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STUDY OF FACTORS DETERMINANT OF SILICEOUS ELECTRICAL PORCELAIN RESISTANCE TO STRUCTURAL DEGRADATION

The subject of this study was investigation of the factors that have a decisive influence on the resistance of siliceous porcelain to degradation processes. There was tested material C 110 type, which is widely used for the production of low-voltage (LV) elements such as insulators and bushings. On the basis of mechanical-acoustic and microscopic research of small-sized samples, which were subjected to compression, there were distinguished successive stages of degradation of the material structure. In the authors' opinion, they have a reference to the ageing process, taking place during many years of work under operating conditions. Thus, it was possible to assess the structural factors that determine the durability and reliability of LV electroinsulating elements. The results were related to electrical aluminous porcelains.

Keywords: porcelain insulating materials, ageing processes, acoustic emission (AE), optical microscopy

1. Introduction

The history of porcelain produced in Europe dates back 300 years. Raw material composition of siliceous porcelain was almost unchanged until today. It includes kaolins and ball clays in amounts about 50%, nearly 25% of feldspar fluxes and similar amount of quartz filler. Occasionally several percent of cullet is also added. Such material, defined as C 110 [1], is widely used for the production of low-voltage insulators, elements for telecommunication engineering and various kinds of bushings. For this reason, material does not necessarily have excessive technical parameters. However, all the components used in power networks are expected to characterise a high level of durability and reliability.

Studies aimed to explain the strength of porcelains have been carried out since the 19th century. Excluding the impact of the defects, there were proposed three main theories [2]. The oldest is mullite hypothesis, which connects growth of the strength with increase of mullite content [3]. Realization of this concept can be recognised aluminous C 120 type material, with a high - above 30% - content of the mullite phase [4]. This is achieved by replacing quartz to alumina in the porcelain composition of raw materials. The second theory - matrix reinforcement hypothesis - the theory of structural compressive stresses in the matrix (pre-stressing effect) on the boundaries of quartz grains, despite many years of research, remains controversial. Moreover, it can refer only to the siliceous materials. The disadvantageous role of quartz in aluminous electrical porcelains was clearly confirmed [5, 6]. This work is a contribution in explaining the validity of matrix reinforcement hypothesis. The last theory, dispersion-strengthening hypothesis of the porcelain material, treated as granular composite, is commonly recognized. As a strengthening phase a fine-grained corundum (α-Al_2O_3) is commonly used. Dispersion strengthening has been successfully performed in the case of aluminous porcelain C 130 type [1]. Raw material composition of siliceous porcelain and typical aluminous C 120 type material is generally similar, but quartz is entirely replaced by metallurgical alumina. In consequence ratio Al_2O_3:SiO_2 in the composition increases to approximately 1:1. In the case of high strength C 130 type porcelain - enlarged content of alumina is applied. It is used in the raw material composition in the form of so called ceramic alumina, in place of the metallurgical one. This material has such a high resistance to ageing processes, that accuracy of the technological process is decisive for its sustainability.

In the case of different siliceous porcelains content of the mullite phase is generally constant - about 20%. There is no efficient dispersion, chemical, and fiber system of structural reinforcement as in the case of aluminous C 130 type material. The glassy matrix is reinforced neither by an increased amount of alumina in the material composition, nor by a numerous dispersed needle-shaped crystals of mullite. Taking into account controversial role of quartz, it is difficult to answer unambiguously the question regarding the factors that determine the resistance to ageing processes, that condition the operational sustainability. Limited resistance to ageing processes was established in the case of much stronger aluminous porcelain of the older generation [4-6]. Application of mechanoacoustic method made possible to determine the factors that influence the functional parameters and operational durability of C 110 type porcelain. Verification of the results was possible due to comparison with the structure images of the insulators made from siliceous porcelain, after many years of operation.

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2. Experimental procedure

Investigated samples of siliceous porcelain were subjected to mechanical-acoustic measurements, on a special two-channel measuring system, using the technique of acoustic emission (AE). Small-sized samples of porcelain were put to slowly increasing compressive stress (v ≈ 200 kPa/s), with simultaneous registration of the force in one channel, and AE descriptors in the second one. The process was stopped at different stages of the structure degradation, else was continued to the destruction of the sample. Specimens, that were not destroyed, were subjected to detailed study. Microscopic analysis of the structure allowed to study the effects of stress action. Intended for testing samples or fragments thereof were flooded in quickly gelling epoxy resin. In order to better illustrate the weak effects of degradation, there was applied resin with added fluorescent agent, visible under UV light.

During several stages polishing - in the first step - diamond suspensions of downward order of granulation were used. The final surface treatment was performed using colloidal solution of silica. Complete microscopic investigation included application of visible and UV light. Examination revealed the effects of growing structure damage and increase of cracks. On this basis there was executed explanation of the subsequent stages of the porcelain degradation.

Mechanical-acoustic and microscopic research enabled the documentation and description of the correlation between the increasing external load and the processes of structure degradation. Effects which are reflected in the AE activity. Acoustic method is in particular suitable for the investigation of the destruction of ceramic materials, due to the fact that initiation and growth of micro-cracks belong to the main sources of AE signals. Damage of the material structure is mainly connected with formation and growth of micro-cracks, that is reflected in the acoustic activity. In the consequence, the acoustic method is particularly effective for the investigation of gradual destruction of brittle materials, such as porcelains.

