Arch. Metall. Mater. **64** (2019), 1, 191-196

DOI: 10.24425/amm.2019.126237

P. PAPLIŃSKI*, J. WAŃKOWICZ*, P. RANACHOWSKI**#, Z. RANACHOWSKI**

INVESTIGATION OF MICROSTRUCTURE OF ZnO VARISTORS TAKEN FROM SURGE ARRESTER COUNTERS

The paper presents investigations of microstructure of varistors of damaged surge arrester counters. A similar ZnO varistor, not subjected before to operation, was a point of reference in this research. The results of investigations of the ZnO varistors show an untypical phase composition of their material, which was characterized by unsatisfying homogeneity and cohesion. The degradation processes of varistor material in the subsequent stages were recognized and described. A harmful impact of humidity inside the untight surge arrester counter on its operation and its ZnO varistors was proved. Some conclusions being the result of the operation checking of surge arrester counters were presented too.

Keywords: surge arrester counter, ZnO varistors, microstructure of ceramics, ceramic material degradation

1. Introduction

A surge counter is a device designed to work together with a surge arrester. Dynamic development of power electronics and metrology facilitated the implementation of a series of solutions for surge counters, combining their existing feature, i.e. counting of current pulses (number of operations), with the simultaneous possibility of reading the current flowing through the arrester during its operation [1,2]. A separate group of surge counters comprises devices equipped with measuring transducers from which a signal is transmitted via a connector galvanically connected with a leakage current analyser [3]. The newest group of surge counters includes measurement counters from which a signal is transmitted via a teletransmission connection to a receiving sensor located outside the surge counter. However, the subject of this paper covers only surge counters that are currently in operation, in which ZnO varistors are used for the counting and measuring of circuits. This approach was based on the experience gained in assessment of the aging effects of the ZnO varistors coming from gapless surge arresters [4,5].

In the initial period of introducing the counters into operation, the function of this devices was limited merely to counting the number of operations of the surge arrester, it works in tandem with. At first, the mechanical and electronic design of the counter was not so complicated, and it consisted mainly of metal spring elements and sections of varistors made of silicon carbide (SiC). Design solutions were subjected to numerous modernization processes, and – for a long time – no standardization documents that would include the requirements for the surge counters were developed. Therefore, when designing newer and newer versions of the counters, the document drafted by the manufacturer of these counters (technical acceptance requirements) formed the primary basis.

Issues related to the tightness of the surge counters were treated very superficially by manufacturers. It was believed that correct installation of the elements inside the counters, together with the gaskets used, was sufficient to ensure their tightness. Laboratory tests of the dismantled surge counters and visual inspection of their internal elements, both electrical and mechanical ones, often showed the presence of humidity and related corrosion of metal elements.

Due to the loss of tightness, varistors with resistance-variability properties deteriorating as a result of progressive degradation also become moistened. In consequence, the counter activation threshold is changed, and the counter reaction threshold is usually increased. The most adverse effect of incorrect operation of the counter may be the loss of electrical continuity between its upper and lower terminals. This is similarly also in the case of corrosion of metal spring elements.

Due to their design, the surge counters get untight during operation more frequently than the surge arresters they work with [6]. At the same time, there are no standards applicable only to the surge counters that would organize the principles of their design as well as electrical and mechanical requirements. Damage, including damage to the varistors, relating to the loss of tightness of the surge counters, determines the importance of the problems faced by design engineers of new design solutions.

The effects of electric aging, which are strongly visible especially in varistors of older generation, result not only from the long-term load of service voltage, but also from the action of

---

* INSTITUTE OF POWER ENGINEERING - RESEARCH INSTITUTE, 8 MORY STR., 01-330 WARSZAWA, POLAND
** INSTITUTE OF FUNDAMENTAL TECHNOLOGICAL RESEARCH PAS, 5B PAWIŃSKIEGO STR., 02-106 WARSZAWA, POLAND

Corresponding author: pranach@ippt.pan.pl

current pulses (impulse degradation) [7]. Many years of research, including observations of the electroluminescence effect, showed that a flow of current through varistors is usually of a pathway nature. The presence of current flow paths may lead to strong thermo-mechanical stresses, especially in certain areas [8]. This is a consequence of the heterogeneity in the structure of the varistor material in different scales. Paths can combine and create the so-called hot spots, where the stresses are cumulated.

