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EVALUATION OF THE MULLITE HYPOTHESIS IN RESPECT OF ELECTROTECHNICAL PORCELAINS

OCENA MULITOWEJ TEORII WZMOCNIENIA W ZASTOSOWANIU DO PORCELAN ELEKTROTECHNICZNYCH

The paper presents the evaluation of the mullite hypothesis explaining the strength of porcelains. There was researched the influence of the mullite phase on the short- and long-term mechanical strength of electrotechnical porcelain of different types (C 110, C 112, C 120 and C 130). The total mullite phase content, the size and distribution of precipitates and dispersed single crystals in the glassy matrix were considered. Mechanoacoustic and microscopic techniques as well as ultrasonic testing were used during the investigation. The role of the mullite phase in the increase of strength and resistance to aging processes of electrical porcelain of various types was described. Mullite hypothesis is valid in reference to siliceous (C 110), cristobalite (C 112) and aluminous C 120 type materials of a typical raw components content and phase composition. In the case of modern strengthened C 120 and C 130 type aluminous materials advantageous are only dispersed fine mullite needles. The precipitates of mullite phase, especially of bigger size, are undesirable.
Keywords: electrotechnical porcelain, porcelain degradation, acoustic emission (AE), microscopic analysis

W pracy przedstawiono ocenę teorii mulitowej wzmocnienia porcelany, w odniesieniu do tworzyw elektrotechnicznych. Przedmiotem badań był wpływ fazy mulitowej na krótko- i długotrwałą wytrzymałość mechaniczną elektroporcelan rodzaju C 110, C 112, C 120 oraz C 130. Rozpatrywana była sumaryczna zawartość fazy mulitowej, wielkość i rozłożenie jej wydzieleń oraz niezaglomeryzowanych kryształów w osnowie szklistej. W badaniach wykorzystano metodę mechanoakustyczną, techniki mikroskopowe (MO i SEM) oraz metodę ultradźwiękową. Przedstawiono rolę fazy mulitowej w podwyższeniu odporności na procesy starzeniowe porcelany elektrotechnicznej różnego rodzaju. Stwierdzono słuszność teorii mulitowej w przypadku tworzyw kwarcowych (C 110), krystobalitowych (C 112) oraz wysokoglinowych rodzaju C 120 o typowym – tradycyjnym składzie surowcowym i fazowym. W zastosowaniu do nowoczesnych, wzmocnionych tworzyw wysokoglinowych rodzaju C 120 oraz porcelan rodzaju C 130 korzystnie działają rozproszone w osnowie, niezaglomeryzowane igłowe kryształy mulitu. Wydzielenia mulitu, zwłaszcza o większych rozmiarach, są niepożądane.

1. Introduction

Studies of the mechanical strength of the porcelain materials, conducted since the 19th century, have led to several major theories concerning the possibility of increasing the mechanical properties of the materials. Independently of the defects, which have a very significant impact on the strength, there are three main hypotheses. They describe the dependency of mechanical properties of porcelain on the phase composition of ceramic body [1, 2]. The first and the oldest – mullite hypothesis is the subject of this work. Matrix reinforcement hypothesis – the theory of structural compressive stresses in the matrix (pre-stressing effect) on the boundaries of quartz grains stirs controversy and may relate only to siliceous materials. In the case of aluminous porcelains a disadvantageous effect of the quartz phase on their strength has been documented [3, 4]. The third dispersion-strengthening hypothesis of the material, treated as granular composite, is widely recognized. A fine-grained corundum (α-Al_2O_3) is used as a strengthening phase.

Mullite hypothesis, that has been developed to explain the mechanical strength of porcelains, is probably the oldest. It was proposed already in 1908 and suggested the strength of the porcelain material was solely dependent on the interlocking fine mullite needles [5]. Growth of the strength was later attributed to increase of mullite content [6]. The mullite - aluminosilicate of aluminum ($3Al_2O_3 \cdot 2SiO_2$) is characterized by good mechanical, electrical and chemical properties. It is resistant to thermal shocks as well. Hence, it has been argued that the strength growths with the increase of this phase content. In fact, a natural tendency of mullite crystals to growth and agglomeration reduces effectiveness of its action. The smaller needles can interlock more efficiently than the larger ones. As a result, temperature of firing and generating the suitable amount of correctly sized needle-shaped crystals of mullite are crucial to achieve the higher strength. There was stated, that small-

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er needle crystals of secondary mullite can increase strength more effectively than scaly crystals of primary mullite [1].

