DC CONDUCTIVITY OF CERAMICS WITH CALCITE WASTE IN THE TEMPERATURE RANGE 20 – 1050°C

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The temperature dependences of the electrical DC conductivity of calcite waste, kaolinite and illite based ceramics were measured in the temperature range of 20 - 1050°C. The ceramic mass that was used was a mixture of 60 wt. % kaolinitic-illitic clay, 20 - 40 wt. % of this clay was fired at 1000°C for 90 min and 0, 10 and 20 wt. % of calcite waste. During heating, several processes take place – the release of the physically bound water, the burning of organic impurities, the dehydroxylation of kaolinite and illite, the decomposition of calcite, and the creation of anorthite and mullite. All of these processes were checked by means of differential thermal analysis (DTA), derivative thermogravimetry (DTG) and thermodilatometry (TDA). At low temperatures (20 - 200°C), due to the release and decomposition of physically bound water, H^+ and OH^- are dominant charge carriers. After completion of release of physically bound water, up to the start of dehydroxylation at the temperature of ~ 450°C, the DC conductivity is dominated by a transport of Na^+, K^+, and Ca^{2+} ions. During dehydroxylation, H^+ and OH^- ions, which are released from kaolinite and illite lattices, contribute to the DC conductivity. Decomposition of calcite runs between ~ 700°C and 900°C. The glassy phase has a dominant influence on the DC conductivity in the fired ceramics. Its high conductivity is determined by the high mobility of Na^+, K^+, and Ca^{2+} ions.

INTRODUCTION

Ceramics containing calcite are often used in the brick industry. It is profitable to use fine-grained waste which is produced in large amounts in limestone quarries. The addition of calcite results in a small irreversible contraction of the ceramic body during and after firing [1, 2]. This is a result of the presence of anorthite which arises at temperatures above 950°C through metastable gehlenite [2, 3]. Initially gehlenite appears in an exothermic reaction at 950°C, then anorthite appears at 980°C [4, 5]. The creation of gehlenite and anorthite is accompanied with an increase in the volume [2, 6, 7]. This volume change occurs in the temperature range where an intensive contraction takes place due to sintering and due to the collapse of the phylosilicate lattices. Also quartz reduces the contraction at temperatures above 950°C. So, firm contacts between quartz grains and their surroundings are created [6].

Since the ceramic samples contain kaolinite and illite as plastic components, dehydroxylation takes place in the temperature range of 450 - 650°C. This endothermic process is linked to a significant mass loss and volume change. Kaolinite contracts but illite expands in the dehydroxylation temperature region [8, 9]. Both the metakaolinite and the dehydroxylated illite (metaillite) exothermically collapse above 950°C which is accompanied by a significant volume contraction [6, 10-13]. Another important process is the decomposition of calcite between 750°C and 850°C, which is accompanied by a high mass loss (up to 44 wt. %) and volume contraction [14].

The same samples, which are the objective of this study, have been studied from the point of view of mechanical properties in [6, 11]. So far, data on the electrical properties of clays containing calcite waste have not been probably published. Therefore, the results of our measurements can bring a new view on the processes which take place in such samples during heating. The objective of this paper is an experimental study of the phase development and of the DC conductivity during heating up to 1050°C, in kaolinite and illite based samples with different content of calcite waste.

EXPERIMENTAL

We used three types of samples (Table 1). Clay B1, supplied by LB-Minerals s.r.o. is a component of each sample. As grog we used clay B1 fired at 1000°C with a soaking time of 90 min at the highest temperature. Clay B1 consists of kaolinite (65 wt. %), illite (25 wt. %), muscovite (3 wt. %), free quartz (5 wt. %), and 2 wt. % of undefined filler [15]. Calcite waste comes from washing the crushed limestone in the quarry Omya, a.s., Vápenná, Czech republic.

Table 1. Composition of measured samples (wt. %).

Sample	Clay B1	Grog	Calcite waste
CW0	60	40	–
CW10	60	30	10
CW20	60	20	20

The chemical compositions of clay B1 and calcite waste are in Tab.2. The calcite waste was dried and then milled for 24 h in the laboratory dry ball mill. The mean spherical diameter of the calcite particles is 17.4 μm (measured with the particle size analyzer Mastersizer 2000).

