Development of Low-Temperature, Short-Time Sintering Technology for Zinc Oxide Surge Arrester Blocks to Reduce CO_2 Emissions

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Abstract

In response to recent demands for reducing the environmental impact of manufacturing processes, there is a need to improve the manufacturing process of zinc oxide blocks for surge arresters, particularly reducing CO_2 emissions during the sintering process. This development focused on reducing the environmental impact by lowering the temperature and shortening the sintering time.

To achieve lower sintering temperatures and shorter sintering times compared to conventional sintering patterns, we optimized the formulation and improved the manufacturing process conditions. As a result, we not only reduced and shortened the sintering temperature and time, but also achieved greater uniformity of the sintered body's microstructure and surge absorption performance equivalent to or better than conventional methods, with the expectation of a 50% reduction in CO_2 emissions during the sintering process.

This development contributes to achieving carbon neutrality as a new manufacturing process that significantly reduces environmental impact while maintaining product performance.

1 Preface

Surge arresters play a crucial role in protecting power equipment such as transformers and switchgears from overvoltages generated in power systems, thereby preventing disruptions to the power supply.

Fig. 1 shows the external appearance of a station class surge arrester. The protective function of the surge arrester is carried out by a semiconductor ceramic (hereinafter referred to as a zinc oxide block) with non-linear resistance characteristics, primarily made from zinc oxide (ZnO).

Our company manufactures and sells zinc oxide surge arresters and the zinc oxide blocks incorporated therein. The manufacturing process for zinc oxide blocks requires a high-temperature, long-duration sintering process to achieve surge absorption performance, consuming a significant amount of energy and resulting in CO_2 emissions, which have become a major concern for us. In line with the Japanese government's goal of achieving carbon neutrality by 2050, our company is also promoting energy conservation in its manufacturing processes and working to reduce CO_2 emissions during the production of zinc oxide blocks. This

Fig. 1 Station Class Surge Arrester

The External appearance of the polymer-type surge arrester manufactured by our company is shown.

paper introduces our efforts to reduce CO_2 emissions generated during the manufacturing process of zinc oxide blocks, specifically focusing on low-temperature, short-time sintering, and presents the results of these efforts.

2 Zinc Oxide Blocks

Zinc oxide blocks are the core components of surge arresters, and their excellent voltage-current nonlinear resistance characteristics enable gapless surge arresters. This characteristic is explained by the formation of symmetrical double Schottky barriers at the grain boundaries of the main component, ZnO grains. This occurs because ZnO is an n-type semiconductor, and additive with different valencies, such as bismuth oxide (Bi_2O_3), segregate at the grain boundaries between the grains. Fig. 2 shows the microstructure of a zinc oxide block, and Fig. 3 shows the symmetrical double Schottky barrier model.

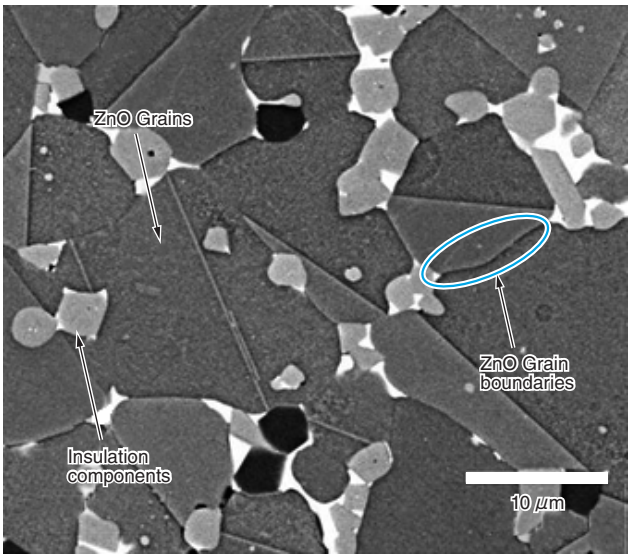


Fig. 2 Microstructure of Zinc Oxide Blocks

A segregate surrounds conductive ZnO grains to form a Grain boundaries, and a symmetric double Schottky barrier is formed.

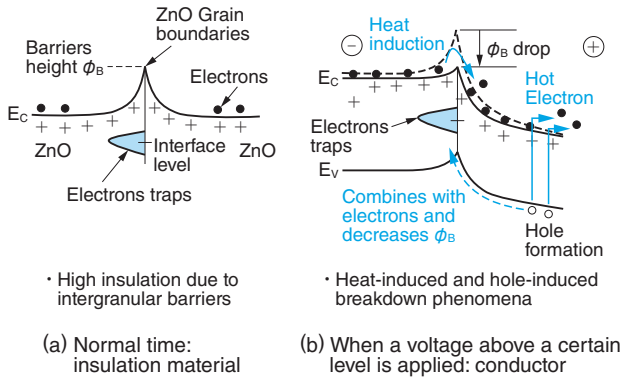


Fig. 3 Symmetric Double Schottky Barrier Model

Normally, high insulation is shown by a Grain boundaries barrier, but when a voltage above a certain level is applied, the width of the barrier narrows, electrons move due to tunnel effects, etc., and become conductive.