There is known the number of works which have confirmed the mullite theory. At the same time the authors of the other articles did not observe the growth of strength with increasing content of mullite phase [2]. Moreover, there was suggested that microstructure parameters like amount, dispersion and size distribution of grains and precipitates of the particular components of the body have bigger effect on its properties [7].

The controversy about the mullite theory of the porcelain strength can result from the degree of dispersion and distribution of mullite in the ceramic body. The authors of the publications most often did not carry out a detailed analysis. It is known, however, that the individual needle crystals, more or less evenly distributed in the glassy matrix, operate in a different way than the mullite precipitates of differentiated size. It should be also added that the quartz material (C 110) was mostly the object of the research, although of the different raw components, technology and phase composition.

The mullite precipitates are a typical constituent of all porcelain materials. The C 110 quartz material contains about 20% (volume) of the mullite. The C 112 cristobalite material contains from 25 up to 35% of mullite in the form of precipitates. In typical aluminous C 120 materials the content is similar and most often it varies from 30 to 35%. The modern reinforced materials of this kind have the mullite amount decreased to about 25% and so have the aluminous C 130 type porcelains of high strength. It should be emphasized that apart from the mullite in the form of precipitates, there are also not agglomerated needle-like crystals, dispersed in the glassy matrix. They constitute the additional fibrous strengthening of ceramic body. Their role is similar to the concrete steel reinforcement. This however refers only to the modern materials of the C 120 type, and the more so to C 130 ones, in which they can amount up to 10%. The quantity of dispersed mullite crystals in quartz and cristobalite porcelains is too low to reinforce the matrix efficiently. In the case of typical aluminous materials of C 120 type, their amount is higher (few percents), but they do not usually affect the short – and long-term strength of the matrix.

2. Experimental

Description of the influence of the mullite on the strength was possible by using complex tests of the structure degradation processes in different porcelain materials. Mechanoacoustic research, supplemented by microscopic analysis and ultrasonic measurements, has demonstrated the usefulness of the evaluation of degradation processes of the material structure [8]. The samples of small dimensions were subjected to slowly increasing compressive loading with simultaneous recording of acoustic emission descriptors. The process was continued to the destruction or was stopped at various stages of degradation of the material structure. Then the samples were subjected to detailed research. Microscopic analysis of the samples enabled determining the effects of stress action.

The measurement of AE descriptors, at very slow increase of mechanical load, of the order of 10^{-2} mm/min, allowed to make the mechanoacoustic tests almost independent of the influence of the experimental factors. At very low velocity of stress increase the process of structure degradation has quasi-static character, which better reflects operational conditions, when ceramic element is under working load. Velocity of stress changes has essential influence on the structure degradation processes.

Application of AE method during slowly increasing compressive stress and comparative microscopic analysis enabled recognition of successive stages of the structure degradation. Worked out method made possible comparison of mechanical and acoustic properties, microstructure, texture, homogeneity and resistance to degradation of different, especially porcelain, materials. On the basis of performed investigation of electrotechnical materials, it could be supposed that there exists similarity between effects of long-term exploitation under working load and material degradation during relatively short laboratory tests. The results were compared with the images of similar materials obtained from insulators after different operation periods [4, 9]. Sequence of degradation effects, concerning mechanics and components of structure, specified during mechanoacoustic examination, occurs for the period of long lasting operation. The required conditions to obtain above similarity are – very slow, quasistatic growth of loading and sensitive monitoring changes of structure by properly chosen AE descriptors. Such measurements should be carried out using specially constructed two-channel experimental set-up [8]. The results of many years studies of materials after long-term exploitation were the reference for the mechanoacoustic experiments [4, 9].

3. Analysis of siliceous and aluminous C 120 materials

As it was already mentioned, the mullite phase in siliceous (C 110 and C 112) as well as typical aluminous C 120 type materials is contained almost only in the form of precipitates. The mullite is the strongest component of such porcelain materials, which contain no or a very low content of the corundum phase. The glassy matrix, with a low amount of dispersed mullite crystals, stays evidently weaker than the mullite precipitates. This affects the mechanism of degradation of such materials. Figures 1 and 2 present exemplary mechanoacoustic characteristics of a typical domestic C 110 and C 120 kind materials of the line insulators. Generally the results are similar for siliceous and typical aluminous materials.

