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MICROSTRUCTURE AND DEGREE OF DEGRADATION OF ZnO VARISTORS IN SURGE ARRESTERS DUE TO OPERATION

The paper presents the test results for the microstructure of ZnO varistors comprising high voltage gapless surge arresters. The tests were performed on varistors produced in different periods and by various manufacturers. The research was inspired by different characteristics of changes in values of current flowing through surge arresters as a function of changes in values of system voltage in a 220 kV substation, and the temperature in a multi-year cycle. Furthermore, the effects of varistor microstructure degradation following a failure of an unsealed surge arrester were investigated. The results provided the grounds for assessment of ZnO varistor microstructure parameters in terms of their durability and resistance to degradation processes.

Keywords: surge arrester, MO varistor, microstructure of ceramics, ceramic material degradation

1. Introduction

ZnO varistors restrict over voltage by conducting current caused by voltage exceeding a threshold voltage value – characteristic of a respective varistor used to protect a specific facility or system. Due to the resistance which lowers exponentially with an increase of voltage, ZnO varistors are suitable for restricting the magnitude of overvoltage – and thus, for surge protection in systems and equipment operated in a very wide voltage range – from a few volts to hundreds of kilovolts. Varistors are distinguished by a relatively simple and inexpensive production process which has been improved and perfected for approximately 40 years. The process consists in grinding, mixing and granulating of raw materials – more than 90% of which is ZnO – using the spray granulation method, and then pressing and firing to sinter ceramic material. Varistor contacts are ground and metalized, and a protective coat is applied on their cylindrical side surfaces. The quantity and homogeneous distribution of doping metal oxides (mainly Bi_2O_3) and maintenance of a required technological regime during the production have a decisive influence on the electrical and mechanical properties of varistors [1].

The zinc oxide is a semiconductor with a wide forbidden band, whereas its grains ranging from several to more than 20 μm resemble irregular polyhedrons. ZnO belongs to non-stoichiometric compounds, and, in principle, contains a minor excess (expressed in ppm) of zinc cations in interstitial positions. The intergranular boundaries and atomic layers that are present play a decisive role for the properties of ZnO varistors. The grain interior is a good conductor, whereas an area of high resistance occurs on grain boundaries due to the electrostatic electric-potential barrier. A few percent of selected doping elements such as Bi, Sb, Cr, Co, Ni or Mn, added in the form of oxides in a suitable production process, has a significant influence on heavily resistive properties of the intergranular boundaries and the conductance of ZnO grains. The homogeneous distribution of doping oxides has a decisive role, which is very difficult to obtain with such a small content thereof. Furthermore, ZnO grains should provide a very narrow grain size distribution. A thin boundary layer between grains with a thickness of approx. 1 nm contains an amorphous phase of Bi_2O_3-ZnO. An excess layer of oxygen occurs therein and a negative electric charge is trapped. The electrostatic electric-potential barrier is formed. For a single intergranular boundary, the limit voltage value is 3.2÷3.4 V [1,2]. With the limit voltage value, the electric field may even reach the value of 1 MV/cm on the boundary layer of a properly doped grain of ZnO. This results in the formation of "hot electrons", which produce holes – tunnels in the valence band due to impact ionization, since their energy is greater than ZnO voids (approx. 3.2 eV). As a result, the electric-potential barrier is suddenly decreased [3]. The complete transition from an isolating to a conducting condition occurs, which is an essential feature of a resistor with a heavily non-linear voltage relation. Such transition occurs in an extremely short period of time (expressed in pico – nanoseconds) and is almost entirely reversible. The current passage is immediately stopped following a voltage drop below a threshold value.

However, varistors, especially the older ones, are subject to ageing and degradation. An increase of conduction losses

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– an increase in conduction current within parts of the characteristics with low current values (densities), may be taken as an example. A series of pulses with a high amplitude and/or with longer duration results in changes in the voltage-current characteristic within the scope of low current values. The flow of surges with a specific polarity results in the constant current voltage-current characteristic ceasing to be symmetrical with changes in polarity [4].

Bearing in mind the possible differences in microstructure and ageing processes occurring within varistors, the varistors obtained from the surge arresters of a number of selected manufacturers were tested. The microstructure of varistors from a surge arrester which had failed due to an unsealed casing was also examined. The results presented herein are a continuation of research on varistor surfaces and spacing-centring elements in damaged surge arresters [5].

