



Research paper

The differences between alkaline- and alkaline-earth-flux effects on high-temperature phase change of clay based ceramic



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ABSTRACT

The differences of the effects of alkaline (illitic clay, K and Ca-Na feldspar) and alkaline-earth flux additions (sepiolitic-dolomite, talc, huntite, hydromagnesite, magnesian clay and Calcite) on the high-temperature-phases (HTP) of ceramic bodies derived from ball clay of Westerwald-(Germany) or Sile (Turkey) area were investigated. This investigation was carried out by X-ray diffraction (XRD) and scanning electron microscopy (SEM) attached with energy dispersive spectrometry (EDS). The type and amount of HTP do not only depend on the type and amount of flux additions alone but also depend on the optimal distribution of these flux cations which are largely determined by the extent of the mixing. No Cristobalite was present and secondary mullite and quartz were the only crystalline phases present in these bodies composed of 50 wt% illite KW and Westerwald ball clay HB or this mixture mixed with 20% K or Ca-Na feldspar. These additions render ≥ 2 wt% K_2O in bulk chemical composition of these alkaline bodies and are enough to inhibit cristobalite formation. The identified major HTP in ceramic bodies derived from 15 wt% Ca carbonate and 5 wt% sepiolitic dolomite, or magnesian clay or talc and Sile ball clay were identified only as melilite (gehlenite) and plagioclase (anorthite) group minerals. The pyroxene group minerals (protoenstatite, clinoenstatite, and diopside) occurred only in the body derived from Sile ball clay mixture mixed with > 5 wt% Mg-Ca flux at over 1000 °C.

1. Introduction

In clay-based ceramics, two different types of HTP may occur depending on whether the ceramic body contains Ca and Mg-Ca flux or not. Ceramic alkaline bodies containing only K- and Na- flux, form eutectic melts (Aras, 2004a; Carty and Senapati, 1998; Allegretta et al., 2016; McConville and Lee, 2005; Wattanasiriwech et al., 2009). In contrast alkaline bodies, alkaline-earth bodies containing Ca and Ca-Mg-flux, form HTP by reactions in the solid state. (Peters and Iberg, 1978; Dondi et al., 1999; Dondi et al., 1998; Riccardi et al., 1999; Cultrone et al., 2001; Trindade et al., 2009; Aras, 2004b; Aras and Demirhan, 2004). The HTP do not only depend on the type and amount of flux materials alone (Fischer, 1987; Zhou et al., 2013; Li et al., 2009; Yamuna et al., 2002; Johnson et al., 1982; Adamo et al., 2013). They also depend on optimal distribution of K, Na, Ca and Mg cations of flux from which themselves are largely determined by the extent of the mixing of clay with these flux materials (Antoni et al., 2005; Carty and Senapati, 1998; Lee and Iqbal, 2001; Iqbal, 2008; Lee et al., 2008).

The alkaline bodies derived from sedimentary clay i.e., ball clay and alkaline flux e.g. illitic clay KW (Wattanasiriwech et al., 2009) and feldspar include porcelain, tile, sanitary ware and tableware. This present work is the follow-up of the investigation on phase change of

alkaline ceramic bodies derived from Westerwald ball clays and the effect of K and Ca-Na feldspar on phase composition (Aras, 2004a). The Westerwald ball clay HB (kaolinitic) and illitic KW and P161 (naturally mixed kaolinite-illite) were selected and laboratory mixture (50 wt%HB + 50 wt% KW = HK) HK was prepared for investigation of previous and this work. The details concerning the geological and mineralogical information of these clays are provided elsewhere (Kromer, 1980; Aras, 2004a).