There was found a correlation between the rate of the increase of cracks and the rate of AE events - number of acoustic events per unit of time [7]. Hence, monitoring of the process of microstructure destruction of ceramic material under load can be realised by registration of this acoustic descriptor and the related parameters. Performed by the authors investigation of different aluminosilicate and corundum ceramic materials, confirmed these relationships [4].

Significant influence on the obtained results has the geometry of specimens. Defects can initiate growth of cracks, therefore the surface of samples must be buffed. Directly affected by compressive force top and bottom surfaces, should be plane and parallel to each other. If this condition is not satisfied enough, there can occur local fracture and splitting off the parts of the stressed sample such as corners or even the whole walls.

Analogies between the effects of long-term work under operating conditions and the compressive stresses in a relatively short lasting laboratory test were proved [4, 6]. Nevertheless, it is essential to apply a quasi-static, very slow growth of stress and – in order to distinguish successive stages of degradation - a precise registration of the AE descriptors. Studies, performed on ceramic aluminous materials, documented this observation. Very slow character of stressing much better reflects operating conditions – when ceramic element is under working load. Images of the structure of analogous materials, taken from the insulators after different periods of exploitation, were compared with the samples subjected to compressive stresses. On this basis were separated various stages of degradation of the material structure. For each of the tested materials, the first stage of investigation were ultrasonic measurements and complete description of the microstructure. It included analysis of the content, distribution and size of the particles of crystalline phases, amount of the glassy phase and characteristics of porosity in the samples. The most interesting phase in siliceous materials is always quartz.

Mechanical-acoustic tests were performed by using two-channel measuring set of a special construction. The mechanical channel contained testing machine INSTRON 3382 with computer control. The steel base, on which the sample was placed, functioned simultaneously as an acoustic waveguide. During the investigation 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 acoustic recording set contained a broad band transducer WD PAC type (pass-band 80 ÷ 1000 kHz), standardised AE analyser and a computer. One second time interval of summing up signals was applied. There were recorded rate of counts, the events rate and the energy of AE signals.

3. Investigated material and ultrasonic control

The subject of study was typical siliceous - C 110 porcelain material. The samples for investigation were cut out from domestic, unexploited low-voltage stand-insulator, produced in 2011. Therefore the set of raw materials and technological processes were common of electrical porcelain. Plastic formation of raw ceramic material and venting in extrusion press were applied. The firing process was performed in a large *Bickley* chamber furnace. The course of the technological process included:

preparation of raw material components and milling → formation of plastic mass - mixing with water → filter pressing → pug pulling - extrusion → drying → profile turing ® drying → glazing → firing (sintering) → cutting and grinding → controlling and tests → assembling.

On the basis of performed ultrasonic testing (UT), general homogeneity of the material could be estimated as satisfactory. Measurements of the acoustic properties of the tested material revealed parameters representative as in the case of insulator C 110 type porcelain [8]. Velocities of the longitudinal c_L and the transverse c_T waves, measured along the lengthwise and lateral directions of the insulator, were equal to 5880 and 5750 m/s as well as 3470 m/s and 3390 m/s respectively. Value of Young's modulus E, calculated on the basis of known dependence [9], was equal to 69 and 65 GPa in different directions, at density of the material ρ = 2.31 ± 0.01 g/cm^3. These values surpass requirements of standards for C 110 type materials - ρ at least 2.20 g/cm^3 and E as a minimum 60 GPa. The uncertainty of measurements for c_L and c_T equaled ±30 m/s, whereas for the calculated value of Young's modulus it was about ±3.0 GPa. The values of damping coefficient α, measured in different directions, showed typical – correct values about 0.6 - 0.7 dB/cm. Parameters of the material in the lengthwise direction were slightly higher. However, this kind of anisotropy is typical for the rod insulators, formed using plastic mass by extrusion. Acoustic parameters and Young's modulus of the tested material correspond to the values typical of older aluminous pocelain. This indicates a high strength parameters and low porosity of the porcelain.

Microscopic investigation of the material was performed in essence in order to recognize the amount and uniformity of distribution of the crystalline phases, glass and pores in the structure. The analysis of the insulator material revealed generally satisfying homogeneity along the length of the rod (macro-scale) as well as sufficient homogeneity in semi-macro scale. Especially the precipitates of mullite were uniformly distributed in the glassy matrix in the micro-scale. The mullite phase was present almost only in the form of precipitates. They were densely distributed and relatively small, predominantly around 10 µm. Mullite occupied 22 ± 3% and was very well associated with the glassy matrix. Precipitates did not contain peripheral or internal cracks. The dispersed single needle crystals of mullite in the glassy phase were sparse and their amount was negligible.

The content of quartz was equal to 20 ± 2%. Considering the size of quartz grains – explicitly dominated fraction of dozen or so micrometers, nevertheless a significant part constituted the relics in the range of 20 ÷ 30 µm. Figure 1 presents distribution of the quartz grains diameter. Unfavorable phenomenon was the presence of agglomerations of larger quartz grains. Additionally, a significant part of the relics exhibited disadvantageous lamellar morphology. In the structure of majority of electrical porcelains, the quartz phase is mainly responsible for internal stresses and the initiation and development of cracks. This is the basic cause of increasing ageing processes with time passing. Significant part of quartz grains contained cracks and was insufficiently associated with matrix. As a result a substantial part of relics fell out during the preparation of surface of the tested samples.

