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Development of engineering ceramics 100% from lignite fly ash and steelmaking EAFC mixtures

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In the present work, the development of ceramics is examined by using two industrial solid by-products as 100% the raw material mixture, a challenge with technological, environmental (sustainable waste management and earth mineral resources conservation) and economic benefits (utilization of largely available industrial secondary resources). Specifically, fly ash derived from lignite-fed power station and electric arc furnace-carbon slag (EAFC) from steelmaking plant, were used as secondary resources. These powdery materials were mixed in various proportions (0-70%wt. EAFC content), cold compacted at 20 tn load using an automated hydraulic press to form a series of 5 cm diam. disc-shaped specimens, and then sintered at three different peak temperatures (1000, 1100 and 1140 ºC) for 3 h. The microstructures produced were studied via SEM-EDS, and specimen physico-mechanical properties were evaluated. For a 50-50%wt. fly ash-EAFC mixture, the experimental data show that as the firing temperature is increased from 1000 ºC up to 1140ºC, the produced specimens hopefully are not deformed during the sintering process. For that mixture, the diametral tensile strength (DTS) increases from approx. 1.5 MPa at 1000 ºC and 1100 ºC up to 7.4 MPa at 1140 ºC. The coefficient of thermal conductivity also remains practically constant up to 1100 ºC, attaining its max. value at 1140 ºC. At this peak temperature, max. DTS was recorded for the 100% fly ash specimens (11.6 MPa). Nevertheless, mixtures containing up to 60%wt. EAFC (at 1140 ºC) seem to maintain satisfactory physico-mechanical properties. SEM micrographs provide an insight in the ceramic microstructural evolution with temperature.

Key words: Ceramics, Fly ash, EAFC, Sintering, diametral tensile strength, Thermal conductivity.

Introduction

Huge amounts of ashes are produced annually from lignite/coal-fired power plants. Fly ash contains several oxides and should be considered as a useful secondary material for industrial use. Several potential applications are examined, such as composites [1], geopolymer-cements [2] and various construction applications [3-5], as well as control of acid generation from sulphidic wastes [6] etc.

On the other side, considerable research has already been conducted on the utilization of metallurgical slags containing aluminosilicates in geopolymers production [7]. Moreover, incorporation of steelmaking dust in ceramic clay bodies has been examined [8-11]. Particularly, the recycling of electric arc furnace-carbon slag (EAFC), one of the major steel-industry powdery residues, is very important. EAFC is an artificial rock-like aggregate with properties similar to real rocks like basalt or granite, produced during the processing of scrap steel in the electric arc furnace with the addition of flux additives, undergoing chelation, successive breaks and classification. Actually, the use of EAF technology in the steelmaking industry has been increasing considerably over the last decades, resulting in the production of significant quantities of solid by-products [12]. So far, especially after 2004, main use of EAFC in Greece is in national highways construction [13].

In the last years, synergy of various mixtures of industrial and/or agricultural wastes containing useful oxides has been under investigation for the fabrication of construction products including ceramics, glass-ceramics and cement-based materials [14-18]. Limited data are reported, however, regarding synergistic utilization of fly ash with steel-industry solid residues in the formation of fired clay ceramics, although appropriate mixture combinations of industrial residues of these categories can be attractive starting materials for ceramics development, taking advantage from differences in their chemical and mineralogical composition [19].

In the current research, the innovative synergistic utilization of lignite fly ash with the metallurgical by-product EAFC is attempted, to develop new materials with potentially interesting properties. From the environmental point of view, both valorizations of these industrial residues to partially alleviate waste management problems and substitution for other raw materials derived from mineral resources can contribute to environmental

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protection and natural resources conservation. Moreover, the low cost of the by-products can give them an advantage over traditional raw materials in possible future large scale utilization as industrial valuable resources. In this study, specimens were prepared from fly ash-EAFC mixtures and their properties were studied as a function of the relative mixture composition and the sintering temperature.

Raw materials and specimen preperation

In Tables 1 and 2, the chemical composition (major oxides) of the secondary resources used as the raw materials for ceramic specimen fabrication is reported.

The raw materials were first ground (< 0.63 mm) in a planetary baw mill for 10 min and then mixtures were formed and cold compacted at 20 tn load using an automated hydraulic press to form 50 mm X 8 mm (diameterXthickness) disc-shaped specimens that were sintered in a programmable electric furnace. The firing program had a first pre-heating step up to 700 ºC to drive off absorbed gases, followed by further controlled heating up to a peak temperature. The specimens were allowed to remain at the maximum sintering temperatures for 3 hrs, and then were gradually cooled in the furnace to room temperature. Specifically, specimens from: a) 50-50wt.% FA-EAFC mixture were fired at three different peak temperatures (1000 ºC, 1100 ºC and 1140 ºC) and b) FA-EAFC mixtures in various proportions (0-70%wt. in EAFC) were sintered at 1140 ºC, and their properties were studied as a function of the firing temperature and the relative mixture composition respectively.

