

Magnetic Films of Cobalt/Aluminum Electrodeposited from the Room Temperature Molten Salts AlCl_3 -BPC- CoCl_2

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The electric conductivities of molten mixtures of aluminum chloride-butylpyridinium chloride-cobalt chloride (AlCl_3 -BPC- CoCl_2) were measured using a computerized direct-current method. The conductivities of all the melts increased with increasing temperature. The electrodeposition of Co/Al films from the AlCl_3 -BPC melt containing a small amount of CoCl_2 has been studied by cyclic voltammetry. Compact and smooth Co/Al thin films could be obtained at a deposition potential of -0.4 V. The surface morphology and the composition of the electrodeposited thin films were studied using scanning electron microscopy (SEM) and atomic force microscopy (AFM). The magnetic properties of the deposited thin films have been investigated via magnetic force microscopy (MFM) and vibrating sample magnetometry (VSM). Higher magnetization and smooth domains of Co/Al layers could be obtained at the deposition potentials of -0.1 V and -0.4 V, respectively.

Key words: Magnetic Film, Room Temperature Molten Salt, Electric Conductivity, Cyclic Voltammetry, Surface Morphology

Introduction

The electrodeposition method has the merits of simple equipment and operation; it is also convenient for obtaining products on substrates possessing big areas. Thus, the electrochemical method will deserve much consideration for preparation of magnetic films. Cobalt is known as a hard magnetic material and cobalt alloys have been shown to have excellent magnetic properties with adequate mechanical durability and corrosion resistance, which are needed for high performance magnetic recording applications [1 – 5].

Due to the ease of large quantity production with a rather simple facility, the electrodeposition method has become one of the main research topics on production of magnetic thin films.

Chloroaluminate molten salts are molten mixtures of aluminum chloride and one or more alkali metal chlorides. These systems are being extensively investigated from both the fundamental and application viewpoints. Chloroaluminate melts have interesting physicochemical properties, such as high electrolytic conduc-

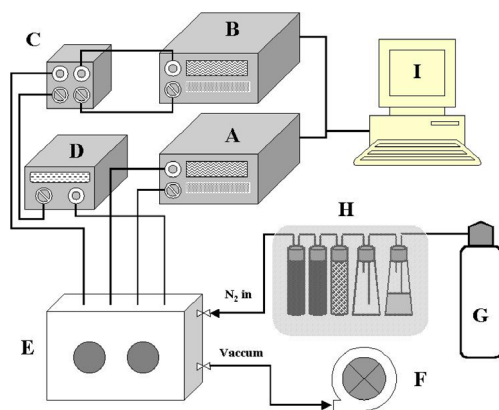
tivities and variable Lewis acid-base properties. These mixtures have lower melting points than most of other molten salts and can be employed as solvents for electrochemical studies, and especially as electrolytes for electrodeposition processes of thin films.

Experimental Section

Molten salt electrolytes of the ternary melts AlCl_3 -BPC (N-butylpyridinium chloride)- CoCl_2 were prepared. Since the chemicals are sensitive to moisture and oxygen, these were prepared in a glove box (H_2O and oxygen levels well below 5 ppm). Aluminum chloride (AlCl_3 , Merck, anhydrous, 95%) was mixed with sodium chloride, and a few g of aluminum powder [7, 8] were used for purification by vacuum sublimation, from which AlCl_3 was obtained as white crystals. BPC (TCI, 98%) and cobalt chloride (CoCl_2 , Merck, anhydrous, 98%) were used as received. In the glove box the electrolytes were prepared by adding CoCl_2 to the binary AlCl_3 -BPC melts on a hot plate at 80°C . A Karl Fischer titrator was used to measure the H_2O content in the melts, and concentrations of the cations in the molten electrolytes were measured by an inductively coupled plasma atomic

Table 1. Water content and the concentration of saturated CoCl_2 in the AlCl_3 -BPC melts.

AlCl_3 -BPC/ mol %	Content of water/ wt %	Concentration of CoCl_2 mg l^{-1}	mmol l^{-1}
40–60	1.59	32.0	1.64
50–50	0.46	25.2	1.29
60–40	2.87	4.58	0.236
70–30	3.21	21.9	1.12

Fig. 1. The apparatus for conductivity determination. A: Multimeter 1, B: Multimeter 2, C: 10Ω standard resistor, D: DC power supply, E: Glove box, F: Vacuum pump, G: N_2 gas, H: Gas purification, I: IBM-PC.

emission spectrometer (ICP-AES); the results are given in Table 1.