Production technology of varistors, improved and optimised for nearly 40 years, is relatively simple and inexpensive. There is used grinding, mixing and granulating of raw materials – using the spray granulation method. Raw materials consist of ZnO (typically more than 90%) and oxides of bismuth, antimony, chromium and other metals in the form of powders. Subsequently take place pressing and firing to sinter ceramics. Plane contacts of varistors are ground and metalized. On their cylindrical side surfaces a protective coat is applied. A decisive influence on the electrical and mechanical properties of varistors have the homogeneous distribution and proportion of doping metal oxides – mainly Bi_2O_3 and Sb_2O_3 – as well as maintenance of a required technological regime during the production process [9].

The effects of degradation are a consequence of numerous processes, in particular, the untightness of the surge arresters or surge counters. These lead to the flow of high short-circuit current and, after a certain time, to a failure. As part of the tests on aging processes, that take place in the material of varistors during their long-term operation, studies of varistors coming from the operated surge counters have been carried out and described in this paper. The examined varistors represented a diverse degree of the degradation of the ceramic material.

2. Experimental

Four ZnO varistors of a leading manufacturer, coming from surge counters, were tested. A reference varistor came from a surge counter that was designed for installation in HV – 110 kV electrical network – Figure 1a. The next two varistors – marked 1 and 2 – operated in adjacent phases of the HV power grid and featured only limited traces of damage in the form of a burnt-out path on the side surface – Figure 1b. The last varistor, marked 3 – Figure 1c, was heavily smoked in the aftermath of fire. It came from a surge counter that had been installed in the 110 kV power grid phase in which, after nearly 10 years of operation, the surge arrester was destroyed.

The surge arresters, which surge counters were in tandem with, worked in a power plant and protected block transformers powered by generators. All four varistors came from surge arrester counters operating at a constant current flow. Under normal operating conditions, the current did not exceed 1.6 mA. It did not cause degradation effects, unlike during power surges – when the current flow could reach up to 10 kA and occur changes in the counter readings. During repeated strong power surges the effects of ageing of the ceramic material may take place as well as damage to the external parts of the varistors i.e. metal contacts and protective coats. It should be emphasized that during nearly 10 years of the varistors' work there occured strong switching overvoltages about the current value of several kilo amperes.