Porosity and its parameters has important influence on the strength and Young's modulus of the ceramic materials. It also indicates the correctness of technological processes, especially firing (sintering). Microscopic investigation proved that the material was very well sintered, porosity was low - about 0.5% - and its parameters were completely correct. Pores were small - usually about 3 mm - and had favourable ovoid shape. Thus, further studies made no sense.

The content of the glassy matrix was high - as compared to other electrical porcelains, even of the same class. It amounted to 55 ± 4%. A high content of the glassy phase has advantageous influence on the cohesion and bonding of all porcelain phases. The material contained small amount of cullet, originating from grinding media. Electrical siliceous porcelains are characterized by significant diversity, but the structure of the tested material can be regarded as homogeneous and representative. The phase composition was in general typical. In Fig. 2 is presented image of the material microstructure.

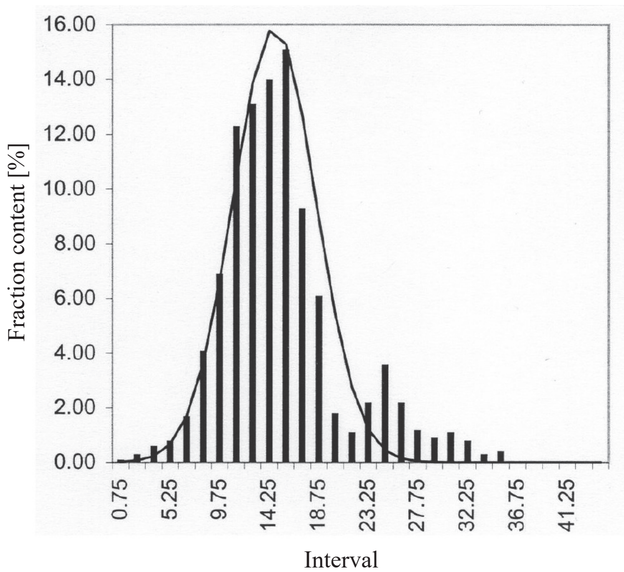

Fig. 1. The size distribution of quartz grains in the tested porcelain. The vertical axis - fraction content in percent, along the horizontal axis - an interval of particle size in microns. The distribution is dominated by two fractions - the size of a dozen or so and 20 - 30 µm. The value of the average is 14.7 µm

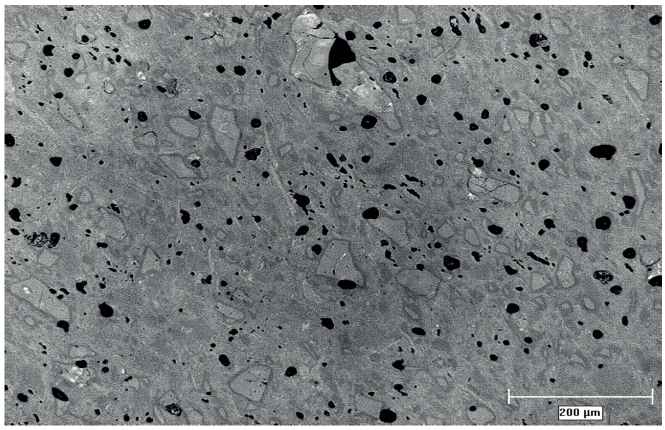

Fig. 2. Image of the microstructure of tested siliceous material, magnification 100x. There are visible brighter quartz relics and darker precipitates of mullite against the background of gray glassy matrix. Black cavities remaining after the crushed out quartz grains occupy about 6% of the surface. Pores are small - a few microns - and cover approximately 0.5%

4. Mechanoacoustic examination

The samples destined for mechanical-acoustic tests had small dimensions - 9.5x9.5x11 mm. Top and bottom areas, being affected by compressive force, were ground to plane and parallel surfaces with an accuracy of 0.1 mm. The compressive strength of the specimens, which were loaded to be destroyed, equaled: 342, 351, 360, 397 and 469 MPa. The value of the average was 384 MPa. This value was beyond expectation high, comparable with the typical strength of aluminous C 120 kind material of the traditional, older type - usually about 400 MPa (over 500 MPa in the case of modern material) [4]. The relative dispersion of compressive strength was typical - 33.1%. Part of specimens, that were not destroyed, were designed for the microscopic examination. The process of compression of these samples was stopped at stresses equal to: 60, 111, 200, 285 and 387 MPa. There were also investigated the larger pieces of destroyed specimens. The study of degradation progresses in the material were carried out in accordance with the previously described procedure.

The mechanical-acoustic characteristics of the individual samples demonstrated considerable diversity. Nonetheless, there were recognized characteristic, successive stages of degradation - the preliminary, the subcritical and the last - critical stadium. Figure 3 presents the course of the rate of AE events versus the increase of compressive stress for the weakest sample. Figure 4 represents the rate of events energy of the other specimen.

