

Electrochemical deposition of superconductor alloy precursor in a low melting molten salt medium

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The applicability of the room temperature molten salt medium based on the 1-methyl-3-ethylimidazolium chloride/ AlCl_3 (MeEtImCl/ AlCl_3) system for the deposition of superconductor alloy precursors (Bi–Sr–Ca–Cu) was investigated. Problems of poor solubility of the constituent metal salts in the neutral melt and aluminium codeposition in the acidic melt were identified for the use of the chloroaluminate room temperature molten salt. Thus, a novel all-chloride molten system (MeEtImCl) was developed in the present work and used at 120 °C. Cyclic voltammetry was used to investigate the suitability of Pt, Al, Ti, Cu and Ag as substrate for alloy deposition and aluminium was found to be the best for depositing alkaline earth metal alloys. The working deposition conditions were a constant potential of -1.72 V for 75 s in an electrolytic bath containing BiCl_3 (0.068 mol), SrCl_2 (0.50 mol), CaCl_2 (0.18 mol) and CuCl_2 (0.050 mol) in 1 kg MeEtImCl (6.83 mol). The compositions of the electrodeposits obtained were in close agreement with the mole ratios of the Bi–Sr–Ca–Cu superconductor alloy precursor.

1. Introduction

Although research and development [1–3] have taken place at a rapid pace since the discovery of superconductivity in ternary metal oxide ceramics by Bednorz and Muller [1], the application of high temperature oxide superconductors is slow due to the difficulties of device fabrication with these brittle materials and the limited current that the superconductor can carry [4]. The formation of thin films at the surface of metallic or semiconductor substrates is one of the most practicable ways of solving these problems, as the underlying substrates can provide the mechanical strength and larger currents can be used due to the increase in the surface area.

Various ways of forming a thin film superconductor have been tried, such as the flux growth method [5, 6], the tap-seed travelling solvent floating zone method [7], physical vapour deposition or plasma spraying procedures [8], or using traditional microelectronic manufacturing methods like screen printing, coevaporation, metalloorganic deposition and various laser techniques [9]. These methods have many drawbacks, such as nonuniform, highly porous and poorly adhered coatings, as well as requiring expensive equipment.

Electrochemical methods [10, 11] offer promising means for the preparation of thin film superconductors on metallic substrates, such as the use of electrophoretic techniques to co-deposit superconductor powders simultaneously with metal deposition [12–15], the aqueous route of electrodeposition of metal hydroxide precursor prior to oxidation [16], and the nonaqueous route of electrodeposition of metal alloy precursor prior to oxidation to form the ceramic

superconductor oxides [17–24]. The electrophoretic technique provides an undesirable heterogeneous composite coating and the precipitation of hydroxide of a given composition ratio requires critical control of the experimental conditions. The two step electrochemical route via electrodeposition of an alloy precursor followed by an oxidation step seems to be the most practicable method as quality control can be exercised in each of the two steps while technological and manufacturing infrastructure available in the electroplating industry can be mobilized once a workable procedure is demonstrated.

As the constituents of the superconductor always include one or two highly electropositive elements, the electrodeposition of their alloy precursors requires an inert medium such as an organic solvent [19, 20] or a high temperature molten salt [5–7, 9, 7–18, 21–24]. Although dimethylsulfoxide has been used successfully as a medium [25, 26], or when mixed with other solvents [27], for electrodeposition of alloy precursors, either by codeposition [19, 20, 23, 28–31] or as a laminate structure [26, 32], its reactivity with the alkaline earth metal alloy precursor led to the incorporation of sulfur, thus affecting the continuity of the superconductor ceramic oxide film formed upon oxidation.

Molten salts provide particularly interesting media for alloy deposition due to their inertness towards alkaline earth metals, good solubility for most inorganic salts and high conductivity that can sustain large currents. However, difficulties for industrial application have arisen due to the need to maintain a high operating temperature. The recent advance in room temperature molten salts based on the 1-methyl-3-ethylimidazolium chloride/aluminium chloride

(MeEtImCl/AlCl₃) system [33–35] provides a promising solvent system suitable for the above application as it has the same advantages as the high temperature molten salt but with the capability of operating at ambient temperature.

In the present work, the most common Bi–Sr–Ca–Cu system was chosen for study and the applicability of the room temperature molten salt based on the MeEtImCl/AlCl₃ system for electrodeposition of the superconductor alloy precursor was investigated and problems facing its use discussed. The working operating conditions of a novel low temperature molten salt system developed in the present work using the all-chloride based MeEtImCl system are given and factors affecting its applicability discussed in the light of the results obtained.