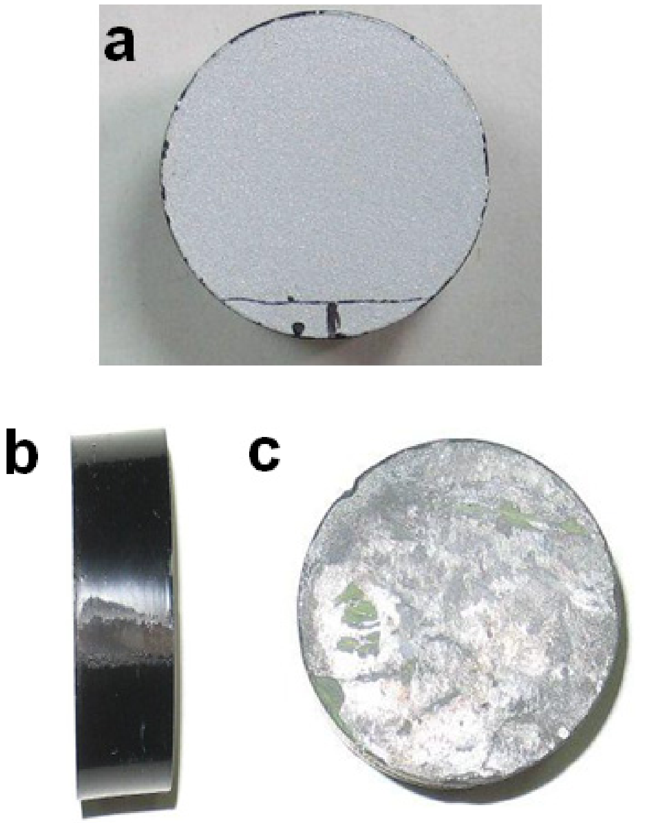

Fig. 1. (a) – Reference varistor – coming from a surge counter that was out of operation. The area from which a block to be tested was cut off is marked on the bottom of the front surface; (b) – varistor 1 – a burnt-out path in the casing material is visible on the side surface; (c) – varistor 3 coming from a destroyed surge counter. The buildups on the front surface is noteworthy

From all four varistors, blocks in the shape of cuboids with a side of 6×6 mm and a length equal to the thickness of the elements, were cut off for the needs of microscopic examinations. In the case of the varistors marked 1 and 2, the samples contained areas of direct over burning in the form of a path visible on their side surface. The blocks were cut off from the varistors with the use of a diamond blade saw with a grain size of 30 μm and then cut with a jigsaw with a working powder having a grain size of 10 μm in oil suspension. The samples prepared in this way were flooded in epoxy resin and then ground on SiC abrasive paper with a grain size of 800, removing a layer with a thickness of approximately 1 mm. The polishing process was carried out using diamond pastes with grain sizes of 10 μm and subsequently 5 μm to remove a layer with a thickness of approximately 150 μm. The final polishing was carried out on diamond pastes with a grain size of 1 μm.

A microscope equipped with a computer image analyser from CLEMEX was used in the tests performed by an optical microscopy method (OM). Images of the microstructure were shown at the magnification 500 times. Nomarski phaseinterference contrast was most frequently used. Then, depending on diverse experimental factors, the aggregates show different shades of grey. Thus, a part of dark areas in the images of the microsections do not, in fact, represent chipping – crushed out elements, but recessed grains, their aggregates, and precipitates with diverse spatial packing, which are present in the microstructure.

Moreover the microhardness of the material was measured. A multi-purpose Struers Dura Scan type microhardness tester was used for that purpose, with a 100 g indenter. A mean value from ten measurements performed and the spread were presented to provide a measure of homogeneity of varistor material.

The visual inspection of microsections proves unsatisfactory micro- and semi-macro homogeneity of the material. The heterogeneities concerned, in particular, the spatial distribution and size of the precipitates of a clearly visible, light doping Bi_2O_3 phase as well as chipping areas associated especially with the crushed out grains of spinel phase.

After analysing the images from the optical microscope, using a computer image analyser CLEMEX type, appropriate reformatting and processing with Photo Paint-Corel, subsequent grey phases in the images of the microstructure of the analysed varistors can be distinguished – Figure 2. The blue phase constitutes crushed out grains from the material matrix and pores. The phase marked yellow is formed by precipitates – bismuth oxide aggregates. This is the most important doping phase in the ZnO varistors. The next phase – spinel ($Zn_7Sb_2O_{12}$) – is marked red. The grey background is the ZnO matrix. Due to a high content of the doping phases, the ZnO matrix accounted only for approximately 70% of the body volume. Most often, the dopes constitute only a few percentage points of the material and the varistors contain over 90% of ZnO [7,10]. It should be noted, however, that the tested varistors did not come from surge arresters, but from surge counters. This may be the reason for their unusual phase structure. Binary masks, an example of which is shown in Figure 2, facilitate the evaluation of the number and distribution of individual phases forming the varistor material.

