Ceramic Materials and Ceramics Pigments based on high amounts of Industrial and Agricultural wastes

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Introduction

The traditional ceramics are heterogeneous materials, obtained mainly by mixing of three types of natural raw materials (i.e. clays, feldspars and sands). After the firing the final products commonly contain residual undissolved quartz and sometimes traces of feldspars. At the same time the fine clay's crystals react completely and participate in the formation of primary or/and secondary mullite ($3Al_2O_3.2SiO_2$). The formed during the heat-treatment liquid phase, which assures the sintering process, vitrified into amorphous phase. The creation of a high amount of liquid phase (usually between 50 and 65 %) leads to products with low or zero water absorption and 5-15 % closed porosity.

The feldspars are the most expensive raw materials and therefore their replacement can reduce significantly the final costs of ceramics. For this reason, many studies, related to the usage of different alternative fluxing agents (usually between 10 and 15 wt %) were carried out by different scientific teams. Promising results were obtained using soda–lime glass cullet, cathode ray tube of TV or PC monitors and granite cutting sludge. Other works examine the possibility to use industrial streams as Blast Furnace Slag, MSW ashes, fly ashes from thermal stations and various sludge. Usually, these residues are added as inert materials so that the sintering process is related mainly to the presence of traditional ceramic fluxes. However, if the melting temperatures of used wastes are reached they also start to participate in the formation of the liquid phase, which drastically changes the sintering behaviour, the phase composition and the structure of final ceramic. In some cases, this feature gives the exceptional possibility for a total removal of the feldspars and for usage of huge amount of wastes in the batch. In addition, these innovative ceramics are characterised with higher crystallinity and improved mechanical properties. The aim of the present work is to discuss the synthesise and the specific structures of few new ceramics, obtained without traditional fluxes and with high amounts of industrial wastes.

Other interesting trend in the ceramic industry is the usage of different agriculture by-products. Usually, in order to decrease the fuel consumption, these organics residues can be added in the batches for bricks manufacture. However, when their "as it is" combustion is applied for a direct energy production, the resulting ashes also might be used in the ceramic industry. One of the most interesting objects are the rice husks ashes (RHA), which are used in different manufactures due to their high silica content. An interesting example is the synthesize of ceramic pigments. In the present work are reported results for thermal behaviour of similar pigments, because they might be used in the glazing of the described above new ceramics.

Experimental

The possibility to obtain ceramics without feldspars flux, which are characterized with a good degree of sintering and high mechanical properties, is demonstrated with four different compositions. The first ceramic (labelled as CSK-70) was obtained by mixing 70 wt% granulated Blast Furnace Slags (BFS) with 30% refractory kaolin (K), while the second (labelled as CSSK-30) - by mixing 30 % BFS, 40 % quartz sand (S) and 30% K. The other two compositions were prepared using 40% industrial clays and 60% of two different fractions of bottom ashes from Municipal Solid Waste Incinerators (F – fine, below 3 mm and L – large, above 3 mm). The last two ceramics are labelled CLK-60 and CFK-60, respectively. All raw materials were milled and sieved below 75 μm. Each batch was prepared by dry-mixing, homogenization and humidification with 6 wt.% distilled water. Then samples (50 x 5 x 4 mm) were obtained by isostatic pressing at 40 MPa.

The thermal and sintering behaviours were determined by DTA-TG (Netzsch STA 409) and optical dilatometer (Misura ODLT 1400), respectively. The phase composition of ceramics was analyzed with Philips PW 1050 diffractometer, equipped with Cu Kα tube and scintillation detector. The microstructure and the crystal morphology of the final samples (both surface and fracture) were observed by Scanning Electron Microscopy (JEOL JSM 6390) coupled with an energy dispersion spectroscopy equipment (EDS, INCA 350, OXFORD).

The thermal behaviour of the parent rice husks and the resulting pigments were studied with DTA-TG and with hot stage microscopy (Misura HSM 1400). The phase formation was estimated by XRD, using samples heat-treated at different temperatures.

Results and Discussion

The chemical compositions of presented ceramics are very different from the traditional clay-feldspar-sand ceramics. They are characterized with elevated amount of CaO and lower silica percentage as well as with presence of MgO and iron oxides. The DTA-TG results, together with the typical effects of clays and carbonate decompositions at about 550 and 750 ºC, respectively, show new exo-effects in the interval 900-1050 ºC due to the formation of anorthite and/or pyroxenes. At 1100-1250 ºC are observed intensive endo-effects of melting, which are diverse from the larger endo-effects with lower intensity, associated with the formation of feldspar liquid phase in the traditional ceramics. The dilatometric sintering curves highlight that rapid densification carries out in the temperature interval of the melting endo-effects; this also is different from the traditional compositions, where the sintering usually is observed at temperatures higher than one of the feldspar melting.