To match the rated voltage of the surge arrester, it is necessary to appropriately set the reference voltage of the zinc oxide block. In controlling the reference voltage, size control of ZnO grains plays an important role. While ZnO grain diameter generally increases with increasing sintering temperature, grain growth is suppressed by the pinning effect of segregated materials such as spinel particles. Therefore, in order to obtain the desired reference voltage, it is essential to appropriately control the balance between the sintering temperature and the pinned grains.

Furthermore, voids are sometimes observed within the sintered body. When a zinc oxide block receives excessive energy while absorbing a lightning surge, vertical tensile stress is generated within the sintered body. If large voids exist within the sintered body under these conditions, they can become the starting point for fracture. Therefore, in order to achieve a more ideal microstructure, it is desirable to minimize the size of the voids and reduce their number as much as possible.

3 Manufacturing Process

The manufacturing process for zinc oxide blocks is carried out according to the following procedure. Fig. 4 shows the manufacturing flow of a zinc oxide block. First, a molded body is prepared by griding and mixing ZnO as the main component

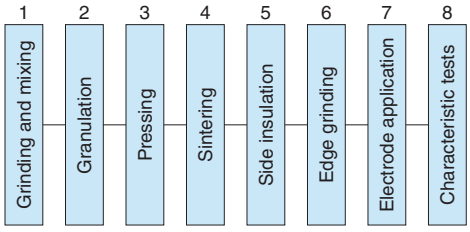


Fig. 4 Zinc Oxide Blocks Manufacturing Flow

The electrical characteristics of zinc oxide blocks are determined by manufacturing conditions for grinding, mixing, sintering, and side insulation of raw materials, and the sintering process accounts for most of the CO_2 emissions during the manufacturing process.

with small amounts of additives such as Bi_2O_3 and antimony oxide (Sb_2O_3). Next, this molded body is degreased and sintered to obtain a dense sintered body. As a final step, side insulation, polishing, and electrode attachment are performed to complete the zinc oxide block. The majority of CO_2 emissions from the block manufacturing process are due to the sintering process. To reduce this environmental burden, this development aimed to reduce CO_2 emissions from the sintering process by 50%.

4 Efforts toward Low-Temperature, Short-Time Sintering

As an approach to reduce CO_2 emissions, we worked on lowering the sintering process temperature and shortening the sintering time. However, low-temperature sintering presents challenges in ensuring densification of the sintered body and maintaining surge absorption performance.

To solve these problems, we optimized the formulation and improved the manufacturing process conditions. In the formulation optimization, we reduced the amount of additives that generate pinning particles that suppress grain growth of ZnO grains and adjusted the formulation of other raw materials. In the improvement of process conditions, we improved the raw material crushing and mixing process and optimized the sintering pattern.

Through these measures, we aimed to ensure sufficient surge absorption performance and discharge withstand capability even under low-temperature sintering conditions.

5 Low-Temperature, Short-Time Sintering Technology

The microstructure and electrical properties of the zinc oxide blocks fabricated in this development were evaluated. Fig. 5 shows the sintering pattern after low-temperature, short-time sintering. To achieve low-temperature sintering, zinc oxide blocks were fabricated under conditions that reduced the amount of additives that generate pinned particles, lowered the sintering temperature from the conventional 1200℃ to 1100℃, and shortened the total sintering time by 40%. Fig. 6 shows the microstructure of the zinc oxide block. Microstructure observation revealed that the ZnO grain size remained the same as that of conventional blocks, and segregated substances such as spinel particles were reduced, indicating uniform dispersion.

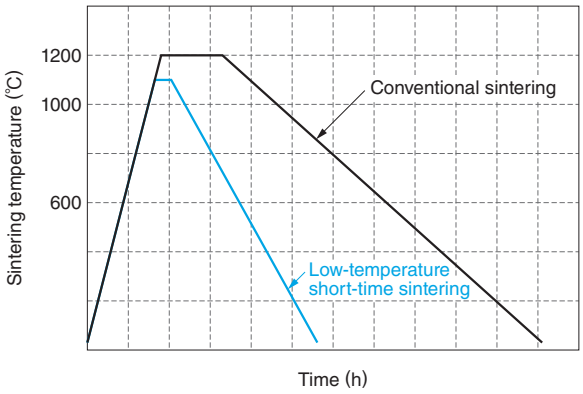
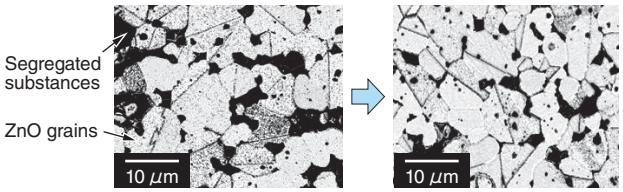


Fig. 5 Sintering Patterns Made by Sintering at Low Temperature for a Short Time

The holding temperature was reduced by 100℃ to reduce CO_2, and the total time was shortened by 40%.