Grog was ground and sieved and then mixed with clay, milled calcite waste, and water to obtain a plastic mass with a water content of ~ 20 wt. %. From the plastic masses, three different compositions of samples were prepared (Table 1).

Samples for electrical conductivity measurements were prepared using a two-part form. After filling its lower 5 mm thick part with the plastic mass, the Pt wire electrodes (diameter of 0.5 mm) were inserted. The distance between these parallel electrodes was 3 mm and their overlap was 15 mm. Then, the upper part of the form is filled with the plastic mass. The final shape of the sample is a prism with dimensions of 10 × 10 × 20 mm with inserted electrodes (Figure 1). This sample arrangement gives a good electrical contact between the measured material and platinum electrodes as experienced in [16]. This arrangement also precludes the access of the air in the electrode area inside the sample.

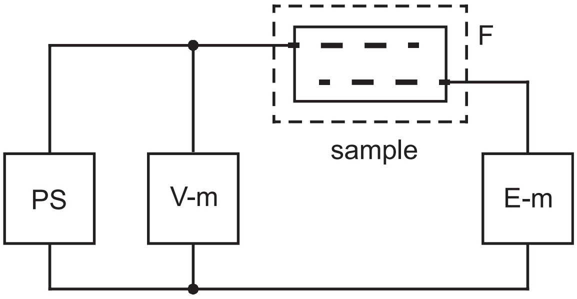

Figure 1. Basic scheme of the DC conductivity measurement; PS – stabilized power supply, V-m – voltmeter, E-m – electrometer, F – furnace.

The volt-ampere method was used to measure the sample resistance, (Figure 1). The measuring circuit was fed using the stabilized voltage source Tesla BS 525. The voltage was recorded with a sensitivity of 1 mV using multimeter Hameg HM 8012. The electrometer Keithley 6514 was used for measuring and recording the current.

The sample was placed in a horizontal furnace heated by silicon carbide rods that were connected, through a power block, to the temperature programmer Grubatec TLK 48. The temperature was measured by a Pt-PtRh10 thermocouple. The heating rate was 2 - 10°C·min^{-1} and the ambient atmosphere was the air.

To avoid the AC heating current influencing the small DC current measured using the electrometer, the measuring period was divided into a time interval of 16 s, during which the heating current was switched on, and a time interval of 4 s when the furnace was switched off using a double-contact electromechanical relay. During these 4 s, the DC current was measured. Thus the DC current was recorded every 20 s.

The conductivity was calculated using the relation

$$\sigma = 12.85\ I/U \tag{1}$$

where U is a measured voltage, I is a measured current, and the numeric value 12.85 is experimentally determined for the given geometrical arrangement that is visible in Figure 1 [17]. In this equation, I is in A, U is in V, and σ is in S·m^{-1}. Measurements were done at linearly increasing temperatures with a rate of 5°C·min^{-1}.

For a better look into phase transitions, TGA and DTA were performed using analyzer MOM Derivatograph 1000 [18]. The green samples were heated up to 1100 °C, which is the highest temperature used in clay ceramic industry, with a heating rate of 5°C·min^{-1}.

The TDA was done on the alumina horizontal dilatometer at the heating rate of 5°C·min^{-1}.

RESULTS AND DISCUSSION

The results of DTA, TGA, and DTG for the ceramic mixtures CW0, CW10, and CW20 are shown in Figures 2-4. In DTA (Figure 2), the release of the physically bound water is registered via endothermic minima between the temperatures 20 - 250°C. It seems that upon adding calcite waste, the content of physically bound water in samples increases. The exothermic reaction between 260°C and 440°C indicates the burning of organic impurities [10, 11]. The next endothermic minima (450 - 600°C) belong to the dehydroxylation of both

Table 2. Chemical composition of clay B1 and calcite waste in wt. %.

	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	K_2O	Na_2O	sulphates	LOI
clay B1	48.6	33.8	2.6	0.8	0.28	0.36	1.98	0.10	–	11.3
waste	0.01	0.08	0.09	0.01	54.55	0.6	0.02	–	0.87	43.77

kaolinite and illite; the dehydroxylation is not influenced by adding the calcite waste. Two endothermic minima of the calcite decomposition are visible between 700°C and 850°C. Both of these minima are more distinct and shifted to higher temperatures at a higher concentration of calcite. A minimum at 740°C indicates the presence of dolomite in the calcite waste. The presence of dolomite is also confirmed by DTG as a two-step process [19] with two minima above 600°C (Figure 3). The exothermic maxima (900 - 1000°C) in the DTA curves belong to the transformation of metakaolinite into Al-Si spinel.

