Sustainable development of P/M ceramics from steel mill scale and lignite fly ash mixtures

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Abstract

In the present work, mixtures of mill scale (MS), an industrial by-product derived from the flaky surface of hot rolled steel, and lignite power station fly ash (FA), both originating from Greek industries, are examined as 100% the starting materials for the sustainable development of ceramics employing powder metallurgy (P/M) fabrication procedures. It should be emphasized that the safe management of such low price and largely available industrial secondary resources by their utilization as 100% the feedstock for another industrial sector (ceramic industry) is strongly prioritized by current EU policies.

FA and MS were mixed in various proportions (30–80% wt. in MS), cold compacted at 20 tn 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°C, 1100°C and 1140°C) for 3 h.

The experimental results are encouraging, showing that the mechanical performance (diametral tensile strength) of the integral ceramic materials so-produced sharply increases, from 0.77 MPa up to as much as 13.42 MPa, with the temperature increase from 1000°C up to 1140°C, for a 50–50 %wt. FA–MS mixture. Scanning electron microscopy mapping enables a better understanding of the microstructural changes occurring at higher sintering temperatures. On the other hand, the coefficient of thermal conductivity increases with temperature and the MS content in the mixture.

Keywords: fly ash, mill scale, sintering temperature, thermal conductivity, diametral tensile strength.

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1 Introduction

Fly ashes (FAs) are annually produced in huge amounts from lignite/coal combustion in power plants. FA contains several oxides and should be considered as a potential raw material for industrial use. Several potential applications are currently examined such as geopolymer cements [1], nickel-based composite materials [2] and in construction applications [3–5]. In recent years, considerable research has been conducted on the utilization of metallurgical slags containing aluminosilicates in the production of geopolymers [6]. Incorporation of steel-making dust in ceramic clay bodies has been considered [7, 8]. The recycling and valorization of solid residues recovered in steel production plants worldwide, such as mill scale (MS), represents a significant issue. In 2006, the global production of MS was 1240 million tons. MS is the flaky surface of hot rolled steel, a porous, hard and brittle coating of several distinct layers of iron oxides (predominantly FeO and Fe_3O_4) formed during the fabrication of steel structures [9]. MS can be used as a valuable secondary material due to its high ferrous oxides content (up to as high as 95%), low impurities and stable chemical composition [10]. Moreover, reduction of this attractive rich in iron by-product for the production of iron has already been carried out, either via hydrogen, or by microwave heating [11, 12]. In Greece, MS is being considered for recycling in the cement industry, steelworks and the chemical industry [13]. Recently, synergy of various mixtures of several industrial solid wastes containing silica, alumina and lime as the predominant oxides has been under consideration for the development of construction materials, including ceramics, glass-ceramics and cement-based materials [14, 15]. In the presence of FA-clay mixtures in particular, waste generated from galvanizing and metal finishing processes, considered to be hazardous due to their toxic metals content, have already been added and thermally treated for the immobilization of toxic metals and the production of building construction materials. However, limited data are reported regarding synergistic usage of FA with steel-industry powdery residues in the formation of fired ceramic bodies. So far, technology for ceramic floor and wall tiles has only been developed based on FA, blast furnace slag from iron and steel industry and iron ore tailings from mines [16]. Nevertheless, appropriate mixture combinations of these industrial residues can be attractive starting materials for ceramic products development. In the current study, an innovative synergistic utilization of lignite FA with MS is attempted in order to make new materials. A potential use of these by-products in large scale and in such a way would constitute a sustainable use of resources. From the environmental perspective, both valorization of these industrial residues to partially alleviate waste management problems and also substitution of other raw materials derived from mineral resources can contribute to both environmental protection and natural resources conservation. Moreover, the low cost of these by-products can give them an advantage over traditional raw materials in possible future large scale utilization as industrial raw materials.

In this study, a mix fly ash with MS in equal ratios (50–50% wt.) is used in order to examine the properties of specimens formed in three different sintering

temperatures namely, 1000°C, 1100°C and 1140°C and various proportions of FA and MS (30% wt. to 80% wt. in MS) and study of property dependence as a function of composition and sintering temperatures.

It is noted that in the metallurgical waste (MS), many different types of metal oxides exist which, at high sintering temperatures may form new and interesting phases which may impart superior properties to the materials. Several parameters control the final material properties, the most important of which are a) composition, b) particle size and particle size distribution, c) compaction ratio and d) sintering temperature and sintering time. Besides thermodynamics, diffusional phenomena may be controlling the formation of phases and microstructure (micro porosity). So, this being a very complicated system, the present study attempts a first look at this new system.