The XRD results elucidate high amounts of anorthite solid solutions and pyroxenes, which is untypical for the traditional ceramics, where the main crystal phases are mullite and quartz. All samples demonstrate a good degree of sintering, which also is unusual because the residual amorphous phase in new ceramics is below 55-60 %. However, this peculiarity can be explained with the substantial phase formation (at about 10-15 %), taking place during the cooling as well as with their lower viscosity at the sintering temperate.

The good degree of sintering were confirmed by SEM-EDS. In Fig. 1-a is shown the smooth and well sintered surface and absence of open pores of CSK-70, while in Fig. 1-b is elucidated the high crystallinity in the surface. The fracture of CLK-60 is presented in Fig. 1-c and shows mainly closed spherical pores with size between 20 and 100 µm, which are characterized with rough and polycrystalline surface (Fig. 1-c).

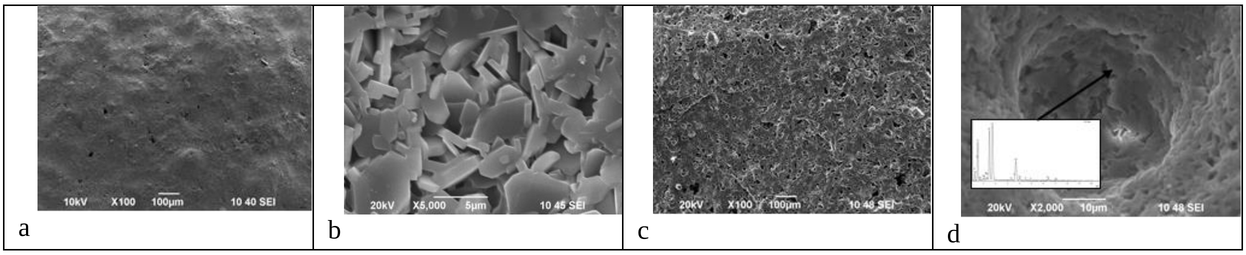

Fig. 1 Structure of the studied ceramics

The DTA and XRD results with the pigments highlight that the substitution of traditional SiO_2 sources with RHA show no significant variation up to 1000-1100 ºC. However, at higher temperature is observed acceleration of the phase formation, coupled in some cases with earlier melting. The last effect might favour the glazing at lower sintering temperatures.

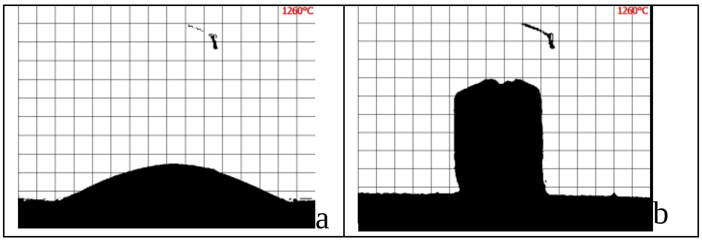

Fig. 2 HSM images of pigments at 1260 ºC.

Typical HSM silhouettes, corresponding to 1260 ºC of iron-rich pigments, obtained with (a) and without RHA (b) are presented in Fig. 2. These result demonstrate that the samples, obtained using rice husks ashes is totally melted, while the “traditional” product yet is in the beginning of the melting process.

Conclusions

The phase compositions of studied ceramics are completely different from these of traditional tiling ceramic materials. The main crystal phases in the new compositions, instead quartz and mullite, are anorthite solid solution and pyroxenes. In addition, the amounts of residual vitreous phase are inferior than one in the well sintered usual compositions. Notwithstanding, the studied samples are characterised with a negligible open porosity (between 0.3 and 2 %) and about 20-25 vol % closed porosity. The new ceramics are characterised also with fine-polycrtalline structure in surface, fracture and pores. In this case, due to crystallization process, taking place during the cooling additional crystallization induced pores are formed.

The possibility to combine the synthesis of the new ceramics with glazes with pigments, based on rice husks ashes is also proposed since these pigments sometimes melt at lower temperature.

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