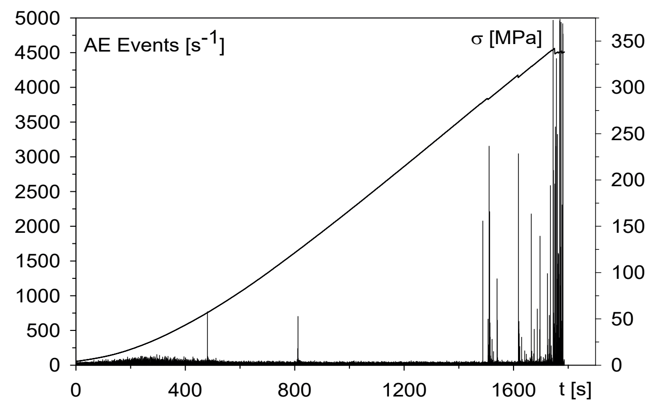

Fig. 3. Mechanoacoustic characteristics of the weakest specimen - compressive strength equal to 342 MPa. Linear scale of AE events

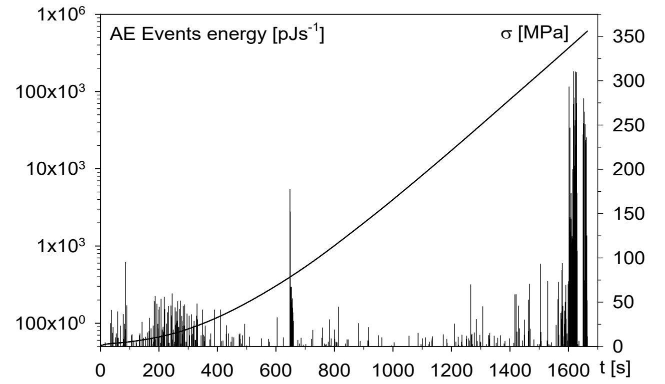

Fig. 4. The rate of events energy in one-second intervals as a function of the stress increase for the sample destroyed at 351 MPa. Logarithmic scale is used for the EA descriptor

The first, preliminary stadium of porcelain degradation is typical - intensity of AE signals is low. It occurs mainly as a result of the internal stresses, created during the manufacturing processes in the micro-scale of the material. Relaxation of these defects can occure at a relatively low energy threshold. Even small compressive stresses, that act on the sample, can cause increase of already existing microcracks and rise of a new ones. Such effects in operation – under working load are slow and take years. The preliminary stage of degradation of siliceous porcelain samples takes place up to 60 ÷ 100 MPa for various specimens. The microscopic examination proved that there occured degradation of important share of quartz. Cracking and crushing out of quartz grains was the source of AE signals. This effect referred particularly to the small grains - of the size of several microns. Susceptible to degradation were the grains with a lamellar morphology. The most resistant to failure and separation from the matrix were the grains of an middling size between 20 and 30 mm, distinguished by the regular shape and typical morphology. Besides quartz, there occured crushing out of almost all particles of cullet. Mullite precipitates were not affected by degradation. They had a coherent structure and were well combined with the glass matrix. Damaged and crushed out elements of the structure covered over 10% of the area of tested surfaces of the stressed samples. In figure 5 is presented material of the sample loaded up to 60 MPa.

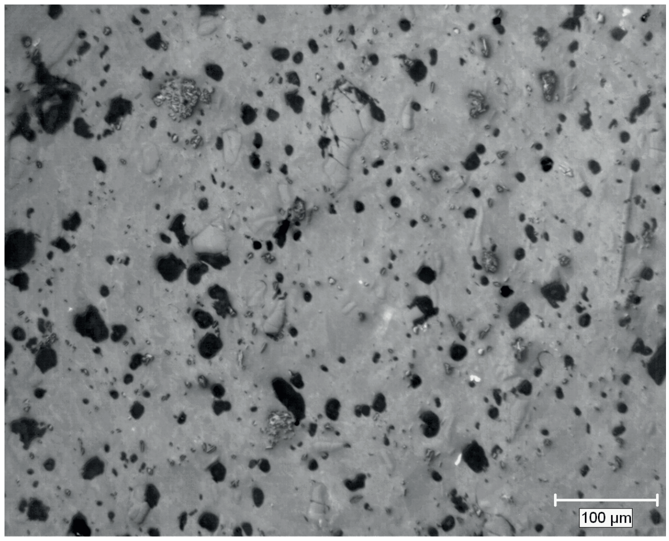

Fig. 5. The structure of siliceous material loaded up to the preliminary stage of degradation, magnification 200x. Numerous damages and crushed out grains of quartz are visible. Dark cavities cover about 10% of the surface

The next, subcritical stadium of the structure degradation is closely connected with the homogeneity of the sample structure in micro and semi-macro scales. This stage takes the longest, goes after the preliminary period and lasts to the start of the critical stadium. Subcritical stage of destruction demonstrates in general low acoustic activity. The stronger signals are sparse - Fig. 3 and 4 - and are connected with the greater cracks, generated during splitting off the walls, their fragments or the corners from the specimens.