2 Raw materials and specimen fabrication

Tables 1 and 2 show the chemical composition of raw materials. In table 2, for MS only the composition of 12 oxides, highest in composition, is reported.

Table 1: Chemical composition of fly ash used.

No	Constituent	(%)	No	Constituent	(%)
1	SiO_2	34.85	7	K_2O	1.51
2	CaO	19.19	8	TiO_2	0.71
3	Al_2O_3	14.17	9	Na_2O	0.42
4	Fe_2O_3	11.23	10	P_2O_5	0.26
5	SO_3	6.26	11	BaO	0.16
6	MgO	2.58	12	MnO	0.09

Table 2: Chemical composition of mill scale used.

No	Constituent	(%)	No	Constituent	(%)
1	$FeO\text{-}Fe_2O_3$	94.32	7	P_2O_5	0.14
2	MnO	1.28	8	CrO_3	0.10
3	SiO_2	0.98	9	Na_2O	0.07
4	CaO	0.53	10	NiO	0.05
5	Al_2O_3	0.17	11	MgO	0.05
6	CuO	0.14	12	ZnO	0.05

Raw materials were first ground (grain size < 0.63 mm) in a planetary baw mill for ten minutes and then mixtures were formed and cold compacted at 20 tn load using an automated hydraulic press to form disc-shaped specimens 50.0 mm x 8.0 mm (diameter x thickness). Different combinations of specimens were prepared as a function of sintering temperatures (1000°C, 1100°C and 1140°C) and the MS percentage in the FA–MS mixture (30, 40, 50, 60, 70, 80% wt.). The specimens so-produced were sintered in a programmable electric furnace for final consolidation. The firing program had a first pre-heating step up to 700°C to drive off absorbed gases, followed by further controlled heating

up to the maximum sintering temperature. The specimens were allowed to remain at this maximum sintering temperatures for 120 min. Then, the pellets were gradually cooled in the furnace to room temperature.

3 Results and discussion

The determination of physico-mechanical properties, including shrinkage, weight loss, water absorption capability, and porosity was conducted on fired disk-shaped specimens according to the ASTM C67: Standard Test Methods for Sampling and Testing Brick and Structural Clay Tile, while the thermal conductivity coefficient (k) was measured at 25°C 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 DTS measurements are 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.

3.1 Diametral shrinkage

Figure 1 shows the effect of sintering temperature on diametral shrinkage of disc specimen containing 50% wt. FA and 50% wt. MS, while in Figure 2, the dependence of diametral shrinkage from the FA–MS composition, is expressed. It is noted that shrinkage is increased with the sintering temperature and decreased with MS content in the mixture. Small shrinkage is observed up to 1000°C leading to conclusion that these materials retain their shape in the area of 1000ºC and possible applications involving their use as engineering materials should not pose any problems as far as dimension tolerances are concerned.

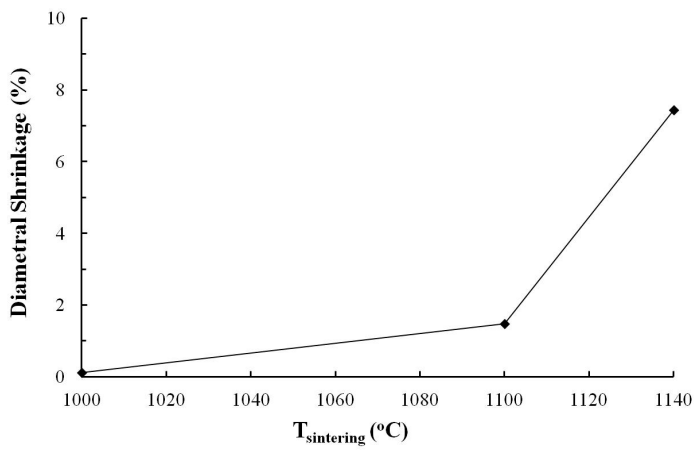


Figure 1: 50% wt. FA and 50% wt. MS.

