INNOVATIVE PROCESSING OF LIGNITE COMBUSTION ASHES TOWARDS CERAMICS SYNTHESIS

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In the present study, novel two-step sintering of lignite combustion highly-calcareous ashes is investigated. So far, solid-state sintering of fly ash through conventional thermal treatment has already been considered for the development of ceramic materials. Although conventional sintering is generally a preferred manufacturing technique for industrial ceramics, a new two-step method is proposed in the last few years for sintering dense and fine ceramic microstructures. Innovative processing of ashes – produced in massive quantities from lignite-fed power generation units – in the elaboration of value-added ceramic materials represents a challenge with important environmental, technological and economic aspects, due to the intrinsic characteristics of these industrial by-products. For that purpose, disc-shaped compacts from fly ash, bottom ash and ash mixtures were prepared by cold pressing, and then consolidated using two-step sintering procedures: the specimens were first heated at a higher temperature to achieve an intermediate starting density, then cooled down and held at a lower temperature to approach higher densities. The sintered specimens were characterized by means of XRD and SEM-EDX analyses as well as shrinkage, apparent density, water absorption capability and Vickers microhardness measurements. According to the results, effectively solidified ceramic materials are obtained with interesting specific microstructural features and properties.

Keywords: Two-step sintering, lignite combustion ashes, ceramics.

INTRODUCTION

Management of fly ash and bottom ash, produced in massive quantities from lignite combustion for power generation, is of great environmental concern, as only a limited amounts of ashes are currently used, while the rest is landfilled, a situation that will possibly cause severe long-term environmental effects (Zacco *et al.*, 2014, Karapanagioti *et al.*, 2012, Sun *et al.*, 2011, Polic *et al.*, 2005). Nevertheless, the chemical, mineralogical and morphological properties of these by-products render their valorization as secondary raw materials into value-added products a challenge with important technological, environmental and economic aspects (Karayannis *et al.*, 2012, Blissett and Rowson, 2012, Badanoiu and Voicu, 2011, Ahmaruzzaman, 2010, Komnitsas, 2009).

In particular, the utilization of lignite combustion ashes for ceramics production represents a significant research area. So far, solid-state sintering of fly ash through conventional thermal treatment has already been considered for the development of ceramic materials. Although conventional sintering is a generally established manufacturing technique for industrial ceramics, a new two-step method (TSS) was proposed in the last few years for sintering powdery materials to produce dense and fine ceramic microstructures without detrimental final-stage grain growth, thus leading to improved mechanical properties (Chen and Wang, 2000). 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 or even for pore size control. The feasibility of densification without grain growth relies on the suppression of grain-boundary migration while keeping grain-boundary diffusion active. The two-step sintering procedure appears an important milestone for modern technical ceramics, and its feasibility has been verified in various ceramic systems (Domopoulou *et al.*, 2014, Kim *et al.*, 2014, Xiong *et al.*, 2013, Isobe *et al.*, 2012, Zhang *et al.*, 2012, Lourenco *et al.*, 2011, Li *et al.*, 2010, Maca *et al.*, 2010, Li *et al.*, 2008, Mazaheri *et al.*, 2008, Wang *et al.*, 2008). The efficiency of this method is considered more pronounced in ceramics with crystalline phases of higher symmetry, whereas its applicability is questioned only when the activation energy for consolidation is higher than that for grain growth. This new process provides 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.

In the present research, innovative two-step sintering of lignite high-Ca fly ash and bottom ash is attempted. This rich-in-Ca ash composition can possibly be expected to yield an interesting mineralogy in the sintered materials, while the Ca-bearing phases may also act as a flux enabling melting to begin at lower temperatures, thus using less energy. Furthermore, the low thermal conductivity of the ashes, as they are mainly consisted of hollow sphere-shaped particles (cenospheres), should also influence the sintering result. In previous studies, ashes of similar composition have been tested by the authors for microwave as well as conventional furnace sintering (Karayannis *et al.*, 2013a, Karayannis *et al.*, 2013b, Moutsatsou *et al.*, 2008). By heating the lignite ashes under investigation employing the two-step method, interesting solidification processes, microstructure and properties can be attained. The sintering results are evaluated as a function of the two-step sintering program employed and the ash specimen composition.

EXPERIMENTAL

Materials

The fly ash (FA) utilized as a secondary raw material in the present research, a fine powder, was obtained by the electrostatic precipitation of dust-like particles from the flue gases of a lignite combustion power plant situated in Northern Greece (Region of Western Macedonia where the main lignite deposits of the country are located). The bottom ash (BA) that was used, a granular material much coarser than FA and also formed during lignite firing, was removed from the bottom of dry boilers of the same power plant. The chemical analysis results for these ashes are given in Table 1. It can be seen that, particularly FA, is characterized by high % CaO content, similarly to other fly ashes from Northern Greece power units belonging to Class-C ashes (ASTM C 618). BA is less abundant in Ca, but contains higher residual (unburned) carbon (≈5%).

