

The effect of sintering processes of lignite calcareous ashes on the production of ceramics

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Abstract

Two-step sintering (TSS) and microwave (MW) heating process are two new techniques, promising approaches to obtain effectively densified ceramics. TSS is characterized by the absence of the final stage of grain growth occurring upon the conventional sintering and by the development of nanograin microstructure. MW energy offers many advantages for effective and rapid, thus eco-friendlier and economic sintering of materials over conventional processing. This process, by its selective and volumetric heating, can reduce the sintering time considerably, enhance the solidification efficiency and improve physical and mechanical properties. In the present research, compacts prepared from lignite combustion Class-C ashes originated from West Macedonia – Greece were sintered employing the aforementioned alternative sintering procedures and compared to similar specimens that were conventionally sintered. The ceramic microstructures obtained were characterized by means of XRD and SEM-EDX analysis, as well as by density measurements conducted using the Archimedes method. The effectiveness of the solidification process was thoroughly studied and is discussed here, and the specific microstructural features attained are compared between each other and evaluated in relation to the sintering method applied. The results show that the valorization of lignite calcareous ashes into ceramic materials is feasible through different sintering techniques.

Keywords: sintering, lignite calcareous ashes, two-step sintering, microwave, ceramics.

1 Introduction

Approximately 500 million tons of coal fly ash and 100 million tons of lignite fly ash are produced annually worldwide, and the particular amount is predicted to increase in the near future. Ash is formed by combustion of coal and especially of low calorific value lignite, in the respective power stations, as a waste product, specifically: a) fly ash, about 80% of the total ash amount, entrained in the gas flow and collected by electrostatic precipitators; b) bottom ash, the remaining, a dark gray, granular, and porous material. The management of ash remains a major problem in many parts of the world [1-4], as only a small amount of fly ash is currently recycled in cement industry as cement additive, as well as for production of paving slabs and ready mixed concrete, while the remaining ash is disposed of in repositories. Research is therefore needed to develop applications that can exploit this industrial by-product as a secondary raw material. In order to extend the utilization of ash, several procedures have been considered [5-11]. One possible application could be the elaboration of

ceramics by employing sintering processes that are extensively examined here. The large amount of ceramics produced supports this endeavor.

Conventional solid-state sintering is a generally established manufacturing technique for industrial ceramics, tiles etc. For the development of fired ceramics, lignite ashes appear attractive candidate secondary materials, given that silica and alumina are among their main components. However, the incorporation of fly ash in the clayey raw materials for brick production has rarely exceeded a 30 %, mainly due to a certain incompatibility of the ash with the clay mixtures, especially with regard to a reduced plasticity at high levels of ash leading to extrusion difficulties. Recently, research has been undertaken on the development of ceramics starting 100% from various Class-F ashes through conventional sintering procedures [12-18].

In the last few years, a new **two-step sintering (TSS)** method was proposed for the thermal treatment of powders to produce dense and fine ceramic microstructures without detrimental final-stage grain growth, thus leading to improved mechanical properties [19]. This sintering method uses two steps in the heating schedule: the sample is first heated to a higher temperature to achieve an intermediate but sufficiently high starting density, then cooled down and held at a lower temperature to approach full densities. The feasibility of densification without grain growth relies on the suppression of grain-boundary migration while keeping grain-boundary diffusion active. This two-step sintering procedure appears an important milestone for modern technical ceramics [20-27]. The characteristics of this method provide sufficient motivation to investigate its potential for the treatment and valorization of industrial by-products in ceramics development, as an efficient alternative to currently employed traditional heating procedures.

Moreover, **microwave sintering (MW)**, can be an efficient, economic and valuable approach for the “greener” processing of some powdery materials [28-31]. Actually, microwave radiation is emerging as a novel and innovative technology, widely applied in various fields. Indeed, a growing interest in the sintering of various ceramics, glass-ceramics, nano-ceramics and bio-ceramics through microwave processing is reported [32-37]. Microwave energy offers many advantages for eco-friendlier processing of materials over conventional processing. In fact, microwave processes, with their selective and volumetric heating, can enhance the solidification efficiency and reduce the processing cycle time considerably, thereby resulting into substantial energy and cost savings. Rapid heating that is possible upon microwave sintering can favour densification while limiting excessive grain coarsening. Therefore, high densities can be attained with a fine grain structure, thus improving mechanical properties and enhancing product quality. Research is currently extended on the potential use of microwave technology as an energy-efficient alternative to conventional heating technologies employed in the processing and treatment of waste by-products. Combustion ashes, in particular, can be considered as secondary raw materials for the development of ceramic crystalline structures, substituting traditional heating by microwave-assisted rapid sintering technology.