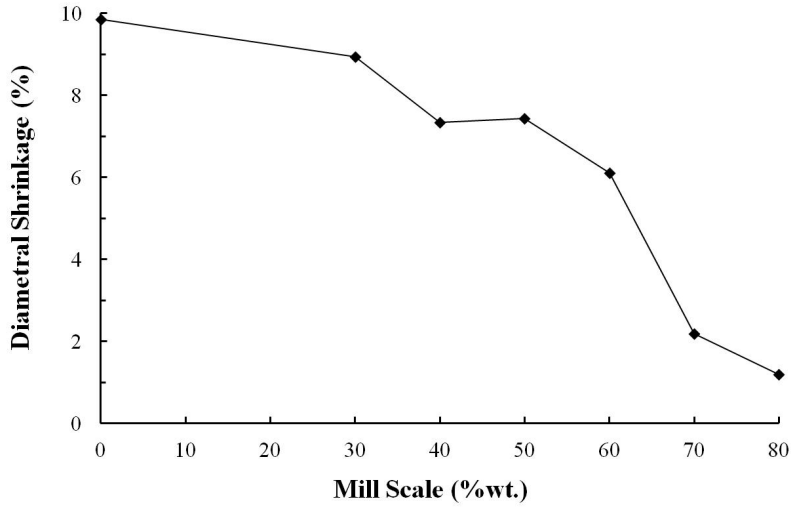


Figure 2: Diametral shrinkage at 1140°C.

3.2 Bulk density and porosity

Figures 3 and 4 show the effect of sintering temperature on the bulk density of specimens prepared for each of the three above mentioned combinations. Density remains almost constant up to 1000°C, increasing rapidly after that up to 1140°C and increases with the MS content in the mixture.

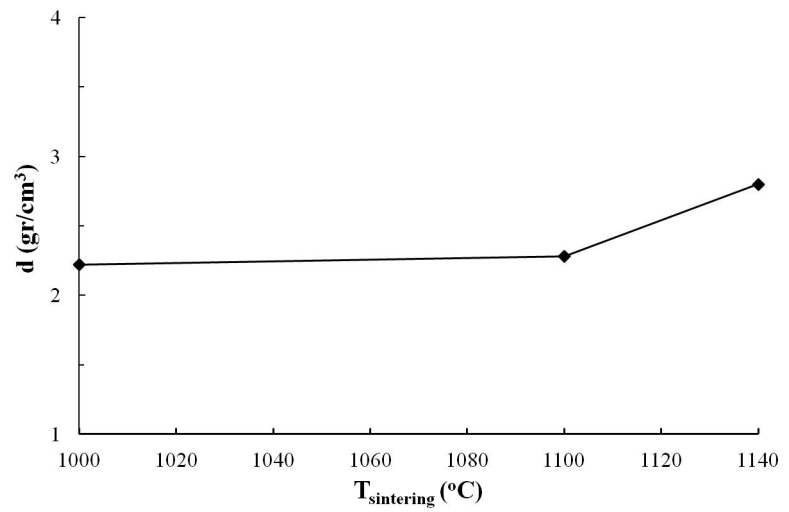


Figure 3: Bulk density 50% wt. FA and 50% wt. MS.

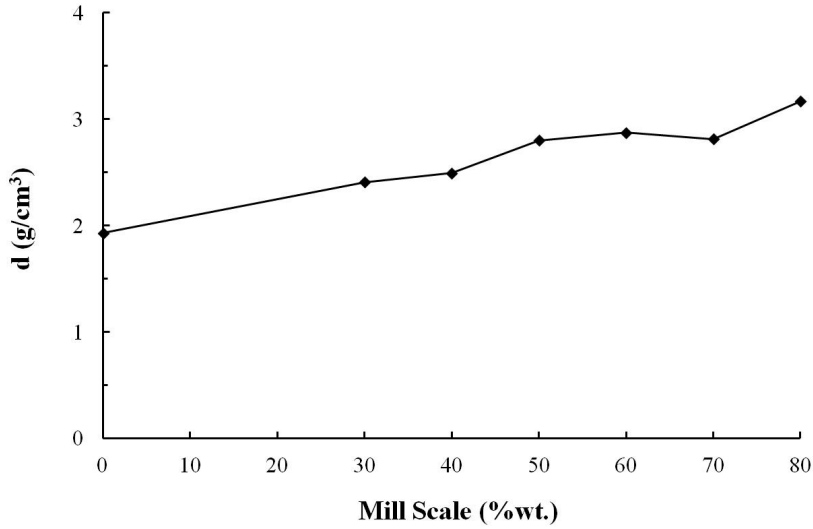


Figure 4: Bulk density at 1140°C.

