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CERAMIC INSULATION COATINGS ON VERY THIN NB_3SN WIRES FOR LTS COILS

Lutfi ARDA[1,a,*], Omer CAKIROGLU[2,a] and Sahin AKTAS[3]

[a] *National High Magnetic Field Laboratory, Florida State University, 1800 E. Paul Dirac Dr., Tallahassee, FL 32310, USA*
[1]*Bahcesehir University, Faculty of Arts and Science. Besiktas Campus, 34349, Besiktas, Istanbul, Turkey*
[2]*Istanbul University, Hasan Ali Yücel Faculty of Education, 34452, Beyazıt, Fatih, Istanbul, Turkey*
[3]*Sahin Aktas, Marmara University, Art and Science Faculty, 34722 Ziverbey, Kadıköy, Istanbul*

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Abstract: Ceramic insulation coatings on very thin Nb3Sn wires which are 0.001 mm (0.004”) in diameter were investigated by reel-to-reel sol-gel dip coating system. Varying thickness from submicron to several of microns sol-gel zirconium based ceramic coating has been successfully applied to Nb3Sn wires at the National High Magnetic Field Laboratory. Ceramic insulations were prepared using solutions of Yttrium and Zirconium based organometallic compounds. The film thickness was controlled by number of coating, withdrawal speed and solution chemistry.

[*] Corresponding author. Fax: +90-212-381 0300, e-mail: lutfi.arda@bahcesehir.edu.tr

Crack-free, dense and ~ 546 nm coating was obtained with appropriate dilution of solutions. The surface morphologies and microstructure of all samples were characterized by ESEM, DTA, TGA and XRD. Resistance was measured using of HP 4339 A High Resistance Meter.

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Keywords: Nb_3Sn wire, Sol-gel, Y_2O_3-ZrO_2, Insulation, LTS coils

INTRODUCTION

Nb_3Sn wires have been used many applications. One of them is coil fabrication by using "Wind and React", W&R technique. For Coil fabrication, one of the most important part is insulation [1-3] which is made from E-glass, S-glass, standard quartz by a vacuum impregnation with a resin and ZrO_2 and ZrO_2 based ceramic coating. ZrO_2 based ceramic coating have superior properties such as corrosion resistance, high hardness, chemical and thermal stability, ionic and electrical conductivity [4-6], therefore many researcher have studied ZrO_2 based ceramic thin and thick films with different thickness on the glass, wires, tapes, and single crystal by using various methods. These methods include chemical vapor deposition (CVD), spray pyrolysis, electron beam evaporation, sputtering, plasma spray and sol-gel method. Among these methods the reel-to-reel, continuous sol-gel technique is the most promising for low cost, long length, low temperature processing, versatility in coating different substrate materials and simplicity for insulation coating [8-14].

These properties of sol gel method make useful for high temperature compatible insulation. In previous study, we have developed and used MgO-ZrO_2 insulation coating on Stainless Steel for a 5 T superconducting $Bi_2Sr_2CaCu_2$)8+& (Bi2212) insert magnet which generated 5.11 T in a 25.05 T background magnetic field [15,16], SnO_2-ZrO_2 insulation coating on the continuous tube forming and filling (CTTF) Cu/MgB_2 wire which we fabricated and tested of W&R first MgB_2 coils in U.S.[17] and Y_2O_3-ZrO_2 insulation coating on CTTF Monel/Fe/MgB_2 wire at the National high Magnetic Field Laboratory (NHMFL).

The cubic phase of ZrO_2 is above 2370 °C and demonstrates the better insulation properties among different ZrO_2 modification. Stabilization which is the subject of wide scientific investigation, of cubic phase of ZrO2 have been achieved using doping of MgO, Y_2O_3, CaO and rare earth oxides [7, 14]. Zr and Zr based compounds such as MgO-ZrO_2, Y_2O_3-ZrO_2, SnO_2-ZrO_2, InO_2-ZrO_2 and the others RE_2O_3-ZrO_2 are compatible with high processing temperature and low temperature (4.2) K. Among those insulation coating Y_2O_3-ZrO_2 has high electrical resistance and adhesive strength which are GOhms, 2.400 MPa respectively [8, 13].

In this study we have investigated processing, characterization and sol-gel parameters such as solution properties, withdrawal rate, drying, heat treatment, annealing condition of the submicron thickness Y_2O_3-ZrO_2 insulation coating on very thin Nb_3Sn wires using reel-to-reel sol-gel technique.

