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Microwave-assisted synthesis and sintering of mullite

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Abstract

Mullitization behaviour of a mixture of clay and alumina as the starting materials was examined by microwave heating of (a) mixed powder and (b) compacted powder samples for different soaking times. X-ray diffraction results showed that in compacted samples mullitization process was completed after 20 min heating with a density of about 87%. Densification and microstructure of samples with different green densities heated in a microwave oven and conventional electric furnace were compared. Results showed that the grain growth of mullite was restricted by microwave heating.

Keywords: D. Mullite; Microwave heating; Powder and compacted samples; Microstructure

1. Introduction

Mullite $3Al_2O_3{\cdot}2SiO_2$ is one of the extensively studied crystalline phases in the Al_2O_3–SiO_2 binary system [1–3] and a promising ceramic with good chemical, mechanical and electrical properties [4–8]. It is also used for high temperature applications due to its low thermal expansion, high creep resistance and good thermal shock behaviour [9,10]. Kaolin is a main source for synthesizing mullite and during heating some changes take place in its chemical and mineralogical composition [11]. The formation of mullite from reaction sintering of kaolin and alumina confirms a good way of combining reaction and densification mechanisms [12–18]. These inversions and transformations depend on a number of factors, among which are the temperature and duration of heating, the atmospheric conditions, chemical composition and form of the precursor material, and the dopants which are frequently added to accelerate the reaction [19].

Microwave technique has been extended as one of processes for synthesis and sintering of oxide materials. Microwave irradiation was found effective to produce the zeolite from coal fly ash in a short period [20,21]. Reaction sintering of $(3Al_2O_3 + 2SiO_2)$ powder compacts was studied using either a conventional electric furnace or a 2.45 GHz microwave furnace [22]. The decrease in temperature associated with a microwave effect was ≈50 °C. This much lower temperature difference was attributed to the experimental conditions used in particular the choice of a frequency of 2.54 GHz instead of a higher frequency which is suitable to detect the microwave effect.

In microwave processing energy is directly transferred to the material through interaction of electromagnetic waves with molecules leading to heating. With use of microwave for sintering a dense material with improved microstructure can be obtained in a much shorter time as compared with the conventional processes.

In this work the synthesis and sintering of mullite ceramic from the reaction sintering of clay and alumina heated by microwave energy and electrical furnace has been reported.

2. Experimental procedures

Mullite ceramics were prepared by reaction sintering of clay and alumina as the starting materials. The chemical composition of alumina (α-Al_2O_3, $d_{90} < 10$ μm) and clay (Zenouz, Iran, $d_{90} < 3.5$ μm) is shown in Table 1. Powder mixtures were ball-milled for 2 h in deionised water, dried at 100 °C for 24 h and pressed uniaxially between 127 and 764 MPa to form pellets of 10 mm diameter. Fig. 1 shows the arrangement of the microwave system used in the present work. Alumina and clay exhibit low dielectric losses (0.1 ± 0.03 and $\ll 1$, respectively) and are

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Table 1
Chemical composition of raw materials.

Oxide	Al_2O_3	SiO_2	Fe_2O_3	TiO_2	MgO	CaO	NaO_2	K_2O	L.O.I.
Clay	39.22	48.46	0.2	0.25	0.3	0.5	–	1.1	9.97
Alumina	98.7	0.07	0.035	0.015	–	0.04	0.43	–	0.7

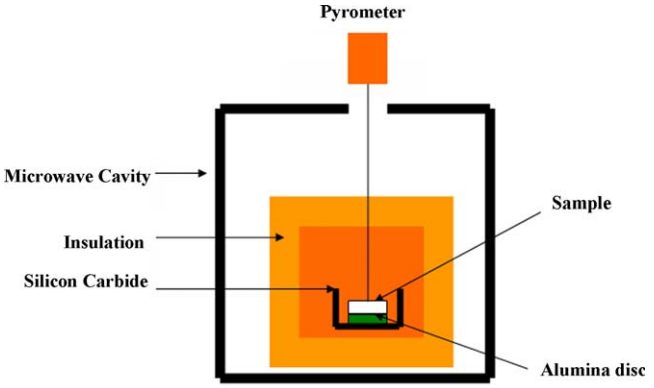

Fig. 1. Schematic diagram of microwave system.

