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Electrodeposition of Al-Sc alloys from LiCl-KCl molten salt containing AlCl₃ and ScCl₃

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Abstract

To investigate co-electrodeposition of Al and Sc ions, voltammogram measurements were carried out in LiCl-KCl molten salt containing AlCl_3 and ScCl_3 at 723K. In the voltammogram measurements, a cathodic current of Al ions and formation of Al-Sc alloys were observed from 0 V and -0.2 V vs. Al/Al(III), respectively. Sponge-like electrodeposit formed on the Cu substrate cathode under the condition of a constant potential electrolysis at -0.4 V. The contents of Al and Sc in the electrodeposit were 73.6 and 8.8 at% by EDS analysis. The X-ray diffraction pattern of the electrodeposit fits the patterns of Al and Al_3Sc .

Keywords: Molten Salt, Al-Sc alloys, Co-electrodeposition, LiCl-KCl melt

1. Introduction

Scandium (Sc) is one of the rare earth (RE) elements and it is present in the earth crust at about 18-25 ppm, a larger proportion than that of tin and lead. Scandium is strongly active like other RE elements, with Sc oxide displaying different properties than the oxides of other elements, both optically and magnetically¹⁾. It also has the characteristic that the ionic radius is the smallest among the RE elements and the electronegativity is high. Applications of Sc include GSGG (Gadolinium Scandium Gallium Garnet($Gd_3Sc_2Ga_3O_{12}$)) laser single crystals^{2,3)}, metal halide lamp phosphor^{4,5)}, addition to aluminum (Al) in Al Alloys⁶⁾, and others. The addition of Sc improves the functionality of these materials to achieve excellent performance characteristics.

The mechanical properties and corrosion resistance of Al and Al alloys are improved by Sc addition, as has been established by numerous reports⁷⁻¹¹⁾. The standard electrode potential of Sc/Sc³⁺ (-2.08 V) is more negative than that of Al/Al³⁺ (-1.66 V)¹²⁾, however, the corrosion resistance is improved by adding Sc to Al. Electrochemical studies of the RE elements in LiCl-KCl molten salt have been widely reported¹³⁻¹⁵⁾, and Al-RE alloys formation have been reported by RE electrodeposition on Al cathodes. Harata et al. reported Al-Sc alloy formation with a liquid Al cathode in CaCl₂-Sc₂O₃ molten salt at 1173 K.¹⁶⁾ Castrillejo et al. also reported Al-Sc alloy formation in LiCl-KCl molten salt at 723 K and 773 K¹⁷⁾. In that report, the potential region for co-electrodeposition of Al ions and Sc ions can be explained by voltammogram measurements, however, Al-Sc electrodeposits formed by co-electrodeposition have not been reported. The Al₃Sc, Al₂Sc, and AlSc₂ are formed by potentiostatic and galvanostatic electrolysis using Al working electrodes. There are few reports that Al-Sc electrodeposits are formed by co-electroreduction of Al ions and Sc ions, and if Al-Sc alloy films can be formed by co-deposition of Al and Sc ions, it will not be necessary to use an Al electrode as a substrate metal. The applicability will be broadened since the corrosion resistance of various metal surfaces can be improved by electroplating of Al-Sc alloys. In this study, the electrochemical behavior of Al and Sc was investigated in LiCl-KCl molten salt, which has a wide electrochemical potential window and co-electrodeposition of Al-Sc alloys was carried out by constant potential electrolysis.

2. Experimental

The LiCl (Kanto Chemical Co., 99% pure) and KCl (Kanto Chemical Co., 99% pure) were used after drying at 393 K for 24 h. The LiCl and KCl salts were mixed in a molar ratio of 58 : 42 in an alumina crucible (Nikkato Corporation, SSA-S(99.6% Al₂O₃)), and melted at 723 K under Ar gas. To remove impurities from the mixed molten salt electrolyte, pre-electrolysis using glassy carbon electrodes was carried out by a constant voltage of 3.0 V for 4 hours. The ScCl₃ (Sigma-Aldrich, 99.99% pure) and/or AlCl₃ (Kanto Chemical Co., 99.8% pure) were added to the LiCl-KCl molten salt in amounts corresponding to 0.1 mol% and 0.3 mol%, respectively. A schematic illustration of the

electrochemical cell is shown in Fig. 1. The cell consists of three electrodes and is filled by Ar gas. The electrolyte temperature was measured by an R-type thermocouple inserted into an alumina tube and controlled at 723 K within an error of 1 K.

