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Influence of microstructure on the properties of siliceous electrical porcelain

Abstract. *The paper presents the microscopic and mechanoacoustic study of degradation processes of the porcelain material C 110 type. Small-sized samples, derived from the low voltage insulator, were subjected to a slow, quasi-static compression, with simultaneous recording of acoustic emission descriptors. There were distinguished consecutive stages of the material degradation. Obtained results were compared with the images of the microstructure of low-voltage insulator materials after many years of operation. On this basis, there were distinguished the factors determinant of the short-term strength of porcelain and its resistance to ageing processes under operating conditions.*

Streszczenie. *W pracy przedstawiono mikroskopowe oraz mechanoakustyczne badania procesów degradacji w tworzywie porcelanowym rodzaju C 110. Próbki małogabarytowe, pochodzące z elementu elektroizolacyjnego niskiego napięcia, poddawane były powolnemu, quasi-statycznemu ściskaniu, z jednoczesną rejestracją deskryptorów emisji akustycznej. Na podstawie badań mikroskopowych ściskanych próbek wyróżniono etapy degradacji materiału. Wyniki konfrontowano z obrazami mikrostruktury tworzywa izolatorów niskonapięciowych po wieloletniej eksploatacji. Wyróżniono czynniki mające wpływ na wytrzymałość krótkotrwałą oraz odporność tworzywa na starzenie się w warunkach eksploatacyjnych. (**Wpływ mikrostruktury na właściwości kwarcowej porcelany elektrotechnicznej**).*

Keywords: electrical porcelain, microscopic analysis, acoustic emission, degradation of the porcelain.
Słowa kluczowe: porcelana elektrotechniczna, badania mikroskopowe, emisja akustyczna, degradacja tworzyw porcelanowych.

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Introduction

The composition of European hard porcelain - with a high content of clay minerals - was finally developed around 1720. Besides clay raw materials - in the amount of about 50% - there is used about 25% of feldspar fluxes and the same quantity of quartz as a filler. These proportions have remained valid until today, with changes of ±10%. Electrical siliceous porcelain C 110 type, akin to the traditional, is widely used primarily for the production of low-voltage (LV) insulators, insulators for telecommunication engineering and bushings [1]. These elements do not need to have high mechanical strength, but they are required to show high durability and reliability. The typical composition of raw materials of electrical C 110 type porcelain contains about 35% of kaolins, around 20% of refractory plastic clays, less than 20% of quartz sand and feldspar fluxes in the amount of about 25%. Sometimes a few percent of cullet is also used.

Studies explaining the mechanical properties of the porcelain materials have been conducted since the 19th century. Independently of the defects, having a major impact on the strength, there were formulated three major theories [2]. The first and the oldest - mullite hypothesis - connects the strength with mullite content (realized in aluminous C 120 type material [3, 4]). The next theory - matrix reinforcement hypothesis - pre-stressing effect on the boundaries of quartz grains, remains controversial. The third, dispersion-strengthening hypothesis of the porcelain material, is widely recognized and realized in aluminous C 130 type material. A fine-grained corundum (α-alumina) filler is commonly used as a strengthening phase.

Electrical C 110 type porcelain of different producers contains generally constant amount of the mullite phase - about 20%. There is no effective chemical, dispersion and fiber system of reinforcement as in the case of C 130 type material. Considering the controversial role of quartz, it is not easy to answer the question of the factors that determine the short-term strength and resistance to ageing processes under operating conditions. Even in the case of C 120 type material of the older generation, limited resistance to degradation processes was demonstrated [4, 5]. The use of mechanoacoustic method enabled to determine the factors which are decisive for the functional parameters and operational durability of siliceous porcelain. Comparison with the images of the structure of siliceous porcelain of the insulators after many years of operation enabled the verification of the results.

