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CHARACTERIZATIONS OF CERAMIC INSULATION COATINGS ON STAINLESS-STEEL TAPES FOR MAGNET TECHNOLOGY

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Abstract: Characterizations of high temperature ceramic insulation coatings were investigated by surface conductivity, electric strength, dielectric constant, mass lost and corrosion techniques. $MgO\text{-}ZrO_2$ was coated on Stainless-Steel-304 (SS) tapes by reel-to-reel sol-gel process for investigation of characterizations of $MgO\text{-}ZrO_2$ as insulation coatings. Tapes were produced several dips for application of HTS/LTS high field insert coils and magnets. Solutions were prepared by using Mg and Zr based precursors, solvent and chelating agent, then the insulations was coated on long-length SS substrate. Characterizations of electrical strength and dielectric

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constant were tested by using standardization equipment. Thermogravimetric (TGA) analyzes in air and in nitrogen was done. The effect of corrosion test according to the standardization of ASTM B 117 was studied. Surface morphology of micrographs of corrosion test samples was examined using ESEM.

Keywords: Electrical properties; dielectric constant; TGA analyzes; corrosion resistance; MgO-ZrO_2.

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INTRODUCTION

MgO-ZrO_2 was insulated on SS by using continue sol-gel dip coating at room temperature. Coated material exhibits interesting properties such as a high and adjustable dielectric constant, mass loss and corrosion resist. These characterizations make the materials interesting for different electronic applications such as capacitors [1] and magnet coil [2, 3, 4].

Ceramic-based reel-to-reel continuous sol-gel coating technique was developed for producing in Wind and React (W@R) magnet coils for HTS/LTS at National High Magnetic Field Lab.[5]. The high temperature ceramic insulation of the MgO-ZrO_2 was coated on long-length Stainless-Steel-304 (SS) tapes by using sol-gel process. The essential parameters of the characterizations of these coatings are electrical conductivity [6, 7], electric strength [8, 9, 10], dielectric constant [11, 12, 13], mass loss [14] and corrosion resistance [15, 16]. Electric strength and dielectric constant of the coatings depend on the insulation thickness, stress and temperature [2, 12, 17, 18]. Mass loss relies on the preparation of coating as varying of precursors and annealing of coating [19]. Corrosion resistances of the tapes depend on coating quality, kinds of coated materials and substrate [2, 3, 10]. The advantages details of the sol-gel process are seen in References [12, 17, 18]. ZrO_2 based coating and its compounds (MgO-ZrO_2) have widely used due to their excellent performances; such as chemical stability, mechanical strength and ionic conductivity [20, 21, 22]. Pure zirconium has three crystal phases at different temperatures. This material has monoclinic structure at low temperature (~1170°C), tetragonal on intermediate temperature (1170 to 2370°C), and it shows cubic phase at high temperatures (>2370°C). The transformation from the phase of tetragonal to monoclinic is rapid [23]. So volume of structure increase that causes extensive cracking in the material. This behaviour causes the destroying the mechanical properties of fabricated components during cooling and various stress [24]. It makes pure zirconium useless for application. Several oxides (MgO, CaO, Y_2O_3, earth oxide) added into zirconia, its structure changes and the high temperature cubic structure zirconium can be uphold to room temperature, which shows significantly stabilize, better insulation, and lower conductivity [12, 25, 26]. ZrO_2 has superior properties such as corrosion resistance, less mass loss, high hardness, high/low temperature, electrical insulation, high conductivity and large relative dielectric constant. Dielectric constant of crystal phase ZrO_2 is 19, 20, 37 and 38 for orthorhombic, monoclinic, cubic and tetragonal phase, respectively [27]. MgO increases the corrosion resist [2, 12]. The coating porosity and thickness play important roles on the corrosion behavior of ZrO_2 coatings [2, 8, 10, 12, 18]. These characterizations make the materials interesting for different electronic applications such as capacitors and magnet coil.

The aim of this work was to study the surface conductivity, electric strength and dielectric constant of MgO-ZrO_2 insulation coatings. Thermogravimetric (TGA) analyzes in air and in nitrogen was carried out and the effect of corrosion was studied. The surface morphology of samples was presented for the homogeneous sol-gel MgO-ZrO_2 insulation coatings.