difficult to heat in a microwave furnace at room temperature, therefore SiC crucible with a high dielectric loss (300 ± 50) was used as a susceptor [23–25]. The temperature measurements were carried out using an optical pyrometer (Model: RAYR312MSCL2G) focused through a hole in the top of insulation on the surface of the sample. Fig. 2 shows a temperature versus time curve of microwave heating. The conventional heating process was carried out in an electrical furnace with 10 °C/min heating rate and 2 h soaking time at 1400 °C. The green densities of the compacted samples were determined from the dry masses and dimensions of these specimens. The density and porosity of sintered specimens were measured after 5 h boiling and a 24 h soaking in water, according to ASTM C373-88. The phase evaluation was investigated by means of X-ray diffraction method (Siemens, D500 system) using Cu Kα radiation working with 30 kV accelerating voltage, a 25 mA current and 2° 2θ/min. Mullite formation progress was examined by considering the intensity ratio of ΣImullite/(ΣImullite + ΣIalumina) peaks. For this means, the planes (1 1 0), (1 2 0), (2 1 0) and (0 0 1) for orthorhombic mullite and (0 1 2) and (1 1 3) for rhombohedral alumina, was used. The

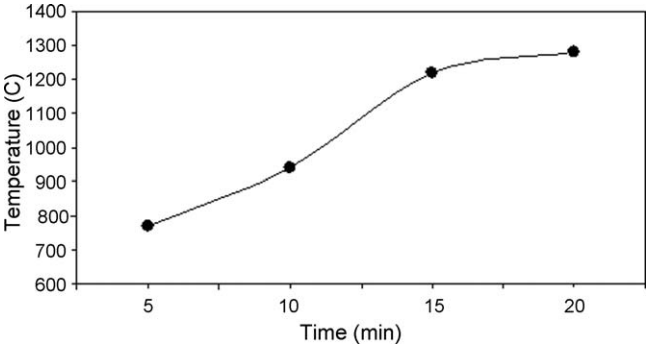

Fig. 2. Microwave heating curve.

microstructure of sintered specimens was observed by SEM (Stereoscan 360, Lecia Cambridge Instrument) on the polished and thermal-etched (1100 °C for 20 min) surfaces.

3. Results and discussion

Figs. 3 and 4 exhibit the result of phase composition of powder (PS) and compacted powder (CS) samples pressed at 127 MPa and heated in the microwave oven for different heating times. It is observed that the mullitization progress in bulk samples is higher than that of powder samples as the intensity of alumina peaks (especially for (0 1 2) plane) decreases in the former. For all heating times, the mullitization behaviour of CS samples is higher than that of PS samples (Fig. 5) and the mullitization is completed in the CS samples only after 20 min heating (from room to maximum temperature of 1280 °C). The advanced mullitization behaviour of CS samples as compared with PS samples can be attributed to the fact that the temperature in a dielectric material composed of more than one dielectric constant region is different while the local temperature depends most importantly on the local dielectric constant and other secondary properties such as heat capacity and density [26]. The accomplishment of mullitization in microwave-heated samples after 20 min and reaching to