The Sile ball clay was used in alkaline earths bodies. The details concerning the geological and mineralogical information of this clay is provided elsewhere (Ece et al., 2003). In the alkaline-earth flux bodies, it is well known since the Roman period, that 10% fine calcite affect the physical properties of fired ceramic bodies positively (Schmidt-Reinholz and Schmidt, 1997). With lower alkaline earth contents, however, there is growing tendency towards formation of glass phases, but the presence in particular of magnesium firstly inhibits the melt forming action of the alkaline flux and diverts glass formation in the direction of feldspar formation. Fischer (1987) pointed out 1% wt CaO, 0.3 wt% MgO, 1.5 wt% K_2O and 0.9 wt% Na_2O likewise at first formed feldspar with increasing amounts up to 950 °C, which was then however absorbed in vitrification. Numerous scientists investigated the alkaline earth flux effects on physical properties by using conventional ratios of

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the additions in their studies from 5% to 15% (Schmidt-Reinholz and Schmidt, 1997; Dondi et al., 1998; Cultrone et al., 2001; Aras, 2004b; Aras and Demirhan, 2004). Dondi et al. (1999) pointed out that the amount of anorthite decreases when CaO is low as < 5 wt% or very high > 15 wt%. In earlier work, Aras and Demirhan (2004) found that anorthite content decreased with increasing magnesian clay content changing from 12 wt% to 15 wt% in the body containing 15 wt% Calcite.

The aim of this integrative study is to determine HTP and HTP changes (i.e., HTP evolution) in ceramic bodies containing alkaline and alkaline-earth flux materials and ball clay by using XRD and SEM techniques. Thus, the determined HTP sequence were discussed on the basis of the result of previous and present work and literature data. The chemical formulas and crystal systems of the identified newly-formed minerals in these bodies of present work are given in.

2. Materials and methods

The raw materials used in the present investigation, Westerwald and Sile ball clay were supplied by company WBB-Fuchs GmbH, and Çanakkale-Ceramic-Plant respectively. The complete characterization of the used individual Westerwald ball clays are described in a large number of studies Rohstoffmerkmale of DKG and the used ones are P161 (Nr-75), Hermanton HB 40/42 (Nr-105) and Kreuzton von Niederdresselndorf KW (Nr-56) (Kromer, 1979). The used mixtures of Westerwald ball clays formulas, chemical and mineralogical composition are given in Table 2 and Table 3. The further geological and mineralogical characterization of this clay was reported in detail by Kromer (1980). The total 6 four alkaline bodies were prepared and investigated in this study; the first one is 50% HB + 50% KW = HK and this mixture also mixed with 20% K and Ca-Na feldspar and first, second and third one are labeled as HK, HK + KF and HK + CN F and the fourth one naturally mixed kaolinite and illite (P161) is also mixed with 20% K and Ca-Na feldspar and fourth, fifth and sixth ones are labeled as P1, P1 + KF and P1 + CN F.

The Sile ball clay used in tile production in Çanakkale Ceramic Plants was labelled as Sile ball clay (224) and the others additions were labeled as quartz sand (501), feldspar (761), and calcite (401, 441) in the data sheet of Kalemaden Company. The complete characterization of the used Sile ball clays was reported by Ece et al. (2003). The body formulas of the prepared bodies are given in Table 4 and also the same raw materials are used for investigation of the effects of magnesian clay addition on physical properties of the ceramic bodies by Aras and Demirhan (2004). The 7 alkaline earth bodies were prepared, fired and investigated in this study, these bodies were derived from Sile ball clay and alkaline earth flux minerals and these 7 alkaline-earth bodies together with 6 alkaline-bodies; total 13 samples were investigated in this work (Table 4 and Table 2).

All raw materials were crushed, grounded and finally then sieved using 300-mesh sieves. The mixtures (Tables 1, 2,) were prepared by wet ball milling with distilled water (1,1) for 30 min and using alumina balls as grinding media. The resultant slurries were oven-dried overnight at 110 °C, powdered in a porcelain mortar and sieved to pass – 100 mesh (150 µm). The resulting powder was moistened by spraying with distilled water (6 wt%) and uniaxially pressed at 40 MPa in a steel die as rectangular samples (30 g each) of 80 × 18 × 8 mm. All green bodies and two powders HK and P161, after drying in an oven at 110 °C, were fired and heated in electrical kiln and Anton-Paar oven respectively with firing schedules below.