The electric conductivity was determined by the four-electrode direct method previously reported by Hsu and Yang [9]. For the measuring system shown in Fig. 1, a programmed computer was utilized. The cell constant was measured to be 286.82 cm^{-1} by use of 0.1 molar KCl solution at 25°C . In the four electrode system the reference electrodes were Ag-AgCl and platinum. The applied current (Hewlett-Packard E3616A supplied) was 2.5 A. Two multimeters (Keithley, Model 2000) were employed to keep the potentials for the cell constant independently of the capillary current. The electric conductivity of the AlCl_3 -BPC- CoCl_2 melts was measured at various compositions and temperatures.

A tungsten wire (1 mm dia., Nilaco Co., 99.95%) was used as the working electrode in investigating the electrodeposition of Co/Al layers. An aluminum wire (1 mm \varnothing , Nilaco Co., 99.99%) was utilized for the $\text{Al}/\text{AlCl}_4^-$ electrode, which was used in the 2:1 AlCl_3 -BPC mixtures. The substrate of copper was washed with 50% v/v HCl solution for 10–30 s, and then cleaned with acetone and distilled water. A potentiostat-galvanostat (EG&G, Princeton Applied Research Model 273A) was used for cyclic voltammetry and preparation of the Co/Al layers (see Fig. 2). The morphology of the electrodeposited layers was measured by a scanning electron microscope. Atomic Force Microscopy and Mag-

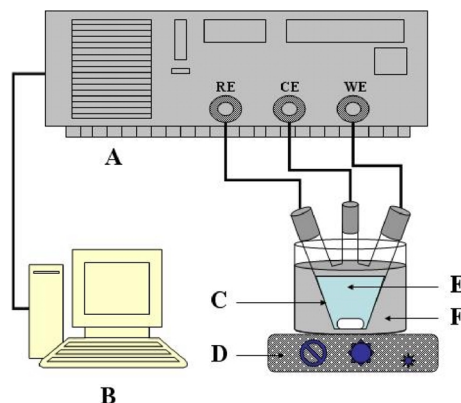
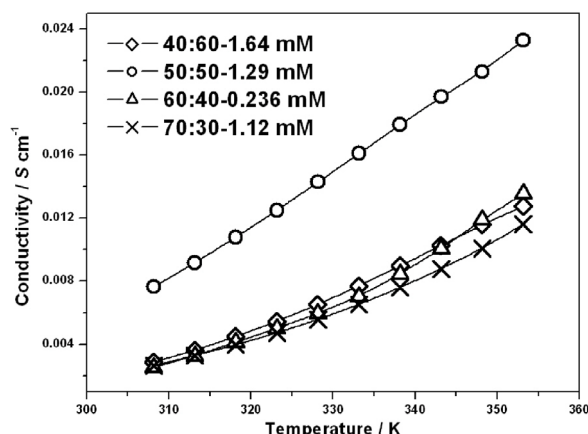


Fig. 2. Schematic diagram of the apparatus for electrodeposition. A: Potentiostat EG&G, B: Computer, C: Three-electrode electrochemical cell, D: Stirring hot plate, E: Molten salt electrolytes, F: Silicone oil.

Fig. 3. The electrical conductivity of the molten mixture system AlCl_3 -BPC- CoCl_2 as a function of the temperature at some different compositions.

netic Force Microscopy were utilized to investigate the surface microstructure and domain of the electrodeposited layers. The magnetic property of the Co/Al layers was measured by a vibrating sample magnetometer.

Results and Discussion

Electrical conductance mechanism

In Fig. 3, electric conductivities are shown as a function of the temperatures at four compositions (AlCl_3 -BPC- CoCl_2 =40:60-1.64 mM, 50:50-1.29 mM, 60:40-0.236 mM, 70:30-1.12 mM); the conductivities increase with increasing temperature, as usual.

In Fig. 4, the electric conductivities vs. the composition of AlCl_3 in the ternary melts are shown at

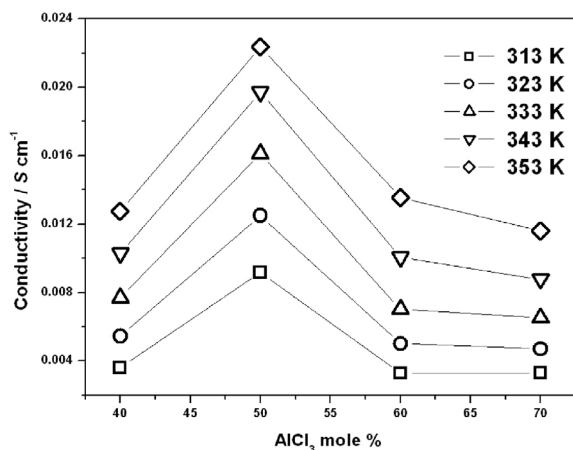
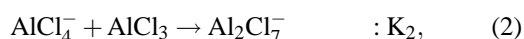
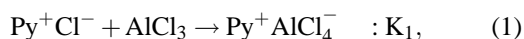