EXPERIMENTAL PROCEDURE

Two types of solution, dilute and normal, were prepared. Dilute solution is obtained by adding 5/5 isopropanol to normal solution. The normal coating solution consists of 2/10 mol MgO and 8/10 ZrO_2. Solution was prepared by using zirconium tetrabutoxide, isopropanol and acetone. Several Mg and zirconium tetrabutoxide precursors were used as precursors, which were prepared as homogenous solution by magnetic stirring at 18 ºC for 10 hors period at 100 rpm. After the preparation of sol-gel solutions, SS-304 tapes, 5 mm width and 0.0254 mm thickness, were wiped with acetone in order to clean surface for ceramic insulation coatings. Then SS tape was dipped into solution and pulled out through the tree-zone furnace in non-vacuum withdrawal speed of 0.65 m/min. The details information of solution preparation, insulation process and insulation coating set up is seen in References [8, 10, 12]. Test samples were cut 10 cm in length from coated commercial SS tapes and the insulation layers were removed from the both ends. Test couples produced for 4, 8 and 12 dip samples. SS ribbons were made into couples form a capacitance. Short time method was performed to determine the dielectric strength of the insulated samples.

Measurements were carried out by using equipment of Modal 6517A Electrometer/High Resistance Meter, 3100 Handheld Capacitance meter and Model 248 High-Voltage (±1.5V to 5kV) Supply. Resistance, capacitance and HVbd were measured at least three times. The surface conductivity was calculated ($\sigma = 1/\rho$) from surface resistivity. The dielectric constant of samples was calculated ignoring the changing of capacitor gaps due to do pressure.

$$\varepsilon_r = \frac{Cd}{\varepsilon_0 A} \quad (1)$$

Where, C is capacitance, d is twice the insulation coating thickness, ε_0 is permittivity of free space (8.854 10^{-12} F/m), A is coated area in the sandwich, ε_r is dielectric constant of insulation coatings in Eq. (1).

Insulation layers were removed from MgO-ZrO_2 coated on SS. Then, using Shimadzu-TG50 A, Thermogravimetric (TGA) analyzes in air and in nitrogen with a speed of 10 °C/minutes up to 1000 °C was performed.

The effect of corrosion of $MgO-ZrO_2$ insulation coating was performed at 200 hours according to the standardization of ASTM B 117 by using Erichson Corrosion Testing Apparatus for Salt Spray Test Model 606. Figures were presented with and without corrosion test samples.

RESULTS AND DISCUSSIONS

a. Electrical Characterization

Electrical properties of ceramic insulation coatings depend on coating thickness, cracks in coatings dopant materials, pressure and temperature. Surface conductivity increases with insulation coatings decrease, which is strongly depends on pressure. As seen in Fig.1, surface conductivity starts to goes up the

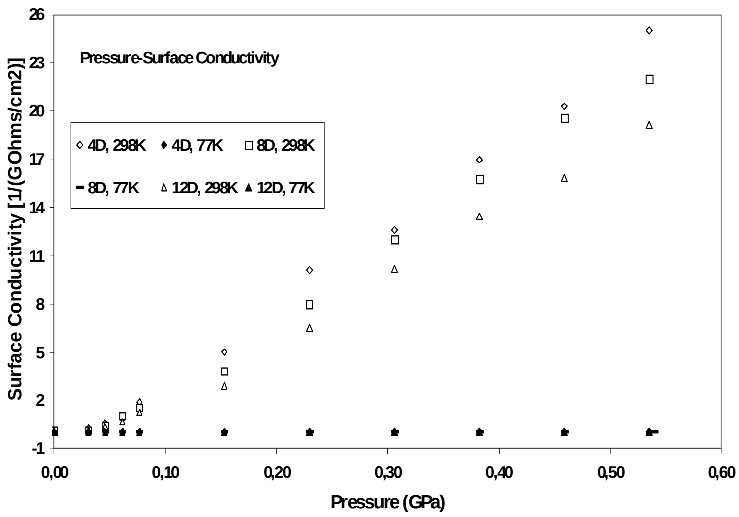


Fig. 1. Surface conductivity as a function of pressure. When insulation coating increses, surface conductivity decreases. $MgO-ZrO_2$ coating strongly depends on pressure.

vicinity of pressure 0.08 GPa at 298K. It is supposed that the holes in insulation influence the surface conductivity at 298 K. Electric strength ($E = V/d$) should be constant, but it slightly exhibit differences for three dips at 298 K and 77 K, as seen in Fig.2. When coating thickness increases, electric strength increases.

