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Low Temperature Dolomitic Ceramics

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Abstract

New building material composed of clay and dolomite at the variable mass ratio $C/D = 1/9$–$9/1$ is developed. At the firing temperature of 720°C the interaction between the components takes place resulting in the formation of structure which ensures high mechanical strength of the material obtained. The structure is composed of both the 'old' structure of carbonates and new formations such as calcium silicates, calcium aluminates and MgO in fine crystalline or amorphous state permeating through the 'old' structure. The mechanical strength of the fired material subjected to hydraulic hardening with following drying increases per 200–300%. © 1998 Elsevier Science Limited. All rights reserved

1 Introduction

By firing dolomite in dependence on temperature materials of various composition can be obtained for use in a variety of applications.[1] Numerous studies dealing with firing of dolomite hydration and hardening of products obtained have been carried out.[2–6] Semifired dolomite is processed by firing dolomite up to 750°C. Main phases it contains are MgO, $MgCO_3$ and $CaCO_3$.[2,3] Material exhibits low density 2·78–2·85 g cm^{-3} and great chemical activity. In confirmity with Ref. 4, if dolomite is fired up to 700°C and mixed in water, complete hydration of MgO takes place during 3 days but dolomite fired at 1450°C takes water about 61% of theoretically possible during a year.

By firing dolomite at the temperature 800–850°C, material containing MgO, CaO and $CaCO_3$ is obtained.[3] Complete decarbonation of dolomite appears at 900–1000°C and main phases material contains are CaO and MgO.[2,5,6] Sintered or dead burned dolomite containing coarse crystalline inactive MgO (periclase) occurs at 1400–1500°C.[3] By firing dolomite containing clay, the phase composition of material is more complicated. Along with the above mentioned phases also calcium silicates and aluminates can form.[7]

In the present paper the development of dolomitic ceramics containing dolomite and clay in various ratio as well as study of their properties and phase composition are reported.

2 Experimental Procedure

The batches for obtaining ceramics were prepared using dolomites and low melting clays of various deposits of Latvia. The average chemical compositions of clays and dolomites are listed in Table 1. Initially grinded and dried clay and dolomite were weighed in mass proportions of clay/dolomite (C/D) from 1/9 to 9/1 milled in the ball mill to the fineness to pass through sieve from 16 mesh. Specimens for each of batches were die pressed at 20 MPa to form cylinders 36 mm in diameter and about 24 mm in height, dried and fired at temperature of 720°C for 2 h. After hardening part of specimens were dried at 60°C for 24 h. All three groups of specimens after firing, after hydraulic hardening (in wet state) and after hydraulic hardening (dried) were subjected to the compressive strength measuring. The strength values represent the average of three tested samples.

Differential thermal analysis (DTA) and thermogravimetric analysis (TG) of raw materials, batches and materials obtained were carried out in air using a heating rate of 10°C min^{-1}. Finely powdered alumina was used as reference substance.

X-ray diffraction analysis (XRD) was performed using monochromated CuK_α radiation. Reflections between 20 and 70°(2θ) were measured. Free CaO was determined by saccharate method.

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Table 1. Chemical composition of clays and dolomites (mass%)

Component	*Clay*	*Dolomite*
Ignition loss (comprises CO_2)	4·2–7·0	37·7–46·9
CO_2	0·1–1·5	37·5–46·7
SiO_2	57·8–68·2	0·5–9·7
Fe_2O_3	4·9–7·6	0·3–2·3
Al_2O_3	14·2–22·5	0·1–4·1
TiO_2	0·2–1·0	—
CaO	0·8–2·3	26·7–31·5
MgO	1·1–3·4	16·9–20·7
R_2O	3·2–4·3	0·2–0·5

3 Results and Discussion

Figure 1 shows the compressive strength and free CaO of dolomitic ceramics in dependence on dolomite content. Free CaO increases with the increase of dolomite and achieves 1·15% with dolomite content of 90%. The compressive strength of fired samples decreases with the increase of dolomite. However it is sufficiently high yet with dolomite content of 90%—15·2 MPa. After hydraulic hardening the compressive strength of samples rich in clay in a wet state is lower than that one after firing, but remarkably higher of dried samples, especially with great content of dolomite 50–90 mass%.

Figure 2 shows that the compressive strength and content of combined water of the samples of mass ratio C/D = 4:6 increase with the rise of the time of hydraulic hardening. For comparing the compressive strength after firing is given.