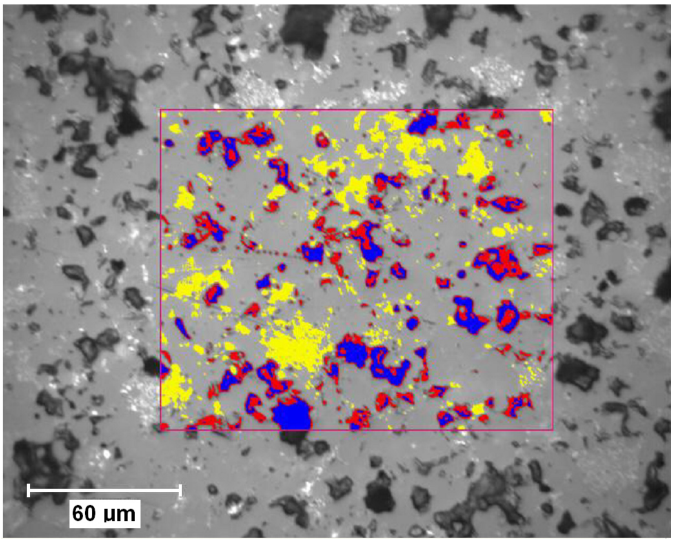

Fig. 2. Typical view of the reference varistor microstructure. A binary mask for colour was applied on the central part of the image, showing the aggregates of the light doping Bi_2O_3 phase – yellow and the spinel phase – red. The areas of chipped elements of the microstructure and scarce pores – in dark blue – cover approximately 6% of the surface. The grey background is the ZnO matrix

The observed microstructure revealed insufficient cohesion. Quite numerous spots of chipping were visible, which are the black areas with a size usually from a few to a dozen or so micrometers. It was associated with the presence of spinel phase. Individual spinel grains had an angular and polyhedral shape and a size of typically a few micrometres, which is slightly less than the ZnO matrix grains. The chipping generally covered grain groups and, together with very scarce and tiny pores, constituted on average 5.8% (from 2 to 8%) of the surface. The spinel phase was present in unexpectedly large quantities. Its non-chipped content, which remained in the microstructure, covered 12.3% (from 11 to 14%) of the surface on average. The initial spinel content in the body can be estimated at 17-18%, of which almost 1/3 was chipped during the preparation of microsections, although, a special – gentle polishing procedure was applied to samples previously flooded in epoxy resin.

The basic doping phase in varistor oxide materials is Bi_2O_3. In the tested samples, the precipitates of bismuth oxide were distributed very heterogeneously. They were also very diverse in shape and size. The average content of Bi_2O_3 was 10.8% (from 8 to 16%). It should be emphasized that the content of Bi_2O_3 in typical varistor materials is approximately 1 to 3% [7,10]. Figure 3a shows the percentage shares of the tested phases in 10 observation fields of the reference varistor sample.

The microstructure of the material, both in the micro- and semi-macro scales, may be evaluated unfavourably, since it is insufficiently compact and homogeneous. Heterogeneity may indicate unsatisfactory mixing of powder components of varistor composite before its pressure forming and subsequent sintering. The brittleness of the spinel phase and its large clusters also suggest a non-optimal selection of sintering conditions, e.g., temperature, time, atmosphere, and their derivatives. However the reference varistor material showed the microhardness on the medium level – of HV1 = 141.6±3.6.

The samples from varistors 1 and 2 contained a material from the areas of direct over burning in the form of a path visible on their side surface, as well as from a slightly distant zone. Generally, the degree of the degradation of the material in both samples was similar, i.e. subcritical. However, at the same time, the microstructure parameters were significantly diversified, depending on the field of observation. This resulted from both – the insufficient homogeneity of the tested material and the degradation effects. The content of individual phases in different measuring fields changed quite widely – Figure 3b.

Only the part of the spinel phase that remained in the microstructure (non-chipped) was quite homogeneously distributed, which is similar to the reference material – Figure 3a. However, its content halved with the number of chipped microstructure elements increasing more than twice. On the other hand, the average Bi_2O_3 content, despite a significant spread, remained at the same level as in the reference sample – approximately