2. Subject and methodology of tests

The comparison tests were performed on two randomly selected ZnO varistors comprising a stack of varistors in a single type of surge arresters, i.e. GXAS 96 for 110 kV networks installed in feeder bays. The first of them was manufactured in the USSR in the years 1980÷1990. It comes from the oldest series of ZnO varistors that were operated in Poland. The second was manufactured by ZWAR Przasnysz in the years 2003÷2007. Both tested varistors came from surge arresters in stock and have not been operated.

In addition to the varistors from older surge arresters, a Japanese medium voltage stock varistor (MV) from 2010 was also tested. Another varistor selected for testing came from a high voltage (HV) 220 kV surge arrester of a renowned manufacturer and was manufactured in 2013. It failed in 2016 following about six months of operation. The failure involved a fire caused by fault current. As a result of combined electric, thermal and mechanical stress, a group of varistors became cracked in the stack of this surge arrester. One of the varistors damaged was examined in three areas – at the location of strong structural damage, at a short distance from the damaged location, and where the microstructure was almost completely intact.

A microscope equipped with a computer image analyzer from CLEMEX was used in the tests performed using the optical microscopy method (OM). A camera lens with the focal power of 20× was used, which corresponds to the optical resolution of 0.1 μm. In order to minimize the influence of preparations for tests on the condition of the microstructure, only polishing was used during the preparation of the microsections, without grinding. Diamond abrasive slurry with the grain size of approximately 0.5 μm was used followed by a silica gel for the purpose of final surface preparation. A layer with the thickness between 30 and 50 μm was removed depending on the material properties. The visual inspection was performed under magnification from 20 to 500 times. The Nomarski phase-interference contrast was used most frequently, which allows for a good distinction of phases forming the material, and also of structure element chipping and pores [6]. However, the boundaries of individual ZnO grains remain less visible.

The varistor materials tested show a typical structure of multi-phase ceramic materials. Large grains are often surrounded by groups of smaller grains with worse cohesion. This results in deformation in areas with a grain geometry similar to polishing agent particles during grinding and polishing using abrasive slurries with a grain size similar to the base grains. In optical microscopy with a relatively small depth of focus – in comparison with SEM, for instance – areas of fine-grained ceramic structure pitted and deformed by polishing always have a darker form and in fact were not chipped off [6]. It should be noted that, depending on the spatial orientation of boundaries, the pits in the top layer of a produced microsection and the illumination, the grains show different shades of grey. In consequence, many dark areas in images of microsections do not reflect chipping, but pitted areas and grains or groups thereof with a diverse spatial orientation present in the structure.

ZnO grain size and homogeneous distribution of precipitatations of Bi_2O_3 phase were tested using the optical microscopy method. The solidity and degree of sintering of the body, integration of grains and their resistance to chipping off during the performance of surface microsection were evaluated. The examination included the quantity, size and distribution of chipped off elements and pores as well as their variation in different areas of samples. The thickness of the aluminium coated contact layer and the microhardness of materials were measured. A multi-purpose Dura Scan type microhardness tester from Struers was used for that purpose, with a 100 g indenter. A mean value from ten measurements performed and the standard deviation were calculated to provide a good measure of homogeneity of varistor materials.

3. Field test results

Figure 1 shows the parameter measurement results for the mean value of leakage current in gapless surge arresters installed in outdoor feeder bay of a 220 kV substation, in a multi-year cycle. The variability of mean values of current being recorded was considered depending on the temperature and supply voltage. Measured values of such current were within the range of permissible values in the accepted patent application [7]. However, differences in current values were found in two-week measurement cycles. The differences occurred between characteristics of the surge arrester installed in phase T and surge arresters installed in phases R and S. At the same time, greater differences in current were not found between surge arresters in phases R and S. Their characteristics were almost identical. It followed from the information obtained from the surge arrester manufacturer that varistors used for the construction of stacks for phases R and S came from a different production lot than the varistors in the stack for phase T. The differences concerned minor changes in raw materials composition, while maintaining the same production process.