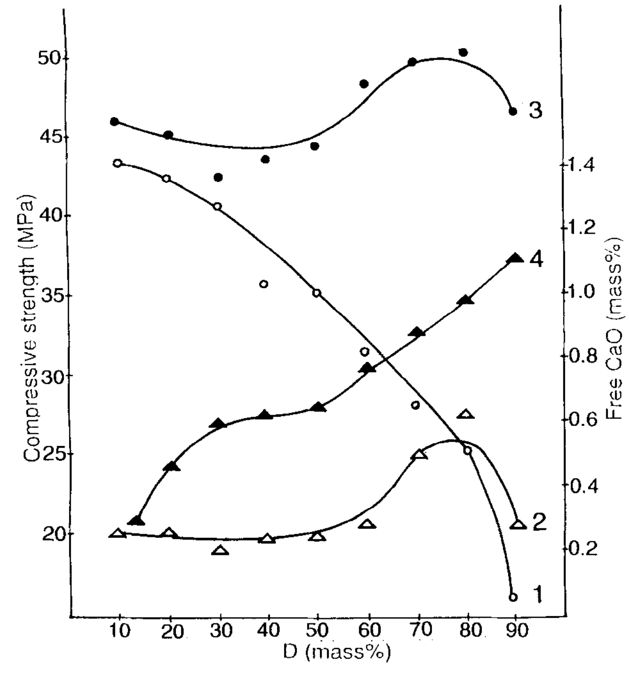

Fig. 1. Compressive strength and free CaO of dolomitic ceramic samples in dependence on dolomite (D) content: 1, fired samples; 2, fired samples after 7 days of hydraulic hardening (in wet state); 3, after 7 days of hydraulic hardening (in dried state), 4, free CaO content in fired samples.

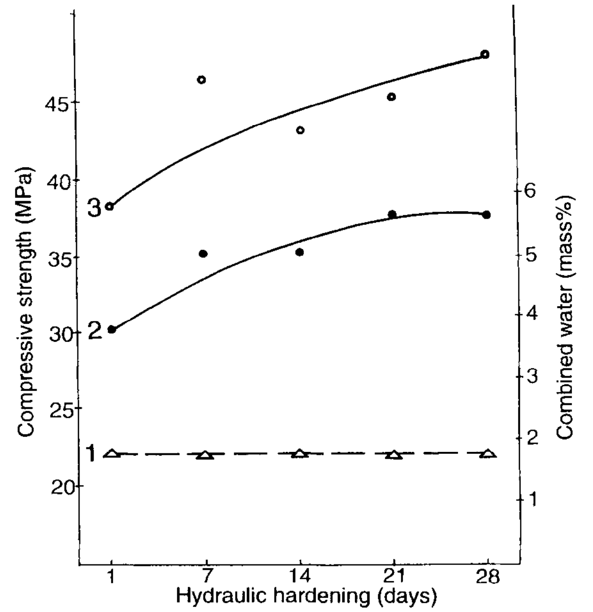

Fig. 2. Compressive strength and combined water of dolomitic ceramic samples. C/D = 4:6 in dependence on the time of hardening; 1, fired samples; 2, fired samples after hydraulic hardening; 3, combined water.

Figure 3 demonstrates the influence of moisture of batches and duration of firing on to the compressive strength of fired samples and allowed to choose optima values. It is obvious that for the composition C/D = 4:6 optima moisture of batches is 9–10%, optima time of firing samples at 720°C is 1–2 h (Fig. 3). It is also stated that the compressive strength of fired samples increases with the rise of the shaping pressure.

Phase composition of raw materials: Kalnciems dolomite (D), Kalnciems clay (C), one of their batches C/D = 4:6 and material obtained determined by DTA-TG and XRD analysis is presented in Table 1. DTA-TG curves of batch C/D = 4:6 and fired at 720°C for 2 h sample are plotted in Fig. 4.

On the each of DTA curves one can notice 3–4 endothermic peaks. On the DTA curves of

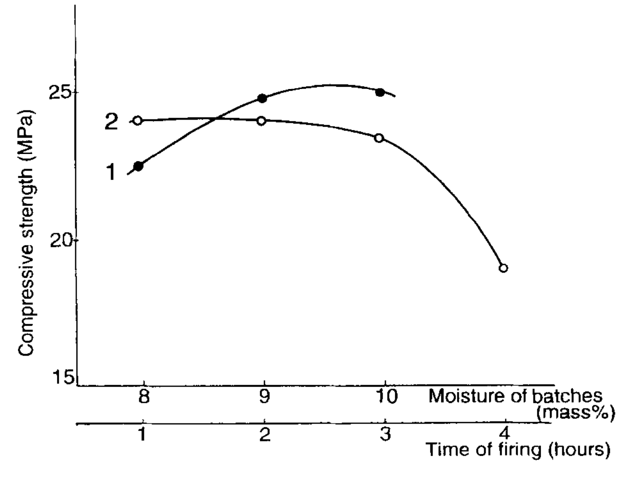

Fig. 3. Compressive strength of fired samples. C/D = 4:6 versus (1) moisture of batches and (2) time of firing at 720°C.