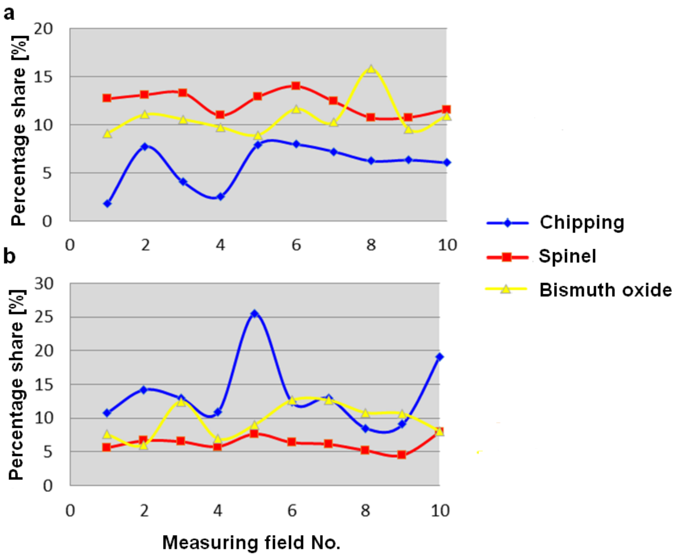

Fig. 3. Percentage share of individual phases in the material samples in 10 observation fields. (a) – The average values for the reference sample are as follows: crushed out elements and pores – 5.8%; non-chipped spinel – 12.3%. The initial structure contained 17-18% of the spinel phase. Bismuth oxide occupied, on average, 10.8% of the surface. (b) – The average values for varistors 1 and 2 are as follows: crushed out elements and pores – 13.6%, non-chipped spinel – 6.3%, and bismuth oxide – 10.8% of the surface

11%, on average. Therefore, it was present in relatively high quantities, but with heterogeneous distributions. Figure 4 shows a typical microstructure of Sample 1 in a zone 1 cm distant from a burnt-out path.

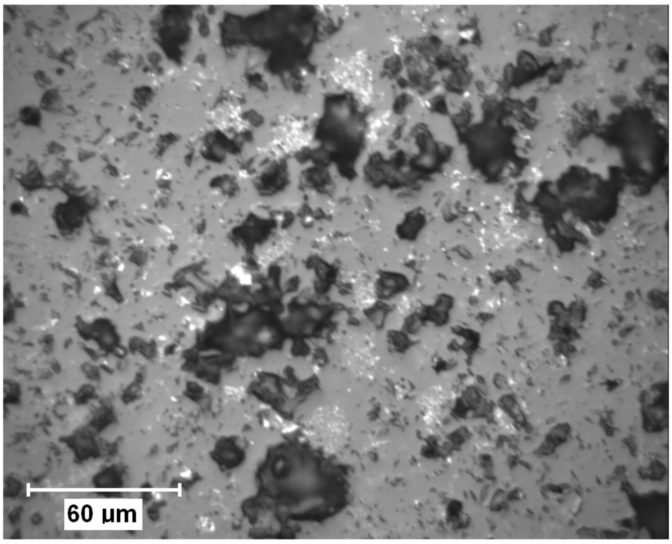

Fig. 4. Image of the microstructure of varistor 1 approximately 1 cm from a burnt-out path. The chipping of microstructure elements accounts for 11% of the surface

In the material of Samples 1 and 2, especially in the vicinity of the path burnt out on the cylindrical surface, the material microstructure significantly loosened, where the microstructure was not compact, cohesive, and homogeneous. The number of chippings – crushed out fragments observed in microsections, increased to a wide range of 8 to 25%-13.6% on average, as shown in Figure 3b. Under the influence of a fault current flow and thermo-mechanical stresses, the next part of the spinel phase was separated from the microstructure. Approximately 1/3 – 6.3% on average, remained out of its original quantity at the level of 17 – 18%. Moreover, the ZnO grains had a small share in the chipped elements of the microstructure – up to 2%. In some areas, peripheral microcracks around the groups of (or even individual) ZnO grains were poorly visible, but they were not chipped from the matrix. Microhardness of the material in the samples of both varistors decreased significantly, while the dispersion of this important parameter increased considerably HV1 = 99.3±8.1.

Heavily smoked varistor 3 was removed from a destroyed surge counter. Highly advanced degradation of the material could be expected there, as a result of combined electric, thermal, and mechanical effects.