Experimental procedure

The samples of C 110 type porcelain were subjected to mechanical-acoustic measurements, using the technique of acoustic emission (AE) on a special two-channel measuring system. Small-sized pieces of the material were subjected to slowly increasing compressive stress in testing machine INSTRON 3382 with computer control. The velocity of the traverse of the machine equal to 0.02 mm/min was applied. Simultaneously with the measurement of the load acting on the sample, AE descriptors were registered. The rate of counts, the events rate and the energy of AE signals were recorded. The process was continued to the destruction of the sample or was stopped at various stages of degradation of porcelain structure. Then the samples were subjected to detailed microscopic study. The samples or fragments thereof were flooded in quickly gelling epoxy resin. There was applied the resin with added fluorescent agent, visible under UV light. The samples were polished in several stages, using diamond suspensions of descending order of granulation and colloidal solution of silica (SiO_2). Detailed microscopic examination, with the use of visible and UV light, revealed the effects of progressive structure damage and growth of cracks. It enabled a complete description of the subsequent stages of degradation.

There exists a correlation between the rate of the increase of cracks and the rate of AE events (number of AE events per unit of time) [6]. Registration of this descriptor and the related ones allows monitoring the process of destruction of the microstructure of ceramic material under load. Examination of aluminosilicate and corundum ceramic materials, carried out by the authors, confirmed these dependencies [3, 4].

The geometry of samples has significant influence on the obtained results. Top and bottom surfaces, being affected by compressive force, ought to be buffed, plane and parallel to each other. Otherwise a local fracture and splitting off corners or even the whole wall of the stressed sample can occur.

Visible analogies between the effects of many years long work under operational load applied to the material and the compressive stresses in a relatively short lasting laboratory test were demonstrated. However, it is necessary to apply a quasi-static, very slow increase of stress. It has been proved by the authors, by investigations on ceramic aluminous materials. Quasi-static character of stressing better reflects operational conditions – under working load. The results were compared with the images of similar materials obtained from the insulators after different periods of operation. Hence, there were distinguished consecutive stages of ageing and corresponding effects of the structure degradation [3, 4]. However, the starting point was detailed description of the porcelain structure with the analysis of the content, size and distribution of crystalline phases as well as pores in the samples. This particularly concerned quartz relics. Its attendance in the structure of porcelain can be one of the main reasons of internal stresses and ageing processes [4, 5].

Examined material

In this work a typical C 110 porcelain material has been studied. The composition of raw materials and technological processes were common of low voltage electrical porcelain. The specimens of small dimensions - 9.5x9.5x11 mm - were cut out from domestic, unexploited low-voltage stand-insulator, produced in 2011.

Ultrasonic control of the acoustic properties of the tested material revealed typical parameters as in the case of insulator siliceous porcelain. The calculated value of Young's modulus E was 69 ± 3.0 GPa, at density of the material ρ = 2.31 ± 0.01 g/cm^3. These values exceed requirements of standards for material C 110 type - $\rho \geq$ 2.20 g/cm^3 and $E \geq$ 60 GPa. Parameters of the material in the perpendicular direction were slightly lower, which is typical for formed by extrusion insulators.

Examination of the material structure was performed essentially in terms of the contents and uniformity of distribution of the crystalline phases in the glassy matrix. The image of porcelain is shown in figure 1.

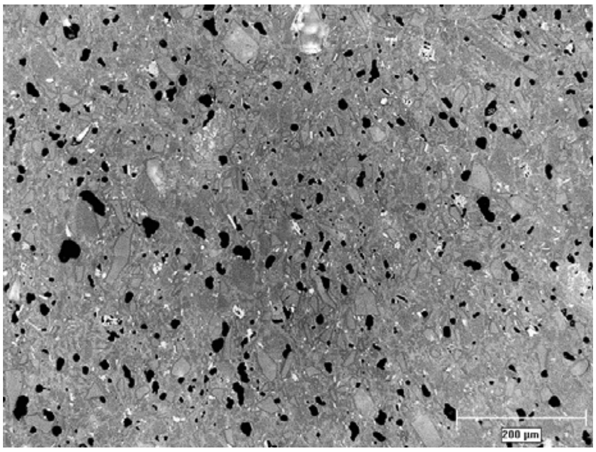

Fig.1. The structure of the sample of C 110 type material, magnification 100x. Bright quartz relics, white particles of cullet and darker mullite precipitates against the background of gray glassy matrix are visible. Dark cavities after the crushed out grains of quartz and particles of cullet occupy about 5% of the surface. Fine pores do not exceed 0.5%