In the present research, compacts prepared from lignite combustion Class-C fly ash and bottom ash mixtures originated from West Macedonia - Greece were heated applying the aforementioned alternative sintering procedures and are compared to similar specimens that were conventionally sintered. The valorization of such ash mixtures as raw materials for the development of sintered ceramics would provide not only environmental but also economic advantages from the low cost of these industrial by-products and from possible energy savings during the ash mixture firing due to the noticeable carbon content of fly ash and especially of bottom ash.

2 Experimental

2.1 Materials

The highly-calcareous fly ash (FA) (Class-C fly ash according to ASTM C 618) was obtained by the electrostatic precipitation of dust-like particles from the flue gases of the Ptolemais lignite-fed power plant situated in Northern Greece (Region of West Macedonia where the main lignite deposits of the country are located).

The bottom ash (BA), a granular material much coarser than FA, was also formed during lignite firing and was removed from the bottom of dry boilers of the same power plant.

The chemical characterization for these ashes is given in Table 1. The SiO_2 and Al_2O_3 content of these ashes originates from the aluminosilicate components of lignite. FA in particular, is characterized by high % CaO (lime) content (similarly to other fly ashes from Northern Greece power units. BA is less abundant in Ca, but contains a higher residual carbon content.

2.2 Preparation of ash compacts

FA/BA mixtures were prepared. Simple fabrication techniques were applied for the compacts preparation: the mixtures were uniaxially cold pressed using a stainless steel die using a hydraulic press (Specac, 15011) to form 13 mm diameter disc-shaped green specimens. The specimen green density and strength were evaluated and the compaction pressure was optimized, so that the pressed compacts had sufficient green density and strength to ensure safe handling and submission to heating.

2.3 Conventional sintering

Upon conventional heating, slow heating rates are normally selected to reduce abrupt thermal gradient that can possibly lead to process-induced stresses. In the present study, all specimens were sintered in a laboratory chamber programmable furnace (Thermoconcept, KL06/13) from room temperature up to 1150 °C with a heating rate of 10 °C/min, and then held at the maximum sintering temperature for 2 h. Finally, they were gradually cooled to ambient temperature. The chosen sintering conditions were optimized on the basis of preliminary experimental trials.

2.4 Two-step sintering (TSS)

The two-step sintering (TSS) procedure was carried out also in the laboratory chamber programmable furnace (Thermoconcept, KL06/13). A temperature slightly lower than the melting point of the ashes was selected for the first sintering step ($T_1 = 1150\text{ °C}$). As soon as T_1 was attained, the samples were rapidly cooled down in the furnace, and held at a lower temperature, that of the second sintering step ($T_2 = 950\text{ °C}$) for 4 h. In order to evaluate the intermediate sintering result at the end of the first sintering step, a series of specimens were sintered only up to 1150 °C and then taken out of the furnace. Finally, the two-step sintered specimens were gradually cooled to ambient temperature in the furnace.

2.5 Microwave sintering (MW)

Microwave irradiation can produce rapid and uniform heating of thick materials, usually at the ISM (Industrial Scientific and Medical) frequency of 2.45 GHz. Actually, microwave energy is delivered directly to the material through molecular interaction with the electromagnetic field, as microwaves can penetrate the material and supply energy, resulting in volumetric heating. Hence, the thermal gradient in the microwave-processed material is the reverse of that in the material processed by conventional heating. In the current research, MW sintering of the green compacts was conducted at 1150 °C for 30 min in a special purpose microwave (2.45 GHz) system design (PHOENIX, Microwave Muffle Furnace) for laboratory rapid heating of materials. Finally, the MW-sintered specimens were gradually cooled to ambient temperature in the furnace.

2.6 Characterization of sintered ash compacts

Phase characterization of green and sintered specimens was realized by X-Ray Diffraction (XRD - Siemens, Diffractometer D-5000). The microstructures produced were studied using Scanning Electron Microscopy (SEM - Jeol, JSM-6400). Shrinkage of the samples was evaluated as the volume change (%) upon sintering. Apparent density was measured according to the Archimedes principle by means of a specific apparatus (Shimadzu, SMK401-AUW220V).

3 Results and discussion

The mineralogical composition, as determined via **XRD** analysis, of green (A), conventionally sintered (B), sintered only up to 1150 °C, TSS-sintered (C) and MW-sintered (D) specimens, prepared of FA/BA mixture (1/1), is shown in Fig. 1.

The intense presence of lime (CaO) in the raw materials is clearly depicted in the diffractogram corresponding to the green specimen (Fig. 1A).