Image analysis of the samples loaded up to 285 MPa and 387 MPa showed that further, relatively small degradation - in a wide range of stress - undergoes only the quartz phase. Circumferential and internal cracks are generated and increase in the grains. Thorough examination, using UV light, proved that in the material structure occur centres of cracks. These are the regions of loosened structure - the agglomerations of the larger grains of quartz, which crack with increasing stress and are being separated from the glassy phase. The cracks that can propagate into the matrix are initiated in these regions. These cracks, growing gradually in the matrix, are one of the most important factors in the process of degradation. Their rapid rise takes place during the critical stadium and leads to the sample destruction. Figure 6 presents the area of loose structure - the center of large cracks in the material of the sample, loaded up to 387 MPa.

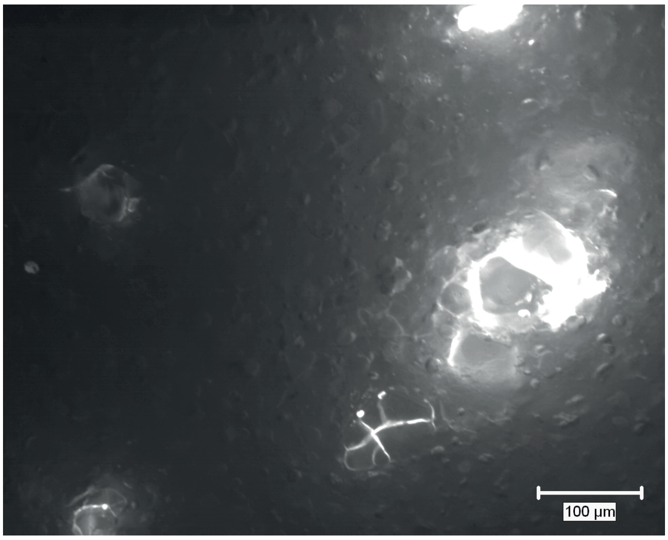

Fig. 6. Microscopic image of the material of the sample loaded up to 387 MPa, in UV light, at a magnification of 200 times. There is visible the area of loose structure - a cluster of large grains of quartz and distinctive grain cracking. Resin with addition of a UV fluorescent was used

The preliminary stadium of degradation was connected mostly with the effect of small quartz grains damage. During the next - subcritical stage was visible harmful influence of the clusters of bigger quartz grains - of several tens of microns. Destroyed and crushed out components of the structure in the advanced subcritical stage comprised about a dozen percent. The strongest constituent - the mullite phase remained without any damage. Figure 7 presents central part of the sample that was stressed up to 285 MPa. Advancement of degradation processes in its structure can be specified as average. There should be emphasized that these effects are limited only to the quartz phase and not numerous particles of cullet.

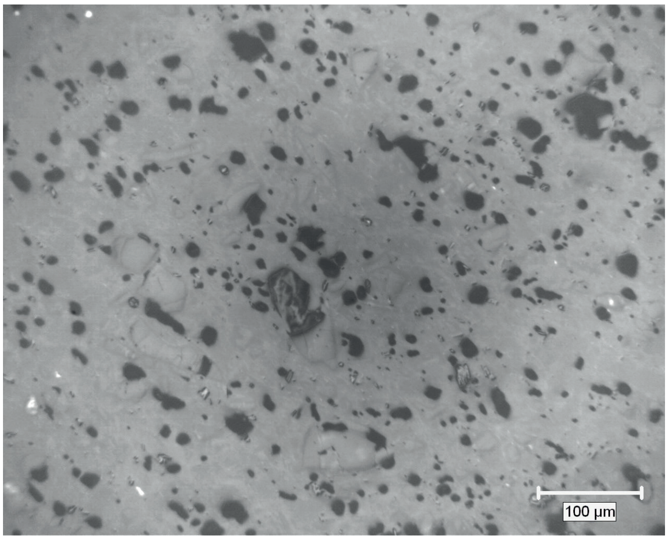

Fig. 7. Microstructure of the sample stressed up to 285 MPa, at a magnification of 200 times. Dark areas representing cracked and crushed out grains of quartz and their fragments as well as cullet fragments comprise above 11%. The mullite phase and the glassy matrix remain unaffected

Sometimes, during the subcritical stage, a local fracture and splitting off the corners or even the whole wall of the stressed sample can occur. This effect is followed by strong AE signals, and is visible on the stress increase curves as a characteristic faults (leaps) – Fig. 3. In the vicinity of the broken off portion are then shaped large cracks. However they are typical for the critical stadium of degradation. Figure 8 shows a marginal area of the sample, loaded up to 285 MPa, in the area adjacent to the separated portion of the wall. Visible large cracks are not characteristic effect of the subcritical stage. There is also evident the typical area of loose structure.