Varistors in the surge arresters tested are sensitive to temperature variations. On the other hand, changes in the supply voltage do not have a significant influence on the current characteristics for medium current. Similar discrepancies in the characteristics were found for the maximum and harmonic current in the paper [7]. The phenomena and differences found in the current values under operating conditions became an inspiration to undertake more detailed research consisting of the identification and documentation of varistor microstructure parameters.

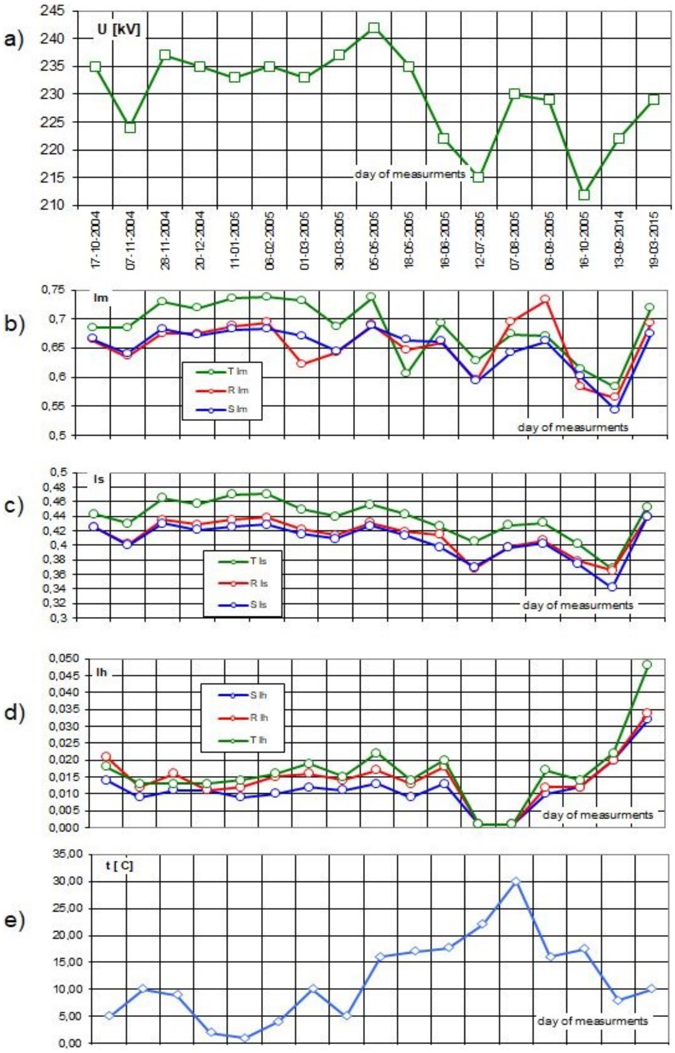

Fig. 1. Leakage current measurements results for gapless surge arresters installed in overhead 220 kV feeder bay, a) power network voltage of 220 kV when measuring current, b) I_m, c) I_s, d) I_h, e) the ambient temperature when measuring current

4. Testing varistors from older surge arresters

The first and oldest of the varistors tested came from a gapless surge arrester manufactured in USSR in the 1980s. Figure 2 shows a typical image of the microstructure of a Russian-made varistor magnified 500 times. A grainy structure of the material is visible. ZnO grains are frequently within a few to a dozen or so micrometres and clearly differ in size. Their typical size is approximately 10 μm. Some grains have peripheral cracks and in general are less integrated than in the material of the remaining varistors being tested. A smaller quantity of light Bi_2O_3 oxide occurs in addition to the primary phase of ZnO. The contents of this phase are a few percent. Nevertheless, its quantity varies in different areas being observed. Light precipitatations of the doping oxide are usually from a few to a dozen or so micrometres in size. Some of them have peripheral cracks and are less integrated with the grains of the primary phase. This is also evident in a greater number of light-phase grains present, especially with greater sizes, in areas of more chipping. It should be noted that dopants of other oxides also occur on the boundaries of ZnO grains and on their edges, in triple spots affecting the material properties. Homogeneity of the material – both in the micro- and semi-macro scale – is insufficient. Significant differences in the contents of doping precipitatations, pores and chipping in structure elements were found in individual areas under observation. The material solidity should be assessed as unsatisfactory, which was heavily influenced by the raw mass homogenizing process as well as agglomeration parameters and the grain recrystallization effect.