The microscopic phase analysis of the examined samples of the insulator material revealed generally satisfying homogeneity. The quartz content was equal to 20 ± 2%. Clearly dominated fraction of the size of dozen or so micrometers, but also a significant portion accounted the relics in the range of 20 ÷ 30 µm. Unfortunately, there occurred agglomerations of larger grains and significant part of the relics exhibited unfavourable lamellar morphology. Important part of quartz relics was insufficiently connected with matrix and contained cracks. In consequence significant amount of quartz grains fell out during the preparation of surface of the tested samples. Mullite phase in the form of precipitates occupied 22 ± 3%. Relatively small precipitates, mostly around 10 µm, were densely and uniformly distributed in the material structure. They were very well connected with the glassy phase and did not contain internal or peripheral cracks. The porosity was correct - about 0.5%. The content of the glassy matrix in the material amounted to 55 ± 4%. It is the high quantity as compared to other electrical porcelain materials, even of the same class. The material contained small amount of cullet (from grinding media). Electrical C 110 type porcelains are characterized by great diversity [7] , but tested material was in general typical and homogeneous.

Results and discussion

The compressive strength of the samples, loaded until a complete destruction, was equal to: 342, 351, 360, 397 and 469 MPa. The mean strength was equal to 384 MPa. The relative dispersion of compressive strength was comparatively low and equalled 33.1%. Besides the damaged samples, a group of specimens was selected for the microscopic investigation. The compression process of these samples was stopped at different levels of stresses: 60, 111, 200, 285 and 387 MPa. The applied procedure enabled a detailed study of degradation progress in the porcelain material, subjected to increasing load.

Mechanoacoustic characteristics of tested samples showed differentiation. However, three consecutive stages of degradation could be recognized – the preliminary, the subcritical and the critical one. Figures 2 and 3 present the course of the rate of AE events versus the increase of compressive stress for the weakest and the strongest specimens.

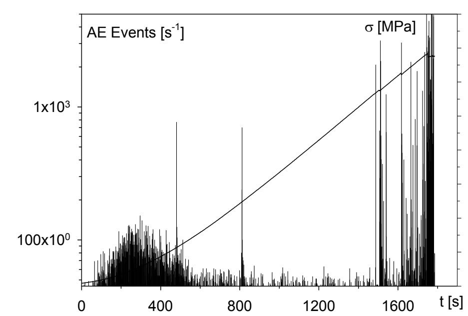

Fig.2. Mechanoacoustic characteristics of the weakest C 110 type material sample of the strength 342 MPa. The course of AE events presented in logarithmic scale

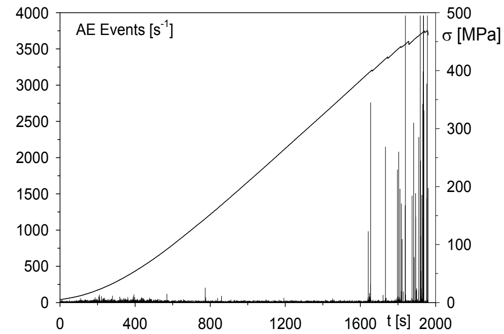

Fig.3. Mechanoacoustic characteristics of the strongest C 110 type material sample of the strength 469 MPa. The course of AE events presented in linear scale

The first - preliminary stage of the material degradation is characterized by low intensity of AE signals. Defects, created during the manufacturing processes, may start to develop at low energy threshold and under small stresses acting on the sample. Under operational conditions growth of microcracks is slow and takes many years. The first stage of material degradation occurs up to 60 ÷ 100 MPa for different samples. The microscopic analysis revealed that the source of AE signals was degradation of significant part of quartz phase. Destruction and crushing out concerned quartz grains, mainly the small ones - of size below 10 μm, and especially of lamellar morphology. The most resistant proved to be the grains of an average size about 20 ÷ 30 μm, having favourable ovoid shape and usual morphology. There also took place crushing out of nearly all cullet fragments. The degradation did not affect mullite and glassy phases. Destroyed components of the structure comprised over 10% of the compressed samples.