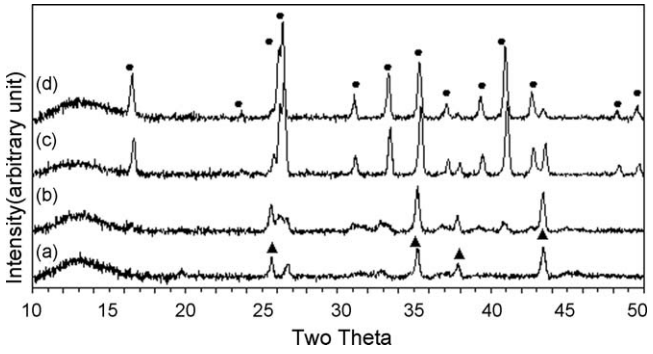

Fig. 3. X-ray diffraction patterns of powder samples (PS) heated in microwave furnace for different soaking times from room to maximum temperature: (a) 5 min (770 °C), (b) 10 min (940 °C), (c) 15 min (1218 °C) and (d) 20 min (1280 °C), ▲: alumina, ◆: quartz and ●: mullite.

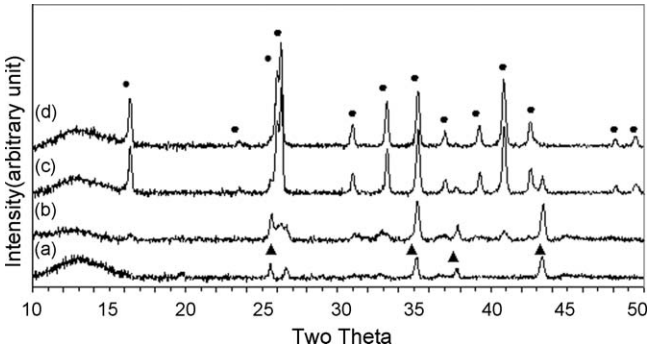

Fig. 4. X-ray diffraction patterns of compacted samples (CS) heated in microwave furnace for different soaking times from room to maximum temperature: (a) 5 min (770 °C), (b) 10 min (940 °C), (c) 15 min (1218 °C) and (d) 20 min (1280 °C), ▲: alumina, ◆: quartz and ●: mullite.

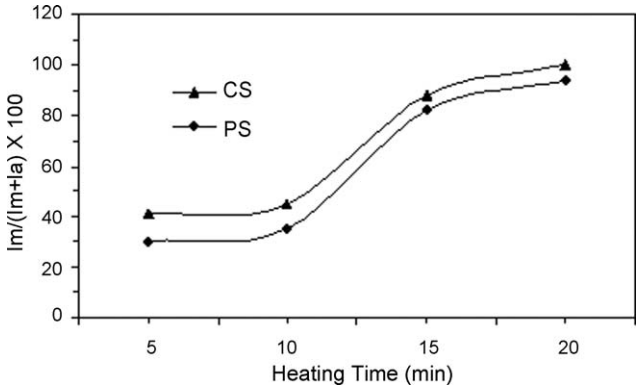

Fig. 5. Formation of mullite vs. heating time (equivalent temperatures are shown in Fig. 2) (Im: integrated intensities of mullite and Ia: integrated intensities of alumina).

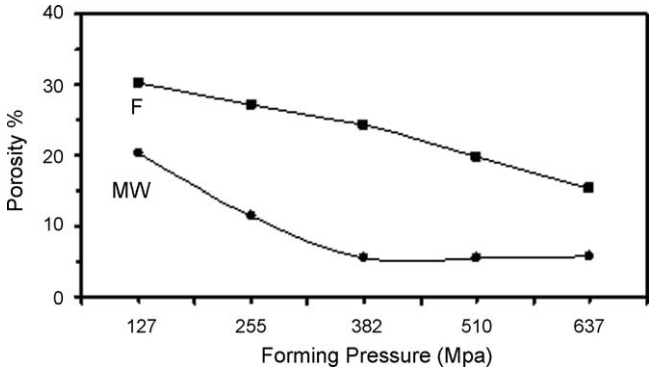

Fig. 7. Porosity of samples pressed at different pressures and sintered in microwave furnace (MW) for 20 min and reached to the maximum temperature of 1280 °C, and conventional furnace (F) at 1400 °C (2 h soaking time).