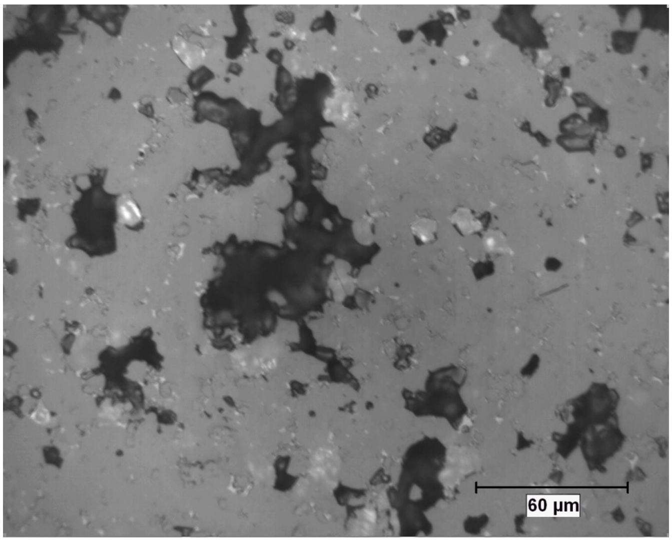

Fig. 2. An image of material microstructure in the varistor manufactured in USSR. Light precipitatations of Bi_2O_3 doping oxide, black pores with a regular shape and dark areas with chipped off or loosened structure elements of a diverse, usually irregular shape are visible

Dark pores with a correct size and oval shape are distributed quite heterogeneously. Their contents measured in 10 measuring points vary from 1.5% to 4.6% of the microsection surface. The mean value is 2.9%. Dark areas of chipping in structure elements (often partial) have an irregular shape and most frequently cover a few ZnO grains. Their size is strongly diversified, in general reaching a few dozen micrometres. Chipped off and heavily loosened elements of the structure constituted between 12.8% and 21.3% of the microsection surface. The mean value was 17.2%. The test results show poor homogeneity of the body and its unsatisfactory cohesion.

The second tested object was a domestic varistor, manufactured around the year 2000. Figure 3 shows a typical image of the microstructure of a domestic varistor magnified 500 times. A grainy structure of the material is visible; however the size of ZnO grains is within 10 µm, and most frequently reaches approximately 4-5 µm. A small quantity of the light Bi_2O_3 phase also appears nearby the primary ZnO phase. The contents of this phase do not exceed 1%, whereas the size of its precipitatations is most frequently a few micrometres. The material structure – both in the micro- and semi-macro scale – can be described as quite homogeneous and solid, considering a moderate quantity of chipped off or strongly loosened elements of the body. Hence, the degree of material agglomeration can be deemed as correct.

Fine, black pores with a correct oval shape are distributed homogeneously. Their contents measured in 10 measuring points vary from 0.5% to 1.0% of the microsection surface with the mean value of 0.7%. In general, the size of pores remains at a level from fractions to single micrometres. Dark areas of chipping or heavy loosening of structure elements – very visible in Figure 2 – have a polyhedral shape and usually cover a few ZnO grains. Their size is diversified and remains from a few to 30 µm at the most. The measurement of the quantity of dark areas performed for 10 measuring areas showed a similar content thereof – at the level of 10.5 ±1.0% of the microsection surface. This confirms very good homogeneity of the body and its satisfactory cohesion.