In the CW0 sample, which does not contain calcite, TGA (Figure 4) records a mass loss due to the release of the physically bound water and a mass loss of the constituent water during dehydroxylation. As visible in Figure 4, the endothermic decomposition of calcite, which occurs in the samples CW10 and CW20, is accompanied by a high mass loss.

DC conductivity is extremely sensitive to the water content and products of its dissociation (Figure 5 and Figure 6). The removal of the physically bound water is accompanied by a rapid decrease of H^+ and OH^- content in samples which results in a significant decrease in the electrical conductivity with increasing temperature (up to 200°C). In this temperature region, H^+ and OH^- ions are dominant charge carriers. At 50 - 60°C, a maximum of the conductivity appears, in all samples. Probably, in this temperature range, the decomposition of water is more rapid than its diffusion to the surfaces of samples. The temperature range of this maximum depends on the concentration of calcite waste in samples. In samples containing calcite waste, the maxima are shifted to higher temperatures in comparison to the sample with no calcite waste by 40 - 50°C. This means that for an effective dissociation of water molecules a higher energy is needed in the samples containing calcite waste. It is in accordance with DTA results (Figure 2) where the enthalpy of this process is higher for CW10 and CW20 than for CW0. This first stage of releasing the physically bound water is finished at 180 ± 15°C in CW0 and at 200 - 210°C in CW10 and CW20.

At increasing temperatures (up to 305 - 310°C), the DC conductivity increases in an Arrhenius-like manner with an activation energy of 1.15 eV. In this temperature region, alkali ions (K^+ and Na^+), present in the samples, are already sufficiently mobile as to essentially contribute to the DC conductivity. However, in the samples CW10 and CW20, an anomaly in the temperature dependence of the DC conductivity at ~ 300°C indicates the second stage of releasing and dissociating the more firmly bound physically bound water. These processes result in the association of alkali ions with OH^-; resulting in NaOH or KOH complexes that are electrically neutral and do not contribute to the DC conductivity [20]. Due to these processes, the DC conductivity temporarily decreases. The temperature range and intensity of this anomaly depends on the concentration of calcite waste, in CW0

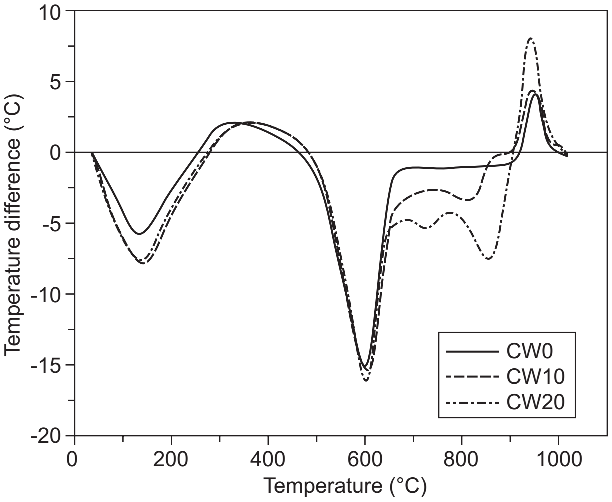

Figure 2. DTA diagrams of CW0, CW10, and CW20.

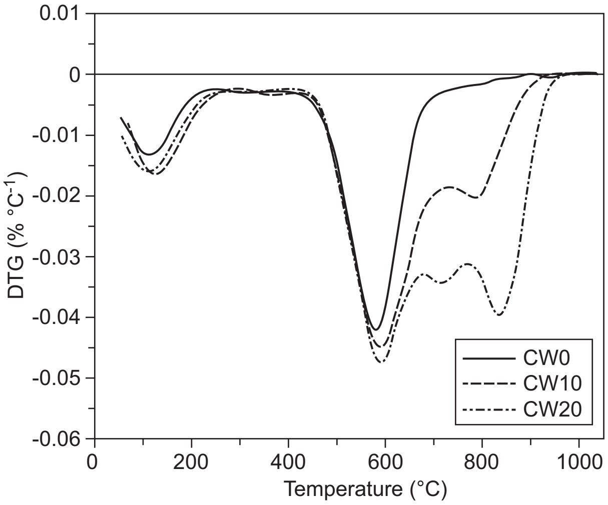

Figure 3. DTG diagrams for samples CW0, CW10 and CW20.