EXPERIMENTAL PROCEDURE

Short samples of about 10 cm in length and 0.004” in diameter were cut from Nb_3Sn wires. These short samples were ultrasonically cleaned in dilute HNO_3 solution and pure acetone in order. Two types of solution were prepared, dilute and normal. The normal coating solutions consists of %3 mol Y_2O_3-ZrO_2. The Y_2O_3-ZrO_2 solutions and polycrystalline powder samples were synthesized by sol-gel process using Yttrium Acetate and Zirconium tetrabutoxide. For normal solution Yttrium III acetate 99.99% was dissolved in isoproponal at room temperature for duration of 90 min. $Zr[O(CH_2)_3CH_3]_4$ was then added Glacial acetic acid (GAA) and Acetyle acetone were used as chelating agent in solution, dilute solutions are obtained varying ratio (10, 20,….50)/50 isoproponal to normal solution and then stirred with a magnetic stirrer for 24 hours at room temperature until a transparent solution was obtained. The pH of the solutions was measured by standard pH meter. Viscosity of the solutions was varied by adding isoproponal.

Y_2O_3-ZrO_2 film was coated with sol-gel method by using vertical three-zone furnace as seen in Fig.1. Furnace zone temperatures can be adjusted from 450-650 at bottom to the top. The film thickness on the wire was controlled by the withdrawal speed, the number of dipping and the dilution of solution. Process was repeated several times in order to achieve dense and uniform coating.

The thermal behaviour of the exrogels of these solutions which were dried at room temperature for 5 days was studied by using differential thermal analysis (DTA, Perkin Elmer series 7) and thermogravimetric analysis (TGA,

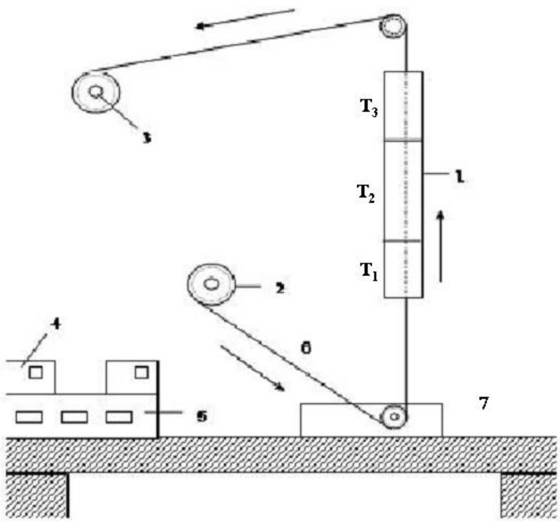

Fig. 1. The continuous, reel-to-reel sol gel coating system;(1) a three-zone-furnace, (2) pay of spool, (3) take-up spool , (4) two electric motor for spool, (5) furnace controllers, (6) tapes or wire being insulated and (7) solution tank.

Perkin Elmer series 7) techniques. X-ray diffraction profiles of powder samples and insulation were recorded using a Rigaku diffractometer with CuK$_\alpha$ radiation. Data for powder samples were collected at a room temperature over the range 18° < 2θ < 82° in 0.02° steps, with an integration time of 0.5 seconds. Surface morphology, thickness and stochiometry of coating films were observed by using the Environmental Scanning Electron Microscope (ESEM, electro scan model E-3 and Jeol-5910LV), the Tencor Alpha-step 200 profilemeter, and the Energy Dispersive Spectroscopy (EDS).

Table I. Properties of YSZ insulation coating on very thin Nb_3Sn wire by sol-gel method. Dilute solutions are obtained 50/50 isoproponal to normal solutions.