A tungsten rod (Niraco, 99.9% pure, ϕ 2 mm) or Cu plate (Niraco, 99.9% pure) and a glassy carbon plate (GC, Tokai carbon, GC-20) were used as the working and counter electrodes, respectively. Pure Al wire (Koujundo Chemical Laboratory Co., Ltd., 99.999% pure, ϕ 2 mm) was used as the reference electrode in molten salts containing Al ions. A tungsten rod (Niraco, 99.9% pure, ϕ 2 mm) was used as the reference electrode in the molten salts without Al ions. The potential during the electrochemical measurements was controlled by a Hokuto-Denko HZ-5000 potentiostat. Voltammograms were measured at a potential range of 0.5 to -1.5 V vs. Al/Al(III) with a scan rate of 0.02 V s^{-1} in the molten salt containing $ScCl_3$ and/or $AlCl_3$. Constant potential electrolysis using a working electrode of Cu plate (Niraco, 99.9% pure, electrode area 2 cm²) and counter electrode of Al plate (Niraco, 99.9% pure, electrode area 4 cm²) was carried out at the potential of -0.4 V for 1 hour. The formed electrodeposits were analyzed by energy dispersion spectroscopy and observed by scanning electron microscopy (SEM-EDS, JEOL JSM-6510LA) and X-ray diffraction (XRD, Bruker D2 phaser, Cu-K α radiation).

3. Results and discussion

Voltammograms on the W electrode in the LiCl-KCl molten salt electrolyte containing $ScCl_3$ and/or $AlCl_3$ are shown in Fig. 2 a) and b), here the potential was scanned from 0.5 V to -1.5 V at a scan rate of 0.02 V s^{-1} , and voltammograms in the LiCl-KCl molten salt without additives and with $ScCl_3$ were measured by the W quasi-reference electrode, the potential axis was calibrated at the Li deposition potential and normalized with the Al/Al(III) potential axis.

The voltammogram in LiCl-KCl molten salt electrolyte (Fig. 2 a)) shows that the cathodic current increases from potentials of -1.4 V and the anodic current increases from a very similar potential. It is considered that these currents correspond to Li electrodeposition and dissolution reactions, this Li electrodeposition is similar to the report of Chen et al. with a similar molten salt system.¹⁸⁾ The voltammograms in the LiCl-KCl molten salt containing $ScCl_3$ and/or $AlCl_3$ are shown in Fig. 2 b). The voltammogram in the electrolyte containing $AlCl_3$ is shown by the green dotted line including the portions from the a1 to a4 peaks, the cathodic current increased slightly at 0 V (a1), exceeded -1.0 V without any steep increase, peaked after the current increased again from -1.15 V (a2), and increased sharply from -1.3 V. After the potential reversal, a large anodic current flowed from -1.45 V, and the current increased from -1.1 V (a3) and 0 V (a4) to peak. The small cathodic current and the large anodic current from 0 V would correspond to an Al electrodeposition reaction and dissolution reaction of the electrodeposited Al. The increase in the cathodic current from -1.3 V and in the anodic current from -1.45 V are considered to represent Li electrodeposition and dissolution of electrodeposited Li,

the current peaks at -1.2 V (a2) and at -1.1 V (a3) are thought to arise from Al-Li alloy electrodeposition and dissolution of electrodeposited Al-Li alloys. The voltammogram in the electrolyte containing ScCl_3 is shown as a blue dotted line including the b1 and b2 peaks, the cathodic current gradually increases from a potential of -0.8 V (b1), after a reverse scan the anodic current peak was recorded at -0.7 V (b2). These currents may correspond to a reduction reaction of Sc(III) and dissolution of deposited Sc, Castrillejo et al. also reported the reduction potential of Sc(III) with potentials close to the results here.¹⁷⁾ The voltammogram in the electrolyte containing ScCl_3 and AlCl_3 is shown by the red solid line including the portions from c1 to c6, the current peaks at -0.28 V (c2) and at -0.18 V (c5) are considered to correspond to an electrodeposition reaction of Al-Sc alloys and dissolution reactions of the deposited alloys. The current of the electrodeposition and dissolution of aluminum are observed at around 0 V, however there is no electrodeposition current that can be ascribed to Sc. A summary of the potentials and their reactions in the voltammogram of Fig. 2 b) is shown in Table 1. The cathodic and anodic current couples at -0.28 V (c2) and -0.18 V (c5) were observed when both ScCl_3 and AlCl_3 were added to the electrolyte. The potential of the current couples is more positive than the potential of the current couple which was observed as a reduction current of Sc(III) and an oxidation current of Sc when only ScCl_3 was added to the electrolyte. Therefore, the cathodic current is considered to be an alloy formation current with Al and Sc.