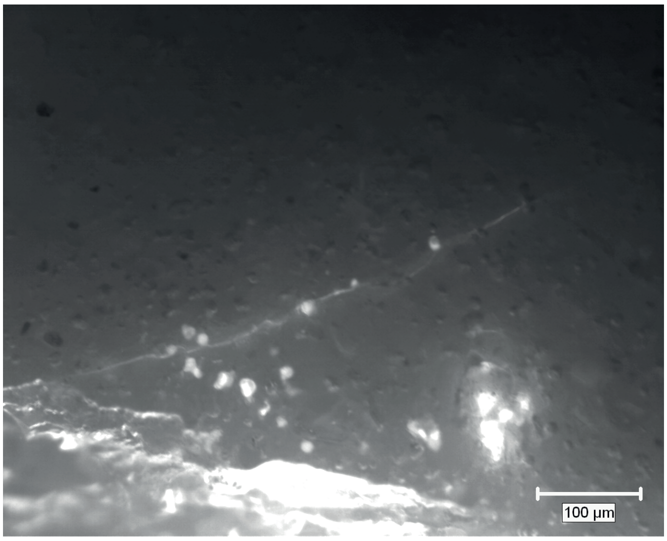

Fig. 8. Microscopic UV light picture of the material of the sample loaded up to 285 MPa, at a magnification of 200 times. The area in the immediate vicinity of the broken off fragment is visible. In addition to cracking, takes notice characteristic area of loose structure at the bottom right of the image. It is clearly visible due to applied resin with added fluorescent agent, visible under UV light

The last - critical stadium was connected with strong acoustic activity. Throughout the whole stage occured, usually with short breaks, strong AE signals. The final effects of degradation concerned scope of stress of tens of megapascals and took place till the destruction of the sample. There happened a splitting off the greater fragments of the stressed specimens, visible in the stress increase curves – faults in Fig. 3. To recognize the effects of the degradation of the structure were used microscopic examination of the sample, the load on which at 387 MPa was quenched - at an earlier phase of the critical stage. Further information was obtained from studies of the larger fragments of the strongest specimen, which was destroyed at 469 MPa. It was found that the regions of loose structure, that include agglomerations of the bigger quartz grains were the main source of big cracks, which grow in the material matrix. The basis of the process of critical degradation of the structure was quite prolonged development of the large cracks and creation of the whole fragments of the fractured material, that can be easily broken off.

Quite numerous precipitates of mullite - the strongest phase of silicious porcelain - had small size and very well combined with the glassy matrix. In consequence they did not undergo degradation even during the critical stresses. They efficiently strengthened the structure causing the deflection and crack growth inhibition. Cracked quartz grains and crumbled elements of the structure facilitate cracks propagation. The porcelain matrix was separated from almost all cullet particles, and about half of the quartz phase (~9%), especially particles of lamellar morphology and small size. During the critical stage, area of damaged, separated and crushed out elements of the structure comprised over dozen percent of the observed surfaces. Nevertheless, the most destructive and essential process, being the source of the strong AE signals, was formation and growth of big cracks in the porcelain matrix, facilitated by previously destroyed components of the structure.

In the case of the sample with the highest strength (469 MPa), the agglomerations of the larger grains of quartz, forming a loose structure centers, occurred very rarely. The homogeneity of the material, observed in micro and semi-macro scales, was high. Therefore, the mullite phase distribution was the most advantageous, although very small number of individual crystals of mullite in the glassy matrix – typical for such type materials. This structure showed high resistance to compressive stress, even higher than in the case of the typical strength of aluminous C 120 kind material of the traditional, older type - generally about 400 MPa (in the case of modern material - over 500 MPa) [4]. Figure 9 shows the highly cracked microstructure of the fraction of the strongest sample. Beside the distinctive macro-cracks, plurality of the parallel cracks of the matrix are visible. Characteristic course of the cracking is a reflection of the loading direction.

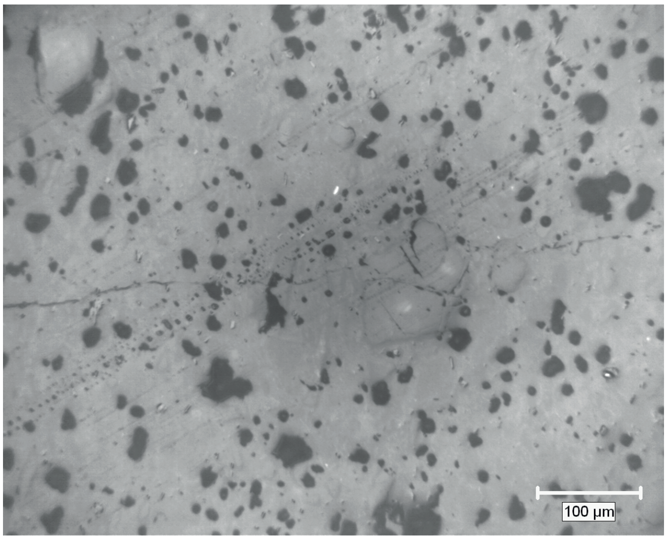

Fig. 9. Heavily fractured microstructure of the strongest sample fraction, at a magnification of 200 times. Separated and crushed out elements of the structure comprise about dozen percent of the surface

Mechanoacoustic research proved quite good resistance of the tested siliceous porcelain to the degradation processes. The destruction occurred at a relatively high values of the stress, after the long stages of the structure degradation. A very important role played homogeneous distribution of the phases in the semi-macro and micro-scale. The matrix turned out to be fairly resistant to the development of cracks formed inside and on the boundaries of quartz grains. Its serious degradation took place only during the critical stage. The mullite phase, in the form of small precipitates, effectively reinforced the glassy matrix. Both these phases - mullite and glass - accounted together nearly 80% of the material, and they determined its mechanical properties. It should be emphasized significantly higher strength of mullite as compared to the glassy matrix and lack of the effects of the mullite precipitates degradation in the compressed samples. Agglomerations of large grains of quartz, forming area of loose structure and in consequence centres of cracks, proved to be the most harmful inhomogeneity, able to restrict the strength of the samples.