As predicted, the degree of the material degradation in the sample could be described as highly advanced subcritical, and close to critical. There appeared strong loosening and mechanical weakening of the material, the initial compactness, and cohesiveness of which were already low. At the same time, the microstructure parameters were diversified, depending on the field of observation. In particular, the fields of the areas of the crushed out elements of the material varied widely – Figure 5. This was a consequence of both – strong thermo-mechanical stresses as well as the insufficient homogeneity of the tested material.

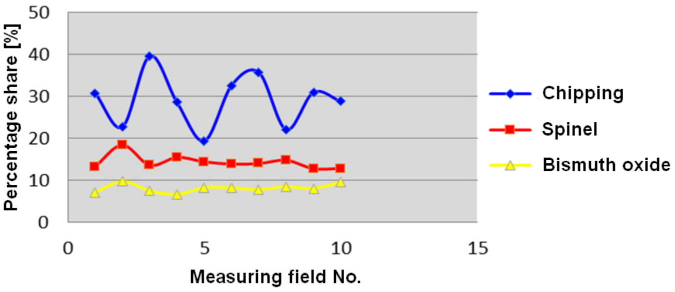

Fig. 5. Percentage share of individual phases in the material of varistor 3 in 10 observation fields. The average values are as follows: chipping and pores – 29.1%, non-chipped spinel – 14.4%, and bismuth oxide – 8.2% of the surface

Only the part of the spinel phase that remained in the microstructure was quite homogeneously distributed, which is similar to in the material of the remaining samples – Figures 3a and 3b. However, contrary to the expectations, not only its content was not subsequently reduced, but it was even higher than in the reference material (approximately 12%). In Sample 3, the spinel phase accounted from less than 12% to approximately 19%, on average 14.4%. Therefore, only approximately 3% of the original spinel content (17-18%) was chipped. A possible explanation for this quite surprising phenomenon is a significant improvement in the binding of the spinel grains with each other and with the ZnO matrix grains as a result of melting and recrystallization effects. This could have happened in the aftermath of a sharp rise in temperature during a fault current flow and as a consequence of fire.

Bismuth oxide, which accounted for almost 11% in both the reference material and the structures of Sample 1 and 2, was still present in significant quantities – approximately 8%.

High weakening of the compactness and loosening of the material microstructure is clearly visible in Figures 6a and 6b. The number of crushed out elements observed in the microsections increased to a wide range of 19 to 40% of the surface, 29.1% on average. Thus, almost 1/3 of the material, under the influence of strong thermo-mechanical stresses, was separated from the microstructure and was chipped when polishing the microsections. However, the loss in the doping phases, Bi_2O_3 and spinel – was small – approximately 2.5% and 3%, respectively. In particular, the ZnO matrix was severely degraded. The chipped ZnO grains constituted, on average, about 24% of the original content of approximately 70% of the material volume. Microhardness of the material in the sample 3 underwent subsequent decrease, with considerable dispersion of this parameter HV1 = 79.0±7.4.