maximum temperature of 1280 °C can be noticeable since as reported [7] the clay and reactive alumina completely reacted at 1600 °C after 3 h heating and formed mullite phase. Since the size and volume of pores are different in CS and PS samples (CS sample has a lower porosity than PS sample due to the compaction process) then the local electrical field strength which affects upon thermal processing differs higher due to the existence of the various volumes of solids and pores in CS and PS samples. Further evidence from Fig. 5 reveals that mullite formation is accelerated above 10 and below 15 min heating which is due to the increase of equivalent temperature from 940 to 1218 °C. Figs. 6 and 7 show the result of density and porosity of samples (pressed at different loads) heated in the furnace at 1400 °C holding for 2 h and in the microwave oven after 20 min heating (from room temperature to 1280 °C). In all experiments microwave heating was performed at 120 °C lower temperature as compared with furnace heating because of the enhanced sintering behaviour upon microwave heating at lower temperatures than furnace heating. The results obtained from densification experiments (Fig. 6) reveal that compacted powders sintered in microwave furnace exhibit enhanced densification as compare with those sintered in the electrical furnace. In this case 87% theoretical density was obtained after 20 min heating (from room temperature to 1280 °C) in microwave conditions. A further observation arising from Fig. 6 reveals that powder sample pressed at 255 MPa and heated for 20 min in the microwave oven has a density equal to 2.57 g/cm^3, while to achieve almost the same density

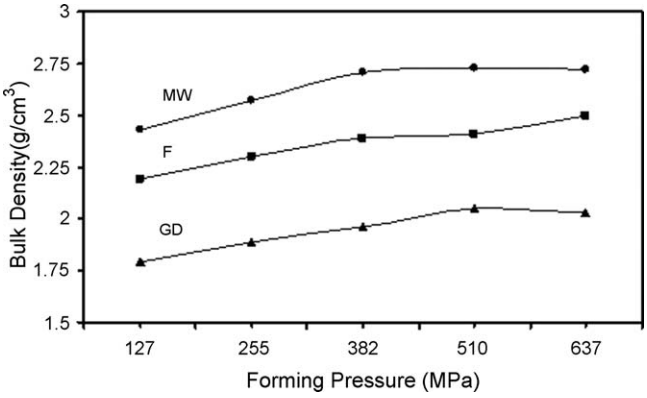

Fig. 6. Bulk density of samples pressed at different pressures before heating (GD) and after sintering in microwave furnace (MW) for 20 min and reached to the maximum temperature of 1280 °C, and conventional furnace (F) at 1400 °C (2 h soaking time).

