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Organic free montmorillonite-based flexible insulating sheaths for Nb_3Sn superconductor magnets

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ABSTRACT

Nb_3Sn is a superconductor that exhibits higher performances than NbTi alloy currently used in superconducting magnets, regarding both the critical magnetic field and critical current. However, Nb_3Sn is an intermetallic compound prepared by thermal treatment, which loses ductility and plasticity once reacted. Since organic materials cannot be used as insulating sheaths and applied before the thermal treatment required for the synthesis of Nb_3Sn, a clay mineral-based organic-free sheath was prepared, which can be applied to Nb_3Sn magnetic coils prepared by the wind & react method, before the thermal process. This process allows for facile shaping of the superconductor precursor, before reaction, along with the application of the insulating coating, the sintering of this coating being achieved by the thermal treatment required for the synthesis of Nb_3Sn. This process has been designed for industrial developments and facile scale-up. The final material is an organic-free ceramic ribbon that can be stored before further use as an insulating sheath of Nb_3Sn wires, and electrical and magnetic tests on both the material and a specific demonstrator made with a 20 m superconducting reel, demonstrate that this material can be used as an insulating sheath, with no side-effect on superconductor properties.

1. Introduction

1.1. General background

Large research programs have been initiated within the last years to expand the technology of high field dipole magnets, especially for the future upgrade of the Large Hadron Collider (LHC) (Canfer et al., 2008; Devred et al., 2004, 2006; Loveridge et al., 2008). In this domain, scientific, engineering and industrial challenges are taken to their apex, and cannot be compared with any other magnetic application worldwide. Indeed, the whole magnetic system includes 1234 fifteen meter long dipolar magnets, weighting 34 t each, and 392 main quadrupolar magnets, all been made with superconducting wires, for a total of 7000 km of multi-strand cables cooled with 94 t of liquid helium in order to generate a 12,000 A steady current. Current magnets installed at the LHC, which led recently to the experimental validation of the Higgs boson, are based on NbTi technology but this material reaches its limits at 10 T, the critical magnetic field beyond which the material loses its superconducting properties. As access to smaller components of matter will require higher energy, the next generation of magnets will require materials that could keep superconductivity above these critical fields to allow for a higher current intensity being provided for higher magnetic fields (Devred et al., 2005). Until now, the best candidate remains Nb_3Sn, an intermetallic compound of the A15 family, which keeps superconducting properties at 12–15 T (Ashkin and Gavaler, 1978; Boutboul et al., 2008; Dew-Hughes, 1975; Echarri and Spadoni, 1971; Godeke, 2006; Hulm and Matthias, 1980; Kunzler, 1961; Matthias et al., 1954, 1963; Muller, 1980; Van Kessel et al., 1978). Unlike other candidates like high Tc superconducting ceramics or MgB_2, the technology for the manufacturing of Nb_3Sn strands is well developed and hundreds of meters can be manufactured at the industrial level. Nevertheless, the use of these materials for the design of large dipoles and quadrupole elements is still facing numerous technological challenges (Breschi et al., 2009; Caspi et al., 2007; Felice et al., 2007; Ferracin et al., 2007; Hafalia et al., 2005; Miyazaki et al., 2008; Nobrega et al., 2007, 2008).

1.2. Preparation and properties of Nb_3Sn

Nb_3Sn strands are prepared with two methods that both involve a direct reaction between niobium and tin at 600–700 °C under neutral atmosphere for several days. In the Powder in Tube (PIT) route (Zlobin et al., 2005), the strand before reaction, is made of Nb-X tubes (X: Ti or Ta) filled with a mixture of Nb and Sn powders, embedded in a high quality copper matrix. After reaction, the tubes are laminated into wires. In the Internal Tin Diffusion (ITD), the strand consists of Nb-X filaments embedded into a mixed Cu and Sn matrix, surrounded by an Nb-X barrier which separates the multi-filamentary

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zones from a stabilizing, high quality Cu matrix. Upon heating, tin diffuses through the copper matrix up to the niobium wires where it reacts, giving a block that is further laminated into wires.

1.3. Challenges for using Nb_3Sn in magnetic reels

The design of all magnets requires very specific dimensional criteria, to fulfill strict parameters for the magnetic field geometry, which implies the bending of Nb_3Sn strands with a high curvature radius. Unfortunately, as Nb_3Sn is an intermetallic compound that becomes brittle upon reaction, this material can hardly been engineered once reacted, because any strain will create defects and crystalline dislocations that hamper dramatically the superconducting properties. Therefore, the sheath must be initially wound around the cable, this cable been further shaped and bent to achieve the magnet geometry before the thermal treatment that will synthesize the Nb_3Sn phase. This method named “wind & react” (Devred, 2002), prevents obviously from using any organic sheath or any material containing organic components, because the thermal treatment under neutral atmosphere would leave behind carbon residues that would hamper electrical insulation. Moreover, the sheath must be flexible enough to allow winding, without cracks, but it must respect also excellent dimension constraints, and exhibit high mechanical strength to resist magnetic strains that will be generated under current.

As the magnet scale, forces and manufacturing route present real challenges for the conductor insulation technology, one method relevant to the current technology, has been explored until now. This method is based on the post-impregnation with resin of a glass fiber matrix. If it allows one to use current organic materials, its application remains confined to small demonstrators and it could not be applied for large scale manufacturing (Canfer et al., 2008). Hence, the real challenge was to develop an organic-free solution, based on ceramic components that could fulfill the complete and drastic bill of specifications.

