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Solid solution limit of Fe_2O_3 in mullite crystals, produced from kaolin by solid state reactions

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ABSTRACT

Porcelain, wall/floor tiles, and roofing tiles are classified as traditional ceramics and are produced from natural raw materials such as clay, quartz, and feldspar. The raw materials are selected by the oxide content which provides the desired properties of the final product. However, impurities such as Fe_2O_3 and TiO_2 may have a significant influence on both physical/mechanical properties and aesthetic appearance. Fe_2O_3, which is of particular importance, causes black maculation formation in tablewares, in which whiteness is essential. The only way to overcome the black maculation is to corrupt the Fe_2O_3 crystal structure and to employ $Fe^{2+/3+}$ cation, making a solid solution with a host crystal (i.e. mullite-$3Al_2O_3{\cdot}2SiO_2$). The aim of this study is to identify the solubility limit of Fe_2O_3 in mullite crystals. With the scope of the study, an illite/kaolinite was utilized by adding an increasing amount of Fe_2O_3 (e.g. 1–2–4–6–8–10 wt%) into the recipes fired at 1300 °C for 3 h after homogenization. According to the mullite phase content, it is concluded that ~ 5 wt% of Fe_2O_3 could be dissolved in mullite crystal structure on the basis of the Rietveld refinement of the XRD patterns.

1. Introduction

Kaolinitic clays and kaolins are the basic constituents of traditional ceramic production [1]. Kaolen is a large group of 1:1 layered clay minerals including kaolinite, dickite, nacrite, and halloysite. In this group of raw materials, even kaolinite is the representative mineral, mineralogical compositions, and phase characteristics are changeable. Mullite ($3Al_2O_3{\cdot}2SiO_2$) is the major crystalline phase when kaolinitic clays are fired above 1000 °C. Qualitative and quantitative phase contents of the fired kaolins are depended on the structural characteristics of the starting minerals (i.e. crystallinity, crystallite size) chemical composition and the thermal cycle [2]. Mullite is a critical phase for traditional ceramic microstructures. Due to having needle-like crystals, it increases the strength of the fired white wares.

During the firing of the kaolins, the type and quantity of secondary phases may have great effect on the thermal behavior of the raw materials [3]. Iron oxide is particularly important [4,5]. Fe_2O_3 can exist in the raw materials either as mineral compounds or associated with the silicate structure. The presence of Fe_2O_3 in the kaolins not only promotes the amount of mullite phase at lower temperatures (1050 °C) but also improves the growth of the mullite crystals at higher temperatures [6].

Never the less the presence of iron oxide is not desired because it causes grey-black maculation in tableware, in which whiteness is essential [7,8]. In order to overcome the maculation, the iron atom must be avoided to form an oxide form but must make a solid solution with a host crystal such as mullite or anorthite (CaO. $Al_2O_3{\cdot}2SiO_2$) [9–11]. Naturally occurring mullites contain transition metal oxides such as Fe_2O_3, Cr_2O_3 or TiO_2 [12]. Studies of various authors show that mullite incorporates up to about 12 wt% of Fe_2O_3, depending on the raw materials, mullite production route and calculation technique (i.e. Mossbauer spectroscopy or XRD) [13,14]. Schneider and Roger had studied the crystal chemistry of synthetic mullites with XRD and Electron Paramagnetic Resonance (EPR) techniques. Incorporation of mullite caused a stronger expansion effect on c lattice parameter rather than a and b. This was interpreted as a substitution of Fe^{3+} for Al^{3+} [15]. Parmenter et al. used Mossbauer spectroscopy and XRD to study Fe- and Cr-substituted mullites, which were produced by a sol-gel route. They interpreted that both Fe^{3+} and Cr^{3+} had a partial replacement with Al^{3+} and the axial distortion of the Al-octahedra was enhanced compared to pure mullite. Iron was only observed as Fe(III) [16].

The objective of this paper is to observe the role of Fe_2O_3 during the heat treatment of kaolin raw material which is used in the whiteware production and to determine the solid solubility limit of Fe_2O_3 in the final microstructure of kaolin, sintered at 1300 °C.

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2. Experimental

Only kaolin was being used as a component in order to compose mullite. To examine the effect of the Fe_2O_3, hematite (Merck) was added to this material in weight percent of 1, 2, 4, 6, 8 and 10. In order to shape easily, 1 wt% of polyvinyl alcohol (PVA) was added to kaolin and hematite. 20 mm diameter pellets were pressed after homogeneous mixing.

In order to determine the phase evaluation, shaped pellets were sintered at 1000–1100–1200–1300 °C after drying at 80 °C for 24 h. Samples were fired at the peak temperature for 3 h with a heating and cooling rate of 5 °C/min. Water absorption and porosity values of the fired samples were measured by standard boiling and Archimedes method. Thermal behavior of Fe_2O_3-free and 1 wt% Fe_2O_3 added samples were determined with Differential Scanning Calorimeter (DSC) (Seteram Labsys-Evo) and Thermo-Mechanical Analyzer (TMA) (Seteram Setsys). Samples were heated up to 1400 °C with a heating rate of 10 °C/min. The chemical composition of the raw materials was identified with x-ray fluorescence technique (XRF) (Panalytical Axios).