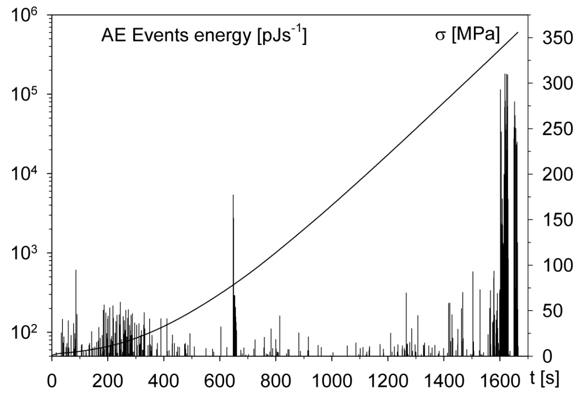

Fig. 1. Rate of of AE events energy in one second periods of time (pJ/s) versus compressive stress increase of typical quartz porcelain. Sample was destroyed at the stress 351 MPa. There was used logarithmic scale for AE descriptor

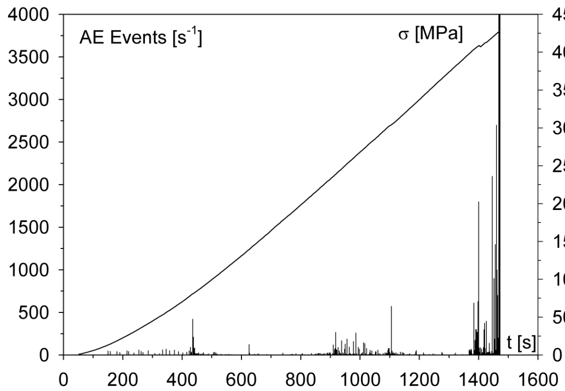

Fig. 2. Mechanoacoustic characteristics of typical domestic aluminous material C 120 type. Compressive strength of the sample equaled 429 MPa

The analysis of mechanoacoustic characteristics of various materials showed that the process of structure degradation progresses in three stages. The subsequent stages of destruction are determined as initial, subcritical and critical [8-10].

The initial degradation stage corresponds to usually weak signals, which are generated by microcracks of low energy of activation. Their initiation and growth are the consequence of strain relaxation, mostly in the microscale, introduced into ceramic body during the technological processes. It usually refers to the interphase boundaries. The signals of the initial stage reflect almost only degradation of quartz phase. It was found that larger grains are more resistant to degradation than the small ones - of several microns size. In the case of aluminous and crystobalite materials, peripheral cracks of quartz grains develop more easily than the internal ones, which appear in higher stress. This relationship is more complex in quartz materials, which contain more glassy phase. However, in the case of bigger grains the internal cracks dominate compared with the smaller ones in which more cracks can be observed at the boundaries. The mullite phase remains without any damage. As a consequence of primary degradation stage, the amount of crushed out structure elements increases by a few percents. A similar effect occurs during the subsequent stages of degradation.

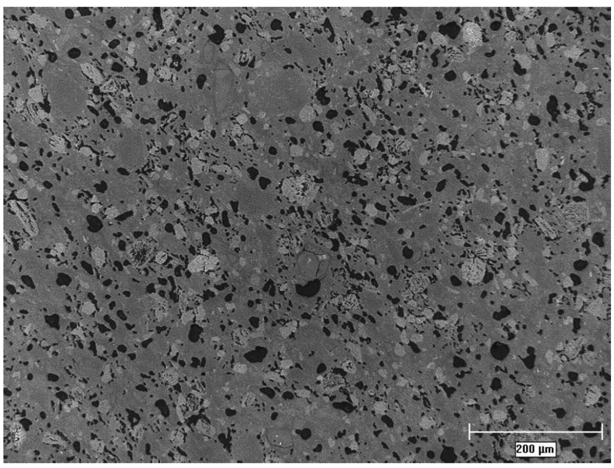

Fig. 3. The structure of C 110 type material of the rod of line post medium voltage insulator of 1981, magnification 100 times. Almost a half of the quartz phase was crashed out, while the mullite phase was not damaged. Intensive cracking inside and around the bright quartz grains is seen

The long-term subcritical stage generally reveals a low level of acoustic activity. The microscopic analysis of the samples structure proved that almost only the quartz phase undergoes degradation in a wide range of stresses [9]. Smaller grains crack more easily, particularly at the boundaries. Figures 3 and 4 show the structures of C 110 and C 120 materials of the rods of the insulators after many years of exploitation. The material reveals an advanced subcritical stage of degradation.

