Witold MIELCAREK, Krystyna PROCIÓW, Joanna WARYCHA
Instytut Elektrotechniki, Oddział Materiałoznawstwa Elektrotechnicznego we Wrocławiu

Ceramic separators to place between green compacts during varistor sintering

***Abstract**. ZnO metal oxide varistors are created using typical ceramic technology. During the process of sintering the green compacts may glue together and stick to each other so hard that they cannot be separated without damaging the varistor. This can be avoided in several ways but none is satisfactory and good enough as ones are not effective, while the other ones are simply inconvenient.The developed ceramic separators can be applied in multiple uses. In essence they are made of the same ceramic as varistor but doped with sinter-resisting component which causes the separators and sintered varistors do not stick together. They are reliable, economical and do not impose chemical contaminants to varistors.*

***Streszczenie.** Warystory ZnO są wytwarzane typową technologią ceramiczną. Podczas wypalania wyprasek warystorowych może dojść do takiego spieczenia się sąsiadujących ze sobą wyprasek, że rozdzielenie ich bez uszkodzenia staje się niemożliwe. Jest kilka sposobów radzenia sobie z tym problemem jednak żaden nie jest wystarczająco satysfakcjonujący. Niektóre są nieefektywne, inne wręcz nieekonomiczne. Przekładki ceramiczne proponowane w ramach tej pracy są wytworzone z ceramiki o składzie zawierającym składnik ceramiki warystorowej utrudniający proces spiekania i zapobiegający przywieraniu wypalanych warystorów. Przekładki te są niezawodne, ekonomiczne i nie wprowadzają chemicznych zanieczyszczeń do wytwarzanych warystorów. (**Przekładki ceramiczne stosowane przy wyrobie warystorów**)*

Keywords: ceramic separators of green compacts, metal oxide varistors, sinter-resisting component
Słowa kluczowe: przekładki ceramiczne wyprasek, warystory tlenkowe, związek trudno spiekalny

Introduction

ZnO metal oxide varistors are made using typical ceramic technology, The ZnO mixture with a small amount of other metal oxides is pressed in discs of variable size and thickness and then sintered at about 1250 °C [1,2,3]. During the process of sintering the green compacts may glue together and stick to each other so hard that they cannot be separated without damaging the varistor. Varistors stick together due to presence of Bi_2O_3 which is one of the principal constituent of ZnO varistors. The Bi_2O_3 melts down at 825 °C and is cleared out from varistor body just to sublimate on its surfaces [4]. Sublimated Bi_2O_3 partly liquates and penetrates into adjoining varistors causing that they adhere together.

Therefore applying suitable separators to prevent the green varistor compacts from sticking to ceramic cassette or to each other is essential. While designing such separators it is key to keep in mind that varistor ceramic shrinks by approximately 20 vol% during the sintering [5]. Moreover they should not introduce any chemical impurities to the varistor.

There are several ways of avoiding this problem. First is by separating green compacts using spoiled varistors with stripped out electrodes. The other way to keep the two pieces of varistors apart is to separate them with material that is to burn out during varistor sintering. Finally, the sintered and then grinded varistor granulate sprinkled over the surface of green compacts can help, however none of these methods is effective and convenient enough.

For example, sprinkling the surface of every green compact with prior sintered and grinded granulate impose additional amount of labor and material costs as the varistor granulate is composed not only of ZnO but also of other metal oxide dopants like Bi_2O_3, Sb_2O_3, Cr_2O_3, Co_2O_3 MnO_2 and NiO [6,7]. Furthermore, the stick-on particles of granulate are still to be removed.

Using a finished varistor for separating the green compacts brings about more challenges. Using spoilage for this purpose requires the removal of electrodes. And still, this sort of separators will not be in proper size due to ceramic densification which causes that their sizes are about 20% smaller than the green compacts to be separated.

The single use separators are ineffective simply through the lack of materials that would properly separate compacts during the whole time of varistor sintering as this type of separators are usually made of organic materials which burn out at 600^{o}C or even lower temperatures, while the most critical moment during varistor sintering takes place at about 825^{o}C when Bi_2O_3 melts. Furthermore being of single use they are uneconomical and hostile to environment.

Experiment

To solve the problem of the effective separation of green varistor compacts during sintering various material compositions were tested. As the Sb_2O_3 is known for forming with ZnO spinel [8] which hinders the process of varistor sintering a mixture of ZnO with Sb_2O_3 was tried first. The crystal phases originating during sintering of the mixture were identified using X-ray powder diffraction (XRD) method. The results of the approach are presented in Table 1 and Figs 1-3. As can be seen (Fig. 1a and b) separators sinter unevenly, in some cases their material migrate to varistors (Fig. 2a) or they are too brittle to multiply usage (Fig. 3b).