The determination of shrinkage, weight loss, water absorption capability and porosity was conducted on fired disk-shaped specimens according to ASTM C67: Standard Test Methods for Sampling and Testing Brick and Structural Clay Tile. In particular, open porosity and total porosity were determined by immersion of the specimens in cold (24 hrs) and boiling water (5 hrs). The thermal conductivity coefficient (k) was measured at 25 ºC using the guarded heat flow meter method (Anter Unitherm Model 2022) in accordance with the ASTM E1530: Standard Test Method for Evaluating the Resistance to Thermal Transmission of Materials by the Guarded Heat Flow Meter Technique. All diametral tensile strength (DTS) measurements were conducted using the Brazilian test, which is an indirect test method according to ASTM D3967: Standard Test Method for Splitting Tensile Strength of Intact Rock Core Specimens. The laboratory testing equipment is a UTS Instron 3382 with a load capacity of 10 KN.

Table 1. Chemical composition of fly ash (FA) used.

Constituent	(%)	Constituent	(%)
SiO_2	34.85	K_2O	1.51
CaO	19.19	TiO_2	0.71
Al_2O_3	14.17	Na_2O	0.42
Fe_2O_3	11.23	P_2O_5	0.26
SO_3	6.26	BaO	0.16
MgO	2.58	MnO	0.09

Table 2. Chemical composition of EAFC [13].

Constituent	(%)	Constituent	Percentage
CaO	35.6	CrO_3	1.1
Fe_2O_3	27.9	TiO_2	0.4
SiO_2	11.1	P_2O_5	0.3
Al_2O_3	9.0	SO_3	0.3
MnO	4.3	BaO	0.1
MgO	3.8	V_2O_5	0.1

Results and Discussion

Diametral shrinkage

Fig. 1(a) shows the effect of sintering temperature on diametral shrinkage of 50-50%wt. FA-EAFC specimens, whereas in Fig. 1(b), the dependence of diametral shrinkage on the FA-EAFC relative composition at 1140 ºC is expressed. No shrinkage is observed at 1000 ºC and 1100 ºC, leading to the conclusion that these materials retain their shape in the area of 1100 ºC and possible applications involving their use as engineering materials should not pose any problems as far as dimension tolerances are concerned. At 1140 ºC, diametral shrinkage reaches a minimum for high EAFC proportions in the mixture (> 50%wt.).

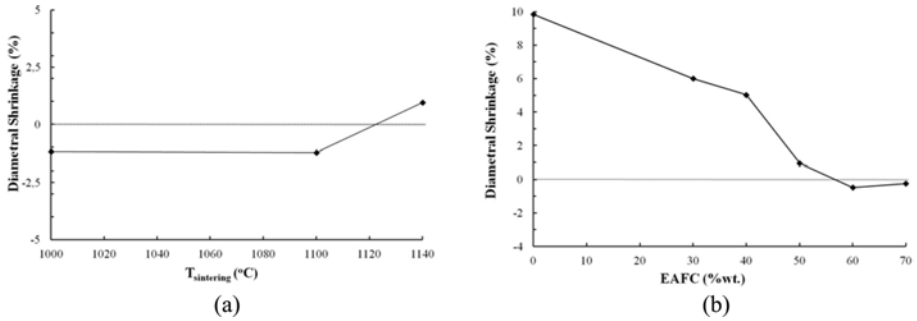

Fig. 1. Diametral shrinkage (%) as a function of (a) sintering temperature (50-50%wt. FA-EAFC mixture) and (b) % EAFC content (at 1140 ºC).

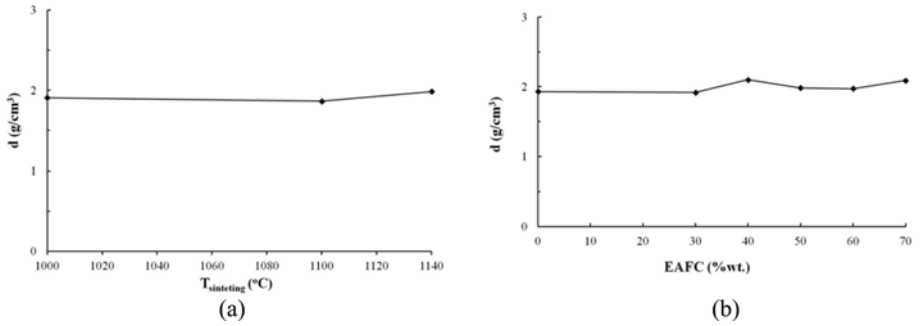

Fig. 2. Bulk density as a function of (a) sintering temperature (50-50%wt. FA-EAFC mixture) and (b) % EAFC content (at 1140 ºC).