Figures 5 and 6 show the effect of sintering temperature on the open and total porosity of specimens prepared for each of the three above mentioned combinations. Open porosity and total porosity were determined from the immersion of the specimens in cold (24 h) and boiling water (5 h). Porosity is decreasing with temperature up to 1140°C, while it remains almost constant with the increase of MS content in the mixture.

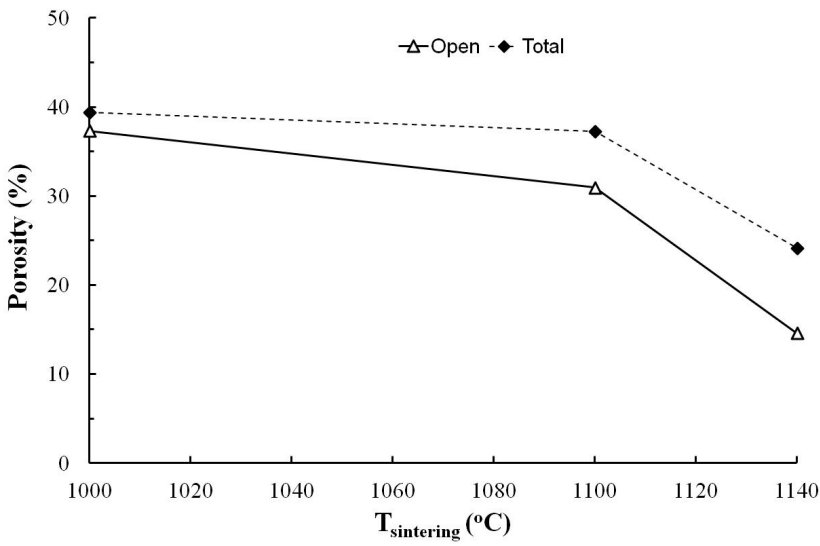


Figure 5: Porosity 50% wt. FA and 50% wt. MS.

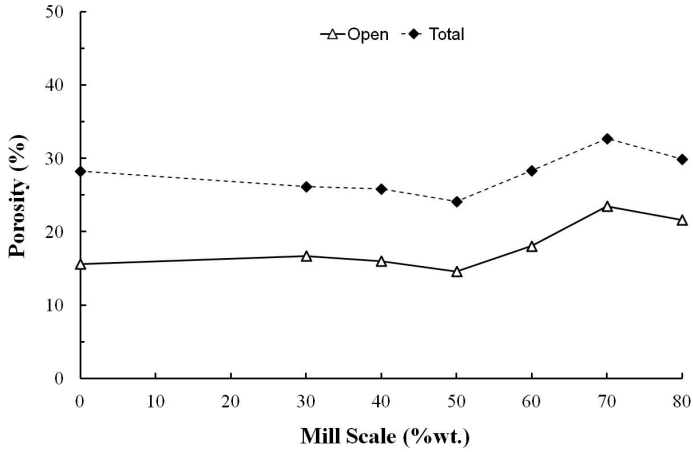


Figure 6: Porosity at 1140°C.

3.3 The coefficient of thermal conductivity

As the bulk density increases and porosity decreases, for small changes in density and porosity and without substantial changes in phase composition in the specimens, it is expected that the coefficient of thermal conductivity would also increase. This is what is observed in Figure 7. The coefficient of thermal conductivity from 1000°C to 1100°C increases by 32.5%. Although the coefficient of thermal conductivity remains low, retaining the thermal insulation capabilities of these materials, the percent increase of the coefficient of thermal conductivity is much larger than the corresponding one in the bulk density (4.5%). In Figure 8, thermal conductivity remains constant up to 40% wt. in MS, increasing its value for higher concentrations in MS.

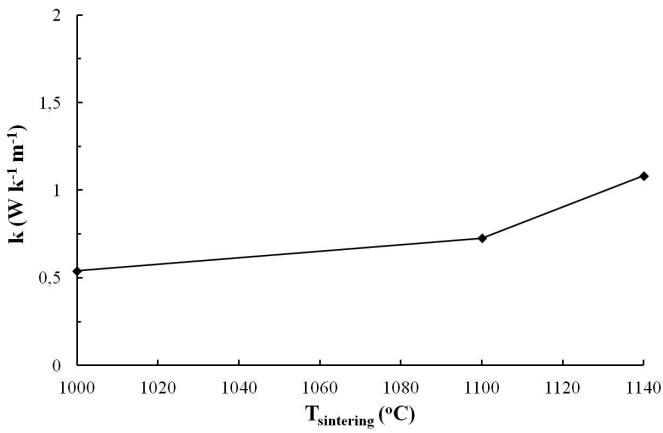


Figure 7: Thermal conductivity coefficient 50% wt. FA and 50% wt. MS.