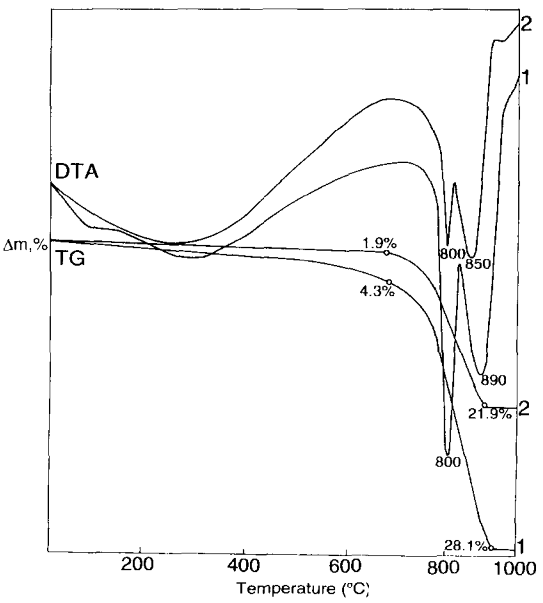

Fig. 4. DTA-TG curves of (1) C/D = 4:6 batch and (2) fired at 720°C for 2 h sample.

dolomite, clay, batch C/D = 4:6 and fired sample bright endoeffect in the range 20–740°C is related to dewatering and dehydration of clay minerals. Two sharp endothermic peaks in the regions 790–820°C and 830–890°C are assigned to dolomite and calcite decarbonation, respectively. A weak peak on the DTA curve of clay at 575°C is attributed to the $\alpha_{\text{quartz}} \rightarrow \beta_{\text{quartz}}$ inversion. On the DTA curves of hydrated C/D = 4:6 samples occurs new endothermic peak, in the range 400–420°C attributed to dehydration of $Mg(OH)_2$ (Table 2).

The increase of mass loss of hydrated and dried samples in the region of 20–380°C allows to assume the presence of calcium and magnesium hydrosilicates and hydroaluminates. It is to be noted that about 4% of $CaCO_3$ is decomposed and amount of decomposed $MgCO_3$ encountered from TG curve is greater than that connected in $Mg(OH)_2$.

By analysing the XRD patterns it is found that dolomite, calcite, quartz exist in all samples. In samples of clay and batch also illite and kaolinite are recognised. New formed phase MgO is detected in fired at 720°C samples. After hydraulic hardening of fired samples no new phases are revealed perhaps due to their amorphous or fine crystalline character.

From the results it can be deduced that the relatively high mechanical strength of low temperature dolomitic material is ensured by it specific structure composed of both the 'old' structure of carbonates and new formations in amorphous or fine crystalline state which permiate through the structure of carbonates.

The highest compressive strength the dolomitic ceramics exhibit after hydraulic hardening and drying. In dependence on composition it makes about 200–300% of the compressive strength of fired material.

4 Conclusions

1. Low temperature dolomitic ceramics—new building material composed of clay (C) and dolomite (D) at the variable mass ratio C/D = 1/9–9/1 is developed.
2. At the firing temperature 700–750°C the interaction between components takes place resulting in formation of structure which ensures high mechanical strength of the material obtained. This structure is composed of both 'old' structure of carbonates and new formations such as calcium silicates and aluminates as well as MgO in fine crystalline or amorphous state permeating through the 'old' structure.
3. Dolomitic ceramics possess hydraulic properties. After hydraulic hardening of fired material

Table 2. DTA-TG and XRD data of raw materials, batch C/D = 4:6 and materials obtained

Sample	*Endoeffect in the temperature range 20–740°C*	*Mass loss (%)*	*Endoeffect in the temperature range 700–920°C*	*Mass loss (%)*	*Phase*
Kalnciems dolomite (D)	320	2·3	820, 890	40·5	dolomite (d/n = 2·89;2·19;1·80 A°) quartz (d/n = 3·36;4·25;1·82 A°)
Kalnciems clay (C)	260, 575	4·7	790, 830	9·7	dolomite kaolinite (d/n = 2·89;2·19;1·80 A°) quartz calcite (d/n = 3·04;2·25;2·09 A°) illite (d/n = 10·0;4·49;3·33 A°)
Batch	280	4·3	800, 890	28·1	dolomite calcite quartz kaolinite illite
Fired at 720°C, 1 h	300	1·9	800, 850	21·9	dolomite MgO (d/n = 2·106;2·43;1·485 A°) quartz calcite
Fired and hydrated 7 days	320, 420	7·8	800, 880	22·5	dolomite $Mg(OH)_2$ quartz calcite

in a moist environment the mechanical strength increases essentially in dry state.

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