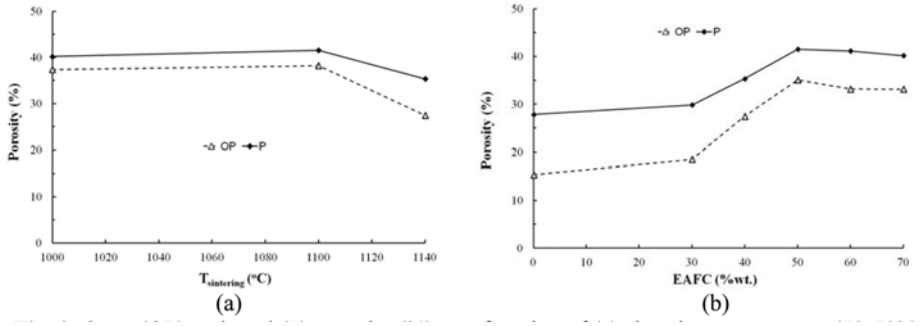

Fig. 3. Open (OP) and total (P) porosity (%) as a function of (a) sintering temperature (50-50%wt. FA-EAFC mixture) and (b) % EAFC content (at 1140 ºC).

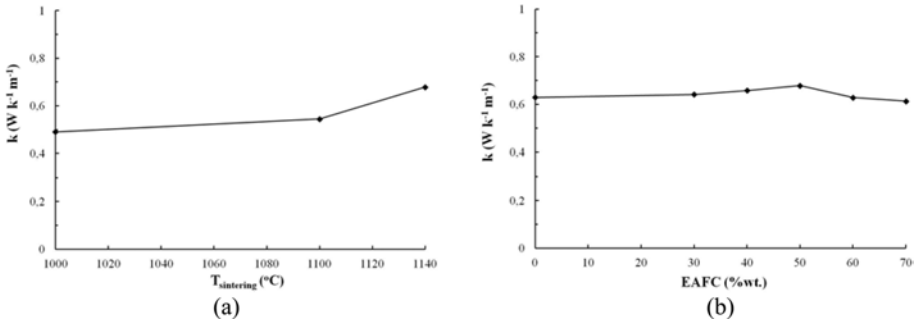

Fig. 4. Coefficient of thermal conductivity (k) as a function of (a) sintering temperature (50-50%wt. FA-EAFC mixture) and (b) % EAFC content (at 1140 ºC).

Bulk density and porosity

In Figs. 2(a) and 2(b) the bulk density of sintered specimens is presented. Density seems to be unaffected from the raise in sintering temperature and only slightly affected by the change in the mixture composition.

Figs 3(a) and 3(b) provide the specimen open and total porosity. For the 50-50%wt. FA-EAFC mixture, porosity is constant with sintering temperature up to 1100 ºC and decreasing at 1140 ºC, due to higher densification. On the other hand, porosity increases at 1140 ºC by increasing the EAFC content in the mixture from 30% to 50%wt., whereas further EAFC addition does not significantly alter specimen porosity.

The coefficient of thermal conductivity

The coefficient of thermal conductivity (k) of sintered specimens (Fig. 4(a)) follows porosity and density variations with firing temperature, as expected. It is noted that k increases by 11.2% from 1000 ºC to 1100 ºC and by 24.4% up to 1140 ºC. In all cases, thermal conductivity of the ceramics developed is maintained at low levels, thus retaining the thermal insulation capability of the materials. At 1140 ºC, the thermal conductivity remains almost constant by varying the EAFC percentage the mixture (maximum value: 0.678 W/m.K).