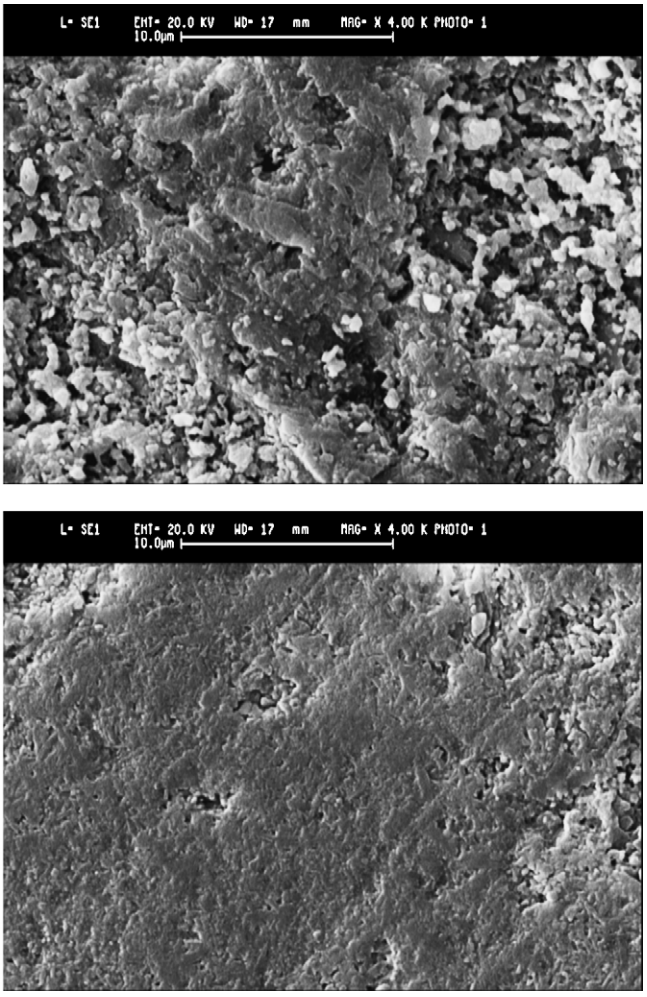

Fig. 8. SEM micrographs of powder samples pressed at 127 MPa (a) and 637 MPa (b) and heated in microwave for 20 min and reached to the maximum temperature of 1280 °C.

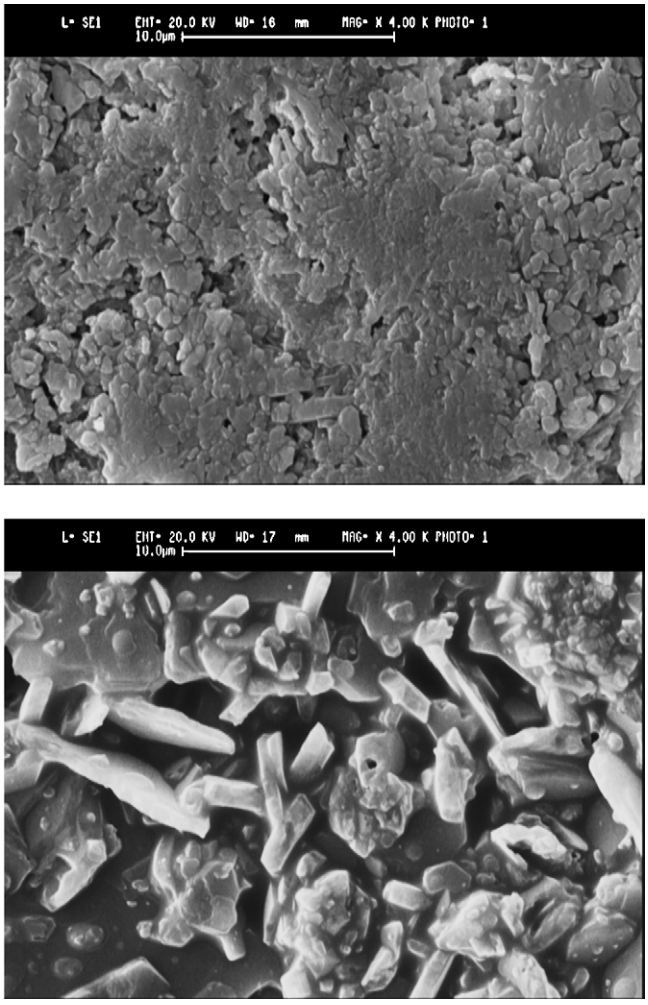

Fig. 9. SEM micrographs of powder samples pressed at 127 MPa (a) and 637 MPa (b) and sintered in furnace at 1400 °C for 2 h.

