Alumina-Mullite Porcelain as a Compromised Product for High-Voltage and Low-Sintering Insulators

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Development of ceramic materials for high-voltage insulators tends to substitute the quartz portion with alumina in order to achieve greater product reliability. However, the compositions with high alumina content require additional processing or increasing sintering temperature resulting in an economic disadvantage for the alumina porcelain. The introduction of alumina-mullite porcelain is another alternative which reduces structural stresses induced by quartz and, at the same time, lower the operating cost. This work will present the effect of changing composition by varying the amount of raw materials on the fired strength along with an evaluation of phases and microstructures. The results will give practical guidance for the manufacturers who need to improve their products for high-voltage applications with a slight change in the sintering conditions.

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1. Introduction

The importance of electrical energy in our society requires the sustainable availability in a high level of safety in the power plant for production and transmission. Two important functions of high-voltage insulators are to insulate the active components and to care for the mechanical fixation.\(^1\) High electrical and mechanical strengths are of importance for the insulators to fulfill these functions. In high-voltage applications, esp. in the severe condition e.g., the case of a sudden temperature increase and long-term performance, quartz porcelain caused serious problems in decreasing strength due to microcracks initiated by structural stresses.\(^2\) This is due to the quartz inversion (573°C) resulting in a quartz particle volume decrease of 2% and the β- to α-cristobalite (225° – 250°C) producing a large volumetric change of 5%.\(^3\) Thus, the way to reduce the structural stresses is that crystalline quartz was replaced by alumina as the strength carrier. The basic substitution of quartz for alumina was volume-for-volume substitution. It is expected that this substitution would provide a matrix of glass and mullite in an equivalent volume to alumina substituted for flint.\(^4\) This concept is a basic for this research to improve alumina-mullite porcelain for high-tension application. Therefore, the first goal is to develop a free-of-quartz microstructure.

The use of alumina as a substitute for quartz in porcelain insulators has been developed extensively since 1921.\(^5\) Although several results had been accomplished providing technical advantages, the commercial applications still require the formula modification related to process conditions of each manufacture. This is due to the compositions with high alumina content requiring an additional processing or increasing sintering temperature. The other goal of this work is to modify the compositions for economical operating cost and reduction of structural stress. The portion variations of the triaxial blends of clay, feldspar and a filler material, i.e., quartz or alumina, will affect their microstructures, i.e., an occurrence of mullite, alumina, quartz and glassy phase, which, in turn, will change the electrical and mechanical strengths of the insulators. The structure-property relationship plays a crucial role and influences on the reliability of the insulators. The purpose of this work is to present the connection between microstructure and physical properties of the insulators.

2. Experimental procedure

The basic criteria for introduction of the alumina-mullite porcelains were to form by the commercial processes of extrusion, to vitrify at 1230°C and to have low loss in manufacture. For this experiment, the MT-1 composition was an original formula for modification. Throughout this work, the amount of feldspar was kept at the constant value of 30 wt.%. The amount of ball clay content was varied between 40 and 30 wt % to observe a change in the green strength of the specimens. The substitution of flint for alumina was volume-for-volume substitution; for example, \((3.96/2.65) \times (\% \text{ flint}).^3\) Thus, the 22 wt% of alumina (A-21) in the formula MT-2 and -3 replaced the 15 wt% of flint in the formula MT-1. The amount of alumina in the formula MT-4 was calculated based on the 20 wt% of flint. Table 1 shows the compositions used for the modification.

The local ball and china clays, blended feldspars, local flint

<table>
<thead>
<tr>
<th>Table 1. Four Formulas Used to Modify the Insulator Bodies</th>
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<td>Raw materials (%)</td>
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<tr>
<td>Ball clay</td>
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<tr>
<td>Kaolin</td>
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<td>Feldspar</td>
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<td>Flint</td>
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<tr>
<td>Alumina (A-21)</td>
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<tr>
<td>Al₂O₃·3SiO₂</td>
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<td>K₂O·Na₂O</td>
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and alumina A-21 were used as the starting materials. All raw materials were characterized to determine their particle sizes and shapes and chemical compositions using light scattering technique (Mastersizer S, Malvern) and scanning electron microscopy (SEM; JEOL, JSM 5410). The alumina A-21 powders were wet-ground for 24 hrs to deagglomerate their particles. The 0.24 wt% of Darvan C (ammonium polymethyleneacrylate) was used as a dispersant for the alumina slip. The non-plastic portion, i.e., feldspar and flint, including kaolin, were poured to the alumina slip and milled for another 3 hrs. The ball clay was, later, added to the system, milled again for another 14 hrs and, then, passed through the sieve sized 120 mesh (150 microns) to separate fine sand and the organic matters, i.e., coal and root residues. The slip was soaked in the plaster mold to reduce its moisture content down to a range of 16-18%. A stiff paste was, finally, extruded into the small bars with a diameter of 25 mm and a length of 115 mm. The rod specimens were dried and fired at the temperature of 1230°C for 2 hrs under the reducing atmosphere.