The diametral tensile strength (DTS)

Fig. 5(a) shows the effect of the sintering temperature on the diametral tensile strength (DTS) of specimens containing 50% wt. EAFC, whereas in Fig. 5(b), the dependence of DTS on the relative FA-EAFC composition at 1140ºC is expressed. From Fig. 5(a), DTS is strongly enhanced (by approx. 400%, from 1.48 MPa up to as much as 7.43 MPa) when increasing the sintering temperature from 1100 ºC to 1140 ºC. On the other side, specimens

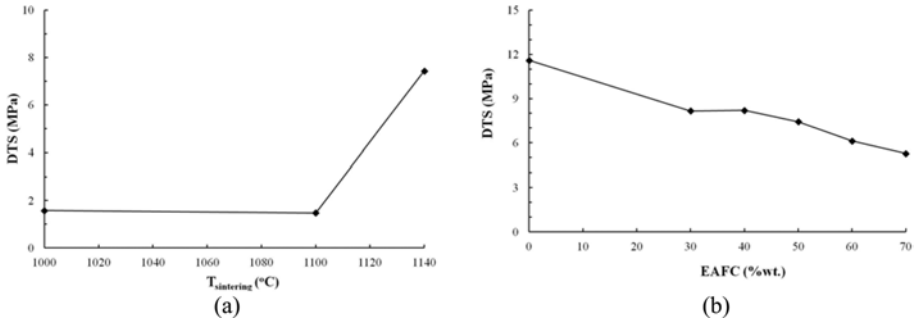

Fig. 5. Diametral tensile strength (DTS) as a function of (a) sintering temperature (50-50%wt. FA-EAFC mixture) and (b) % EAFC content (at 1140 °C).

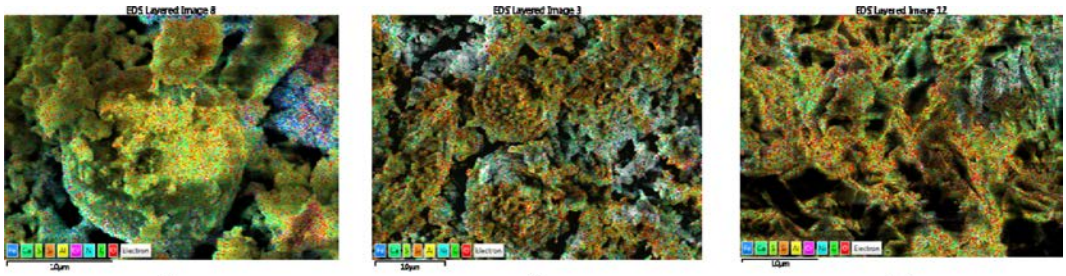

Fig. 6. EDS layered SEM micrographs of ceramic microstructures obtained from 50-50%wt. FA-EAFC mixture sintered at (a) 1000 °C, (b) 1100 °C and (c)1140 °C.

from rich-in FA mixtures exhibit clearly higher DTS values 1140 °C. Variations in bulk density and porosity do not seem to fully explain these findings that should also be attributed to phase changes occurring in the mixture, especially at this sintering temperature.

In Fig. 6, EDS layered SEM images of specimens from 50%FA-50%EAFC mixture sintered each time at 1000 °C (a), 1100 °C (b) and 1140 °C (c), do not reveal significant changes in porosity with firing temperature, but rather an extended diffusion between the different phases of fly ash and electric arc furnace carbon slag, leading to formation of an interconnected network and 1140 °C, binding the ceramic materials, thus explaining the remarkable increase in DTS respectively.

It is noted that many different types of metal oxides exist in the industrial by-products mixture, which, at high sintering temperatures possibly form new and interesting phases imparting superior mechanical performance to the materials. Certainly, several parameters control the final material properties. The most important are a) composition, b) raw material particle size distribution, c) compaction ratio and d) sintering time and temperature. Moreover, diffusional phenomena mainly control the formation of phases and microstructure (microporosity). At higher temperatures, liquid phase sintering may also occur, thus creating a complex system that should further be investigated.

Conclusions

Specimens fabricated from low-Ca FA and EAFC mixtures appear to be promising novel ceramic materials for appropriate applications, taking into consideration DTS strength and the coefficient of thermal conductivity results.

For the 50-50wt.% FA-EAFC mixture:

- The DTS strength remains almost stable from 1000 °C to 1100 °C, but is strongly enhanced by approx. 400% from 1100 °C up to 1140 °C.
- All specimens fabricated retain their shape upon sintering, while changes in porosity and bulk density are practically limited for sintering temperatures up to 1100 °C, becoming sensible at 1140 °C.
- The coefficient of thermal conductivity is increased (by 11.2%) as the sintering temperature is raised from 1000 °C to 1100 °C, having a further increase (by 24.4%) from 1100 °C up to 1140 °C. Values are maintained at low levels, which are encouraging for thermal insulation applications.

Techniques used in powder metallurgy can be employed to fabricate novel materials from lignite fly ash and the metallurgical by-product EAFC, possessing acceptable mechanical strength for new applications. This promotes the concept of circular economy, making good use of industrial by-products and contributing to conservation of earth natural resources.

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