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ELECTROCHEMICAL SYNTHESIS OF Nb_3Sn COATINGS ON Cu SUBSTRATES

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Abstract

This work aims at contributing to the development of superconducting Nb_3Sn thin films for possible applications, as for instance in superconducting radio frequency (SRF) cavities. The synthesis of Nb-Sn coatings was carried out on copper substrates by electrodeposition from 1-Butyl-3-methylimidazolium chloride (BMIC) ionic liquids containing $SnCl_2$ and $NbCl_5$. Cyclic voltammetric curves were recorded to identify the reduction potentials of Nb and Sn ionic species. Electrodeposition was performed at 40 and 400 mA/cm^2 and 130°C. The CV demonstrated that BMIC has a suitable potential window for co-deposition of Nb and Sn. The electrodeposited coatings showed a cubic Nb_3Sn phase with (211) preferred orientation, a disordered orthorhombic $NbSn_2$ phase and Sn-Cu phases. Film thickness was from 200 to 750 nm. These results suggest that electrodeposition of Nb-Sn coatings on copper substrates could be a suitable route to one day replace the current expensive Nb SRF cavities.

Keywords: Nb_3Sn; ionic liquids; 1-Butyl-3-methylimidazolium chloride; Niobium; Tin; electrodeposition.

1. Introduction

The intermetallic compound Nb_3Sn is a high performing superconducting material, which finds wide application in Nuclear Resonance Magnetic devices, high field laboratory magnets, but also fusion and accelerator magnets. Moreover, manufacturing film-based superconducting radio frequency (SRF) structures remains the "holy grail" for accelerator physicists. The main reason is that copper cavities coated with Nb_3Sn films in principle would be more efficient and far less expensive than the current Nb cavities.

To the authors’ knowledge, the manufacturing of Nb_3Sn films has not succeeded yet. Deposition of Nb_3Sn layers was carried by CVD [1,2] and magnetron sputtering [3]. However, film-based SRF cavities have not yet equaled the performance of conventional bulk niobium cavities [4].

Kolosov et al. electrodeposited Nb and Nb_3Sn from high-temperature molten salt solutions, but due to the aggressive conditions of deposition, relatively few substrates can be utilized. The most promising alternative to those high temperature electrolytes are low temperature ionic liquids [5, 6, 7]. Early attempts to deposit Nb-Sn alloys from ionic liquids resulted in Nb-Sn coatings containing the superconducting Nb_3Sn phase [8,9,10]. However, the same authors declared that the reproducibility of the process was not acceptable. More recently Lewis basic melt was also tested [11]. Nevertheless, no indication of the total thickness of the film was given, which is a property of great interest to make the approach eligible for applications and further development to the industrial scale.

This work capitalizes on the decade-long effort at Fermilab in Nb_3Sn research and development for high field accelerator magnets [12]. The results herein presented originated from trying to experimentally verify a flux pinning model in A15 superconductors [13].

The present paper describes the electrodeposition of Nb-Sn thin films from a novel ionic liquid consisting of $SnCl_2$, $NbCl_5$ and BMIC. This method aims at obtaining directly and reproducibly Nb_3Sn coatings on any conductive substrate without the need of a high temperature post-processing and on complex 3D shapes with high aspect ratio. Especially the latter goal cannot be achieved with the classical metallurgical techniques due to the intrinsic brittleness of Nb_3Sn.

2. Experimental setup

The experiments were carried out by using BMIC as ionic liquid (>98%, Sigma-Aldrich) containing either anhydrous $SnCl_2$ (98%, Sigma-Aldrich), anhydrous $NbCl_5$ (99%, Sigma-Aldrich) or both. The chemicals were mixed in a glove box (argon atmosphere) by magnetic stirring at 100°C for 24 hours. Electrochemical measurements and deposition experiments were done in an electrochemical cell sealed to the ambient atmosphere. In the following, when not otherwise specified, % stands for mol.%.

Cyclic voltammetries (CVs) were performed at 100°C and 10 mV/s using a three-electrode cell. Cu foils (99.95%) were used as cathodes. The exposed area was 1 to 2 cm^2. As counter and reference electrodes, a Sn foil and a Pt wire were used, respectively.

The electrodeposition was carried out from a 85 % BMIC - 10 % $NbCl_5$ - 5 % $SnCl_2$ using a two electrodes cell configuration. Cu sheets (99.95%) were used as substrates. Experiments were done in galvanostatic mode at 40 and 400 mA/cm^2 and 130 °C.