2. Experimental details

2.1. Chemicals and electrode preparation

The MeEtImCl was prepared using procedures as previously reported [33, 34]. All the chemicals used were AR grade and obtained from the Aldrich Chemical Co. (Milwaukee, WI). Chlorides of calcium, strontium, bismuth and copper were used as received, while 1-methylimidazole was purified by distillation. Various working electrodes such as platinum, silver, copper, titanium and aluminium were used for the investigation. All working electrodes were decreased with acetone prior to use. The reference electrode was a Ag/Ag⁺ electrode immersed in the MeEtImCl melt. The counter electrode was a platinum foil. All experiments were carried out at 120 ± 2 °C with scan rate kept constant at 50 mV s⁻¹.

2.2. Electrochemical apparatus and SEM studies

All the experimental operations including weighing, stirring, temperature control and electrochemical experiments were performed in an argon filled glove box under positive pressure. The argon gas was recirculated continuously through the Dry-train Purifier Hawthorne, (Vacuum/Atmospheres Co., Hawthorne CA) to remove oxygen catalytically and adsorb moisture by molecular sieve. Cyclic voltammetry was performed using a PAR175 universal programmer and a PAR363 potentiostat/galvanostat with voltammograms recorded by a LY16100-II X–Y recorder and monitored by a Keithley 182 sensitive digital voltmeter.

A constant potential of –1.72 V vs the Ag/Ag⁺ reference electrode in MeEtImCl was applied to the cathode for 75 s for the electrodeposition of the alloy precursors on selected substrates. The deposit was then rinsed using acetonitrile and kept in a desiccator prior to investigation using a Cambridge Stereoscan 360 scanning electron microscope. The atomic per cent of Bi, Sr, Ca and Cu was determined using an energy dispersion X-ray microprobe attached to the SEM.

3. Results and discussions

3.1. Investigation of the molten salt system

To be useful for the deposition of superconductor alloy precursor, the molten salt system must have a low melting temperature, with good conductivity, wide electrochemical window, inertness towards the alkaline earth metal alloys and with satisfactory solubility for all the constituents of the metal salts present in the superconductor alloy precursor. Chloride salts were chosen in the present study as high purity salts are available commercially.

The first molten salt system to be investigated was the room temperature molten salt MeEtImCl/AlCl₃ system. Although the neutral melt of MeEtImCl/AlCl₃ gave the largest electrochemical window, the solubility of halide salts was rather poor in the melt. The acidic melt with excess AlCl₃ over MeEtImCl is a good solvent. However, even in an acidic melt, the solubilities of calcium chloride and strontium chloride were low and the saturated solution of calcium chloride contained only 0.072 mol of calcium chloride dissolved in a MeEtImCl/AlCl₃ melt containing 0.45 mol MeEtImCl and 0.55 mol AlCl₃. In addition, calcium and aluminium could be codeposited from the acidic melt even in the presence of a small amount of CaCl₂ (0.07 mol CaCl₂ in 0.55/0.45 mol of AlCl₃/MeEtImCl, respectively). The codeposition of Ca and Al is clearly indicated in Fig. 1 that shows the appearance of an additional deposition peak at –0.2 V and a composite stripping peak at –0.3 V with the addition of CaCl₂ to the acidic melt. The Al deposition peak remains unchanged at –0.62 V, whereas its stripping peak potential is shifted from –0.1 to –0.3 V due to alloying with calcium that had deposited at –0.2 V prior to Al deposition. Moreover, both the

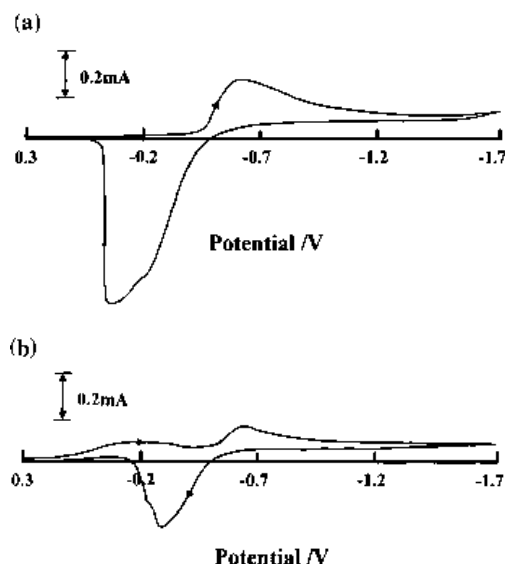


Fig. 1. Voltammograms showing the codeposition of aluminium with calcium in the acidic melt (W.E.: Pt, $A = 0.16 \text{ cm}^2$; R.E. = (Al/AlCl₃ + MeEtImCl = 0.6:0.4); AgCl, $T = 25 \text{ }^\circ\text{C}$). (a) AlCl₃:MeEtImCl = 0.55:0.45. (b) 0.07 mol CaCl₂ in 1 kg melt (AlCl₃:MeEtImCl = 0.55:0.45).

depositing and stripping currents were depressed upon alloying with calcium.