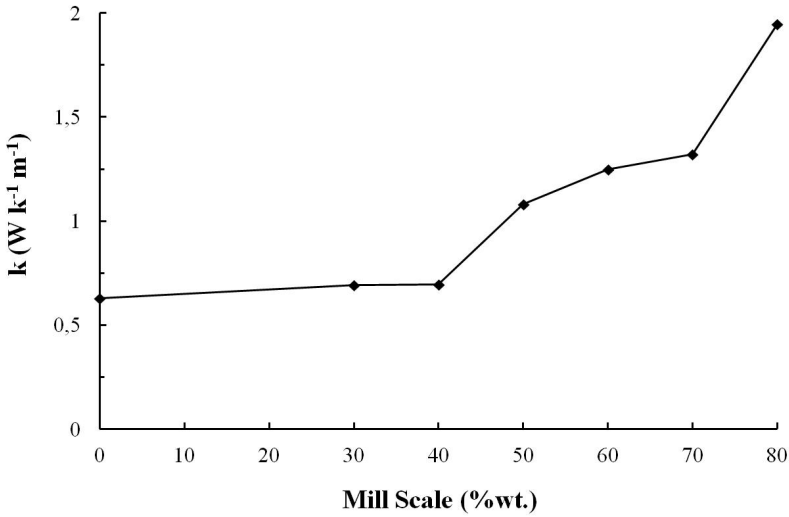


Figure 8: Thermal conductivity coefficient at 1140°C.

3.4 The Diametral Tensile Strength (DTS)

Figure 9 shows the effect of the sintering temperature on the diametral tensile strength (DTS) of the disc specimens containing 50% wt. MS while in Figure 10, the dependence of DTS from the FA–MS composition, is expressed. In Figure 9 it is noted that changes in the DTS are very pronounced, especially between 1000°C and 1140°C. As the sintering temperature of the specimens is increased from 1000°C to 1100°C, the DTS increases from 0.77 to 2.96 (284%). Best DTS

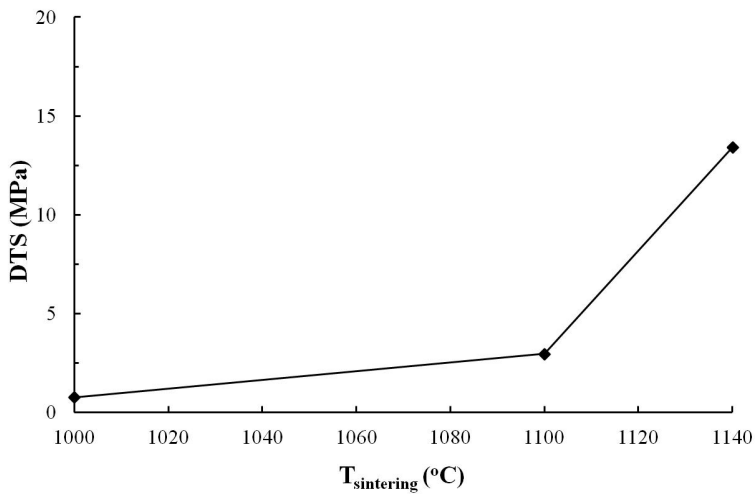


Figure 9: DTS 50% wt. FA and 50% wt. MS.

values are observed by adding MS up to 60% at 1140°C sintering temperature (Figure 10). On the other hand bulk density and porosity changes do not explain such a dramatic increase for the DTS, as the sintering temperature is increased from 1000°C to 1140°C. It is possible that more pronounced changes in the physico-mechanical properties of these exciting new materials may be occurring at the sintering temperatures examined.