The second – subcritical stage of the structure degradation is the longest, follows the preliminary period and lasts to the beginning of the last - critical stage. This phase of destruction shows low AE activity. Rare stronger signals follow only the fracture and splitting off the walls or the corners from the sample. During this period, in a wide range of stress, takes place further damage of quartz grains. There are created peripheral and internal cracks in the grains. Detailed microscopic examination, with the use of UV light, showed that in the material are present centres of cracks - regions of loosened structure. The agglomerations of the larger grains of quartz are their source. In these areas, the cracks in the matrix are initiated. Development of the cracks in the matrix is one of the determinants of the advancement of the structure degradation and they rise sharply at the time of the critical stage.

During the preliminary stage mainly small quartz grains are damaged. Subcritical stage showed harmfulness of the presence of large quartz grains - above 30 μm, particularly in agglomerations. In the case of the samples, stressed up to the advanced subcritical stage (285 and 387 MPa), the area of damaged, separated and crushed out elements of the structure equalled about a dozen percent. The effect of degradation of mullite phase was not registered. In figure 4 is presented central part of the sample loaded up to 285 MPa.

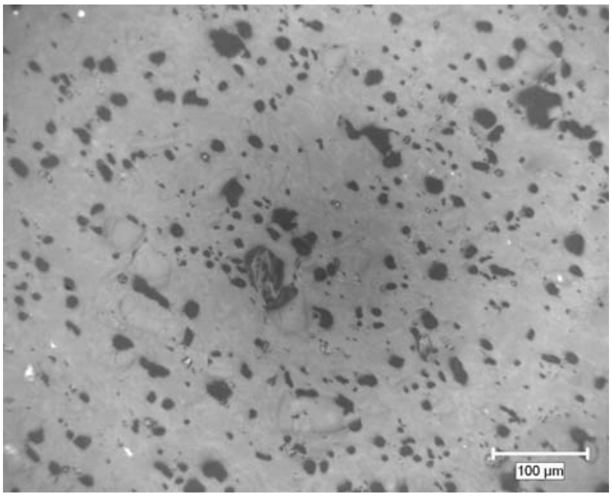

Fig.4. Structure of the central part of the sample loaded up to 285 MPa, magnification 200x. Dark areas remaining after crushed out grains of quartz and their fragments as well as cullet particles cover above 11%. There are no degradation effects of the glassy matrix and mullite phase

The last one - critical interval, shows the high level of the acoustic activity. This stage covers a wide range of stress - tens of megapascals and lasts up to the destruction of the specimen. It is related to the gradual fracture and a splitting off the greater pieces of the stressed specimens. This effect is visible on the stress increase curves as a characteristic faults (leaps) – figures 2 and 3. To identify the critical effects of degradation, there were tested sample loaded up to 387 MPa and the larger fragments of the destroyed samples. The main source of the growth of big cracks proved to be the regions of loosened structure, containing agglomerations of large quartz grains. The essence of the critical degradation was a relatively long-term development of large cracks in the matrix and the creation of entire blocks of the fractured material, which easily underwent breaking off. The area of damaged, separated and crushed out elements of the structure achieved nearly 15% of analyzed surfaces. It included almost the whole cullet and about half of quartz. However, the most important and destructive effect, followed by the strong AE signals, was formation and growth of big cracks in the porcelain matrix. Their propagation was facilitated by damaged components of the structure. Precipitates of mullite, having small size and very well integrated with the matrix, did not undergo degradation. They effectively deviated rising cracks and hampered their increase. Figure 5 shows the structure of the piece of the destroyed sample with the highest strength.

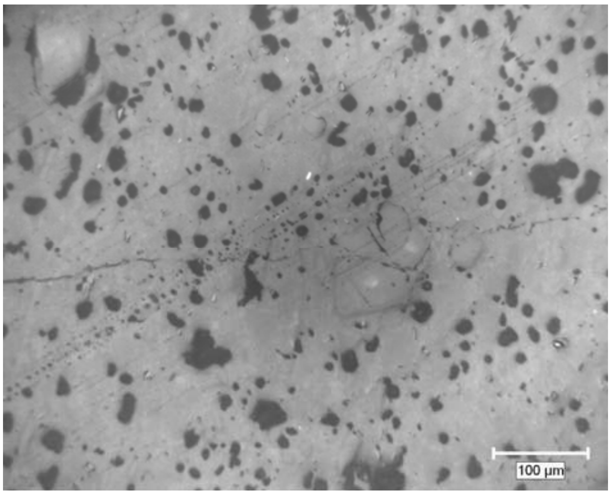

Fig.5. Severely cracked structure of the fragment of the sample, which was destroyed under stress 469 MPa, magnification 200x. Big, cracked quartz grains are explicitly visible. Parallel course of the matrix cracking results from the direction of the load