(2.5 g/cm^3) in conventionally heating the temperature of 1400 °C with soaking time of 120 min is required. The mentioned above implies that in microwave heating the reduced activation energy for sintering and enhanced mechanisms that lead to densification such as volume and grain boundary diffusion are appeared due to a microwave effect in presence of an external electrical field. It is obvious that if the resultant densities from heating of the samples in microwave oven are due only to indirect heating from the susceptor, then the density values would be identical to those for the conventional heating. On the other hand, contrast with conventional heating, the preferential interaction of the microwaves with the porosity also serves to accelerate densification [26]. Fig. 8 depicts there is no sharp difference between the resultant microstructure of samples pressed at 127 and 637 MPa and sintered in the microwave furnace for 20 min from room temperature to 1280 °C. The resultant microstructure of samples sintered in the electrical furnace at 1400 °C for 2 h (Fig. 9) represents a remarkable contrast between the samples pressed at different loads. In this case sample pressed at 637 MPa (Fig. 9b) exhibits a microstructure containing of needle-shaped particles. The appreciably smaller grain sizes of samples pressed at 637 MPa and sintered in microwave (Fig. 8b) rather than that heated in furnace (Fig. 9b) may be attributed to the faster heating rate of the former (64 rather than 10 °C/min). Fast heating causes a suppression of surface diffusion and coarsening mechanisms that exist at lower temperatures [27]. Reaching fast to higher temperatures encourages boundary and lattice diffusion mechanisms that lead to rapid sintering with little or no coarsening. Furthermore, with regard to density and microstructure results (Figs. 6, 8b and 9b) it is observed that the densification rate for microwave-heated samples is significantly higher than the grain coarsening relative to samples heated in the electrical furnace.

4. Conclusion

Phase progress results showed that the mullitization was completed in the compacted powder after 20 min heating in microwave furnace, whereas at the same heating conditions alumina peaks were detected in the powder sample confirming an incomplete reaction. The higher density was obtained at a lower temperature by microwave heating rather than conventional heating. The microwave process led to a reduction of 120 °C in sintering temperature for a given value of density. The final density of the samples pressed at various loads and sintered in the microwave furnace was higher than those sintered in the electrical furnace. The microstructural observations showed that mullite grains grew dramatically with the increase of the green density in conventionally sintered samples, while the faster heating in the microwave furnace appeared to be helpful to reduce of grain growth.

References

[1] I.A. Aksay, J.A. Pask, Stable and meta-stable equilibria in the system Al_2O_3–SiO_2, J. Am. Ceram. Soc. 58 (11–12) (1975) 507–512.
[2] R.F. Davis, J.A. Pask, Diffusion and reaction studies in the system Al_2O_3–SiO_2, J. Am. Ceram. Soc. 55 (10) (1972) 525–531.
[3] S.H. Risbud, J.A. Pask, Mullite crystallization from Al_2O_3–SiO_2 melts, J. Am. Ceram. Soc. 61 (1–2) (1978) 63–67.
[4] K.S. Mazdiyasni, L.M. Brown, Synthesis and mechanical properties of stoichiometric aluminum silicate (Mullite), J. Am. Ceram. Soc. 55 (11) (1972) 548–552.
[5] S. Kanzaki, H. Tabata, T. Kumazawa, S. Obta, Sintering and mechanical properties of stoichiometric mullite, J. Am. Ceram. Soc. 68 (1) (1985), C-6–C-7.
[6] T. Ebadzadeh, Formation of mullite from precursor powders: sintering, microstructure and mechanical properties, Mater. Sci. Eng. A355 (2003) 56–61.
[7] V. Viswabaskaran, F.D. Gnanam, M. Balasubramanian, Mullite from clay-reactive alumina for insulating substrate application, Appl. Clay Sci. 25 (2004) 29–35.
[8] H. Kalkanci, S.C. Kurnaz, The effect of process parameters on mullite-based plasma electrolytic oxide coatings, Surf. Coat. Technol. 203 (2008) 15–22.
[9] H. Ohnishi, K. Kriven, T. Nakamura, T. Kawanami, High temperature mechanical properties of mullite ceramics, in: S.R. Somiya, F. Davis, J.A. Pask (Eds.), Mullite and Mullite Composites, Ceramic Transaction, vol. 6, American Ceramic Society, Westerville, OH, 1990, pp. 605–612.
[10] N.M. Rendtorff, L.B. Garrido, E.F. Aglietti, Thermal shock behaviour of dense mullite–zirconia composites obtained by two processing routes, Ceram. Int. 34 (8) (2008) 2017–2024.
[11] C.J. MaConville, W.E. Lee, J.H. Sharp, Microstructural evolution in fired kaolinite, Br. Ceram. Trans. 97 (4) (1998) 162–168.