As none of above solutions was satisfying enough to be applied in the industry another approach was tried. This time a high-temperature ceramics based on mullite ($3Al_2O_3x2SiO_2$), cordierite $Mg_2Al_4Si_5O_{18}$ and corundum Al_2O_3 was utilized. As previously, various compositions and temperatures were tried before the separators with best parameters were identified. Their performance was tested both in laboratory and in industrial settings. Results are presented in Tables 2-4 and Figs 4-8.

a) b)

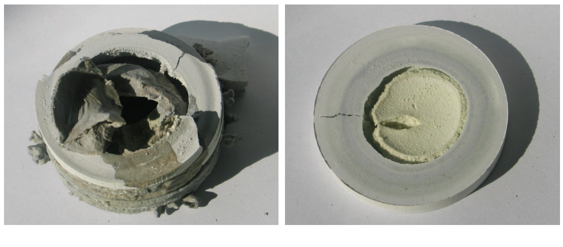

Fig. 1. Separators No 1 (in Table 1) after sintering

Table 1. Ceramic separators made of components typical to varistors $ZnO - Sb_2O_3$

No	Details on separator composition and processing	Observations
1	Separators made from ZnO and Sb_2O_3 mixed at rate: 7 mol% ZnO:1 mol%Sb_2O_3 and sintered at 1240 °C.	The mixture disintegrated during sintering. In effect the separators melted and were damaged during sintering (Fig.1).
2	Separators made from ZnO and Sb_2O_3 mixed at rate: 7 mol% ZnO:1 mol% Sb_2O_3 pre-sintered at 580 °C and sintered at 1200 °C.	The Sb_2O_3 affiliation to ZnO causes varistor components migration to separators (Figs 2a and 2b)
3	Separators made from ZnO and Sb_2O_3 mixed at rate: 7 mol% ZnO:1 mol% Sb_2O_3 pre-sintered at 580 °C, added with 37,5 wt% of ZnO, 10 wt% of $Zn_7 Sb_2 O_{12}$ and sintered at 1240 °C	Rigid, varistor components migrate to separators (Figs 3a and 3b).
4	Separators made from ZnO and Sb_2O_3 mixed at rate: 7 mol% ZnO:1 mol% Sb_2O_3 pre-sintered at 580 °C, added with 10 wt% of ZnO and sintered at 1240 °C.	Rigid, varistor components migrate to separators
5	Separators made from ZnO and Sb_2O_3 mixed at rate: 7mol%ZnO:1mol%Sb_2O_3 pre-sintered at 580 °C added with 50 wt% varistor granulate, 15 wt% Sb_2O_3, 20 wt% of ZnO and 15 wt% of $Mg_2Al_4Si_5O_{18}$ and sintered at 1240 °C.	Rigid
6	Separators made from varistor granulate mixed with 10 wt% of Sb_2O_3 and sintered at 1240 °C.	Rigid
7	Separators made from ZnO and SnO_2 mixed at rate: 2 mol% ZnO:1 mol% SnO_2 and sintered at 1240 °C	Separators and sintered varistors stick together.

a) b)

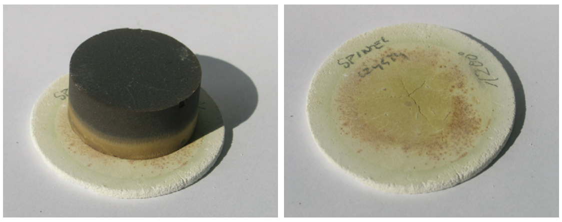

Fig. 2. a/ Penetration of spinel grains (from separator No 2 in Table 1) into varistor yvisible as a light brown ring on varistor body. b/The spinel separator No 2 (in Table 1) after usage

a) b)

Fig. 3. The views of separator No 3 (in Table 1) a/ before and b/ after usage

Table 2. Ceramic separators made of cordierite

No	Details on separator composition and processing	Observations
1	Separators made from cordierite A, sintered at 1250 °C.	Brittle (Fig. 4a)
2	Separators made from cordierite B, sintered at 1250 °C.	Brittle, stick to varistors (Fig. 4b)
3	Separators made from cordierite C, sintered at 1250 °C.	Brittle, stick to varistors
4	Separators from laboratory-made cordierite, sintered at 1350 °C.	Brittle, easily broken (Fig. 5)

a) b)

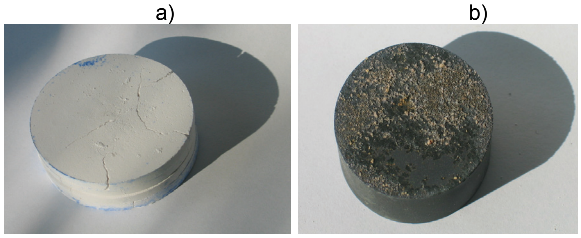

Fig. 4. a\ Separators made of poorly sintered cordierite A, b\ the remains of separator 2 (made of cordierite B) stuck to varistor

