

Dilatometry of stove tile ceramic material Letovice

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Letovice-i kályhacsempe kerámia anyagának dilatometriája

A kaolin és a kvarc fontos szerepet töltenek be a kályhacsempe anyagában, és szembetűnően befolyásolják a dilatogrammot. 900–1100 °C közötti hőmérsékleten megy végbe a spinell és a mullit kialakulása, és megjelenik az üveges fázis is. A minták ismételt égetései nem befolyásolják a dilatometrikus viselkedést, ez arról tanúskodik, hogy a kerámia anyag már az első égetés után stabilizálódik. A 20–530 °C közötti hőmérséklet tartományban az égetett kerámiák lineáris hőtágulási együtthatójának értéke $6,2 \times 10^{-6} \text{ K}^{-1}$.

Introduction

The reliance on the tile stoves in houses appears outmoded if compared to gas or electrical heating. The related energetic problems mandate using some alternative and cheap energy carriers such as wood. Ceramic tile stoves of the classical type not only offer a problem solving option but also are stylish and decorative in the houses.

Ceramic material for such stove tiles is typically made from commercial materials that are mixed by a formula, which was developed through empirical experience during the years of testing until the required quality was reached. A literature search reveals that the ceramic material for tiles was not apparently studied extensively. Furthermore, many of the physical properties remain unknown.

It is assumed that the expected properties of the stove tile material are chemical and heat resistance. As a stove tile undergoes testing to high temperature gradients, on the inner side the temperature may reach 900 °C, while the temperature is only 80–90 °C on the outer side. To stand such temperature difference without damage, the tile must have low thermal expansion.

So it is reasonable to perform thermodilatometric study of the stove tile material to gain more knowledge about processes, which take place during firing. It may be assumed that thermodilatometry is one of the most important methods which can be applied for investigation of sintering of ceramic materials. Axiomatically sintering is accompanied with shrinkage of the sample, and can be successfully measured with a dilatometer [1].

The objective of this article is to provide a dilatometric study of the ceramic material which is used for making fireproof ceramic tiles at the ceramic plant Keramika Letovice (Czech Republic).

Samples and method of measurement

Material for the samples was combined from some commercial raw materials, most of which contain significant part of kaolin. The resulting chemical composition of the dried form is showed in Tab. 1.

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Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	SiO ₂	CaO	MgO	Na ₂ O	K ₂ O	L.O.I.
23,08	1,47	0,68	62,4	1,5	0,4	0,72	2,45	7,3

Table 1. Chemical composition of the green ceramic mixture (mass %)
1. táblázat A kerámia nyersanyag kémiai összetétele (tömeg %)

The samples were prepared from the water suspension by casting to the gyps form. After drying the samples have the dimension 4×4×35 mm. The dilatometric analysis was performed with the push-rod dilatometer [2]. The maximum temperature 1100 °C was reached by a heating rate 5 °C/min.

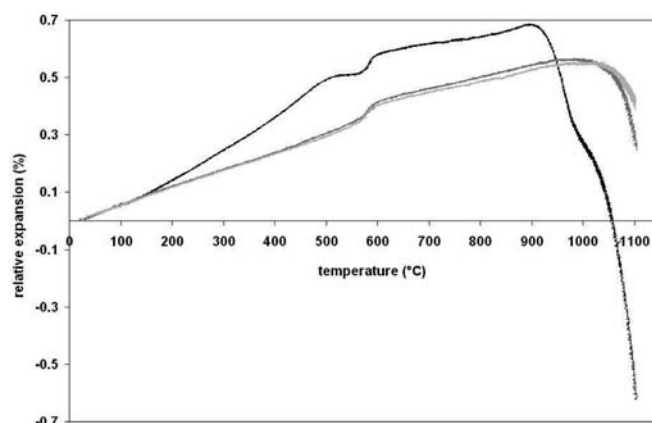


Fig. 1. Dilatometric curves of the 1st heating (black) and 2nd and 3rd heating (gray)
1. ábra Az első égetés (fekete), illetve a második és harmadik égetés (szürke) dilatogramjai

Results and discussion

During the heating, the green sample changed its structure and composition. Thus these changes determined the dilatometric behavior. The results of dilatometric analysis are shown in Fig. 1.

It is known that the physically bounded water escapes from the pores and surfaces of the crystals in the temperature region 20–150 °C [3, 4]. This process did not manifest itself in Fig. 1,

even though the sample contains about 1 mass % of the free water. Dehydroxylation begins after reaching 450 °C. In pure kaolin, dehydroxylation was accompanied with shrinkage of the sample [4, 5]. However in this case, only a short plateau is apparent; then after a steep course of the curve appears. This is caused by the $\alpha \rightarrow \beta$ transition of the quartz at 573 °C. It may be expected that a contraction of the sample takes place after this transition. This is attributed to the fact that the sample contains primarily kaolin. The curve of the first heating however, did not reflect that result. Thus it is assumed that the sample contains significant amount of other minerals, which do not undergo to dehydroxylation and thermal expansion continues over ranges of the heating. At the temperatures 900–950 °C, steep contraction appears apparently caused by the transition of the metakaolinite into spinell and primary mullite [6, 7]. It may be assumed that glassy phase is created at the highest temperatures. That was verified by the second and the third heating curves.

It was discovered that the sample contains significant part of glassy phase and unsolved quartz grains. A presence of the glassy phase causes the softening of the material at temperatures above 1000 °C as recorded by the push-rod dilatometer.

The ceramic tiles are fired two times in the ceramic plant, therefore the test firing was repeated to simulate the industrial praxis. The end result after the second heating does not change the dilatometric properties as evidenced by the two lower dilatometric curves in Fig. 1. The dilatometric line of the fired ceramics is linear in the most important temperature region from an exploitation point of view. A coefficient of the linear thermal expansion is $6.2 \times 10^{-6} \text{ K}^{-1}$ for the fired ceramics in the region of 20–530 °C.

To be able to specify description of dilatometric behavior of the investigated material in greater details, additional analysis, mainly XRD, is necessary.

Conclusion

In the ceramic plant, Keramika Letovice, kaolin plays significant role, in the materials used and markedly affects the dilatometric curve. At temperatures 900–1100 °C creation of the spinell, mullite, and glassy phase occurs. Repeated firings of the samples do not affect dilatometric behavior, which indicates that the ceramic material is stable after the first firing.

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