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

	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O
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

Two-Step Sintering of Ash Specimens

Disc-shaped green compacts (13 mm diameter) from FA, BA and 50-50 wt% FA-BA mixtures were prepared by uniaxially cold pressing in a stainless steel die using a hydraulic press (Specac, 15011), and then consolidated using two-step sintering procedures in a laboratory chamber programmable furnace (Thermoconcept, KL06/13).

A temperature slightly lower than the melting point of the ashes was selected for the 1st first sintering step (T1=1150°C). As soon as T1 was attained, the samples were rapidly cooled down in the furnace, and held at a lower temperature, this of the 2nd sintering step (T2=950°C). Two different sintering programs where tested: TSS1, where the samples remained at T2 for 2h, and TSS1, where the samples remained at T2 for 4h. In order to evaluate the intermediate sintering result at the end of the 1st sintering step, a series of specimens were sintered only up to 1150°C and then taken out of the furnace. Finally, the specimens were gradually cooled to ambient temperature in the furnace.

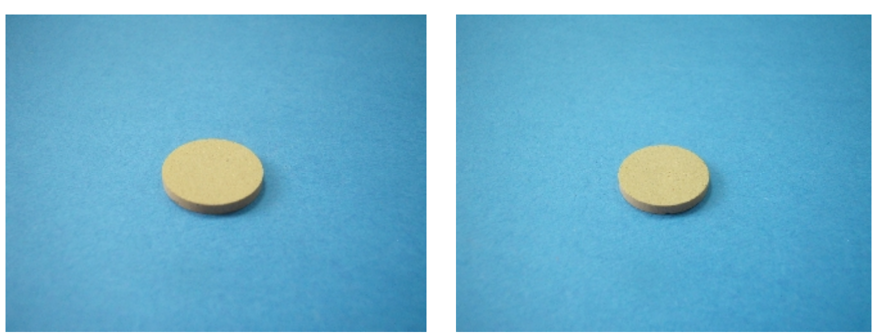
Characterization of Two-Step Sintered Specimens

Phase characterization of green and two-step 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 calculated as the volume change (%) upon sintering. Apparent density was measured according to the Archimedes principle by means of a specific apparatus (Shimadzu, SMK401-AUW220V). In order to determine water absorption capacity, sintered specimens were first oven dried to constant weight, cooled to room temperature, and weighed (W1). Then, the specimens were immersed in distilled water for 24h, and subsequently weighed again (W2), after the excess water had been removed from their surfaces by wiping with a damp cloth. The water absorption (%) was calculated as the increase in mass as a percentage of oven dried mass. Vickers microhardness was measured with a load of 200g and a dwell time of 15s (Shimadzu, HMV-2T). In order to enable reliable comparisons, mean microhardness values were calculated over five valid indentations per specimen.

RESULTS AND DISCUSSION

Photographs of ash mixtures (FA/BA:1/1) sintered through the two-step method (TSS1 (a) and TSS2 (b)) are provided in Figure 1. It can be seen that successfully consolidated integral and similar between them earth-yellowish specimens are obtained.



(a) (b)

Figure 1. Photographs of specimens (diameter: 13 mm) made of ash mixtures (FA/BA:1/1) and sintered via the two-step method: (a) TSS1 and (b) TSS2

The main mineral phases present in the green specimens prepared of ash mixture (FA/BA:1/1), as well as in those sintered only up to 1150°C and in the two-step sintered sintered ones (TSS1 and TSS2), as determined by means of XRD, are shown in Figure 2.