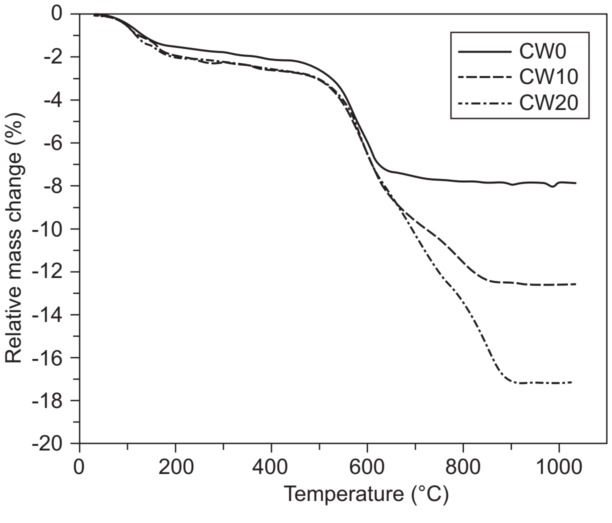

Figure 4. TGA diagrams for samples CW0, CW10 and CW20.

being very small. This anomaly is also present in both green illite and in kaolinite. After heating up to 450°C, the local maximum in these clays disappears because the physically bound water also disappears [21].

At temperatures above 365°C, the dominant charge carriers are alkali ions, especially K$^+$ ions, which are present in a high concentration, and the DC conductivity increases with increasing temperature due to the increasing mobility of these ions. This increase is Arrhenius-like with an activation energy of 1.46 ± 0.06 eV in CW0 and CW10. In this temperature region, Ca^{2+} ions are not very important for DC conductivity because the temperature dependencies of the conductivity of CW0 and CW10 are almost identical. A more complicated behavior of the DC conductivity of CW20 probably results from significant differences in the structure of this sample. At 480 - 580°C, a slight indication of dehydroxylation appears; the onset temperature depends on the concentration of calcite waste. However we can see only a slight change in the slope of the temperature dependencies of the DC conductivity. It probably comes from the association of alkali ions with liberated chemically bound OH$^-$ ions. In this temperature region, the activation energy of the DC conductivity of all samples is 0.74 eV, e.g. it is similar to that of CW0 samples, in the temperature range of 200 - 300°C where a similar mechanism is supposed, e.g. cooperative motion of alkali ions and OH$^-$ ions.

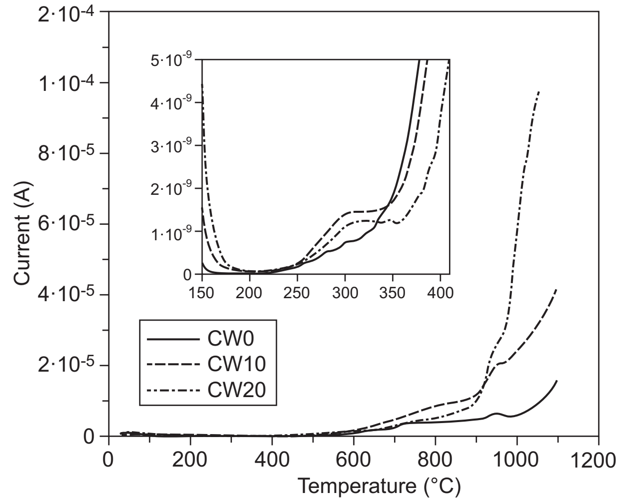

Figure 5. Temperature dependences of the DC current for samples CW0, CW10 and CW20. The inserted picture shows the temperature dependence of the DC current between 150°C and 400°C.