Based on the above voltammogram results, constant potential electrolysis was performed at -0.4 V for 60 minutes in the electrolyte containing ScCl_3 and AlCl_3 . The current density value during the constant potential electrolysis changed with time, and the average current density was 6 mAcm^{-2} . After the electrolysis, a sponge-like grey and uneven surface was observed on the cathode. The electrodeposit was washed with distilled water, dried, and then examined by SEM observation and EDS analysis. The SEM image and analysis results are shown in Fig. 3. From the SEM image, it was observed that dendritic electrodeposits form on the cathode. The concentration of Al, Sc, and O in the electrodeposit were 73.6, 8.8, and 17 at%, respectively by the EDS analysis in the dendritic electrodeposit at the center (middle part) of Fig. 3(a). The composition of the dendritic electrodeposits around the center was not significantly different from that at the center. The oxygen content of 17 at% suggests the formation of oxide of Al and Sc at the electrodeposit surface, likely caused by contact with oxygen at the washing of the electrodeposit. The XRD result to identify the electrodeposit is shown in Fig. 4. Comparing the XRD results with published XRD JCPDS reference patterns, relatively large intensities of $2\theta = 38.1^\circ, 44.8^\circ, 65.1^\circ, \text{ and } 77.8^\circ$ were consistent with (111), (200), (220), and (311) of Al (JCPDS card 4-0787), respectively. It was found that the low intensities of $2\theta = 37.5^\circ, 44.1^\circ, 64.1^\circ, \text{ and } 77.5^\circ$ at positions close to the above were consistent with (111), (200), (220), and (311) of Al_3Sc (JCPDS card 17-412). From these results, it is considered that the main component of the electrodeposit is Al, and that Al_3Sc is co-deposited in parts of it. More than 1600 K is required to form Al_3Sc (melting point of $\text{Al}_3\text{Sc} : 1593 \text{ K}^{19)}$ from Al-Sc melt, however, in this molten salt

electrolysis, Al_3Sc was formed at 723 K. This is believed to be due to the electrodeposition process. Considering the EDS analysis, since the electrodeposit surface contains oxygen, it may be expected that oxide film of Al or Al_3Sc formed, and Al and Al_3Sc are present below the oxide film.

The results of this experiment show that Al_3Sc can be formed by co-electrodeposition even if the substrate material is not Al.

4. Conclusions

The electrochemical behavior of Al and Sc was investigated in LiCl-KCl molten salt containing AlCl_3 and ScCl_3 at 723K. In the LiCl-KCl molten salt containing ScCl_3 or AlCl_3 , a reduction current of Sc(III) or Al(III) flowed from potentials at -0.8 V or 0 V, respectively. In the molten salt containing ScCl_3 and AlCl_3 , reduction current peaks at -0.28 V and an oxidation current peak at -0.18 V are observed, this is considered to be electrodeposition of Al-Sc alloy and dissolution of the alloy. Sponge like electrodeposit was obtained by constant potential electrolysis at -0.4 V in the electrolyte containing ScCl_3 and AlCl_3 , The XRD pattern of the electrodeposit fit with diffraction patterns of Al and Al_3Sc .

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Figure and Captions

Fig. 1 Schematic illustration of the electrochemical cell.

Fig. 2 Voltammograms on the tungsten electrode a) in LiCl-KCl molten salt and b) in LiCl-KCl containing AlCl₃(green dotted line), ScCl₃(blue dotted line), and AlCl₃+ScCl₃ (red solid line).

Fig. 3 a) SEM image of the electrodeposit surface formed by constant potential electrolysis at -0.4V for 1 h in the electrolyte containing ScCl₃ and AlCl₃ and b) EDS profile of the electrodeposit.