Table 3. Ceramic separators made of corundum and mullite

No	Details on separator composition and processing	Observations
1	Separators made of corundum, sintered at 1200 °C	Separators stick to varistors (see Fig.6)
2	Mullite separators sintered at 1350 °C	Brittle, stick to varistors (see Fig. 7)
3	Mullite separators sintered at 1200 °C	Brittle, stick to varistors

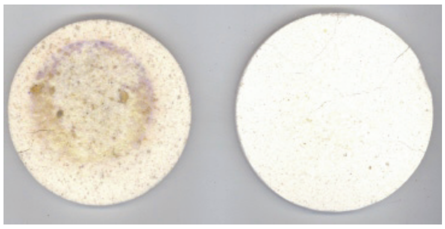

Fig. 5. Separators from laboratory-made cordierite, the trace was left by sintered varistor

a) b)

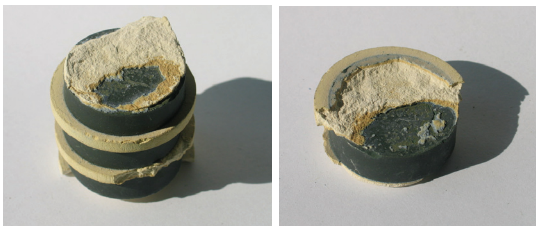

Fig. 6. The view of corundum separators stuck to varistors

a) b)

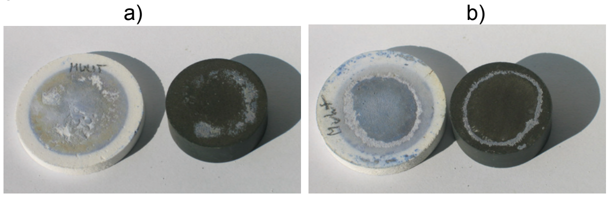

Fig. 7. Mullite separators, traces of stuck to varistor

Finally, compositions: 99 wt% ZnO : 1wt% of sinter-resisting Co_2O_3 or Cr_2O_3 could be recommended for industrial applications. Details on them are shown in Table 4 and Figs 8 a, b and c.

Table 4. Ceramic separators made of ZnO mixed with sinter-resisting component

No	Details on separator composition and processing	Identified crystal phases	Observations
1	Separators made of ZnO doped with 1 wt% of Cr_2O_3 sintered at 1250 °C	ZnO Zincite $ZnCrO_4$ Zincchromatite	(see Fig. 8c)
1	Separators made of ZnO doped with 1 wt% of- Co_2O_3 sintered at 1250 °C	ZnO Zincite $ZnCo_2O_4$ Cobalt spinel	(see Figs 8a)

a) b) c)

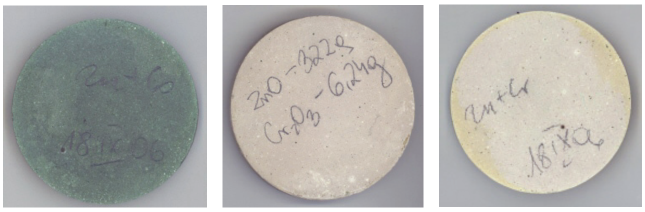

Fig.8. Separators made of ZnO sintered with a) 1 wt %Co_2O_3; b) 1.9 wt % Cr_2O_3 ; c) 1 wt% Cr_2O_3.

Because of the $ZnCo_2O_4$ cobalt pigment spinel occurrence (Fig.8a) in the case of ($ZnO+Co_2O_3$) separators the ($ZnO+Cr_2O_3$) separators composed mainly of Cr modified ZnO and only a small amount of $ZnCrO_4$ are considered most suitable by the authors of this research.

As this approach to the problem adds novelty, the details of the solution were submitted to the Polish Patent Office and are protected by Patent Pending No P 390293 [9].

Conclusions

The best results were obtained with ZnO ceramic doped with sinter-resisting component. Separators made of ZnO doped with sinter – resisting component like Cr_2O_3 or Co_2O_3 effectively separate sintered varistors during the whole period of time of varistor sintering. Separators and sintered varistors do not stick together and do not introduce any chemical impurities to the varistor. In comparison to currently used solutions this is reliable and economical alternative. Details on the technology i.e. material composition, procedure and the stock of machine tools for their processing are given in patent entitled "Ceramic separators to place between green compacts during varistor sintering" which was registered by Polish Patent Office on 27.01.2010 under Patent Pending No P 390293.

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Authors: *dr hab. inż. Witold Mielcarek, prof. IEL, E-mail: mielcar@iel.wroc.pl, mgr inż. Krystyna Prociów, kproc@iel.wroc.pl, dr inż. Joanna Warycha, warycha@iel.wroc.pl, Instytut Elektrotechniki Oddział Technologii i Materiałoznawstwa Elektrotechnicznego we Wrocławiu, ul. M. Skłodowskiej Curie 55-61, 50-369 Wrocław.*