2.1. In-situ high temperature (HTXRD) X-ray diffraction analysis of powder of HK and P161 and ex-situ X-ray analysis of interrupted-quenched samples alkaline and alkaline earth bodies(QSXR)

The in-situ and ex-situ high-temperature X-ray analysis of powder of mixtures samples patterns were obtained with Philips PW 3710

Table 1

The chemical formulas and crystal system of the identified high temperature phases (HTP).

Mineral Group	Subgroup/ polymorph	Chemical formulas	Crystal system
Mullite	Primary mullite	$Al_4 + 2xSi_2-2xO_{10-x}$ ($x \sim 0.4$)	Tetragonal
	Secondary mullite	$Al_4 + 2xSi_2-2xO_{10-x}$ ($x \sim 0.4$)	Orthorhombic
Quartz	Quartz	SiO ₂	Trigonal
	Low cristobalite	SiO ₂	Tetragonal
	High cristobalite	SiO ₂	Tetragonal
Melilite group	Gehlenite	Ca ₂ Al(AlSiO ₇)	Tetragonal
	Pyroxene group	Enstatite	MgSiO ₃
Clinoenstatite		MgSiO ₃	Monoclinic
Protoenstatite		MgSiO ₃	Monoclinic
Diopside		CaMgSi ₂ O ₆	Monoclinic
Feldspar (Plagioclase)	Anorthite	Ca(Al ₂ Si ₂ O ₈)	Triclinic

Table 2

Mineralogical composition of individual Westerwald ball clays and their mixture HK.

Westerwald ball clays ^a	Kao	Illite	I/SMix	Na-Ca	K Feld	Q-Tro-Wyn	Fe-Ti
HB	72	13	3	–	1	8	2
HK = 50%HB + 50% KW ^b	40	21	1	4	–	31	1
KW	7	21	–	8	–	55	–
P161 ^b	41	32	2	1	2	20	1

^a Rohstoffmerkmale of DKG (P161 (Nr-75) HB 40/42 (Nr-105) KW (Nr-56).

^b 20 wt% K and Ca-Na feldspar mixed with HK and P161 and are labeled as HK + KF, HK + CN F, P1 + KF and P1 + CN F.

diffractometer and with high-temperature goniometer and attachment (Anton Parr HTK1200 Graz, Austria) with a Pt/Pt Rh thermocouple. The temperature was controlled with an accuracy of ± 1 K using a Eurotherm temperature controller. An alumina sample holder is used for scanning samples (Cu K-alpha radiation at 40 kV and 35 mA). All the samples were analyzed from 5 to 70° and 5–40° 2θ with a step-size of 0.020° in 2θ and time per step 1.00°/min. Identification of crystalline phases by HTXRD and QSXR was carried out using the ICDD powder diffraction CD-ROM file of Xpert High-Score software. Mineralogical transformations of body constituents after firing were investigated by in-situ HTXRD and ex-situ QSXR to enable a more precise comparison of the X-ray patterns between the bodies fired at different temperatures, the equipment, and analytical conditions were kept identical to the samples employed in the determination of HTP for comparison of relative intensities of reflections of identified phases.

2.1.1. Temperature cycle of in-situ high-temperature X-ray diffraction (HTXRD) analysis of HK and P161 powders

Heating of the HK powder was carried out at 100 °C intervals from 650 °C to 1150 °C. HK powder was brought to the desired temperature at a rate of 2 °C/min. At each set temperature, the sample was allowed to equilibrate for 5 min prior to data collection. After 1200 °C during the cooling period, the sample was examined at 100 °C intervals within the 1200 °C–800 °C range. First examination and the last examination were performed at room temperature. Fig. 1 (left) shows in situ HTXRD patterns of HK clay during heating process up to 1200 °C and cooling down to room temperature (RT).

Heating of the P1 powder was carried out at 50 °C intervals from 700 °C to 1200 °C and this powder was brought to the desired temperature at a rate of 2 °C/min. At each set temperature, the sample was allowed to equilibrate for 5 min prior to data collection. After 1200 °C during the cooling period, the sample was examined at 100 °C intervals

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