Fig. 4 XRD pattern of the electrodeposit formed by constant potential electrolysis at -0.4V for 1 h in the electrolyte containing ScCl₃ and AlCl₃.

Table 1 Relationship between potential and reaction in the voltammogram of Fig. 2 b).

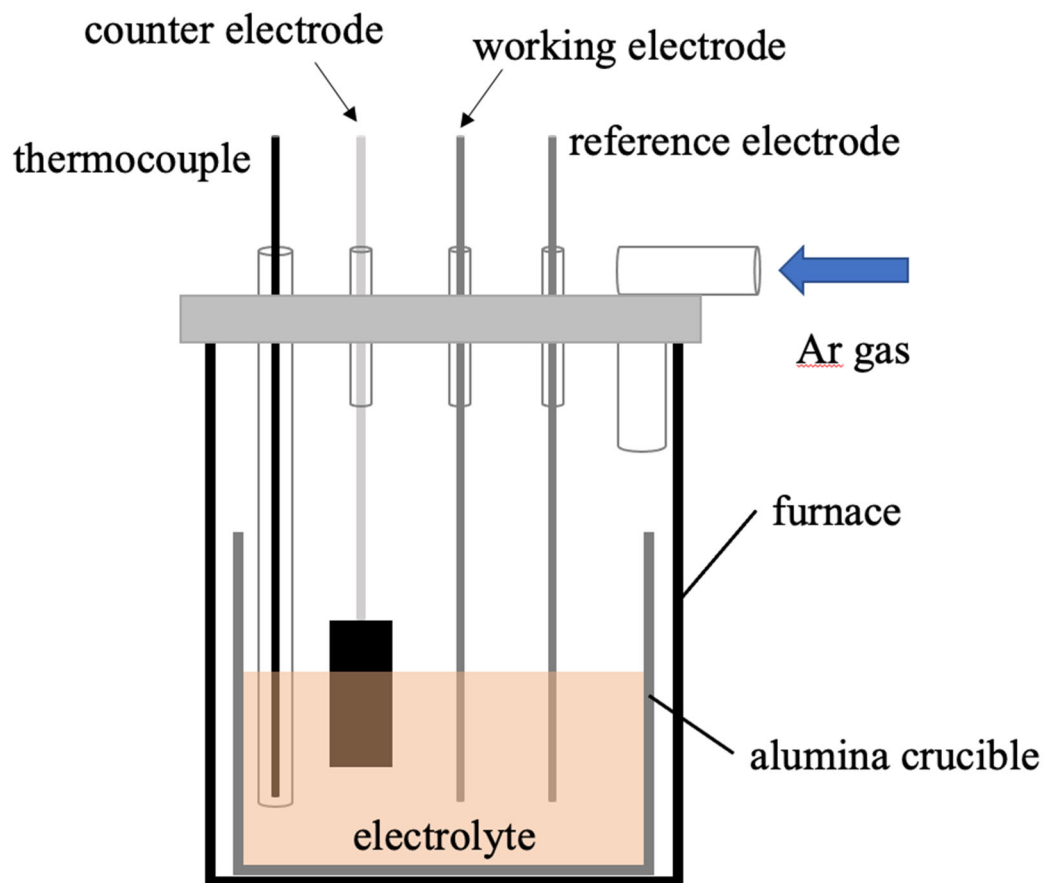


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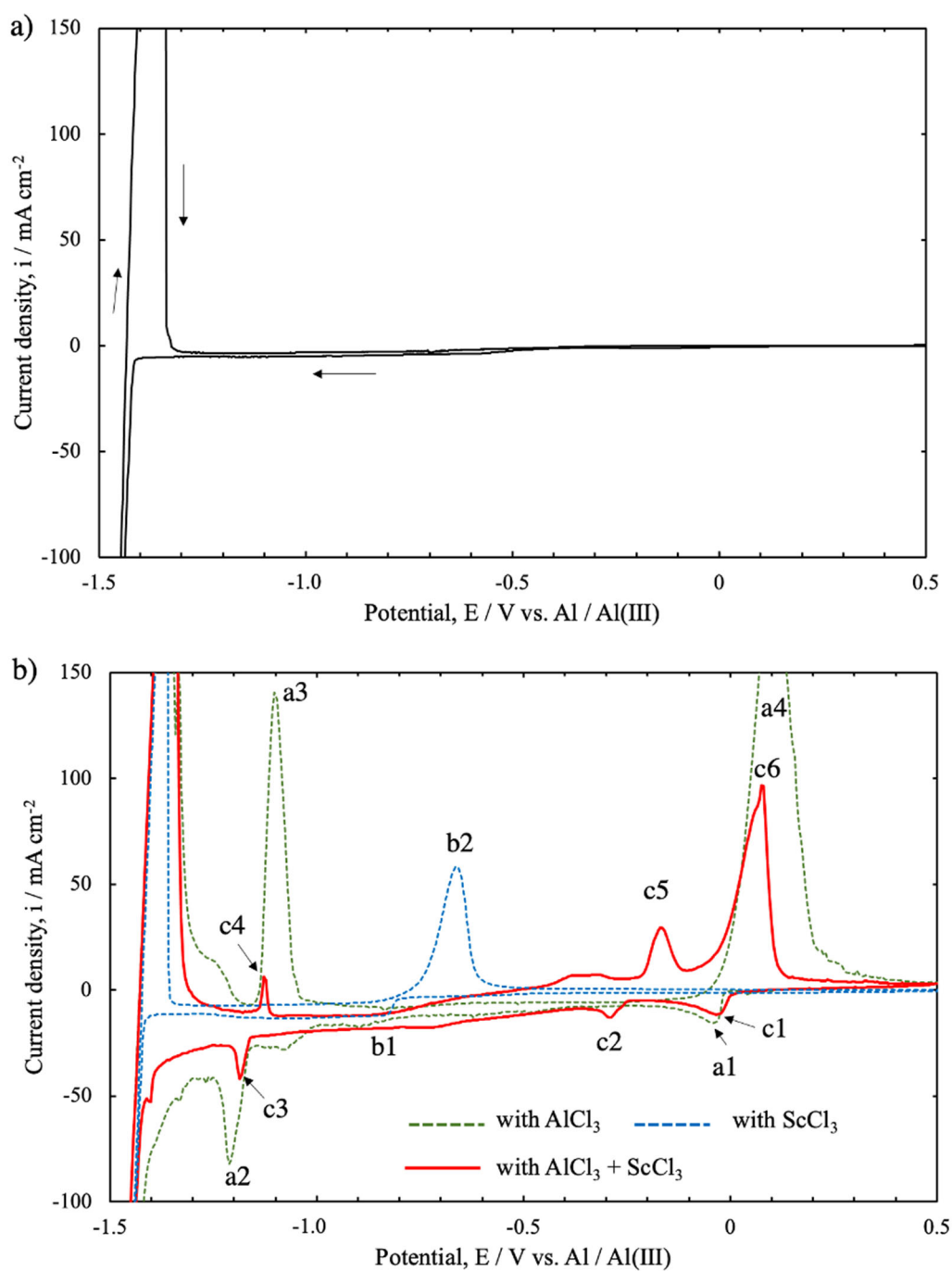


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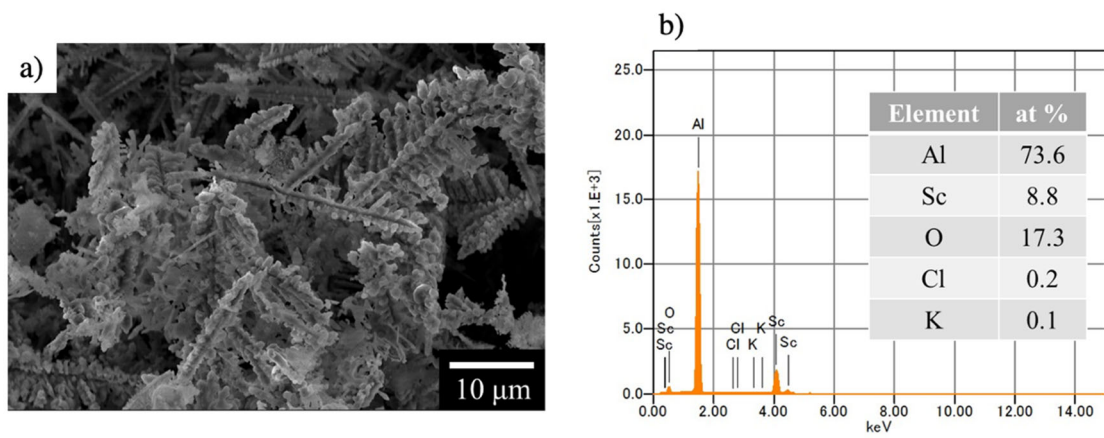