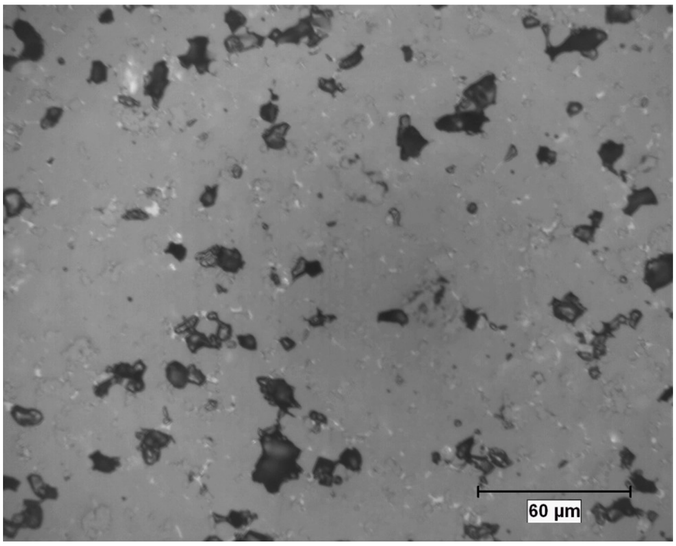

Fig. 3. A typical image of material microstructure in the domestic varistor. Quite homogeneous distribution of fine precipitatations of the light Bi_2O_3 doping phase, small dark pores with an irregular shape and dark areas with chipped off or loosened structure of a diverse size and shape are visible

Microhardness tests confirm this opinion. The mean values of ten measurements performed showed significant differences between the varistors being tested. The domestic varistor shows the hardness of HV1 = 48.7 ±2.4, whereas the USSR-made varistor reaches HV1 = 39.8 ±9.1. Differences in the microhardness indicate a considerably better solidity of the structure of the Polish varistor, but also good homogeneity shown in a small standard deviation of the mean value. The structure of the Russian-made varistor not only had an effect on a lower hardness but also on a significant spread of the measurement results. This indicates a much lower homogeneity of the Russian-made varistor structure. It should be noted that it was manufactured approximately 20 years earlier, and the manufacturing process might have been significantly modified. It is worth noting that the material of both varistors differs in terms of chemical composition – various quantities and proportions of doping phases were used.

5. Testing varistors from newer surge arresters

As expected, the varistor from the medium voltage surge arrester manufactured in Japan in 2010 was distinguished by more a homogeneous and solid microstructure than the two older varistors tested previously. Figure 4 shows a typical image of the microstructure of a Japanese varistor magnified 500 times. The fine-grained structure of the material is a notable feature. The size of ZnO grains does not exceed 5 µm and most frequently reaches approximately 2 µm. The microstructure observed shows high cohesion. Chippings – visible as black areas – are between a few to a dozen or so micrometres in size. They usually cover a few grains and constitute between 0.8 and 1.5% of the surface in the examined fields of observation. Their average quantity is, therefore, very low and constitutes only 1.1% at homogeneous distribution, which proves the material homogeneity well. Fine, black pores are of correct, oval shape and appear in a very small quantity of 0.1%. They are uniformly distributed and their size remains at a level from fractions to single micrometres.

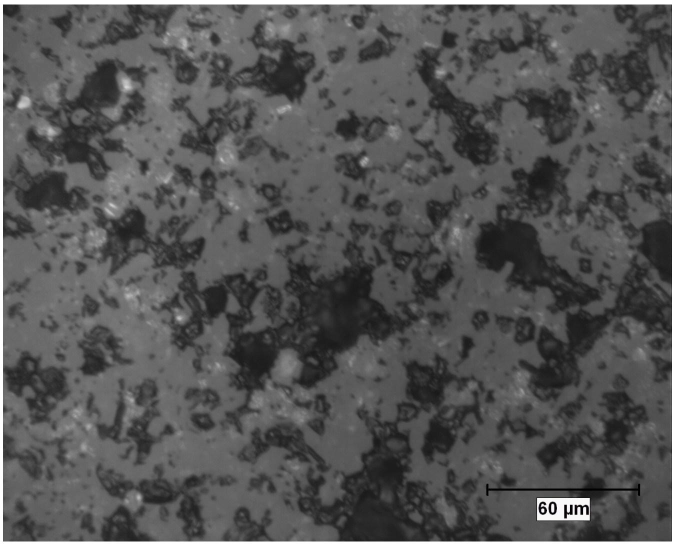

Fig. 4. A typical image of material microstructure in the varistor manufactured in Japan. A homogeneous fine-grained structure and uniform distribution of grains in the light Bi_2O_3 doping phase can be observed. Darker areas show pitted groups of grains with diverse packing. Black chipping and pores are sparse

A small quantity of the light Bi_2O_3 phase also appears nearby ZnO grains. The content of bismuth oxide – which shows high, but homogeneous scattering – is difficult to accurately determine. Its contents range from 1 to 2% in various fields of observation. The size of visible Bi_2O_3 precipitatations is very close to ZnO – below 5 μm.