In all sintered specimens, ceramic microstructures apparently more complex than that of the green ash compacts are revealed (Fig. 1B, C, D and E), as a result of thermal treatment. Major crystalline phases identified are gehlenite, kyanite, magnetite and quartz, and even calcite, calcium aluminium oxide hydrate and a magnesium aluminosilicate compound ($\text{MgAl}_2\text{Si}_3\text{O}_{10}$), while lime practically disappears. Certainly, some of the mineralogical phases detected in the sintered compacts were also originally present in the raw materials. Nevertheless, the intensity of the peaks associated with these phases is clearly higher after sintering.

When comparing the sintered microstructures between each other, it can, first, be stated that the ash mixtures sintered only up to 1150 °C and then taken out of the furnace (Fig. 1C) as well as the TSS-sintered ones (Fig. 1D) exhibit similar mineralogical compositions between them. Therefore, it can safely be concluded that the mineralogical phases identified in the specimens subjected to TSS heating had already been generated during the first sintering step. Moreover, crystallinity in the produced materials is slightly reduced moving from the TSS procedure (Fig. 1D) to conventional sintering (Fig. 1B), and even more upon MW sintering (Fig. 1E). Hence, it seems that, by holding the ash mixtures for a time period at 1150 °C (conventional and MW sintering) rather than at 950 °C (second step of the TSS procedure), some of the crystalline structures progressively decrease thus resulting in relatively more simple ceramic microstructures.

The result of the densification process in the sintered specimens can be evaluated upon microstructural observation using **SEM** analysis (Fig. 2).

From Fig. 2, acceptable ceramic microstructures are obtained for all sintered specimens and the development of diffusion sintering necks that bind the produced materials can be observed. The efficient ash particle packing achieved in the green compacts, as it can be seen from Fig. 2a, should contribute to a successful sintering result. Nevertheless, the consolidation degree upon sintering clearly depends on the heating mode applied, and, in consequence, the sintered density determined varies in the range of 2.3-2.7 g·cm⁻³.

Higher densification degrees are attained after conventionally sintering (Fig. 2b) and especially after MW processing (Fig. 2d) the ash mixtures. Particularly in the MW-sintered materials, quartz crystals are located in a densified matrix mainly composed of gehlenite, while a localized viscous flow, indicative of limited liquid-phase sintering also appears. Therefore, both thermally activated processes, mainly diffusive but even restricted viscous processes, coexist in the bulk of the materials, enhancing consolidation. Such microstructures would be potentially preferred for structural applications demanding reasonably dense ceramic materials combined with the substantial energy and production cost savings from the use of MW technology.

Finer microstructures are obtained when employing the TSS sintering (Fig. 2c). However, Fig. 2c also reveals an interconnected porosity in the TSS-sintered specimens, which exhibits no preferential orientation or shape. Therefore, higher holding times should probably be considered for the second sintering step of the TSS-heating program, in case that higher densification was demanded. On the other hand, such porous sintered-ceramic microstructures offer various advantages for specific applications, including a possible water-purifier performance due to bacteria immobilization properties in their pores, tailored insulation behavior as an alternative solution to reduce the energy consumption of buildings, and thermal shock resistance due to an improved expansion tolerance and a certain decrease in the modulus of elasticity. Moreover, from the economic point of view, a cost reduction is expected by producing objects of a reduced relative density.

In addition, it should be noted that the shrinkage all ash specimens underwent during sintering appears relatively restricted and remains lower than 5%.

4 Conclusions

The results show that the valorization of lignite calcareous fly ash and bottom ash mixtures in synthesizing acceptable ceramic microstructures is feasible through different sintering techniques.

The MW-sintered microstructures obtained from the ash mixtures would be potentially preferred for structural applications demanding reasonably dense ceramic materials combined with the substantial energy and production cost savings from the use of MW technology that could facilitate incorporation of such sintered ash ceramics into the market.

On the other hand, finer microstructures are obtained when employing the TSS sintering, however also exhibiting an interconnected porosity. In this case, the potential advantages of porous ceramic microstructures for specific applications, combined with a cost reduction expected by producing objects of a reduced relative density, should be taken into consideration.

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Table 1. Chemical analysis of Greek calcareous fly ash (FA) and bottom ash (BA)

	SiO₂	Al₂O₃	Fe₂O₃	CaO	MgO	SO₃	Na₂O	K₂O
FA	30.16	14.93	5.10	34.99	2.69	6.28	1.01	0.40
BA	48.63	21.62	7.29	6.83	2.75	2.78	0.89	2.97