Sample ID (NHMFL)	**Coating Material**	**Number of Coating**	**$T_{Furnace}$ (°C)**	**Withdrawal Speed(*m/min*)**	**$R_{Ins.}$ ($10^9\Omega$)**
N-3	Y_2O_3-ZrO_2 (Normal Solution)	6	450, 500, 550	0.65	120
N -6	Y_2O_3-ZrO_2 (Normal Solution)	6	580, 610, 630	0.65	100
N-22	Y_2O_3-ZrO_2 (Dilute Solution)	10	450, 500, 550	0.65	4.0
N-23	Y_2O_3-ZrO_2	4 Dilute 2Normal 3 Dilute	450, 500, 550	0.65	2.0
N-24	Y_2O_3-ZrO_2 (Dilute Solution)	10	450, 500, 550	0.49	0.18
N-26	Y_2O_3-ZrO_2	4 Dilute 2 Normal 4 Dilute	450, 500, 550	0.65	1.8
N-27	Y_2O_3-ZrO_2	4 Dilute 2 Normal 4 Dilute	450, 500, 550	0.81	3.2
N-28	Y_2O_3-ZrO_2 (Dilute Solution)	10	450, 500, 550	1.46	300

RESULTS AND DISCUSSION

Y_2O_3-ZrO_2 insulation coating was deposited on very thin Nb_3Sn wires using the reel-to-reel sol-gel coating system. The insulation coating properties of Y_2O_3-ZrO_2 were summarizes in Table I. As seen in Table I the deposited films with dilute and normal solutions were dried from 450 to 580 °C. They were then exposed to heat-treating temperature in the range of 500-630 °C using in line three zone furnace. The coating process of inline three zone furnace in the continuous reel to reel sol-gel system has several steps: dipping, drying, burn-out, oxidation and bonding of coating to substrate. Those step depending on time and temperature. The best result was obtained N-28 sample which was prepared with 10 dips with dilute solutions. The quality of insulation film depends on withdrawal rate, drying, heat treatment condition and sol structure such as chemical composition, purity of precursor solvent catalyst materials and pH value of starting and stabilized solution. The finale pH value of the yttrium acetate solution was 9.69.

After obtaining Y_2O_3-ZrO_2 powder. The thermal behaviors of the exrogels are analyzed by using DTA and TGA to find the heat treatment temperatures in the zones of furnace. Fig. 2 shows the TG chart for the Y_2O_3-ZrO_2 which are obtained by drying the sol-gel solution at room temperature in air for 5 days. The Y_2O_3-ZrO_2 exrogels were analyzed in the temperature range between 0 and 800 °C under the air. The first weight decrease due to removal of the solvent and evaporation of volatile organic component is seen at 110 °C as shown in Fig. 3. The percentage of lost weight was 12%. The Carbon–based materials were burn out in two steps. First step; the second weight decrease was observed at 130-300 °C. Second step; the third weight decrease was observed at 300-400 °C. The combustion of carbon based materials was completed at 400 °C. The percentage of weight was 36 %. The oxidation was started around 400 °C and finished around 550 °C. The fourth weight decrease with 46 % at 550 °C.

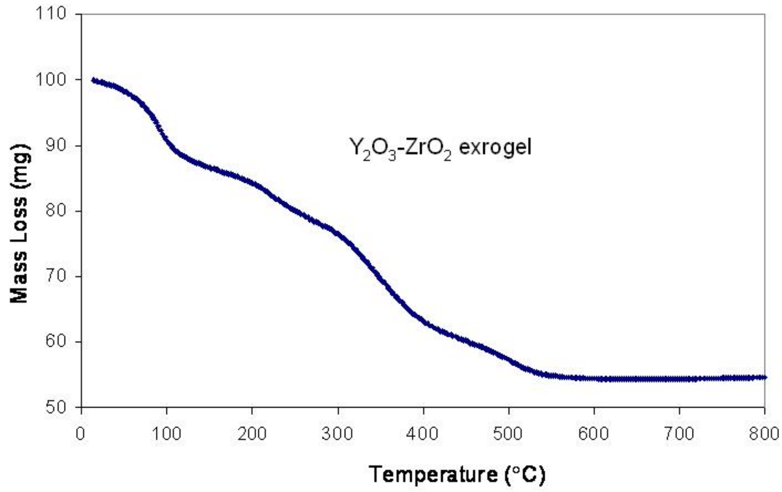

Fig. 2. TG curve of Y_2O_3-ZrO_2 exrogel powder.