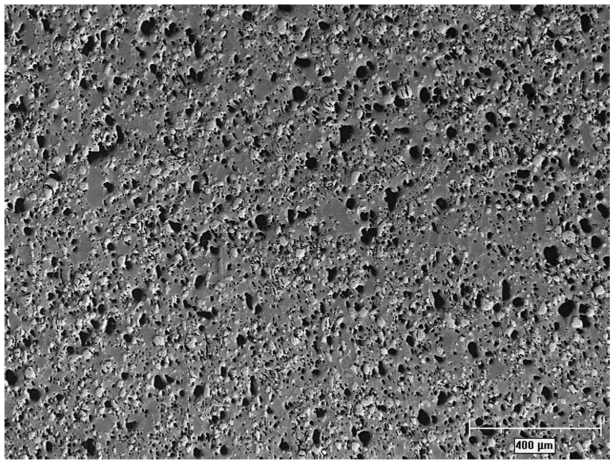

Fig. 4. The structure of C 120 type material of the rod of the long rod high voltage insulator of 1974, magnification 50 times. Advanced ageing processes are visible. More than 1/3 quartz grains was separated from the matrix and crushed out. Numerous fine cracks of the matrix are visible in their vicinity

Stronger AE signals appear only in the final part of the subcritical stage, when cracks generated at crannied quartz grains, begin to propagate into the matrix. Since the glassy matrix has lower strength than the mullite precipitates it is evident that the cracks develop in it. It was confirmed by the observations of materials after many years exploitation – Figures 3 and 4 – as well as the samples in mechanoacoustic experiments [4, 9]. During the critical stage of degradation, the cracks in matrix – initiated in the neighbourhood of quartz grains – propagate, branch and when they reach critical size the sample destruction occurs.

In the considered materials, the mullite precipitates play a substantial role as the structure reinforcement. They are more effective in larger amount, when they are finer and more homogeneously distributed in the porcelain body. It was right confirmed in the mechanoacoustic tests of the quartz C 110 type material.

4. Examination of modern aluminous porcelains

In the composition of modern, reinforced materials of C 120 type and aluminous porcelains C 130 of high strength an increased content of alumina is applied. It is added to the raw ceramic composition in so called ceramic form. This results in the occurrence of fine corundum grains in the material – from few up to more than 25% – as well as in a considerable raise of the strength of glassy matrix. It is due to an increased Al_2O_3:SiO_2 ratio in the chemical composition of the glassy phase and the mentioned occurrence of dispersed needle-like mullite crystals.

Strong AE signals were observed in an advanced part of the subcritical stage of the mechanoacoustic characteristics of the discussed materials – Figures 5 and 6. These signals were stronger than in the case of peripheral or internal cracking of the quartz grains.

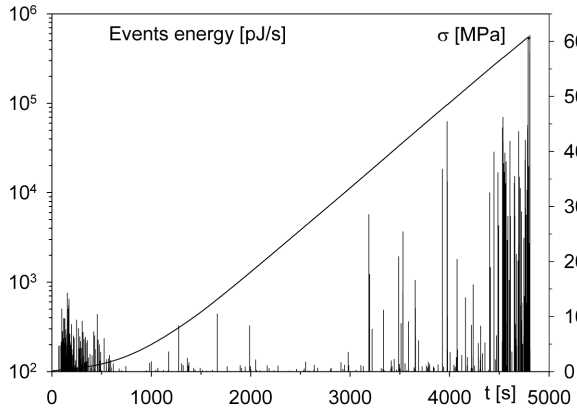

Fig. 5. The course of AE event energy versus the strain increase for the sample of reinforced material C 120 type of the compressive strength 608 MPa

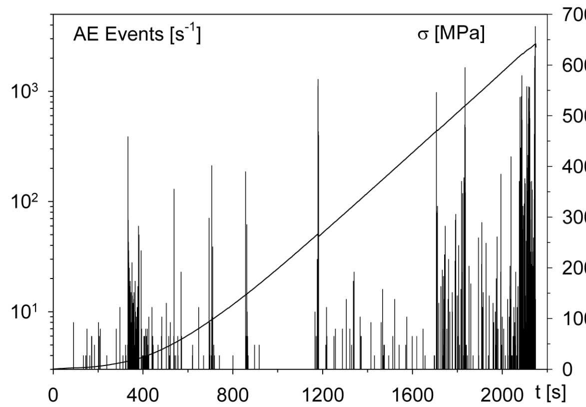

Fig. 6. Mechanoacoustic characteristics of C 130 material sample of foreign production of compressive strength 642 MPa