The physical properties, i.e., water absorption, bulk density, and apparent porosity, were characterized based on ASTM C373–88. The dried and fired shrinkages of the specimens were measured using ASTM C326–82. The modulus of rupture (MOR) of the specimens was measured using ASTM C689–80 (reapproved 1985). The dielectric constant was measured using Impedance/Gain-phased analyzer model 4194A (HP) at a frequency of 1 kHz.

The fired specimens were cold-mounted with the resin typed Specifix–20 and polished using diamond pastes sized 11, 6, 3 and 1 microns. The polished samples were chemical-etched by hydrofluoric acid (HF) at a concentration of 4 wt.% for 5 min. After cleaning the surfaces, the etched specimens were gold-sputtered. Each specimen was characterized using SEM and image analysis (Omnimit 3–4 version 1.5).

3. Results

3.1 Raw materials characterization

Based on the SEM result, the as-received Al₂O₃ (A-21) powders present disc-like primary particles size of 1–5 microns in diameter with particle agglomerates having diameters ≤50 microns (Fig. 1). It was found that the median diameter sizes of the alumina powders were approximately 10.55 microns with a span of 2.18 microns by light scattering technique. After the alumina slip was wet-milled for 24 hrs, the median diameter values of the powders were decreased less than 4 microns. The median diameter sizes of ball clay, kaolin, flint and feldspar were approximately 3.45, 18.09, 14.69 and 9.29 microns, respectively. After the mixed-body slips of all compositions (MT1–4) were wet-milled for 41 hrs, the median diameter sizes of the mixed-body powders were in a range of 2–5 microns.

3.2 Physical and electrical properties of the mixed-body compositions

The physical and electrical properties of four compositions were measured and are recorded and compared with typical electrical porcelain in Table 2. The water absorptions of all specimens are not zero but less than 0.5%. However, they increased with a change in the compositions from MT-1 to MT-4. Typically, the water absorption of the electrical porcelain should be equal to zero as shown in the last column of Table 2. This implies that the substitution of feldspar with alumina including a change in the kaolin content influence on the vitrification of the specimens. In addition, the modulus of rupture (MOR) of the specimens are altered according to the modification in the composition. The MT-2 porcelain specimens exhibit the highest MOR of 165 MPa whereas the MT-4 specimens, the composition with the highest alumina content, present the lowest value of 94 MPa. The dielectric constants of all compositions are comparable to those of typical electric porcelain for high-tension application as shown in Table 2. However, further investigation in dielectric strength and thermal mechanical performance test are required to ensure an endurance of the MT-2 specimen.

3.3 Microstructure evaluation

SEM photomicrographs present the existing phases in the microstructure of the specimens from the four formulas.

![Fig. 1. SEM photomicrographs present the morphology of the as-received alumina (A-21) particles: (a) Alumina (A-21) at the magnification of 5,000x and (b) Alumina (A-21) at the magnification of 500x.](image-url)
tomicrographs of these multiphase microstructures of each specimen were quantitatively measured using optical microscopy and image analysis. The images were, firstly, transformed to the binary color images and, then, the area measurement program was used to quantify the amount of each phase (Fig. 3). However, the limitation of this technique is that the contrast of each phase must be clearly distinguished. As a result, three groups of the multiphase microstructures were categorized as follows: 1) mullite, 2) α-corundum and quartz and 3) pores and matrix including glassy phase. Table 3 compares the amount of a multiphase microstructure of the fired specimens of all compositions, MT-1, -2, -3 and -4. It can be seen that the MT-3 specimens possess the highest amount of mullite (52.5%) and the lowest amount of pores and glassy phase (28.1%).