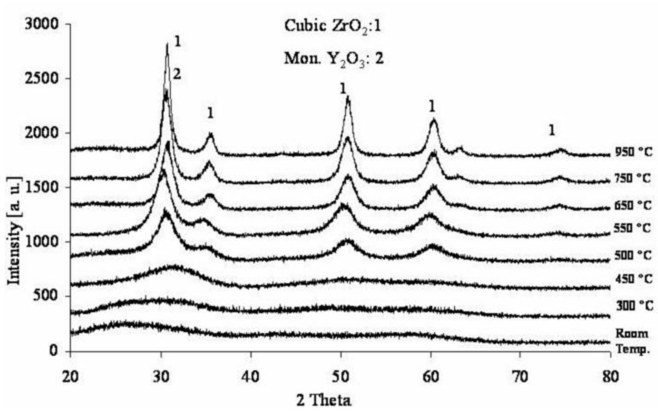

Fig. 3. XRD patterns of Y_2O_3-ZrO_2 powder annealed various temperatures under air.

XRD analysis were used to find phase and crystal structure of the samples. The X-ray diffractions of the annealed samples at various temperatures in the air are shown in Fig.3. The reflections correspond to Cubic ZrO_2, Mon Y_2O_3 structure. The peaks at 30.7°, 35.7°, 50.8° and 60.5° of belong to the cubic ZrO_2 phase and the peak at 30.7° belongs to the Mono Y_2O_3 phase. The high intensity peak observed at 30.7° of the cubic ZrO_2 and Mono Y_2O_3 phase is indexed to be. As also XRD patterns show that the films are at amorphous state at temperature below 450 °C which convert into crystalline phase at 500 °C or higher temperature.

Nb_3Sn wire contains typically several types of contaminants as shown Fig. 4a and b. For success of insulation coating it is essential to develop a scalable surface cleaning procedure to clean the Nb_3Sn wire before deposition of the insulation coating. Several cleaning technique are currently being used for substrate, wire, type…etc. In this study we used simple chemical method which includes dilute HNO_3 solution and pure acetone by using ultrasonic cleaner. It was found the cleaning treatment were removed all of contaminants successfully along surface of Nb3Sn wire as shown Fig. 4a and c which is required for quality bonding between the wire and insulation coating.

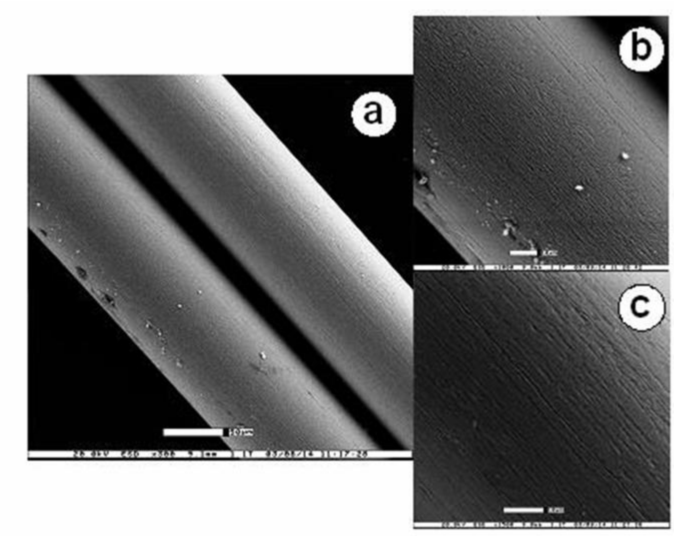

Fig. 4. SEM micrographs a) as received and after cleaned (right) Nb_3Sn wires b) high magnification of as received wires, c) high magnification of after cleaned wires . The wire diameter is 0.004” and the scale bars are 50, 10 and 10 μm, in a, b, and c respectively.

Fig. 5 depicts surface morphologies of N-3 and N-6 samples, As seen Fig. 5 surface is fairly smooth and there are maze of cracks running through the surface most likely due to drying stresses. These cracks was absent in the very thin Y_2O_3-ZrO_2 coating were achieved by diluting solution which are obtained 50/50 isoproponal to normal solution and high withdrawal rate as seen Fig. 6.

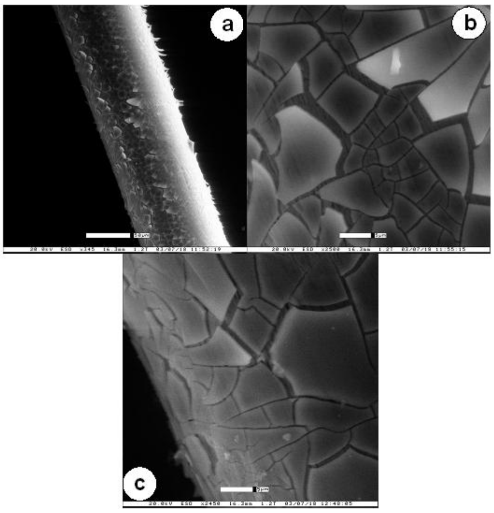

Fig. 5. SEM micrographs were taken from the surface of a) and b) N-3 sample and c) N-6 sample after sol-gel insulation. The scale bars are 50, 5 and 5 μm, in a, b, and c respectively.