Insulators, made of siliceous porcelain, after a long period of operation, were frequently investigated. The most common aim of these studies was to determine causes of failure and to assess the state of their material [8]. In this connection microscopic examinations of the taken samples were carried out and the effects of degradation were evaluated. There was possible to recognise ageing advancement of different phases and to find their connection with conescutive stages of degradation observed during mechanical-acoustic research. Close analogies were found. Long-term degradation - caused by internal stresses, operating loads and devitrification effect - related mainly to the damage of the quartz phase. There were observed numerous cracks at the boundaries and inside the quartz grains. Such effects mostly referred to the preliminary and subcritical stages, documented as a result of laboratory tests. There were recognised many damaged elements of the structure and crushed out during surface preparation. This fenomenon concerned particularly small grains of quartz - of size below 10 mm. But also big quartz grains contained internal fractures and cracks at the boundaries. Their fragments could undergo crushing out as well. Furthermore, particles of cullet were separated from the glassy matrix and crushed out, if only cullet was used in the material composition. Advanced stages of the insulator material degradation were followed by cracks in the glassy matrix. However, the nature, length and quantity of these cracks were diverse. Damaged and cracked components of the structure made propagation of cracks in the matrix easier. Longer, critical cracks which are visible in the structure of broken insulators are like fractures observable in Fig 9. Such cracks can propagate right across all constituents of porcelain structure at great speed.

However, it should be emphasized that mullite, the strongest phase of siliceous porcelain, effectively reinforces the material. Its precipitates are well bonded with the glassy matrix. In consequence, degradation effects were not observed within and at the boundaries of the mullite precipitates. Nevertheless, quartz grains immediately adjacent to the mullite phase are more susceptible to separation than when they are surrounded only by the glassy matrix – binder of porcelain structure.

Figure 10 presents advanced ageing processes in domestic siliceous material of the LV stand-insulator after over twenty years of exploitation. About 1/3 of initial amount of quartz phase (29 – 32%) were damaged and underwent crushing out during surface preparation. Remaining grains contained microcracks, especially peripheral. Structural integrity were much weakened and there were found elongated, nearly critical cracks propagating throughout all phases of the material and only deviated by precipitates of mullite.

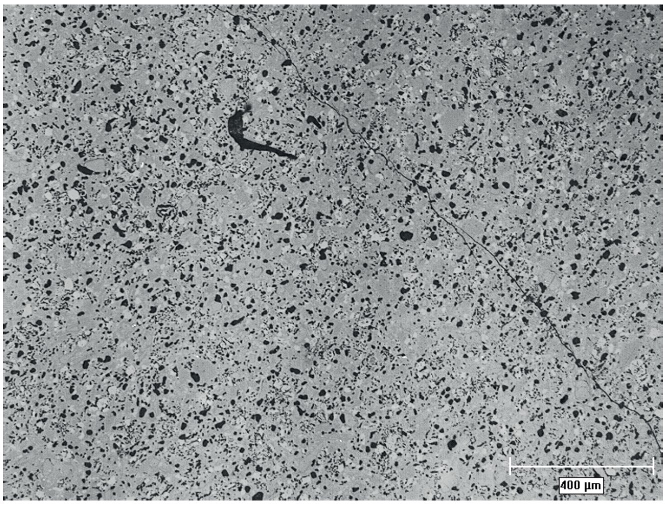

Fig. 10. The image of siliceous porcelain of LV stand-insulator after over 20 years operation period, at a magnification of 50x. Extended crack aswell as black slit, elongated in a direction parallel to the axis of the insulator, are visible. There are a lot of micro-cracks within and at the boundaries of the quartz grains. Black areas that remained after crushed out grains of quartz and cullet fragments cover about 10%

Insulators made of aluminous material C 120 type were studied for many years. This kind of electrical porcelain was widely used in production of a variety of insulators for decades. The course and effects of degradation of typical C 120 material were accurately recognised [4, 6]. Using mechanical-acoustic and microscopic research there were distinguished three successive stages of such aluminous material degradation. The process was in general similar as in the case of siliceous porcelain.

The first - preliminary - stage of the material degradation occurs as a result of the internal stresses, created during the manufacturing processes and existing mainly in the micro-scale. The propagation of microcracks under operating conditions is slow and takes years. The first stage reflects actually only degradation of the quartz phase and it refers mainly to the interphase boundaries. The mullite precipitates remain without any damage. As in the case of siliceous materials they significantly increase the mechanical strength of the porcelain structure.

The second stage of degradation corresponds to the long lasting development of subcritical defects in insulators in service conditions. The growth of microcracks is hindered and the latter branch out on the intergranular and phase boundaries. The microcracks, initiated at the borders of quartz grains, are propagated in the glassy matrix of the porcelain. This effect is simplified by quite frequent, cracked quartz grains. The subcritical stage is closely connected with homogeneity of the sample structure in micro and semi-macro scales. Both stadia are strongly influenced by the contents, size and spatial distribution of the quartz grains and - to a lesser extent - by the mullite precipitates. The decohesion process is inhibited, especially by the mullite phase. In order to cross each inter-phase boundary an appropriate amount of energy is needed.