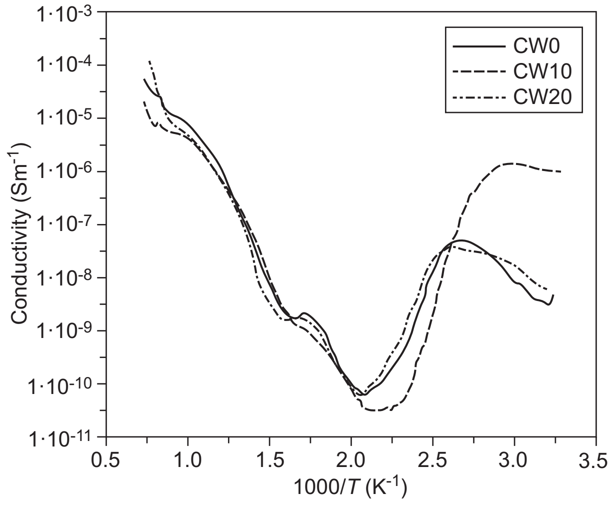

Figure 6. Temperature dependences of the DC conductivity for samples CW0, CW10 and CW20 on the reciprocal temperature.

Above 780°C, the value of the DC conductivity of CW0 only slightly depends on temperature. At 946°C, a small current peak indicates the relatively fast reconstruction of the metakaolinite lattice into the spinel lattice. This peak implies that the shift of Al^{3+} ions into octahedral coordination takes place during the metakaolinite → Si-Al spinel transformation [22]. When these ions are bound in the newly created spinel lattice, the peak of the electrical current vanishes [16]. At the same time, above 870°C, the Ca^{2+} ions, created through the decomposition of CaCO$_3$ get dominant charge carriers in CW10 and CW20. Their conduction activation energy is higher than that of alkali ions but their concentration is high enough to get dominant charge carriers, especially in the glassy phase which develops during firing.

CONCLUSIONS

Temperature dependencies of the electrical DC conductivity of the unfired ceramic mixtures are measured in the temperature range of 20 - 1050°C. The mixtures used contained 60 wt. % of clay, 0-20 wt. % of calcite waste, and 20 - 40 wt. % of the clay fired at 1000°C for 90 min. A special arrangement of electrodes was used for measurements. Near the middle of samples, two parallel Pt wires with a diameter of 0.5 mm, at a distance of 3 mm, and with an overlap of 15 mm, were used as electrodes. The following conclusions relating to DC conductivity can be made:

- At low temperatures (20 - 200°C), due to the release and decomposition of physically bound water, H$^+$ and OH$^-$ are dominant charge carriers. The removal of the physically bound water is accompanied by a rapid decrease of H$^+$ and OH$^-$ content in samples that results in a significant decrease of the electrical conductivity with increasing temperature (up to 200°C).
- Above 200°C, the DC conductivity increases in an Arrhenius-like manner with an activation energy of 1.15 eV. In this temperature region, alkali ions (K$^+$ and Na$^+$), present in samples, are already sufficiently mobile as to get charge carriers.
- At ~ 300°C, the hump on the temperature dependence of the DC conductivity indicates the second stage of releasing and dissociating the more firmly bound physically bound water.

- At temperatures above 350°C, dominant charge carriers are alkali ions, especially K^+ ions which are present in a high concentration, and the DC conductivity increases with increasing temperature due to increasing mobility of these ions. This increase is Arrhenius-like with activation energy of 1.53 eV. In this temperature region, Ca^{2+} ions are not very important for DC conductivity because the temperature dependencies of the conductivity of CW0 and CW10 are almost identical.
- After the completion of release of physically bound water up to the start of dehydroxylation, at the temperature of ~ 450°C, the DC conductivity is dominated by the transport of Na^+ and K^+ ions.
- During dehydroxylation, H^+ and OH^- ions released from kaolinite and illite lattices contribute to the DC conductivity and the activation energy of the electrical conductivity slightly decreases. Above 700°C, the value of conduction activation energy decreases.
- At 946°C, a small current peak indicates the relatively fast reconstruction of the metakaolinite lattice into the spinel lattice.
- Decomposition of calcite occurs between ~ 700°C and 900°C. The Ca^{2+} ions, created through the decomposition of $CaCO_3$ get dominant charge carriers in CW10 and CW20. Their activation energy is higher than that of alkali ions but their concentration is high enough to get dominant charge carriers. The created glassy phase has a dominant influence on the high DC conductivity in the fired ceramics. This conductivity is dominated by the high mobility of Ca^{2+} ions.

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