To solve the problems of solubility and aluminium codeposition, a novel molten MeEtImCl system was developed as the use of an all-chloride melt could enhance the solubility of the chloride salts of superconductor precursors and the removal of AlCl₃ from the salt system could solve the problem of Al codeposition. The drawback is the increase of the operation temperature of the MeEtImCl melt to 120 °C. This is not too high and is acceptable for industrial application.

Using the molten MeEtImCl as the medium, the conductivity of the electrolyte was shown to be satisfactory with $k = 3.746 \times 10^{-2} \Omega^{-1} \text{cm}^{-1}$ at 110.4 °C [34]. Good solubilities of various metal chloride salts such as CaCl₂, SrCl₂, BiCl₃ and CuCl₂ were obtained in the melt at 120 °C as indicated by their working concentrations in the electrolytic bath as given in Table 1.

As the deposition potentials of Ca and Sr and very negative as compared to those of Cu and Bi, they are expected to be more difficult to deposit. Thus, their concentrations in the melt were increased relative to those of Cu and Bi (Table 1). The composition of the melt with appropriate adjustment of their relative mole ratios to those of the Bi–Sr–Ca–Cu superconductor alloy precursor is given in Table 1.

3.2. Selection of substrates

The suitability of different metallic substrates, platinum, copper, silver, titanium and aluminium, were investigated using cyclic voltammetry. As the deposition potentials for Ca and Sr are close to each other but differed significantly to those of Cu and Bi, to obtain reproducible alloy deposition, the deposition potentials for Ca and Sr should be moved positively whereas the deposition potentials for Cu and Bi should be shifted negatively so that one potential can be used for the deposition of all four elements.

The effect of different metal substrates on the decomposition of the melt in the presence of alkaline earth metal chlorides is shown in Figs 2 and 3. The rise in current starting at around –1.5 V was due to the decomposition of MeEtImCl catalytically at the metal substrate surface. For example, silver gave a very rapid increase in current starting from the decomposition potential at –1.25 V (Fig. 2) and was thus not suitable as a substrate for alloy precursor

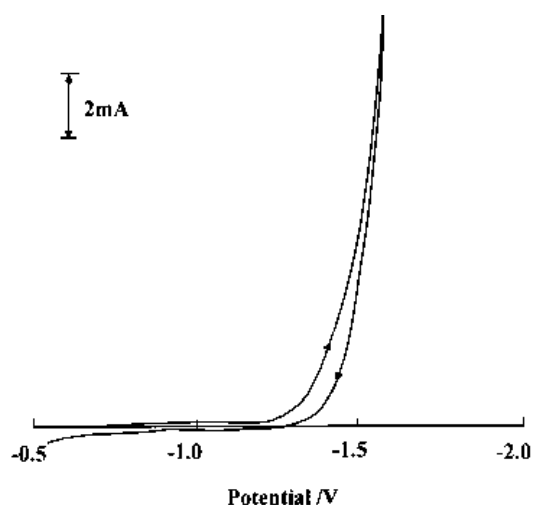


Fig. 2. Voltammogram showing the decomposition of the MeEtImCl melt at a silver electrode ($A(\text{Ag}) = 0.32 \text{ cm}^2$ R.E. = Ag/Ag⁺ in MeEtImCl, $T = 120^\circ\text{C}$).

electrodeposition. With other metal substrates, the decomposition started at about –1.5 V with moderate increase in current towards the negative direction. With the addition of SrCl₂, the current due to the decomposition of the melt was depressed and a deposition peak was observed for all the metal substrates. The appearance of a peak was due to alloying of the substrates by strontium that shifted the deposition potential away from the solvent decomposition potential. However, the extent of the positive shift of the peak potential was decreased in the following order: Al > Ti > Pt > Cu (Table 2). As the use of a more positive deposition potential favoured the codeposition of all four components, the aluminium substrate was chosen as the substrate for subsequent studies. Moreover, the deposition of Sr on Al is enhanced as compared to other substrates and this is indicated by the highest peak current density obtained using Al as the substrate (Table 2).