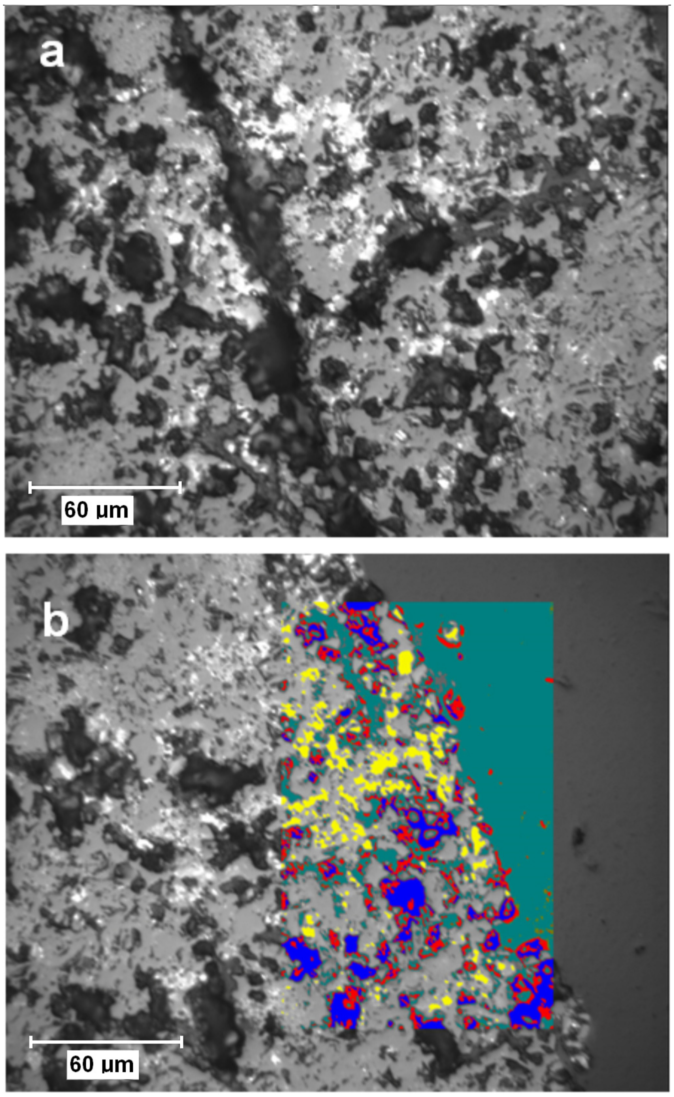

Fig. 6. Images of the boundary area of varistor 3. (a) – long crack initiated and propagating in the place of higher concentration of the doping phases – light Bi_2O_3 and darker spinel. (b) – the front face. The layer of metallization was melted. Grey epoxy resin in which the sample was mounted is visible on the right side. A binary mask presents the doping phases – light Bi_2O_3 aggregates – yellow, spinel – red and crushed out fragments – navy blue. The ZnO matrix is grey. Marked turquoise resin penetrates deep into the sample

Cracks were another effect of far-reaching degradation that was already critical – Figure 6a. Observation of their directions proves that they were formed and disseminated in places with large precipitates of the doping phases – Bi_2O_3 and spinel.

High temperature caused the melting of metallization (contact layer) on the front face of varistor 3. The microstructure in the boundary layer was weakened and loosened to such an extent that deep gaps were formed, through which the resin penetrated deep into the sample. The depth of the heavily cracked layer at the front surface of the varistor reached 80 µm – Figure 6b.

3. Summary

Operational experience proved that, during failure of a surge arrester, the surge counter it works in tandem with is also destroyed, with electronic elements and varistors. Nevertheless, the most common cause of damage to the counters during operation is their untightness. This is mostly due to the design solutions for the counters on the high voltage side. Humidity penetrates into the interior of the counters along the insulator of the upper terminal, in the place of counter sealing and through the counter viewer – not sealed very accurately. Failure to comply with the tightness requirement may result in the potential presence on the upper terminal of the counter over time. This poses a risk of electric shock to the station staff. An additional problem, in contrast to the surge arresters, is the failure to comply with the regime of varistor parameters, when selecting them for the surge counters.

These observations indicate the need for diagnostic tests of the surge counters at least in the time cycles provided for the surge arresters. The tests should include a visual inspection of the counter viewer and a check whether the continuity of the current flowing through the counter is maintained.

Four tested ZnO varistors, coming from surge counters, working in the power plant, had an atypical phase structure of the ceramic body. Content of doping phases was relatively very high. In consequence the ZnO matrix covered only approximately 70% of the body volume. Probable explanation of the unusual phase structure of the varistors can be their application, i.e. in the surge counters, and not in the surge arresters.

The microstructure of the tested material may be evaluated unfavourably – as insufficiently compact and homogeneous. Heterogeneity may indicate unsatisfactory mixing of powder components of the mass before its pressure forming and subsequent sintering. The brittleness of the spinel phase and its large aggregations also suggest a non-optimal selection of sintering conditions, e.g., temperature, time, atmosphere, and their derivatives. Nevertheless, the porosity of the material was low and had proper parameters.