Karl-Fischer analysis was performed to determine the water content using a Mettler Toledo titrator (Model DL31). For electrochemical measurements, a potentiostat/galvanostat (Solartron Analytical ModuLab ECS) was used. The surface morphology was investigated by means of Scanning Electron Microscopy (SEM – Zeiss® EVO 50) equipped with LaB6 source operated at 20 kV. X-ray diffraction (XRD) patterns were acquired using Cu Kα radiation (λ =1.5405 Å) and a powder goniometer (Philips PW-1830) in the 2θ angular range of 30 to 90°. XRD patterns were explained by means of powder diffraction references. Grain size was estimated according to Scherrer equation. Film thickness was measured by X-ray fluorescence using a Fischerscope-XAN®- instrument. Depth profiling analysis was performed by Glow discharge optical emission spectrometry (GD-OES) using a Spectruma GDA750 analyzer. Film composition was also assessed by EDX analysis.

3. Results and discussion

3.1 Cyclic Voltammetry

The cathodic behavior of the ionic liquid solution was investigated by means of CV with the objective to define the potential range for alloy deposition. Figure 1 shows CV curves over the potential range from –0.4 to –3.5 V corresponding to the pure BMIC, BMIC with 10% $SnCl_2$, BMIC with 25% $NbCl_5$, and BMIC with 5% $SnCl_2$ and 21% $NbCl_5$. In pure BMIC, a low current density (c.d.) was observed over the potential range from OCP to –1.9 V, which can be considered a suitable potential window for Nb-Sn deposition. The significant increase of c.d. towards the lower limit of the scanning range might be attributed to the electrochemical decomposition of the traces of water, which are 0.44 wt.%, or to the reduction of ionic liquid itself. By adding 10% $SnCl_2$ to BMIC, a broad reduction wave peaking at about -1.14 V was observed, which can be attributed to reduction of $SnCl_3^-$, which is the main anionic species in this basic melt.

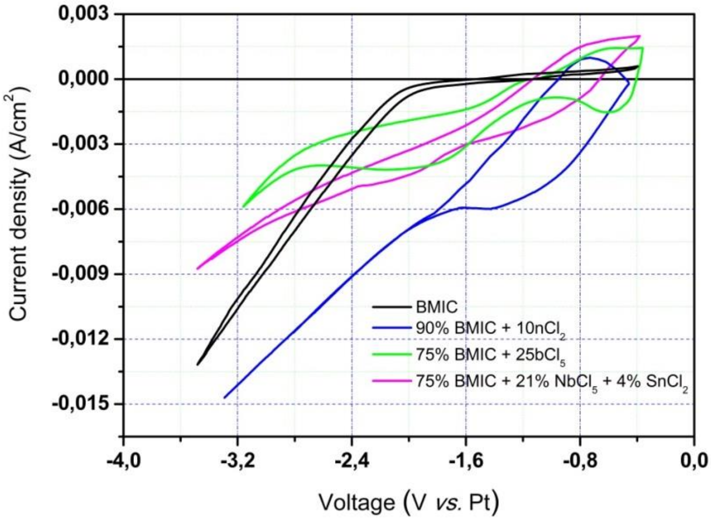


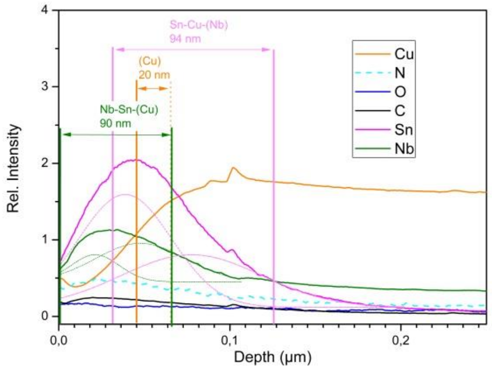
Figure 1. CV curves of pure BMIC (black) compared to: 10% $SnCl_2$ 90% BMIC (blue); b- 25% NbCl5 75% BMIC (green); c- 75 % BMIC - 21 % $NbCl_5$ - 4 % $SnCl_2$ (purple).

By addition of $NbCl_5$ to BMIC two pronounced reduction peaks were observed at -0.6 V and at - 1.96 V vs. Pt. In agreement with Sun et al. [14] and Koichi [11], the two reduction waves can be attributed to the Nb(V)/Nb(IV) and to Nb(IV)/Nb(III) redox couples. Investigating the cathodic behavior of the 75 % BMIC - 21 % $NbCl_5$ - 4 % $SnCl_2$ electrolyte, two reduction waves peaking at about -1.1 V and -2.0 V were observed. The first reduction wave is very close to that of pure Sn(II), while the peak owed to the reduction of Nb(V) to Nb(IV) is not evident. Good overlapping of the reduction waves of Sn(II) and Nb(V) was observed.

