	48.91	95.25	52.47
SiO_2	–	11.64	–	5.90	–	12.22	–	–
CaO	–	1.75	–	2.01	–	0.98	–	1.40
P_2O_5	–	9.93	–	7.07	–	43.85	–	42.74
Fe_2O_3	2.24	1.59	2.02	2.06	4.53	1.38	4.73	3.29

pores having variable sizes. Fe_2O_3 is dissolved within the magnesia network with different amounts of 2.02–2.24% in P1 (analysis No. 1 Table 2) and 4.50–4.70% in P2. Table 2 summarizes the point analysis done on the surface of periclase crystals of P1 and P2 fired at 1300 and 1450°C, respectively. Point analysis No. (1) shows the chemical composition of periclase whereas, No. (2) illustrates those of the matrix. It is also shown from

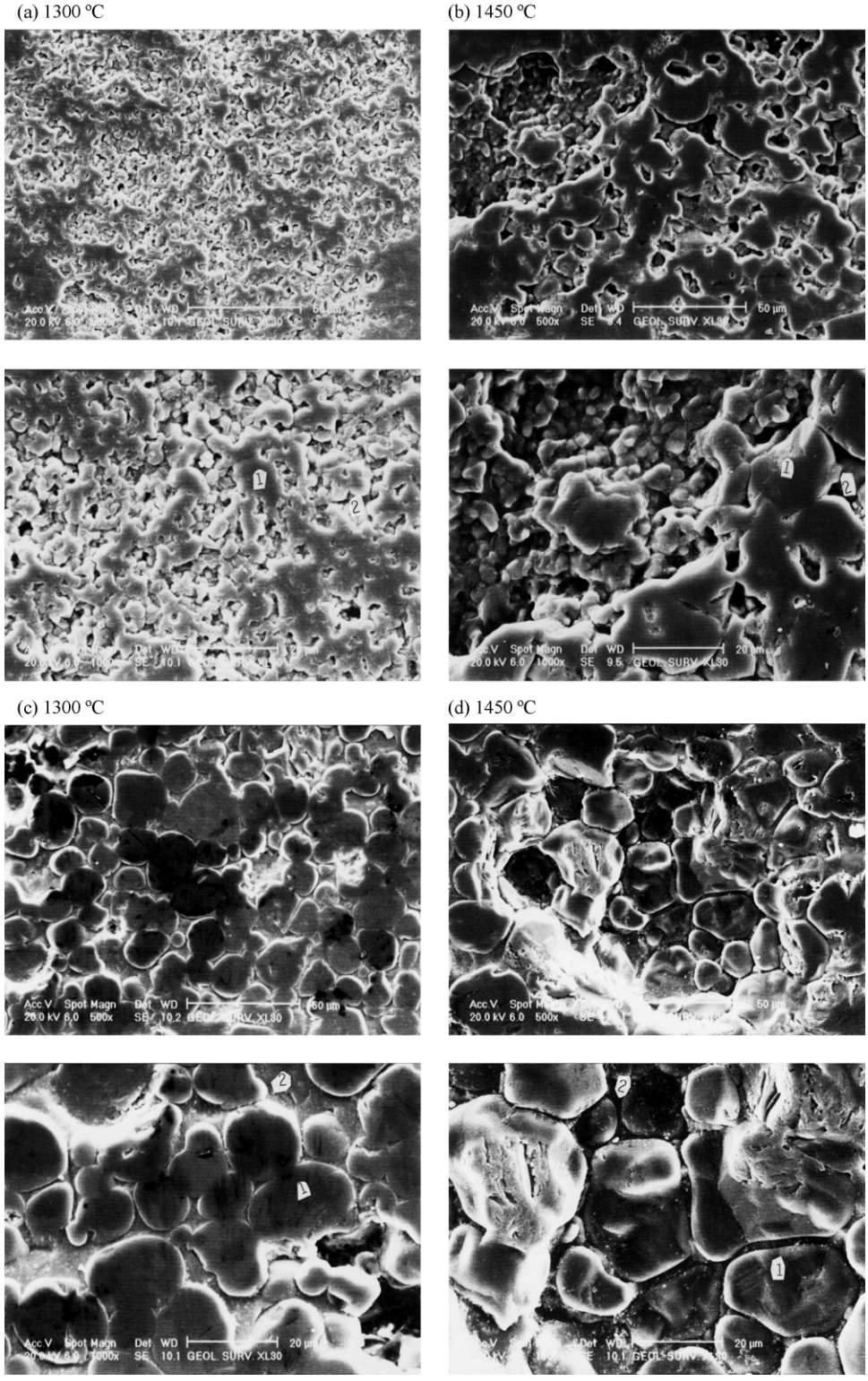

Fig. 7. (a), (b). SEM photomicrographs of P1 magnesia ceramic after firing at 1300 and 1450°C. (c), (d). SEM photomicrographs of P2 magnesia ceramic after firing at 1300 and 1450°C.

Table 2 that these matrices of this ceramics are composed of Mg-rich, Ca-silicate, ferrite and phosphate phases. The formation of such matrix is enhanced in P2 and appreciably interrupts the magnesia network as compared with that of P1.

It is also evident from Fig. 7a–d, that both P1 and P2 sintered bodies show periclase grain growth on raising firing temperature from 1300 to 1450°C. In P1 the grown periclase network enclosed much higher closed pores than in case of P2. Meanwhile, P2 shows more inter- and intra-granular cracking, especially on firing at 1450°C. This lead to decrease the bulk density of the latter sample from 3.20 to 3.02 g/cm^3.

4. Conclusions

1. Dense periclase ceramics containing 93–96% MgO with variable degrees of direct bonding could be obtained by firing brucite including different impurities contents at 1300–1550°C.
2. Doping brucite with 0.50 mol% P_2O_5 has contributed in densification of magnesia ceramics in the presence of magnesia-rich calcium silicate, ferrite and phosphate liquid phase.
3. As the impurity content increases, densification is accelerated and occurred at lower temperature of 1300°C, By rising the firing temperature, relative decrease in bulk density and degree of direct bonding are occurred.

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