The addition of calcium chloride to the MeEtImCl/SrCl₂ melt led to the formation of a broad peak at –1.85 V (Fig. 4(a)), indicating the codeposition of Ca/Sr alloy on aluminium. Further addition of Bi and Cu led to the formation of two peaks at –0.45 V and –0.82 V for Bi and Cu, respectively. However, the alloy peak for Ca and Sr disappeared and the voltammetric current was increased 10 times. Thus, the coverage of the aluminium electrode surface with copper and bismuth made it much easier to accept the incorporation of Sr and Ca.

Table 1. Bath composition for electrodeposition of the superconductor alloy precursor (Bi–Sr–Ca–Cu) at 120 °C

Constituent	BiCl ₃	SrCl ₂	CaCl ₂	CuCl ₂
Concentration (mol kg ⁻¹ MeEtImCl)	0.068	0.50	0.18	0.050
Molar ratio obtained	1.36	10	3.6	1
Mole ratio of Bi–Si–Ca–Cu superconductor	2	2	1	2

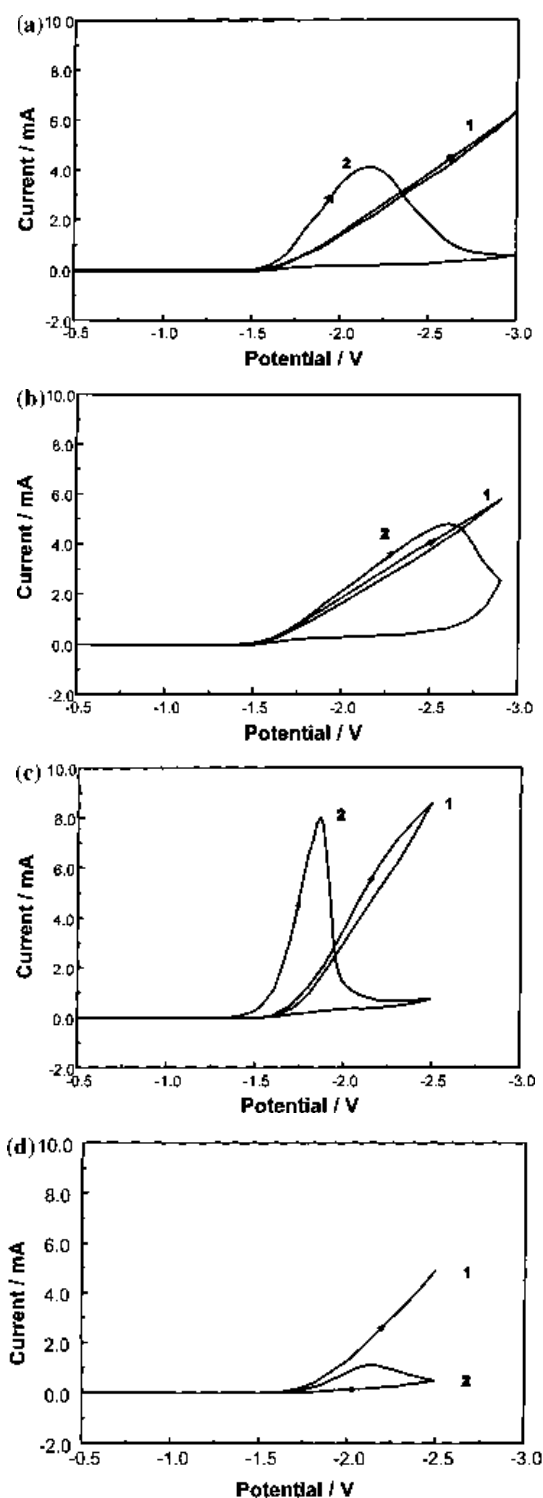


Fig. 3. Effect of the substrate on the decomposition of MeEtImCl in the absence (curve 1) and presence (curve 2) of strontium chloride. R.E. = Ag/Ag⁺ in MeEtImCl, $T = 120^\circ\text{C}$. MeEtImCl, 0.12 mol SrCl₂ per kg MeEtImCl. (a) W.E.: Pt ($A = 0.15\text{ cm}^2$), (b) W.E.: Cu ($A = 0.47\text{ cm}^2$), (c) W.E.: Al ($A = 0.22\text{ cm}^2$) and (d) W.E.: Ti ($A = 0.084\text{ cm}^2$).