3.2 Electrodeposition of Nb-Sn films

By electrochemical deposition at a c.d. of 400 mA/cm^2 for 30 minutes, Nb-Sn films having average thickness of about 200 nm and Nb content of about 17 at.% were obtained. Such non-stoichiometric Nb content with respect to the Nb_3Sn phase can be explained by the presence of Sn-rich phases. In fact, GD-OES depth profiling analysis (Figure 2-a) suggests that a multilayered structure was obtained. The Nb-Sn layer was about 90 nm thick, followed by a Sn-Cu layer about 100 nm thick. The Sn-Cu layer can be attributed to galvanic displacement between Sn^{3+} and Cu followed by thermal diffusion occurring at the operating temperature. Cu diffusion also occurred into the Nb-Sn layer for a depth of about 20 nm. The carbon content across the whole film thickness can be attributed to electrochemical reaction of the ionic liquid itself. A very low oxygen content was measured, confirming the good quality of the film. The XRD pattern (not shown) revealed the presence of a cubic Nb_3Sn phase having (211) preferred orientation (P.O.), of the orthorhombic

$NbSn_2$ phase, and of η Cu_6Sn_5 and ε Cu_3Sn phases. A SEM micrograph of the film surface in Figure 2- b shows good coverage of the substrate. Good adhesion to the substrate was also observed.



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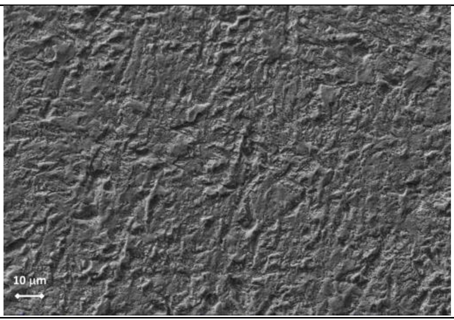

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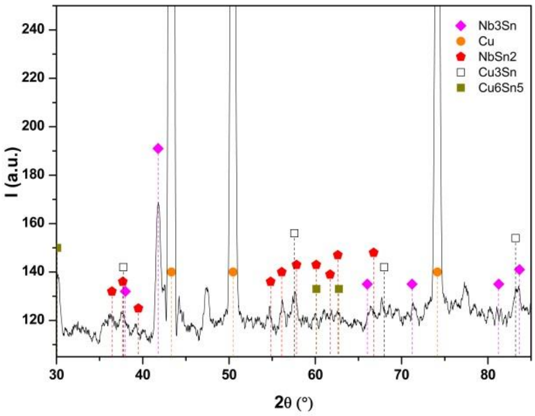

c

Figure 2. GDOES depth profiling analysis (a) and SEM micrograph (b) of Nb-Sn films electrodeposited at 400 mA/cm^2: 17at.% Nb, film thickness 200 nm; c): XRD pattern of of Nb-Sn films electrodeposited at 40 mA/cm2: 28at.% Nb, film thickness 750 nm.

At a c.d. of 40 mA/cm^2 for 10 minutes, the average Nb content increased to about 28 wt.% and the average film thickness was 750 nm. The XRD pattern (Figure 2-c) revealed the coexistence of Nb-rich and Sn-rich phases. In particular, cubic Nb_3Sn having strong (211) P.O. (2θ 41.78°), disordered orthorhombic $NbSn_2$ structure (28.64° - 29.86 ° - 57.87°) and η Cu_6Sn_5 and ε Cu_3Sn phases were observed. Coverage and adhesion to the substrate were good. The crystallite size of the electrodeposited Nb-Sn films, as estimated according to Scherrer, was between 3 and 4 nm at a c.d. of 40 mA/cm^2, and about 15 nm at a c.d. of 400 mA/cm^2.

4. Conclusions

In the present paper, the synthesis of Nb-Sn thin films on copper substrates was presented. Electrolytes consisted of BMIC with addition of $SnCl_2$ and $NbCl_5$ salts. CV curves demonstrated that the BMIC had a sufficiently wide potential window to allow for the electrodeposition of Nb and Sn. The electrodeposited Nb-Sn thin films with average Nb content up to 28 at% consisted in cubic Nb_3Sn structure (A15 phase) with (211) preferred orientation along with disordered orthorhombic $NbSn_3$ phase, and Cu-Sn phases. The Nb-Sn films were homogeneous and showed good adhesion to copper substrates. Average film thickness values up to 750 nm were measured.
Overall, the electrodeposition of Nb-Sn from BMIC was shown to be a promising process for the deposition of Nb_3Sn thin films on copper substrates. In principle this technique is suitable for manufacturing superconductors as surface coatings as opposed to bulk, wires and cables.

Acknowledgments

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