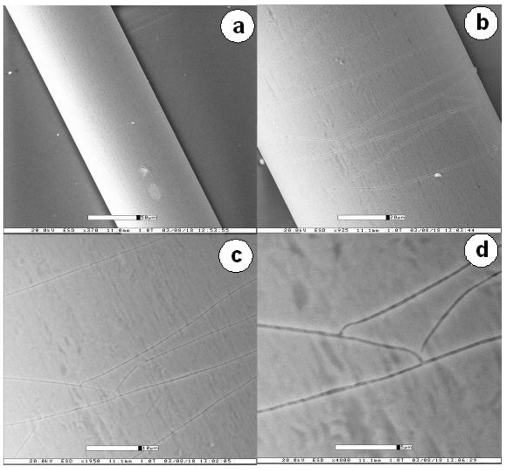

Fig. 6. Surface morphology of the surface of the N-28 sample. The white scale bars are 50, 20, 10 and 5 μm in a, b, c, and d respectively.

Thickness of the coating was controlled by viscosity of solution, number of dipping, changing withdrawal rate and temperature of three-zone furnace. Fig.6 shows the thickness of the insulation coating which was measured as approximately 546 nm for 10 dips dilute Y_2O_3-ZrO_2 solution, three zone furnace temperatures 450, 500, 550 °C from bottom to top respectively and withdrawal rate was 1.46 m/min.

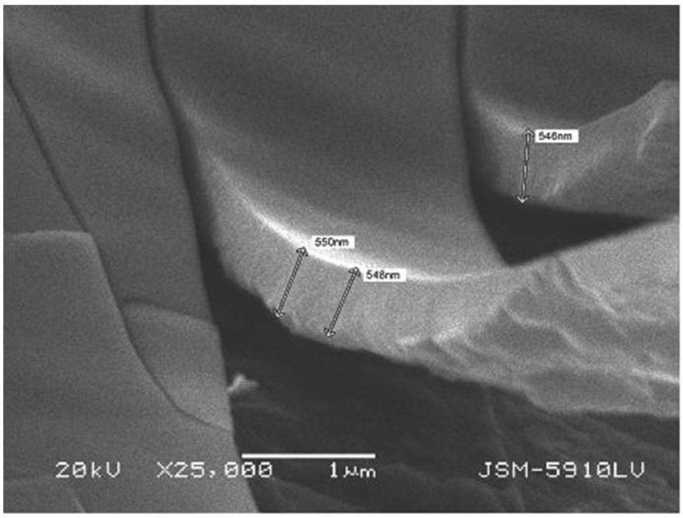

Fig. 7. SEM micrograph of a YSZ coating on Nb_3Sn wires which was 10 dips dilute solution and 1.46 m/min withdrawal speed. The thickness of the coating was approximately 546 nm.

CONCLUSIONS

Nb_3Sn wires were coated by Yttrium-Stabilized Zirconia (YSZ) using reel-to-reel sol-gel dip coating system. YSZ coating were oxidized after drying and heat treating in the range 450-550 °C. The coating films are at amorphous state at temperature below 450 °C which convert into crystalline phase at 500 °C or higher temperature.

The thickness of the film coating increases by increasing the number of dipping, withdrawal speed, and insulation density. When the coating thickness is increased, cracks start to occur. Sizeable cracks were observed on the wires as a result of insulation thickness and withdrawal speed. Crack free and thin sol-gel coating was produced from dilute solutions which are obtained 50/50 isoproponal to normal solution. The insulation layer was observed uniform on the wire by using ESEM.

The thickness of the uniform coating was approximately 546 nm. Cubic ZrO_2 and Mono Y_2O_3 phases were observed in the XRD of the YSZ powder. The average resistance of the 546 nm YSZ coating was obtained 10^{11} Ohms. This value is very high for room temperature resistance of other sol-gel ceramic insulation.

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