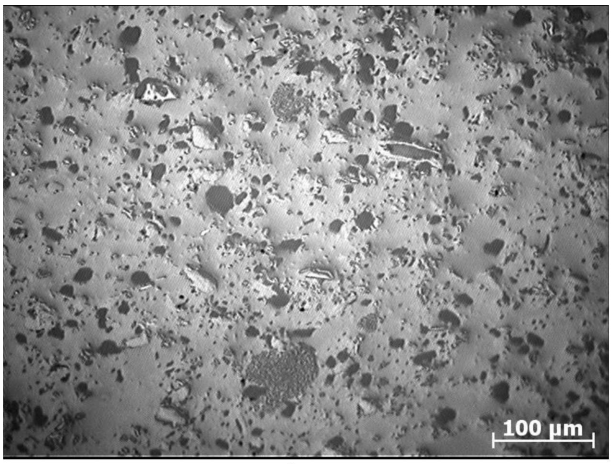

Fig. 7. The structure of reinforced C 120 material loaded up to 521 MPa, magnification 200 times. Dark areas correspond to the cavities after the crushed out particles of cullet and quartz grains. Big, dark and strongly fractured mullite precipitates are easily visible

Microscopic examination of the reinforced C 120 material samples, which were taken from the domestic medium voltage line isolator, revealed the origin of the mentioned AE signals. It was found that the mullite phase underwent a gradual degradation under the load corresponding to the advanced subcritical phase. The microcracks shown in Figure 7 appeared and grew inside some precipitates. Also crushing out of some fragments of the precipitates happened, although uncommonly. Since the precipitates of mullite are strongly bound with the glassy matrix, the cracks at their interphase boundaries are not often observed [10].

Quite similar effects are recorded in the case of C 130 materials. The subcritical stage of degradation, apart from the other effects like cracking of larger quartz grains or the destruction of agglomerates of corundum grains refers, first of all, to the degradation of the mullite phase. Its numerous grey precipitates are distinctly visible in the structure of both domestic and foreign made porcelains. Fragments of some precipitates undergo cracking and crushing out. Because of a strong connection with the glassy phase, the cracks appear mostly inside the precipitates. They rarely undergo even a partial separation out of the matrix. The cracks inside a large mullite precipitate in a small size C 130 porcelain specimen, loaded up to 1144 MPa, are presented in Figure 8.

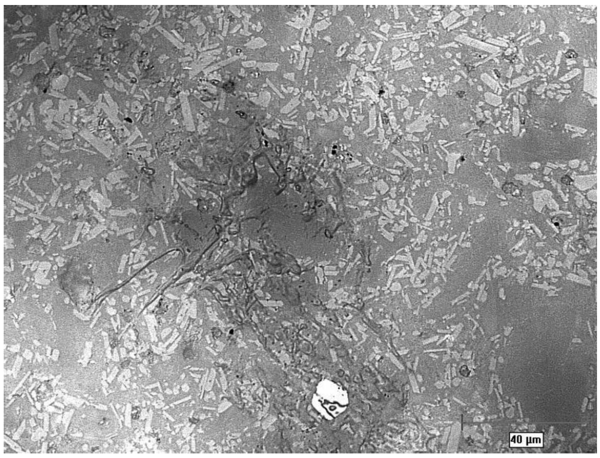

Fig. 8. Cracks in the mullite precipitate, propagating into the matrix, magnification 500 times. The structure of small size sample of C 130 material loaded up to the advanced subcritical stage

The cracks that appeared inside the mullite precipitates grow under the influence of increasing compressive stress and may cause the separation of precipitate fragments. Sometimes they propagate into the matrix, which is visible in Figure 8. The typical effect of strongly advanced degradation of the structure in the subcritical stage, apart from the destruction of most fragments of cullet and quartz grains, is considerable number of crushed out fragments of the mullite precipitates – Figure 9.