[12] T.W. Campos, H. De Souza, P. De Souza, Santoz, mullite development from fibrous kaolin mineral, J. Am. Ceram. Soc. 59 (7–8) (1976) 357–360.
[13] G.W. Brindly, M. Nakahira, Kaolinite–mullite reaction series: I, J. Am. Ceram. Soc. 42 (7) (1959) 311–314.
[14] F. Duncan, K.J.D. Mackenzie, P.K. Foster, Kinetica and mechanism of high-temperature reactions of kaolinite minerals, J. Am. Ceram. Soc. 52 (2) (1969) 74–77.
[15] F. Sahnoune, M. Chegaar, N. Saheb, P. Goeuriot, F. Valdivieso, Algerian kaolinite used for mullite formation, Appl. Clay Sci. 38 (2008) 304–310.
[16] Chen. Yang-Feng, M.C. Wang, M.H. Hon, Phase transformation and growth of mullite in kaolin ceramics, J. Eur. Ceram. Soc. 24 (2004) 2389–2397.
[17] K. Okada, N. Otsuka, J. Ossaka, Characterization of spinel phase formed in the kaolin—mullite thermal sequence, Commun. Am. Ceram. Soc. 69 (2003) 251–253.
[18] Y.-F. Liu, X.-Q. Liu, H. Wei, G.-Y. Meng, Porous mullite ceramics from national clay produced by gelcasting, Ceram. Int. 27 (1) (2001) 1–7.
[19] H.R. Rezaie, W.M. Rainforth, W.E. Lee, Mullite evolution I ceramics derived from kaolinite with added α-alumina and sol–gel precursors, Trans. Br. Ceram. Soc. 96 (1997) 181–187.
[20] M. Inada, H. Tsujimoto, Y. Eguchi, N. Enomot, J. Hojo, Microwave-assisted zeolite synthesis from coal fly ash in hydrothermal process, Fuel 84 (2005) 1482–1486.
[21] N. Enomoto, M. Inada, Y. Eguchi, M. Uehara, J. Hojo, Microwave synthesis of zeolite from coal fly ash and the way to scale up, Trans. Mater. Res. Soc. Jpn. 26 (2001) 1197–1200.
[22] P. Piluso, L. Gaillard, N. Lequeux, P. Boch, Mullitization and densification of ($3Al_2O_3 + 2SiO_2$) powder compacts by microwave sintering, J. Eur. Ceram. Soc. 16 (1996) 121–125.
[23] R.H. Insley, Electrical properties of alumina ceramics, in: L.D. Hart (Ed.), Science and Technology Handbook, The American Ceramic Society, Westerville, OH, 1990, pp. 293–297.
[24] J. Batt, J.G.P. Binner, T.E. Cross, N.R. Greenacre, M.G. Hamlyn, R.M. Hutcheon, W.H. Sutton, C.M. Weil, A parallel measurement programme in high temperature dielectric property measurements: an update, in: D.E. Clark, D.C. Folz, S.J. Oda, R. Silberglitt (Eds.), Microwaves: Theory and Application in Materials Processing III, Ceramic Transactions, vol. 59, American Ceramic Society, Westerville, OH, 1995, pp. 243–250.
[25] G. Zou, M. Cao, H. Lin, H. Jin, Y. Kang, Y. Chen, Nickel layer deposition on SiC nanoparticles by simple electroless plating and its dielectric behaviours, Powder Technol. 168 (2) (2006) 84–88.
[26] T.T. Meek, A proposed model for the sintering of a dielectric in a microwave field, J. Mater. Sci. Lett. 6 (1987) 638–640.
[27] D.L. Johnson, in: G.C. Kuczynski, A.E. Miller, G.A. Sargent (Eds.), Sintering and Heterogeneous Catalysis, Plenum Publishing Corp., NY, 1984, pp. 243–252.