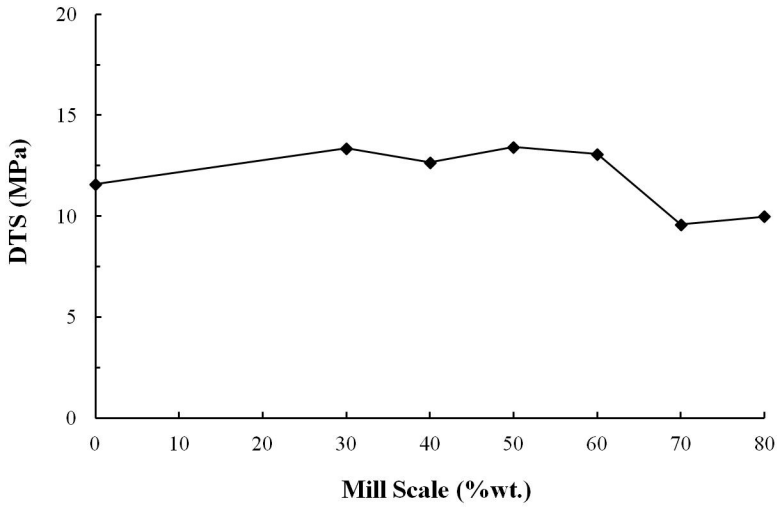


Figure 10: DTS at 1140°C.

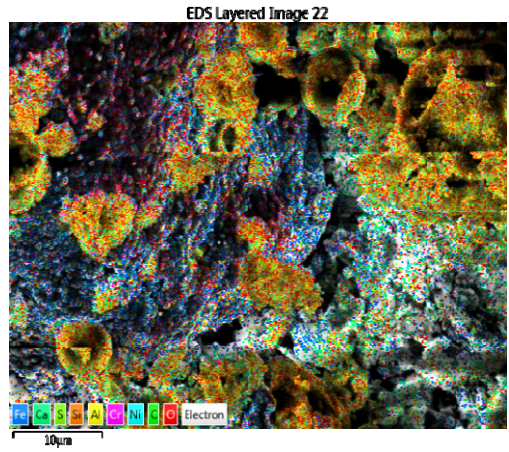
In Figure 11 EDS layered images show that the 50% FA–50% MS mixture sintered from 1000°C (a) through 1100°C (b) to 1140°C (c), porosity decreases and extended diffusion between the different phases, initially existing in the fly ash and the mill scale, is taking place, explaining the remarkable increase in DTS.

4 Conclusions

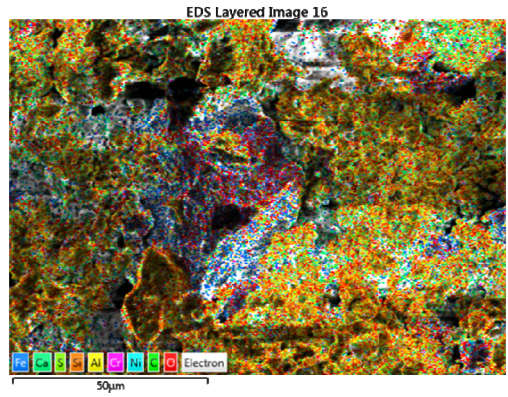
Material specimens fabricated from 60% mixtures of FA low in CaO with 40% of MS at 1140°C sintering temperature, show promising applications as novel materials taking into main consideration the DTS strength and the coefficient of thermal conductivity.

For the mixture of 50% FA–50% MS wt.:

- The DTS strength is increased by 284% from 1000°C to 1100°C and 353% from 1100°C to 1140°C respectively.
- All specimens retain their shape upon sintering, while changes in porosity and bulk density are less than 6% for sintering temperatures up to 1100°C, becoming larger up to 1140°C.
- Changes in the coefficient of thermal conductivity are more substantial (35.2%) as the sintering temperature is increased from 1000°C to 1100°C.



(a)



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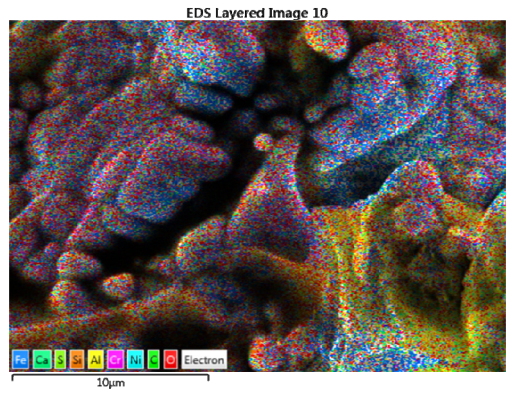

(c)

Figure 11: EDS 50% wt. FA–50% wt. MS sintered from 1000°C (a) through 1100°C (b) to 1140°C (c).

Techniques used in powder metallurgy may be used in order to fabricate novel materials from fly ash and metallurgical by-product MS, possessing high mechanical strength with new applications. This promotes the concept of circular economy making good use of industrial by-products and alleviating mineral natural resources.

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