The glassy matrix reveals a higher strength than the mullite precipitates. The propagation of cracks in the matrix, which brings about the damage of the sample structure, takes place after achieving the critical stage of degradation. The presence of numerous mullite crystals, dispersed in the glassy phase, is important factor, which ensures the high strength of the matrix in the modern C 120 type materials and C 130 porcelains. These needle-shaped crystals become visible only after etching the glassy phase with the hydrofluoric acid – Figure 10.

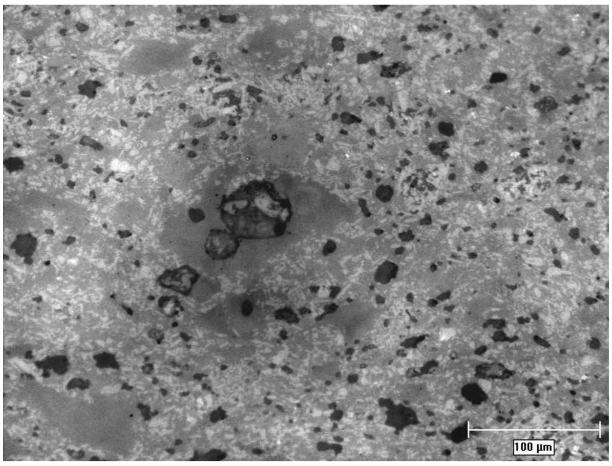

Fig. 9. Dark cavities in the mullite preciptates in the C 130 material of long rod insulator, loaded up to 741 MPa, magnification 200 times. Almost the whole cullet and most of quartz grains are crushed out

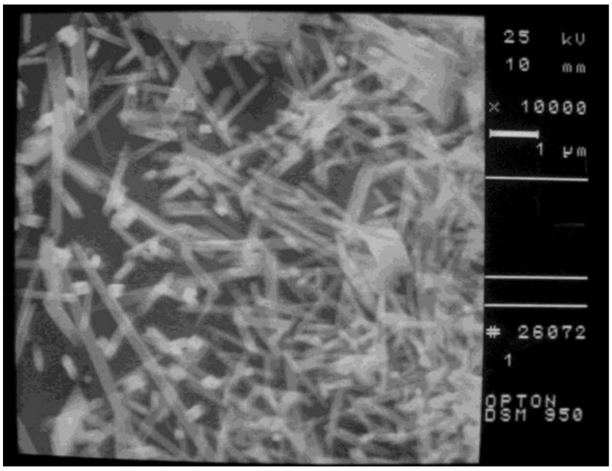

Fig. 10. Fibrous reinforcement of C 130 type material matrix with needle-like mullite crystals. SEM image, magnification 10 000 times. Glassy phase etched in 10% solution of hydrofluoric acid for 20 min

The occurrence of precipitates of the mullite phase, particularly the bigger ones, is disadvantageous and adversely affects the mechanical parameters of the porcelain body. The material matrix reveals a higher strength and resistance to the propagation of cracks than the mullite precipitates. This effect is connected with the presence of numerous resistant grains of corundum in the glassy matrix (dispersion strengthening) as well as high alumina content in its chemical composition. Simultaneously, the dispersed needle mullite crystals in the glassy phase act as effective reinforcement of a fibrous type. Thus, clear assessment of the role of mullite in the discussed materials is difficult.

5. Discussion and conclusions

The considered theory of reinforcement of porcelain with mullite is proper in reference to the electrotechnical quartz (C 110), crystobalite (C 112) and aluminous (C 120) materials of a typical composition. The mullite phase is strongly bound with the glassy matrix, forming a structural reinforcement of the ceramic body as regards the short- and the long-term mechanical strength as well as the resistance to ageing processes. The influence of mullite is more effective when its precipitates are smaller, more numerous and more homogeneously distributed in the ceramic body. In the above mentioned materials the needle crystals of mullite, dispersed in the glassy phase, are sparse and they do not play a significant role as their fibrous reinforcement.

In modern, strengthened aluminous materials C 120 and porcelains C 130 type, the dispersed mullite crystals act as a reinforcement of the glassy matrix. The upper content of the mullite (it can constitute up to 10%), the higher is strength of the material. On the other hand, the presence of the precipitates of mullite, especially bigger – of the size above 30 μm – should be considered disadvantageous. Their strength is lower than the glassy matrix, which is rich in alumina and contains dispersed corundum grains as well as the mullite crystals. Moreover, the mullite precipitates most often adversely affect the homogeneity of the material.

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