Effects of degradation, which were registered in defected varistors 1, 2 and 3 were generally similar to ageing processes in varistors from surge arresters [10]. Under the influence of the combined action of electric, thermal and mechanical stresses, the loosening of the microstructure took place. Degradation concerned mainly grains of spinel phase ($Zn_7Sb_2O_{12}$), and only in the next turn ZnO matrix. Clusters of the spinel grains weaken thermo-mechanical durability of the material. Most of the spinel phase was separated from the loose microstructure. In the case of bismuth oxide, its good binding with the ZnO matrix and its resistance to cracking and separation from the microstructure was confirmed, which was also observed in other varistor materials.

REFERENCES

[1] Surge counter type I 3EX5 050 manufactured by Siemens. Operation Manual No. 1198/RSJ, Berlin, 1998. [In Polish: Licznik zadziałań typu I 3EX5 050 firmy Siemens. Instrukcja obsługi Nr 1198/RSJ, Berlin 1998 r.].

[2] Surge counter type SC 13 manufactured by Bowthrope EMP Limited. Operation Manual No. 066/1, Brighton, 1994. [In Polish: Licznik zadziałań typu SC 13 firmy Bowthrope EMP Limited. Instrukcja obsługi. Nr 066/1, Brighton 1994 r.].

[3] Surge counter type GLX. Data Sheet GLX/06/00, „ZWAR" S.A. Production Plant Z-4, Przasnysz, 1998. [In Polish: Licznik zadziałań typu GLX. Karta katalogowa GLX/06/00, „ZWAR" S.A. Zakład Produkcyjny Z-4, Przasnysz 1998 r.].

[4] Report on evaluation of the technical condition of damaged surge arrester type 3EQ 4 336-3PP42-4TZ-1, factory No. K/35227949, manufactured by Siemens, production year 2013, dismantled from feeder No. 5 Ełk circuit 2 in the 400 kV Łomża Systemowa substation. Compiled by Institute of Power Engineering – Research Institute, February/March 2016. [In Polish: Raport z oceny stanu technicznego uszkodzonego beziskiernikowego ogranicznika przepięć typu 3EQ 4 336-3PP42-4TZ-1, nr fabryczny K/35227949 firmy Siemens, rok prod. 2013, zdemontowanego z pola nr 5 Ełk tor 2 w SE 400 kV Łomża Systemowa. Opracowanie IEn – Ib, luty/marzec 2016 r.].

[5] Study on the revision of gapless surge arrester type VARISIL HI manufactured by Tridelta Parafoudres S.A. Compliled by Institute of Power Engineering – Research Institute, December 2016. [In Polish: Ekspertyza z rewizji beziskiernikowego ogranicznika przepięć typu VARISIL HI firmy Tridelta Parafoudres S.A. Opracowanie IEn – Ib, grudzień 2016 r.].

[6] P. Papliński, P. Ranachowski, Testing of the surfaces of internal elements of surge arresters, Przegląd Elektrotechniczny **5a**, 73-76 (2012). [In Polish: Badania powierzchni elementów wewnętrznych ograniczników przepięć].

[7] L.M. Levinson, editor, Advances in Varistor Technology, Ceramic Transactions, **3** (The American Ceramic Society, Westerville, OH), 22-30 (1989).

[8] S. Boggs, J. Kuang, H. Andoh, S. Nishiwaki, Electro-thermal-mechanical computations in ZnO arrester elements, IEEE Trans. Power Delivery **15** (1), 128-134, (2000).

[9] D.R. Clarke, On the equilibrium thickness of intergranular glass phases in ceramic materials, J. Am. Ceram. Soc. **85**, 485-502 (1999).

[10] P. Papliński, J. Wańkowicz, P. Ranachowski, Z. Ranachowski, Microstructure and degree of degradation of ZnO varistors in surge arresters due to operation, Archives of Metallurgy and Materials **63**, 3, 1267-1273 (2018).