Furthermore, fine light spinel grains $ZnCr_2O_4$ ($ZnO \cdot Cr_2O_3$) of a polyhedral or longitudinal shape are hardly visible in special illumination. Their content is lower than of Bi_2O_3 and they also occur with high scattering. It should be noted that dopants of other oxides are essentially not visible in the microsections. In particular, they appear in the so-called triple points, on the boundaries of ZnO grains and they considerably modify the properties – especially electrical properties – of intergranular boundaries. Both in the micro- and semi-macro scale, the material structure can be assessed as solid and homogeneous, whereas the degree of material agglomeration is entirely correct.

Microhardness tests of materials in the Japanese varistor confirmed the high grade of homogeneity and the cohesion of the body. The mean value of ten measurements performed was HV1 = 195.5 ±1.8. The material is distinguished by a high hardness, whereas a very low value of standard deviation confirms excellent homogeneity of the varistor material.

Another varistor examined came from a high voltage (HV) 220 kV surge arrester of a renowned manufacturer, and was manufactured in 2013. It failed in 2016 following a relatively short period of operation. As already mentioned, a fire broke out due to the fault current flow. The resulting electrical, thermal and mechanical stress caused the cracking of a large number of varistors – Figure 5. One of the varistors damaged was examined within three areas – at the location of strong structural damage, at a short distance from the damage location, and where the microstructure was almost completely intact.

Fig. 5. Fastening elements and damaged varistors following the unsealing, breakdown and fire of an HV surge arrester

Figure 6 shows the fine-grained microstructure of the material within the area farthest away from the breakdown location. The effects of stresses are not visible. The size of ZnO grains is approximately 5 μm. The chipping and areas with a loosened structure, visible as dark areas, are quite scarce – they constitute between 3 and 9% (6.5% on average) of the microsection surface. In general, their size does not exceed 10 μm. Small black pores are of a correct size – from fractions to single micrometres – and have an oval shape. They occupy 0.2% of the microsection surface. The distribution of chipping and pores is homogeneous, whereas their size remains at a correct level. This well proves the general homogeneity of the material, which seems to be only slightly lower than in case of the material of the Japanese varistor.

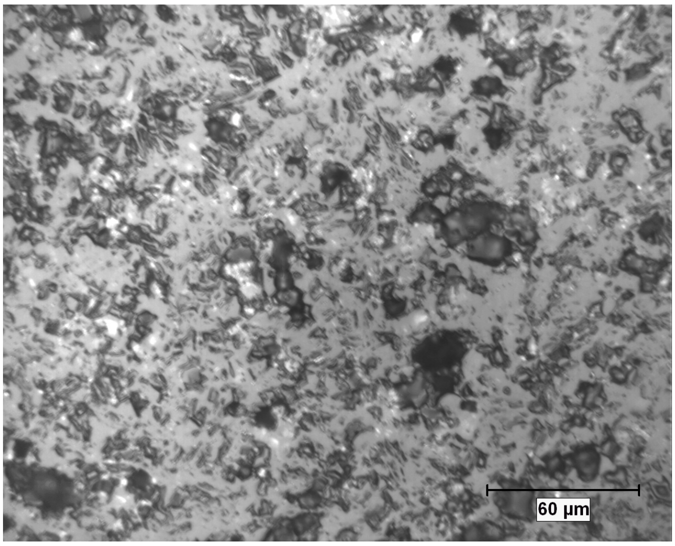

Fig. 6. An image of material microstructure in the damaged HV varistor. An area at a great distance from the breakdown location. The fine-grained microstructure is homogeneous, light grains of the doping phase are uniformly distributed. Darker areas show pitted grains or groups thereof with diverse packing. Black chipping and pores are sparse

A small quantity of the light Bi_2O_3 phase also appears nearby the primary ZnO phase. Bismuth oxide is heavily scattered. Visible precipitatations constitute only a fraction of a percent of the surface, whereas their size is very close to that of ZnO grains and amounts to a few micrometres. Small light spinel grains of a polyhedral or longitudinal shape are also hardly visible in proper illumination. Their size and contents are similar to bismuth oxide, and they appear in a large scattering.