4. Discussion

It is observed that the as-received alumina (A-21) powders consist of large agglomerates; thus, they need to be ground to achieve the primary particles (Fig. 1), enhancing homogeneity and the chemical reactivity of powders. The fine particles also accelerate the sintering process to be able to occur at lower temperatures. Then, the step in charging of raw materials should be of concern because the milling time could be reduced, meanwhile, the obtained slip is still in an optimum condition. The following process is therefore recommended firstly starting with grinding alumina, then, charging feldspars, fine and kaolin and, finally, mixing with ball clays. The sieve separation, particle size testing and specific gravity of the slip are three practical methods used to control the quality and consistency of the body slips.

The aim of this work is to fabricate the electrical insulator bodies that can be vitrified at the temperature of 1230°C. Since the insulator bodies mature are changed not by temperature alone, but by the length of time they are exposed to a given temperature also. Thus, the time-temperature factor, the work heat, should be of concern. With regard to the heating/cooling rates and the reduction atmosphere in this work, thus, the maximum work heat during firing is in a range of Cone 9-11 (1260-1293°C). This work heat is high enough to accelerate the chemical reactions of the bodies during firing e.g., the formation of mullite from kaolin and feldspar, the dissolution of quartz, and the formation of α-corundum. Additionally, the work heat is in the same level as the heat generated to sinter the quartz insulator of the recent production line in the manufacture. This will allow the manufacturers to improve their products with the same firing conditions as usual. Further investigation is still required to optimize the sintering conditions because the heating and cooling rate could be adjusted due to free-of-quartz microstructure. However, an occurrence in the chemical reaction of the insulator bodies, also, depends on the chemical compositions. Based on the chemical composition, it should be noted that the Al₂O₃/SiO₂ and K₂O: Na₂O ratio could play a significant role in densification of tested specimens (Table 1). To achieve high density for the alumina-modified composition at the same firing conditions as the quartz composition, the amount of Na₂O in the K₂O: Na₂O ratio must increase. A change in alkali ratio in the compositions could alter the microstructures and result in a difference in physical properties.

Before the chemical etching, it is found that the pore content in microstructures of all specimens is in the range of 8-12%. After the chemical etching, the amount of pores and glassy phase of each composition are altered. This implies that a difference is due to a significant change in the glassy phase of
each composition. The MT–1 composition, the original formula, has the highest amount of the glassy phase of approximately 31%, causing the lowest water absorption of 0.08%. Conversely, the high value in the amount of glassy phase leads to a weakness in strength. Therefore, the MT–1 specimens exhibit lower MOR than the MT–2 specimens with the amount of glassy phase of approximately 23%.

The MT–3 composition consists of the highest amount of kaolin (18%). The clay relicts were transformed to mullite during the firing process of the specimens. Consequently, the MT–3 microstructure shows the highest amount of the mullite phase of approximately 33% whereas the others possess the mullite content of approximately 46%. However, the kaolin, Al_{2}O_{3}-2SiO_{2}-2H_{2}O, contributes to the aluminum oxide and silicon dioxide ratio in the chemical composition, resulting in an increase in total alumina content and, also, an increase in firing temperature for vitrification. Firing at the target temperature as the others might not be suitable for the MT–3 specimen as indicated from a low value in MOR (136 MPa) and a little change in water absorption (0.36%).

The MT–4 composition was the formula with the highest alumina content of 30%. This requires either a high in heat work or a high alkali content, the fluxing agent, from the feldspar, to vitrify the MT–4 specimen. Regarding the target firing conditions, the MT–4 specimens were improperly fired. This results in the lowest MOR value of 94 MPa, even lower than the MT–1 quartz porcelain.

Regarding the highest MOR value, the MT–2 composition can be a promising composition for the electrical insulator fired at the same conditions as the quartz insulators in recent manufacture. However, the residue quartz still occurs in its microstructure (Fig. 2(b)). The residue quartz may come
from the free silica in ball clay. Thus, to eliminate the residue quartz, a careful screening the ball slip before mixing and an improvement in firing schedule, i.e., a change in cooling rate, are required. A change in the cooling rate could be dissolved the quartz to be fine sizes which the quartz transformation is less severe.

5. Conclusions

Two important properties of the high-voltage insulators are the mechanical and electrical strengths that can withstand the operation, esp. in the severe conditions. The use of alumina as a substitution for quartz in porcelain insulators provides technical advantages but requires more expensive investment in production. The compositional modification using the variation of triaxial clay, feldspar and flint is required for economical operating cost and reduction of structural stresses. The structural related property is the key to accomplish the task. With the target temperature and the work heat of Cone 9-11, the MT-2 composition with a MOR of 165 MPa was found to be a promising candidate for the insulators used for high-tension application.

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References