Many years of testing of the samples of siliceous porcelain, from various insulators after long-term operation, conducted by the authors, confirm the registered sequence of the effects of the structure degradation [7]. Long-term degradation of the preliminary and subcritical stages relates to the damage of quartz phase – cracks at the boundaries and inside of quartz grains. Crushing out of the structure concerned especially the small quartz grains - of size below 10 μm. The others, especially large grains, contain internal cracks and/or cracks at the boundaries. Cullet, if is present in the composition, is also separated from the matrix. Mullite phase is the strongest component of the material, effectively strengthening siliceous porcelain. It is very well associated with the glassy matrix. Nowhere degradation effects were observed inside and at the boundaries of the precipitates of mullite.

When the degradation, caused by internal stresses, operating loads and devitrification effect, reaches an advanced stage - there appear cracks in the glassy matrix. Their propagation is facilitated by damaged and separated grains of quartz and particles of cullet. In the structure of insulators which cracked up, long cracks are observed, similar to those visible in figure 5. Figure 6 shows the advanced aging processes in the structure of the LV draw off insulator after about a 20-year period of operation.

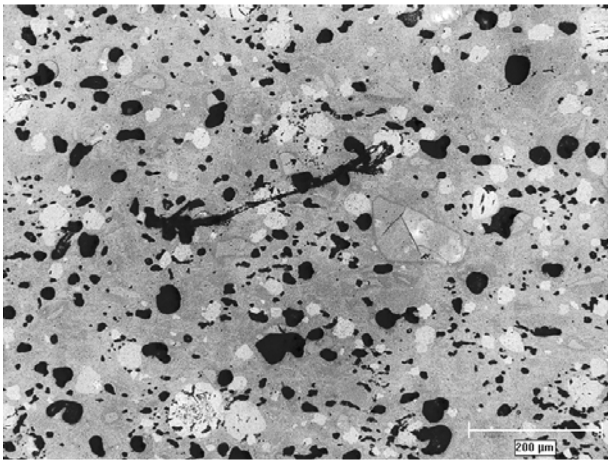

Fig.6. The image of siliceous porcelain of LV draw off insulator after many years' period of operation, magnification 100x. Crack in the structure is visible. Dark areas remaining after crushed out grains of quartz and cullet particles cover about 10%. Numerous particles of cullet and residual quartz grains contain cracks

Conclusions

Based on the mechanoacoustic research and observations of the structure of siliceous porcelains after many years of operation, it is possible to draw conclusions regarding short-term mechanical strength, resistance to structural degradation and operational durability:

- Considering the absence of dispersion strengthening - mullite plays a special role. Precipitates of mullite are well associated with the matrix and the better reinforce the structure, the more uniformly are distributed therein. The most effectively operate small precipitates - about 10 μm. Mullite content in various siliceous porcelains is generally constant at about 20%.
- The optimal size of quartz grains is 20 ÷ 30 μm. Both small grains and the large ones are not favourable, as confirmed by literature data [2, 5]. Agglomerations of large quartz grains operate the most detrimentally. They cause the structure loosening and are the source of big cracks proceeding into the glassy matrix.
- Quartz grains of a lamellar morphology and particles of cullet, regardless of size, act adversely - are poorly associated with the matrix and weaken the structure of the material.
- Porcelain structure shows better cohesiveness when the glassy matrix content is high - more than 50%. The amount of relics of quartz and cullet should be limited in favour of larger quantity of the glassy phase.
- The study showed a very significant role of the homogeneity of porcelain, understood as the distribution of the crystalline phases in the glassy matrix. The phase composition and homogeneity are decisive factors which determine the resistance of the material to the aging processes, and therefore the "lifetime" of the porcelain product, unless it does not contain technological defects.

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