The present report describes a method to manufacture a ceramic insulating sheath with processes that could be easily scaled-up, leading to an organic-free ceramic ribbon that can be stored before further use as an insulating sheath of Nb_3Sn wires, or for other applications. This process associates a glass fiber ribbon that provides a constant thickness, with the impregnation of a dispersion of ceramic precursors. This dispersion must fulfill different criteria: (i) being stable with time, (ii) being rather fluid during the impregnation step, (iii) becoming rapidly rigid to prevent any drip after application, and (iv) being a good electrical insulator after the thermal process.

The present insulating sheath fulfills the required criteria: it resists well to the synthesis of Nb_3Sn (300 h at a temperature range between 600 and 750 °C) that is actually used to achieve the formation of this insulating sheath, it presents a well-defined thickness (around 130 μm) under an 80 MPa pressure, and results of electrical and magnetic tests, validated by assembling a demonstration reel that could conduct a 194 A current under a 11 T magnetic field, in the superconducting state of Nb_3Sn, confirm that the ceramic sheath is not detrimental to the superconducting properties.

2. Experiments

2.1. Materials

An initial set of ceramic precursors was tested to check their adequacy with the expected properties, that is, exhibiting good film properties in the crude state, and providing a good structural evolution upon sintering at low temperature (≈650 °C) under neutral atmosphere, a major challenge for ceramics that are usually sintered in air at higher temperatures. Different raw materials were tested, all based on clay minerals (BIP™ or (BIP Kaol) CGU™ (CGU Kaol) kaolinite, Arvel™ (Arvel Mt) or Expans™ (Expans Mt) Montmorillonite). Compared with synthetic clays, it is well known that properties of natural minerals change with time and from a batch to another one. Therefore, the whole procedure must allow one to adapt the final composition in agreement with a required property. The rheological behavior of the aqueous dispersion was selected as a reference for the further selection of component proportions. As the thermal treatment for the synthesis of Nb_3Sn occurs at a rather moderate temperature, compared with usual ceramic processes, the structuring agent (the clay mineral) had to be combined with a low temperature frit (2495F from Johnson & Mattey: melting temperature at 538 °C). The absence of Boron in the additive, an element that can diffuse under irradiation, was checked before use. The final ceramic sheath was prepared by the impregnation of a 15 mm large (0.12 mm thickness) weaved glass ribbon (Type S2 from Hiltex Technische Weefsels Co.). As these glass fibers are initially coated by an organic layer, this latter was removed before use with a 10 h thermal treatment at 350 °C in air. The fibers became extremely brittle after treatment, but they recovered their initial mechanical properties after a 48 h curing at room temperature under a moderate moisture (Devred, 2002). Nb_3Sn/Cu wires were kindly provided by Alsthom Cie. These wires have an overall section of 0.535 mm^2, with a Nb_3Sn/Cu ratio of 1, and a Nb_3Sn section of 0.267 mm^2.

2.2. Preparation

2.2.1. Preparation of the ceramic dispersions

A typical preparation of the aqueous dispersion was carried out according to the following procedure: (i) 160 g of the sintering frit was poured under strong mechanical stirring into 160 mL of deionized water; (ii) the solution was defragmented for a total active time of 10 min under ultrasounds – 2 s. pulses – with a sonication gun (650 W Vibracell with a 15 mm diameter sonication probe); (iii) the solution was left for 4 h under stirring to allow the pH to stabilize (final pH ≈ 11); (iv) 80 g of clay mineral was slowly added under strong mechanical stirring to avoid the formation of aggregates; (v) the solution was left under sonication for 10 min – same procedure as for (ii) – and stored; and (vi) before use, the solution was stirred for 12 h on a roller stirrer, after the addition of 20 balls of vitreous china (10 mm diameter) for 12 h. In the following, the proportions of components were adjusted according to the experimental points in the phase diagrams.

2.2.2. Design of the impregnation bench

A specific impregnation bench was designed and assembled to allow the impregnation of long length of glass ribbons by the ceramic dispersion. A schematic and a photo of this apparatus bench are displayed in Fig. S1 (in ESI), top and bottom, respectively. The different parts of this system include: (1) an initial roll of the glass ribbon (thermally treated beforehand to remove organics) that can deliver the ribbon with a constant tension through an electromagnetic brake (MAYR, France); (2) a 500 mL beaker of the ceramic dispersion in which the glass ribbon is firstly dipped, then pressed between rolls in order to achieve a good impregnation of the ceramic dispersion; (3) a magnetic stirring to keep the ceramic solution fluid (the specific thixotropic behavior of the ceramic dispersion allows it to gel as soon as the ribbon is pulled out from the beaker); (4) a dryer made of a tube (53 mm diam., 320 cm length) equipped with a seven meter heating wire rolled over a 2.66 m length, heated at 110 °C; (5) an in-line thickness control provided by a laser telemeter (Jeanbrun Automation); (6) a winding system with varying speed set at 30 $cm.min^{-1}$ that allowed us to obtain at the end a full roll of the dried glass ribbon impregnated with the ceramic mixture (clay + frit). A thirty-meter reel of ceramic ribbon was successfully prepared (Fig. S2), the roll being stored before further use. This method allowed us to totally differentiate the preparation of the ceramic ribbon from the winding operation, which provides much more flexibility in the future scale-up process.