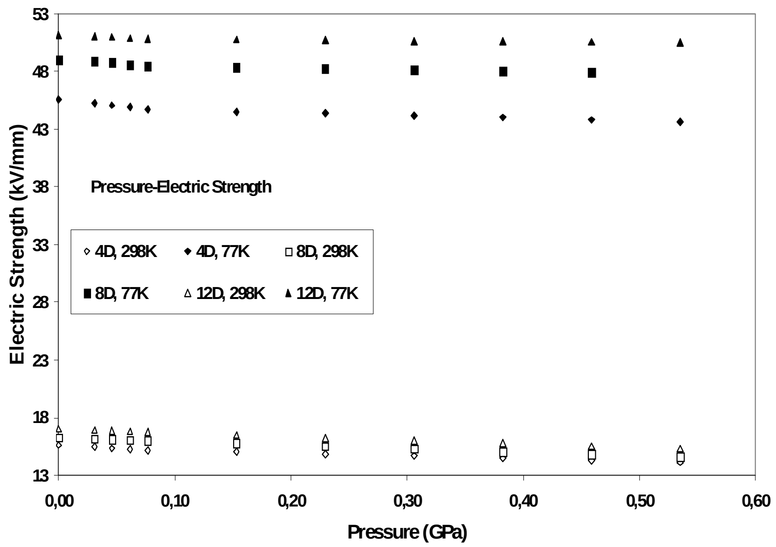


Fig. 2. Electric strength vs pressure with the samples. Electric strength decreases with small ratio decreasing with dip numbers.

Dielectric constant increases with the increase of dip number. These increments are higher between at pressure 0-0.08 GPa than 0.08-0.60 GP, as seen Fig.3. When the samples were cooled from 298 K to 77 K, the values of the surface conductivity and the dielectric constant decreases, the electric strength increase.

The variations of the conductivity, electric strength and dielectric constant are given in Table 1.

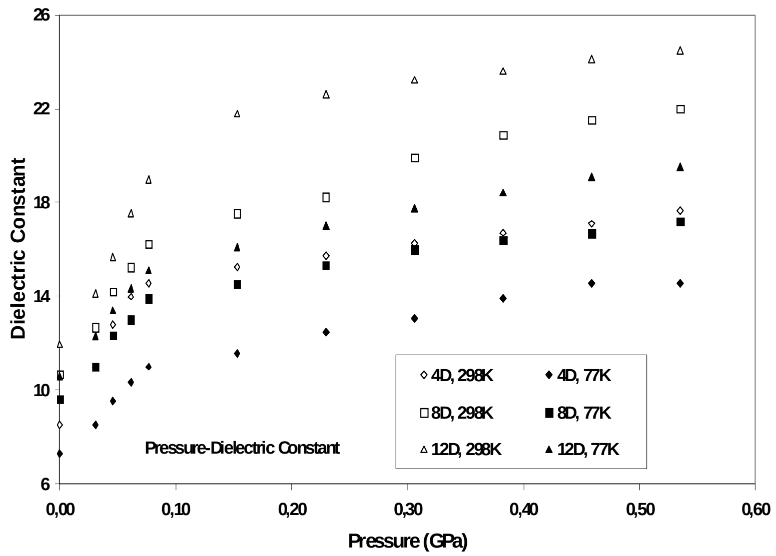


Fig. 3. Dielectric constant vs pressure. At low pressure dielectric constant sharply increase due to do holes in insulation. After 0.15 GPa, they very slightly go up.

Table 1. The average values of measurements of sol-gel $MgO\text{-}ZrO_2$

$MgOZrO_2$	**298 K**			**77 K**		
Dip #	4	8	12	4	8	12
σ ($cm^2/G\Omega$)	0.16→25.0	0.13→22.0	0.12→19.12	0.065	0.055	0.050
Electric Strength (kV/mm)	115.62→14.1	16.27→14.6	17.03→15.13	45.58→43.7	48.96→47.8	51.18→50.5
Dielektric Constant	8.51→17.6	10.67→22.	11.96→24.5	7.28→14.6	9.61→17.2	10.62→19.

b. Mass Loss Characterization

20 mg MgO-ZrO_2 insulation was removed the insulation coating from the coated test samples. Then, mass loss of coating was performed in air and nitrogen. Thermogravimetric (TGA) analyze in air and in nitrogen with a speed of 10°C/minutes up to 1000°C was done by using Shimadzu-TG50 A. As seen in Fig. 4, the first masses losses are starting the decrease at vicinity 90°C in atmosphere and in nitrogen, which is about 2%. It is supposed that the first mass loss is removal of solvents in holes and evaporation of volatile organics. The second masses losses are observed from 7% to 12% for the former 340°C and the latter 440°C. Between these temperatures carbon-based materials were able to born out since their combustion are about at 440 °C. The last step masses loss are between 13%-16% at 620°C - 820°C. The mass loss is 1.98 mg higher in atmosphere than in nitrogen. Mass loss can decrease by arranging the precursors of insulation and anneyling of the coated samples.