Both in the micro- and semi-macro scale, the material structure can be assessed as solid and homogeneous, only slightly inferior to the Japanese varistor. The degree of material sintering is completely correct. This is confirmed by the value of microhardness which amounts to HV1 = 204.5 ±3.7. It is even slightly higher than for the Japanese material (HV1 = 195.5 ±1.8), while the value of standard deviation is two times greater, which proves a little lower homogeneity of the material.

As already mentioned, a zone was examined near the area with a correct, intact structure, where combined electrical, thermal and mechanical stress resulted in significant damage. Figure 7 shows an inlet area of the breakdown passage of the varistor magnified 500 times.

The visible breakdown passage of the varistor has a variable width ranging from a few to more than 60 micrometres. There is a certain quantity of ZnO grains in the centre, which are not chipped off but became remelted as a result of high temperature. Grain joining boundaries cracked at the same time. A large amount of chipping can be observed in the area adjacent to the passage. Grain boundaries were so substantially weakened that, as the microsection was prepared, groups of grains constituting between 17 and 21% became chipped off or strongly loosened. They occupy as much as 19% of the surface.

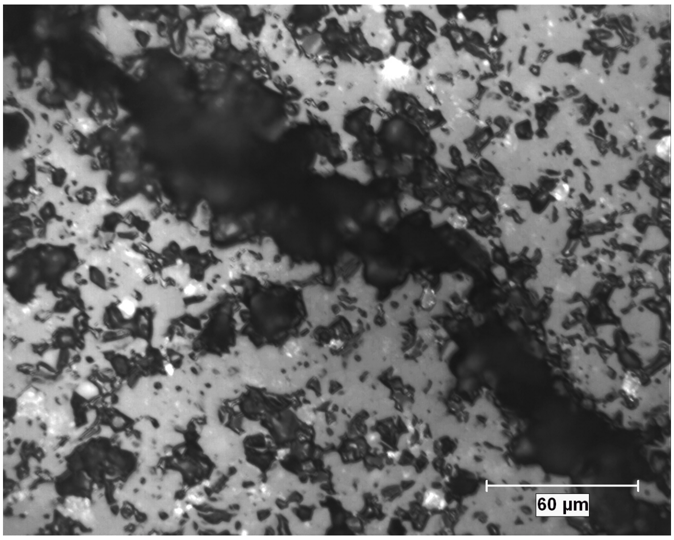

Fig. 7. Damaged HV varistor – an inlet area of the breakdown passage – a microscopic image. A significant quantity of chipped off and strongly loosened structure elements is evident

The remelting effect of a part of ZnO grains is also marked in Figure 8 which shows the material microstructure at a short distance from the passage. Remelted grains, and most frequently entire groups thereof, are still visible in areas at a distance of over one millimetre from the passage. Completely or partially chipped off groups of grains constitute a dozen or so percent (13.5% on average) in this area. Closer observations of the microsections in various illumination led to a finding that chippings are often adjacent to pores or precipitatations of the spinel phase. This proves a weaker bonding with ZnO grains.

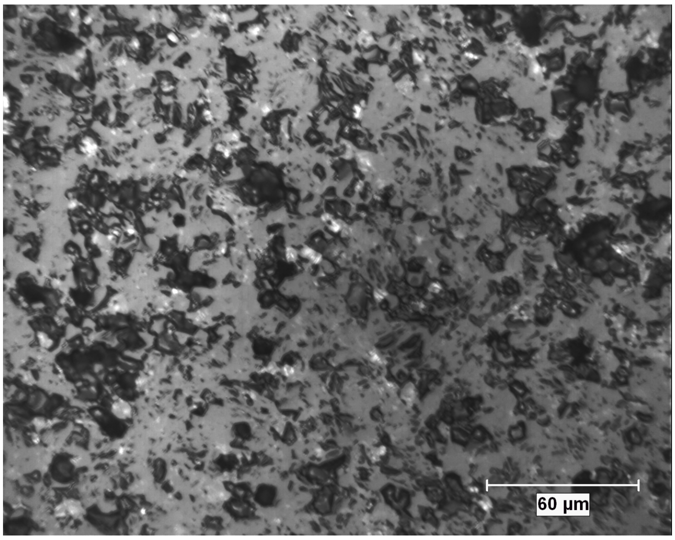

Fig. 8. An image of material microstructure in the damaged HV varistor at a distance of approximately 0.5 mm from the breakdown passage. Chipped off and heavily loosened elements of the structure constitute approximately 13% of the surface. Characteristic groups of remelted ZnO grains are slightly marked. They have a grey colour and are surrounded with thicker black rims. The light Bi_2O_3 phase is very visible