A Panalytical Emperian high-resolution diffractometer was used for the detection of the phases in the fired sample. During the data collection, the diffractometer was operated under the following conditions: voltage and current 45 kV and 40 mA, scanning from 10° to 70° (2θ) with step-size 0.0261 and step-time 97 s, soller slits 0.04 rad, anti-scatter slit ½″ and 2″, and beam mask 10 mm. A reflection-transmission holder was used with 8 rpm. For the phase identifications, Inorganic Crystal Structure Database (ICSD) and International Centre for Diffraction Data (ICDD) PDF-4 + (version: 2012) crystallographic databases were used. Rietveld refinement procedures were performed with the soft wares HighScore Plus V.3.0 (PANalytical, License Number: 10004501), and MAUD (Material Analysis Using Diffraction). In order to obtain reliable results for the quantitative analysis and structure calculation, background, scale parameters, basic phase parameters, microstructure parameters and crystal structure parameters were refined. The refined pattern of the sample with 1 wt% of Fe_2O_3 was given in Fig. 1.

3. Results and discussion

Chemical and mineralogical results of the raw materials were given in Table 1. The main mineral of the kaolin was the kaolinite phase ($Al_2Si_2O_5(OH)_4$), followed by 15.54% illite ($K_1Al_4Si_2O_9(OH)_3$) since 2.24% K_2O and 6.15% quartz (SiO_2). Hematite was highly pure.

Table 1
Chemical and mineralogical constituents of the raw materials.

	Kaolin	Hematite
	Chemical analysis (wt%)	
SiO_2	49.11	
Al_2O_3	35.88	
K_2O	2.24	
Fe_2O_3	0.84	99.5
MgO	0.35	
$TiO_2 + Na_2O + CaO$	0.28	
LOI	11.30	
Total	100.0	
	Mineralogical analysis (wt%)	
Kaolinite ($Al_2Si_2O_5(OH)_4$)	78.02	
Illite ($K_1Al_4Si_2O_9(OH)_3$)	15.83	
Quartz (SiO_2)	6.15	
Hematite (Fe_2O_3)	–	99.5
Total	100	
	Particle size distribution (d_{50}, μm)	
	7.06	20.10

The porosity ratio of the Fe_2O_3-free and 1 wt% Fe_2O_3 added specimens were inversely proportional with the increasing temperature. Moreover, it becomes almost 0% at 1300 °C. Because of the absence of the porosity maker components (such as carbonates and sulfates) within the mixture, and the presence of K_2O at relatively higher ratio, porosity, and water absorption ratio were decreasing as a result of liquid phase formation, particularly in the higher temperatures. On the other hand, Fe_2O_3 shows its fluxing property at 1300 °C [17]. Until 1300 °C, porosity and water absorption rate of the Fe_2O_3-free specimen were relatively low (Fig. 2).

DSC behavior of Fe_2O_3-free and 1 wt% Fe_2O_3 added specimens were similar (Fig. 3). Four endothermic and two exothermic reactions were characterized as follows: At ~ 97 °C evaporation of physical water, at ~ 281 °C combustion of organic matter, at ~ 554 °C removal OH groups from the structure of clay minerals, at ~ 877 °C removal of OH groups from illite structure, At ~ 948 °C complement of OH group removal from kaolinite structure, at ~990 °C formation of new crystals (i.e. mullite) [18]. The highest intensities of endothermic peak at ~ 550 °C and exothermic peak at ~ 990 °C indicate that the kaolinite phase in the raw material was well-crystallized. Moreover, well-crystallized kaolinite shows a slight endothermic reaction before 990 °C. The loss of (OH) from the kaolinite is not accompanied at ~ 550 °C and it may be a small endothermic peak at ~ 950 °C [19]. Even though 1 wt% of Fe_2O_3 addition had no significant effect on reaction occurring temperatures, it decreased the liquid phase formation temperature, which occurred after

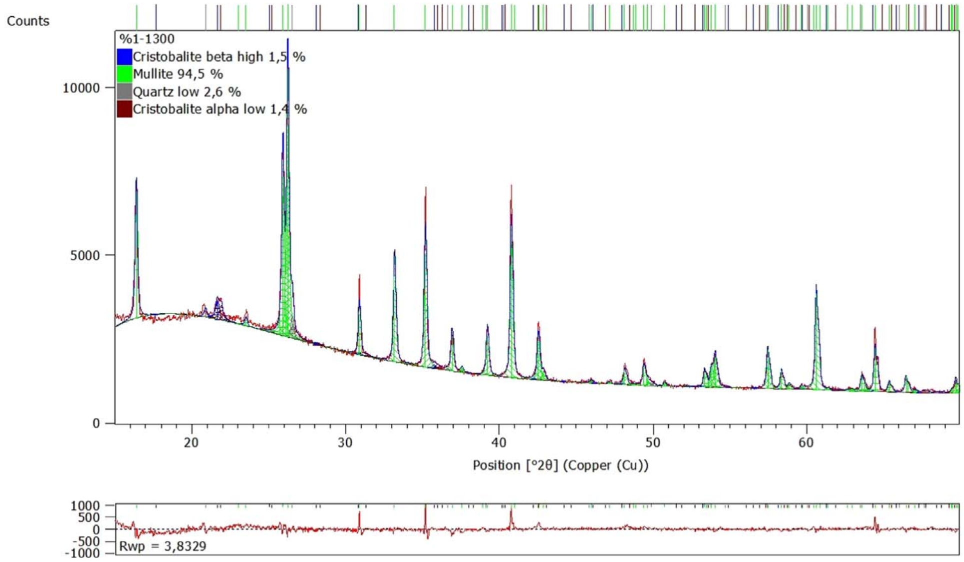

Fig. 1. XRD pattern of the sample 1 wt% added Fe_2O_3 after Rietveld refinement.

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