Fig. 3 a) SEM image of the electrodeposit surface formed by constant potential electrolysis at -0.4V for 1 h in the electrolyte containing ScCl_3 and AlCl_3 and b) EDS profile of the electrodeposit.

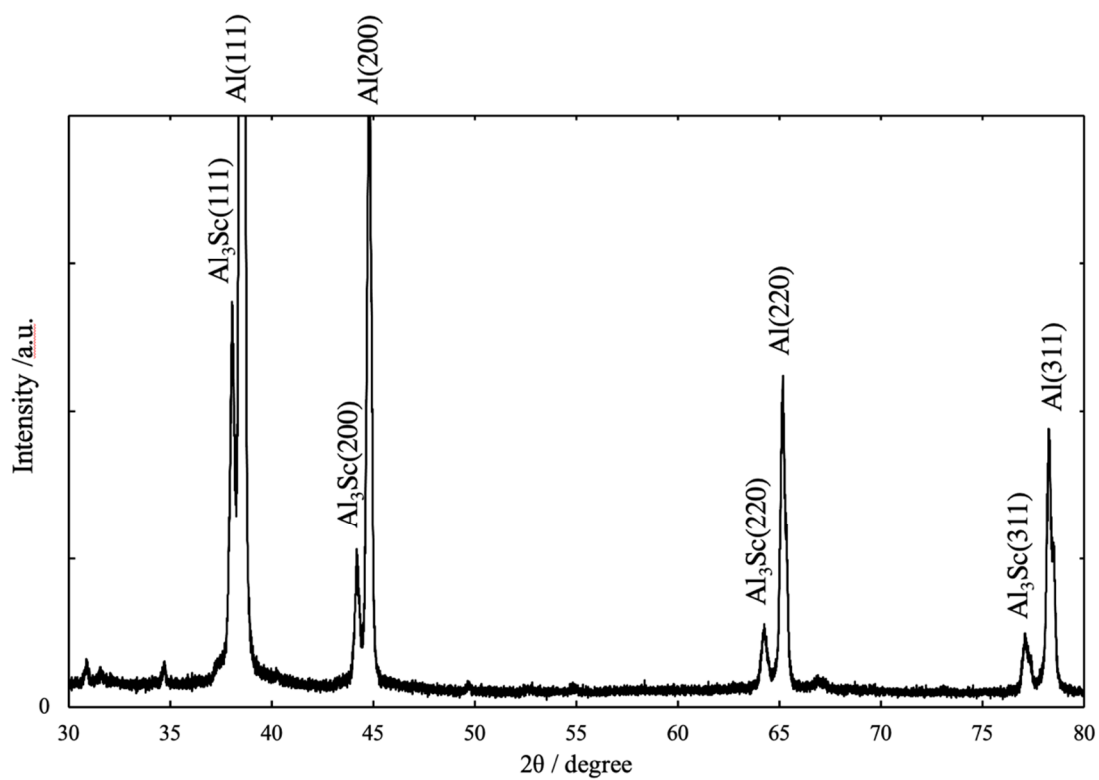


Fig. 4 XRD pattern of the electrodeposit formed by constant potential electrolysis at -0.4V for 1 h in the electrolyte containing ScCl_3 and AlCl_3 .

Table 1 Relationship between potential and reaction in the voltammogram of Fig. 2 b).

Potential range (V)	Electrodeposition and dissolution reaction	Symbol
-0.1 ⇔ 0.2	Al	a1 ⇔ a4 c1 ⇔ c6
-0.28 ⇔ -0.18	Al-Sc alloy	c2 ⇔ c5
-0.8 ⇔ -0.7	Sc	b1 ⇔ b2
-1.2 ⇔ -1.1	Li-Al alloy	a2 ⇔ a3 c3 ⇔ c4
-1.5 ⇔ -1.3	Li	-