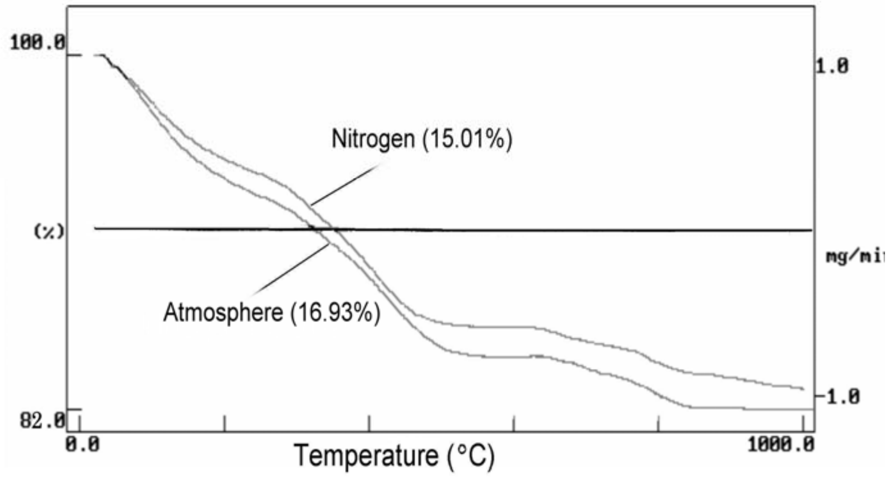
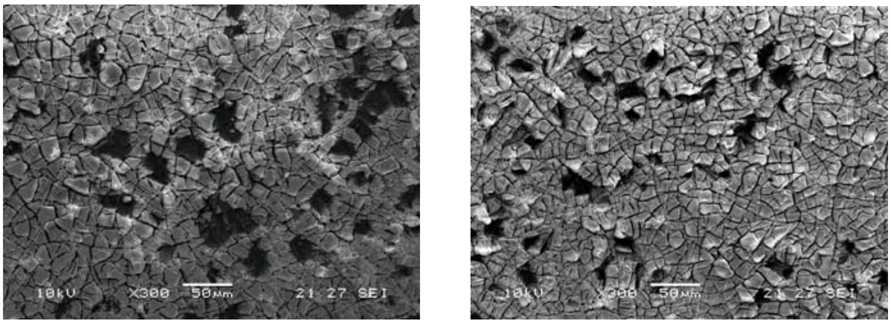


Fig. 4. The percentages of the mass loss of MgO-ZrO_2 insulated coating in air and in nitrogen.

c. Corrosion Characterization

According to the standardization of ASTM B 117, the effect of corrosion of MgO-ZrO_2 insulation coating was performed by salt spray method at 120 hours. Erichson Corrosion Testing Apparatus for Salt Spray Test Model 606 was used in test. Test results are shown that the surface morphology of insulation coating did not affected and the coating did not removed from substrate stainless-steel. Fig. 5 shows the normal and after the corrosion test was carried out of sample.



Corrosion treatment Normal

Fig. 5. SEM micrographs show the insulating coatings normal and after the corrosion test were performed. The scale bars are 50 μm.

CONCLUSION

The high temperature MgO-ZrO_2 insulation was coated on SS-304 tapes at 4, 8, and 12 dips by using reel-to-reel sol-gel technique. Electrical properties of test samples were performed. Surface conductivity increases with decreasing coating thickness. Dielectric constant increases with increasing coating thickness. Surface conductivity sharply increases at low pressure (0-0.08 GPa). Between these pressures, the surface conductivity shows slightly difference due to do holes in insulation. When the samples cooled from 298 K to 77 K, surface conductivity and dielectric constant decreases, and electric strength values increase. The highest surface conductivity was found with sample at 4 dips, which is 25 (GΩ/cm2) at 298 K. The electric strength value at 77 K was found with samples at 12 dips, which is 50.53 kV/mm. The highest dielectric constant was found with sample at 12 dips at 298 K, which is 11.96. Thermogravimetric (TGA) analyzes in air and in nitrogen with a speed of 10 °C/minutes up to 1000 °C was performed and mass loss were 15.01 % in nitrogen and 16.93 % in air. According to the standardization of ASTM B 117, the corrosion test by salt spray test, the surface morphology of insulation coating did not affected and the coating did not removed from substrate stainless-steel. The results show that the higher MgO content and the thicker the insulation coatings, the better the corrosion resistance, which is attributed to the resistance of coatings.

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