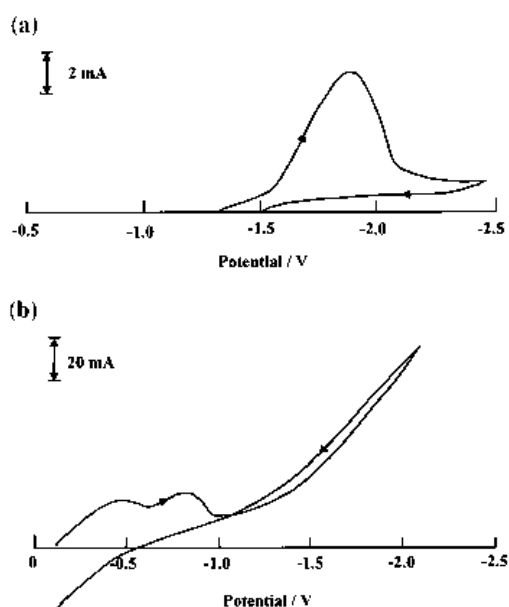


Fig. 4. Voltammograms of aluminium in MeEtImCl melts. $A(\text{Al}) = 0.22\text{ cm}^2$, $T = 120^\circ\text{C}$. R.E. = Ag/Ag⁺ in MeEtImCl. (a) 0.12 mol SrCl₂ + 0.12 mol CaCl₂ in 1 kg MeEtImCl and (b) 0.12 mol SrCl₂ + 0.12 mol CaCl₂ + 0.10 mol CuCl₂ + 0.10 mol BiCl₃ in 1 kg MeEtImCl.

3.3. Composition of electrodeposit

For deposition of four metals simultaneously with an aim to obtain mole ratios close to those of the Bi–Sr–Ca–Cu superconductor alloy precursor, the deposition potential has to be carefully chosen. It should be chosen at a value midway between that of the two easily deposited elements, Cu and Bi, and of the two alkaline earth metals, Ca and Sr, that are difficult to plate. Appropriate adjustment of their relative concentrations in the electrolytic bath is also needed. The deposition potential was chosen at -1.72 V as it was away from the decomposition potential of the melt and with sufficient current for the deposition of Ca and Sr. The deposition time was chosen at 75 s, as a suitable thickness of the thin film was obtained within this period of time.

With the potential controlled at -1.72 V for 75 s, the four constituents of the superconductor precursor were found to be codeposited with alloy composition as given in Table 3. The reproducibility of the deposition procedure was satisfactory as indicated by the relative standard deviation of the results obtained. The mean values of the results are very close to those of the Bi–Sr–Ca–Cu superconductor. Thus, the composition of the Bi–Sr–Ca–Cu alloy precursor has been obtained under the present experimental conditions.

Table 2. Peak current density and peak potential at different metal substrates

Substrate	Peak current density/ mA cm^{-2}	Peak potential/V
Pt	27.8	-2.18
Cu	10.2	-2.60
Al	36.1	-1.86
Ti	12.4	-2.11

Table 3. Chemical composition of electrodeposit of the superconductor alloy precursors obtained in low melting molten salt medium

Element	Atomic percent / %				Mean / %	Relative standard deviation / %	Mean mole ratio
Bi	33.1	33.1	30.7	33.3	32.6	3.8	2.1
Sr	24.8	25.1	29.0	28.4	26.8	8.1	1.7
Ca	15.1	15.5	15.0	17.3	15.7	6.8	1.0
Cu	27.0	28.2	24.0	23.0	25.6	9.3	1.6

4. Conclusions

The following conclusions can be drawn:

- (i) Poor solubility of metal chloride salts was found using the neutral MeEtImCl/AlCl₃ melt and the problem of aluminium codeposition was identified with the use of the acidic melt.
- (ii) A novel low temperature molten salt based on the all-chloride MeEtImCl melt was developed in the present work and it gave satisfactory solubility of the chloride salts of the four constituents of the Bi–Sr–Ca–Cu superconductor at 120 °C.
- (iii) Results from cyclic voltammetry indicate that aluminium is the best substrate for the electrodeposition as compared to Pt, Ag, Cu, and Ti, as it alloys with the alkaline earth metals, leading to anodic shift of the deposition peak and hence less reactivity with the solvent medium.
- (iv) With the deposition potential kept constant at –1.72 V for 75 s in a bath maintained at 120 °C and with a composition of 0.068 mol BiCl₃, 0.50 mol SrCl₂, 0.18 mol CaCl₂ and 0.050 mol CuCl₂, the four constituents of the Bi–Sr–Ca–Cu superconductor alloy precursor were found to be codeposited at mole ratios close to those of the Bi–Sr–Ca–Cu superconductor alloy precursor with satisfactory repeatability of the results.
- (v) The low melting molten salt medium based on MeEtImCl is thus shown to provide a suitable medium for the two stages electrodeposition route for electrochemical formation of superconductor at metallic substrates.

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