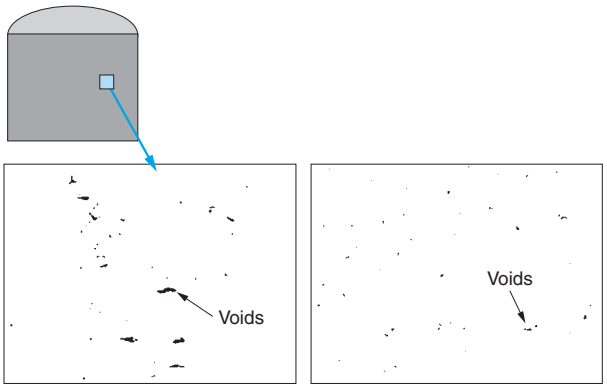
(a) Conventional block (b) Newly developed block

Fig. 6 Microstructure of Zinc Oxide Blocks

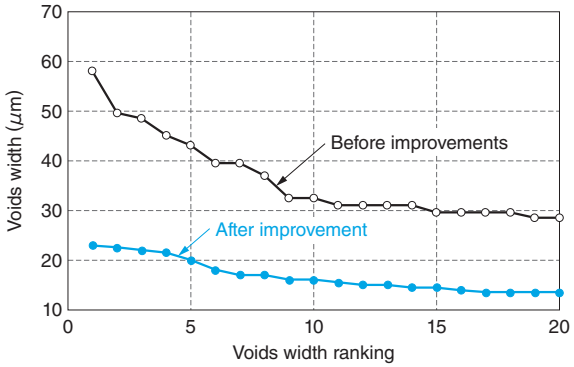
Additive raw materials that generate segregates were reduced, and a decrease in pinning particles was confirmed. Furthermore, an equivalent ZnO grain size was obtained even when the sintering temperature was reduced by 100℃.

Through this development, in order to suppress void generation within the sintered body due to low-temperature, short-time sintering, efforts were made to control the microstructure to achieve densification even at low temperatures, and the raw material powder pulverization mixing process and sintering pattern were improved. Fig. 7 shows binarized images of the microstructure before and after process improvement, and a graph arranged in order from largest to smallest void width. Suppression of coarse void generation and reduction of void number were confirmed from the process improvement, and a more ideal microstructure was obtained.

Furthermore, Table 1 shows the results of the electrical characteristics of the conventional block and the developed block. The deterioration of electrical characteristics due to lower sintering temperatures was improved by repeatedly optimizing the formulation, resulting in better characteristics in both limit voltage ratio and power loss compared to



(a) Before improvements (b) After improvement



(c) Voids width before and after improvements

Fig. 7 **Microstructure and Voids Width of Blocks Sintered at Low Temperature for a Short Time**

We were able to reduce the occurrence of large voids by improving the grinding, mixing, and sintering patterns.

conventional blocks. Discharge withstand tests also met the required specifications, achieving characteristics equivalent to or better than conventional blocks.

These performance improvements are due to the reduction of segregated materials through formulation changes and improvements in the manufacturing process. During surge absorption, surge current selectively flows through conductive ZnO. At this time, the reduction in pinned particles, which are insulating components, and their uniform dispersion, which increases current paths and allows for more uniform current flow, are considered to be

Table 1 **Comparison of Electrical Properties of Developed Zinc Oxide Blocks**

By adjusting the formulation and improving the manufacturing process, good characteristic have been obtained despite short sintering at low temperatures.

Item	Conventional blocks	Developed blocks
Reference voltage (V/mm)	240	240
Limit voltage (p.u.)	1	0.97※2
Power loss (p.u.) ※1	1	0.7※2
4/10 μs withstand capability	Passed	Passed
2 ms withstand capability	Passed	Passed

Note: ※1. 170℃ - charging rate 85%
※2. Performance improved below 1

the factors contributing to the performance improvement.

Through these formulation adjustments and improvements in the manufacturing process, it is expected that CO_2 emissions during the sintering process can be reduced by 50% while maintaining product performance.

6 Postscript

This paper introduces a low-temperature, short-time sintering process technology for zinc oxide block manufacturing. By optimizing the formulation and improving manufacturing process conditions, we anticipate a 50% reduction in CO_2 emissions while maintaining performance equivalent to or better than conventional methods.

Going forward, we will continue to work on further improving manufacturing technology to achieve both reduced environmental impact and high product performance. We will continue to promote technological development so that this development can contribute to achieving carbon neutrality and maintaining a reliable power supply.

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