An area at a distance of approximately 2-3 mm from the passage can be considered as a transition between the damaged and correct microstructure. Such zone is shown in Figure 9. Electrical, thermal and mechanical stress affecting the material did not exceed the mechanical strength of the material and did not cause cracks, but only slight degradation in the microstructure. The weakening of the intergranular boundaries resulted in an increase of chipping to approximately 10% (typically around 6.5%). The microhardness was slightly lower and burdened with significantly greater scattering than in the areas with an intact structure – HV1 = 181.4 ±9.3 (as compared to HV1 = 204.5 ±3.7).

Only a slight reduction in the cohesion and parameters of the material at a short distance from the breakdown passage proves its high resistance to large thermal stress, and in consequence, to mechanical stress associated with fault current. This confirms the high evaluation of the varistor material in the damaged 220 kV surge arrester. This also proves high mechanical and thermo-mechanical strength which the ZnO varistor material should demonstrate. The strength should exceed the values of mechanical stress (tensile and compressive), associated with the passage of strong current through varistor materials, by the highest possible margin.

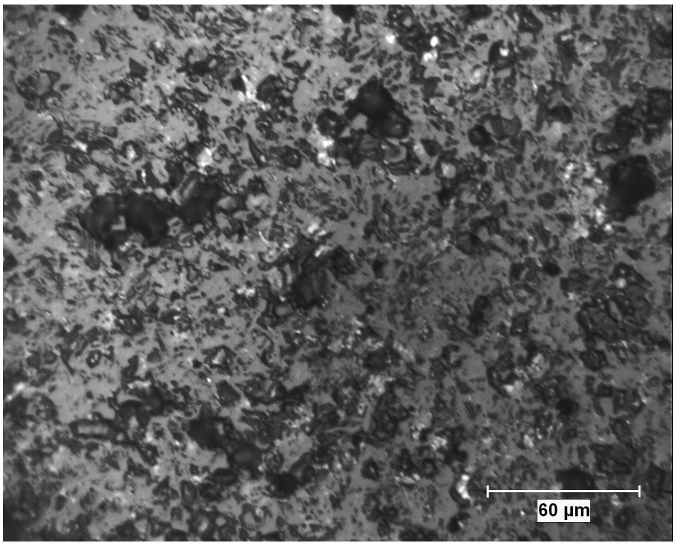

Fig. 9. An image of the material microstructure in the damaged HV varistor at a distance of approximately 2 mm from the breakdown passage. The damaged microstructure is marked only slightly. Chipped off and heavily loosened groups of grains constitute approximately 10% of the surface. Remelted ZnO grains are not visible. Light grains of Bi_2O_3 phase can be observed

6. Summary and conclusions

The varistors examined, coming from different periods and from various manufacturers, are distinguished by a diverse content of doping oxides, microstructure parameters, mechanical properties, and in consequence, various resistance to degradation processes.

Research on surge arresters underway for many years proves that the microstructure and properties – electrical properties in particular – of varistors in surge arresters operating in a single bay in each phase should be as similar as possible.

Elements that weaken the varistor microstructure are significant differences in ZnO grain size, spinel precipitatations and pores to a lesser extent. The Bi_2O_3 phase does not weaken the material, and its precipitatations have essentially a similar size to ZnO grains. Only the oldest of the varistor materials examined – manufactured as late as in the 1980s – raises significant reservations as to the homogeneity and solidity of the microstructure.

From the point of view of resistance to ageing processes, the varistor material should demonstrate the highest mechanical and thermo-mechanical resistance possible. It is mainly conditioned by the homogeneity and solidity of the microstructure. In particular, this applies to the homogeneous distribution of ZnO grain size and the packing of doping oxides, which requires a carefully developed and implemented manufacturing process, including strict compliance with the technological regime at individual stages. It should be pointed out that currently manufactured high-quality varistor materials have proper resistance to combined electrical, thermal and mechanical stress.

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