During the last – critical stadium cracks start propagating rapidly. The single cracks grow, can branch out and join together, even forming a network of cracks. In consequence it can lead to breakage of the insulator or the tested sample disintegration. In figure 11 is presented typical image of aged aluminous material of domestic line insulator after about 30 years operation period. Advanced degradation processes are visible. They are a consequence of high and diversified amount of the quartz phase in the material structure - initial average content 24%. This phase was the main source of internal stresses, initiation and growth of micro-cracks.

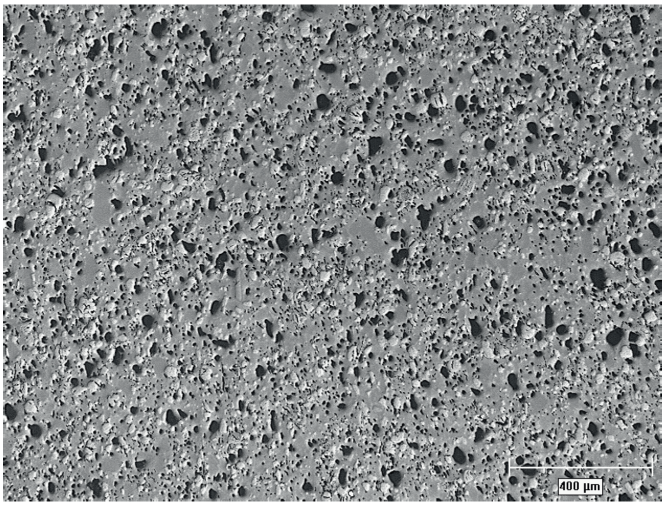

Fig. 11. The image of C 120 type porcelain of HV line insulator after about 30 years operation period, at a magnification of 50x. The effects of the degradation of the structure appropriate to the subcritical stage, with a high degree of advancement. Over 1/3 of the quartz grains (nearly 9%) was separated and crushed out from the structure. In the vicinity of the relics of quartz are present numerous micro-cracks in the glassy matrix

In the case of modern aluminous porcelains, such as reinforced materials of C 120 type and porcelains of high strength C 130 type, an increased content of alumina is applied. This constituent is added to the raw material composition in the special form of ceramic alumina. As a result the structural features of porcelain are changed. The most important effect is occurrence of fine corundum grains in the structure - usually in the amount of dozen or so percent. The next consequence is increased ratio Al_2O_3:SiO_2 in the chemical composition of the glassy phase. Accordingly significant raise of the strength of glassy phase takes place. Another important effect is occurrence of dispersed needle-like mullite crystals in the material matrix. The most important effect of modification of porcelain structure is that its reinforced matrix reveals higher strength than the mullite precipitates. The material has higher mechanical strength and is much more resistant to degradation processes. Ageing process runs in a different way than in the case of the conventional porcelain materials. Although degradation also occurs in three stages, observed effects of the structure damage are different in nature. This problem was recognised and widely documented [4].

5. Conclusions

Siliceous porcelain structure degradation occurs in the conventional - a three-step way. Destruction processes relate mainly to the quartz phase, which plays an important role in

C 110 type materials. In the porcelain structure were found the regions of loose structure, that include agglomerations of the bigger quartz grains. As it was observed, they were the main source of big cracks, which can propagate deeper into glassy material matrix. Critical degradation of the structure was connected with development of the large cracks and creation of the whole fragments of the fractured material.

Hence, the investigation proved crucial role of the homogeneity of the material structure alike in micro, semi-macro and macro scales. This concerns in particular the distribution of the crystalline phases in the glassy matrix of the porcelain. The phase composition and homogeneity are decisive factors which determine the resistance of the material to the aging processes, and in consequence operational durability of the insulator. Assuminng it does not contain technological flaw.

Desirable size of quartz grains is about 20 ÷ 30 μm. Small grains (below 10 μm) and the large ones can act in detrimental manner, which is in accordance with literature data [2, 5]. The most inexpedient are agglomerations of large quartz grains. Matrix reinforcement hypothesis can be valid only in the case of optimal size of quartz grains and when they have favourable ovoid shape as well as the normal morphology. Further important condition is high amount of the glassy phase, surrounding grains of quartz. Generally, the contents of quartz relics and cullet should be limited in favour of larger amount of the glassy matrix, as the material binder (at least 50%).

In the case of siliceous porcelain mullite phase is the strongest and the most resistant to degradation processes. In consideration of the absence of dispersion or fibrous strengthening of the structure, mullite is only one reinforcement. Precipitates of mullite are strongly bound with the matrix and the better strengthen the structure, the more homogeneously are spatially distributed. The most efficiently act small precipitates - about 10 μm, evenly spread in porcelain structure. Amount of mullite in different siliceous porcelains is commonly constant - about 20%. However, single needle-shaped mullite crystals, dispersed in the glassy matrix, are only few. They can not play role as reinforcement of the structure.

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