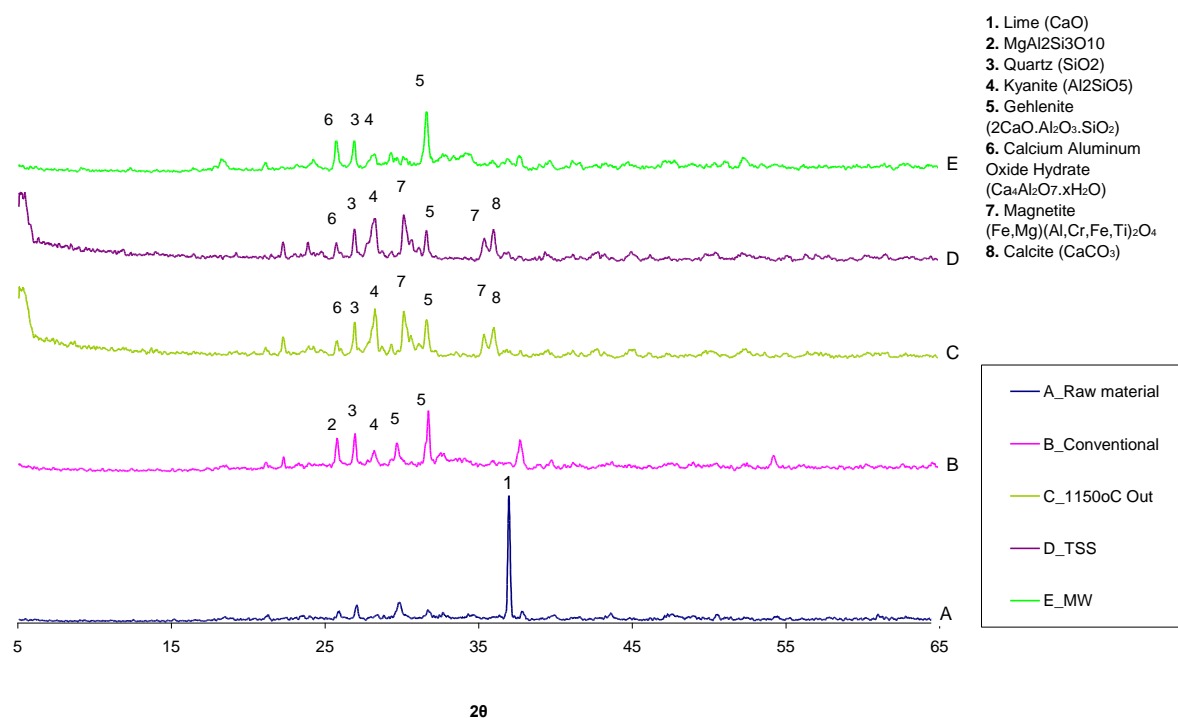
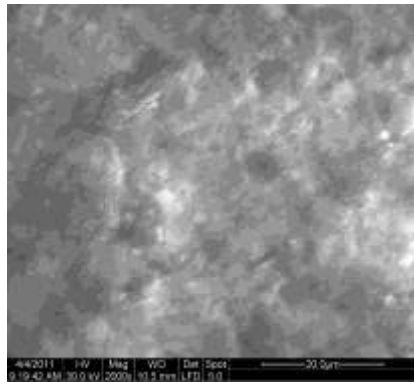
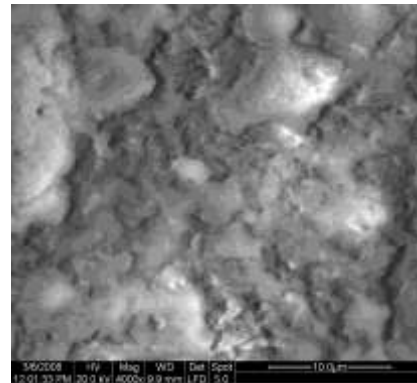


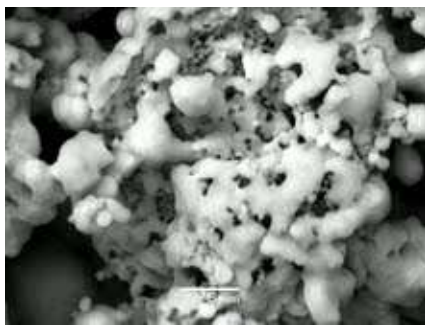
Fig. 1 Typical XRD spectra of FA/BA (1/1) mixtures: (A) green, (B) conventionally sintered, (C) sintered up to 1150 °C, (D) TSS-sintered and (E) MW-sintered



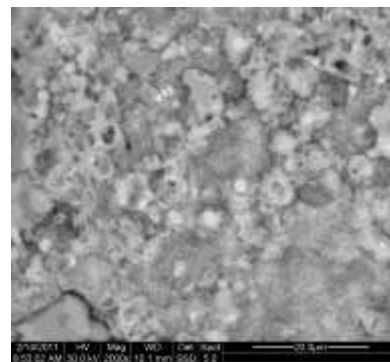
(a)



(b)



(c)



(d)

Fig.2 SEM micrographs of FA/BA (1/1) mixtures: (a) green, (b) conventionally sintered, (c) TSS-sintered and (d) MW-sintered