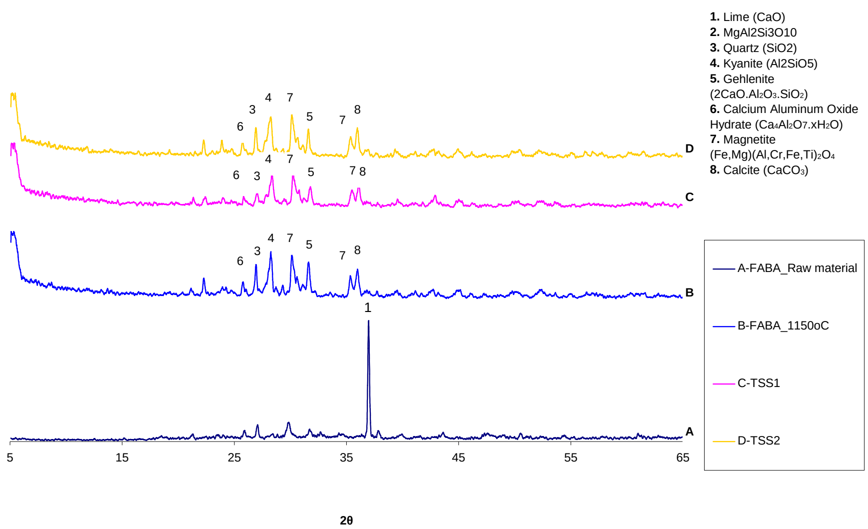
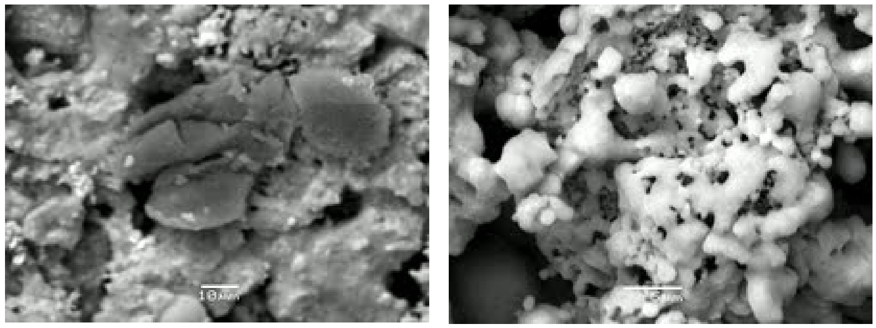


Figure 2. Typical XRD spectra of ash mixtures (FA/BA:1/1):
(A) green, (B) sintered up to 1150°C, & sintered by 2-step method (C:TSS1 & D:TSS2)

Obviously, the intensity of the peak associated with lime (CaO) predominates in the diffractogram of the green specimen (Figure 2, A). This intense presence of lime in the ashes is mainly due to the high percentage of limestone ($CaCO_3$) in the feedcoal (lignite) of the power unit. The ash mixtures sintered only up to 1150°C (Figure 2, B) as well as those sintered via the two-step procedure (Figure 2, C and D) exhibit quite similar mineralogical compositions between them. Therefore, it can be concluded that the mineralogical phases detected in the two-step sintered specimens were already generated in the first sintering step. Actually, an interesting ceramic microstructure and more complex than that of the raw materials is revealed, whose major crystalline phases are kyanite, magnetite, quartz, gehlenite and calcite.

The result of the consolidation process can be evaluated upon microstructural observation of two-step sintered specimens via SEM analyses (Figure 3). From Figure 3, when using the TSS1 heating program (2h-holding-time in the second step), a reasonably sintered and rather rough matrix is shown where quartz crystals are located. On the other hand, a clearly finer microstucture is obtained when the TSS2 program (4h-holding-time in the second step) is employed. Hence, the consolidation process and the specific microstructural features not only depend on the temperatures chosen for the two sintering steps but also on the holding time in the second step. In order to achieve a higher densification degree, even higher holding times should be considered for the second sintering step.



(a) (b)

Figure 3. SEM micrographs of ash mixtures (FA/BA:1/1) sintered using two-step programs: (a) TSS1 and (b) TSS2

Shrinkage of the two-step sintered fly ash specimens is lower than 5%. Density lies in the range of 2.3-2.4 g.cm^{-3}, whereas mean Vickers microhardness attains 120 HV. Water absorptivity varies up to 20 %, strongly depending on the existence of open and interconnected pores that can be verified from the SEM analyses. Moreover, rough pore wall surfaces are frequently indicated in the micrographs, revealing a high specific surface area facilitating water adsorption on the pore wall (following the penetration of water in the open pores and its diffusion along the interconnected pores). Precise preparation of porous ceramics having various pore size and porosity two-step sintering program from Al_2O_3 powder compact are also reported from other researchers (Isobe et al. 2012). From a technological point view, such microstructures may be of interest for porous ceramic applications.

CONCLUSIONS

Lightweight ceramic microstructures with pronounced crystallinity are obtained from lignite high-Ca fly ash and bottom ash employing two-step sintering processes.

The highly-calcareous nature of fly ash and the residual carbon of bottom ash influence the sintering results but do not hinder the synthesis of ceramics via this method.

TSS approach depends on the heating program applied. It should be noticed that sintering time is kept at lower temperatures, thus leading to possible energy consumption reductions. Further investigation of the heating conditions would enable a tailoring of the ceramic microstructures to meet the needs for specific applications.

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