Fig. 4. Electrical conductivities of the molten mixture AlCl_3 -BPC- CoCl_2 as a function of the AlCl_3 mole fraction at some different temperatures.

five temperatures. The neutral melt ($\text{AlCl}_3/\text{BPC} = 1$) has maximum values of the conductivities. This is probably because in the neutral melt the main anionic species is AlCl_4^- . The conductivities of the acidic melts ($\text{AlCl}_3/\text{BPC} > 1$) are slightly higher than those of the basic melts for the AlCl_3 -BPC melts; this may be attributed to the increase in Al_2Cl_7^- in the acidic melts which decreases the viscosity [7,8]. In contrast to the binary system (AlCl_3 -BPC), Fig. 4 reveals that, from the maximum value at the neutral composition, the conductivities decrease a little more in the acidic side than in the basic side. We assume that such species as $\text{Co}(\text{Al}_2\text{Cl}_7)_2$ are formed from Co^{2+} and Al_2Cl_7^- ions, which will increase the viscosities and decrease the conductivities. The acid-base properties of the AlCl_3 -BPC system may be described in terms of the following reactions [9]:



where K_1 , K_2 , and K_3 are the equilibrium constants for the corresponding reactions. Gale and Karpinski *et al.* [15–17] have utilized potentiometric titration based on the acid-base properties to investigate Cl^- , AlCl_4^- , and Al_2Cl_7^- ions in the binary AlCl_3 -BPC melts. $K_3 = [\text{Al}_2\text{Cl}_7^-][\text{Cl}^-]/[\text{AlCl}_4^-] = 3.8 \times 10^3$ at 30 °C; K_1 and K_2 are larger than K_3 . Therefore, some physical properties of the AlCl_4^- ions in the molten AlCl_3 -BPC system may be studied on the basis of the chemical potential.

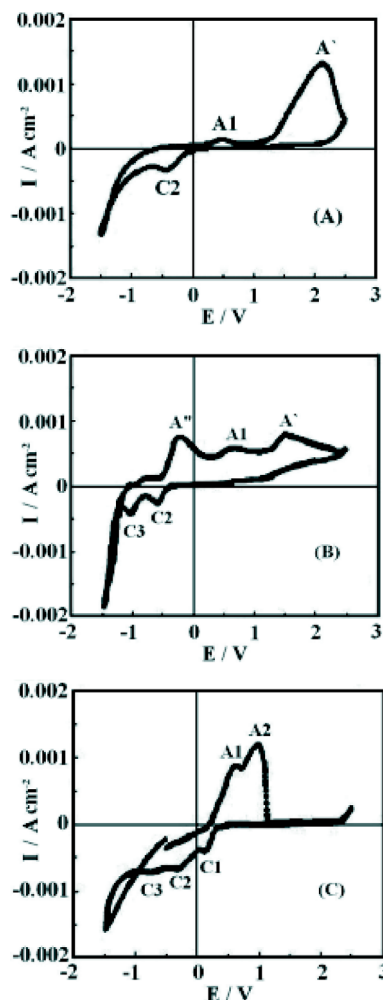


Fig. 5. Cyclic voltammograms recorded with a tungsten electrode in the ternary melt at 40 °C. (A) 40:60 AlCl_3 -BPC melt containing 1.64 mmol/l CoCl_2 , (B) 50:50 AlCl_3 -BPC melt containing 1.29 mmol/l CoCl_2 , and (C) 70:30 AlCl_3 -BPC melt containing 1.12 mmol/l CoCl_2 ; scanning rate: 400 mV/s; reference electrode: $\text{Al}/\text{AlCl}_4^-$.

Any models have been proposed, or the mechanism of electrical conductance in ionic melts; electrolytic conductivity may be strongly related to the structure. Raman spectrum analyses have shown [18] that in the AlCl_3 -MCl ($\text{M}=\text{Li}^+$, K^+ , or BP^+) systems complex ions such as AlCl_4^- and Al_2Cl_7^- are present; in the neutral and acidic melts tetrahedrally coordinated AlCl_4^- and Al_2Cl_7^- complexes are formed, respectively.

Analyses of the electrode reactions

The melt compositions of CoCl_2 for the electrode reaction are given in Table 1; the contents

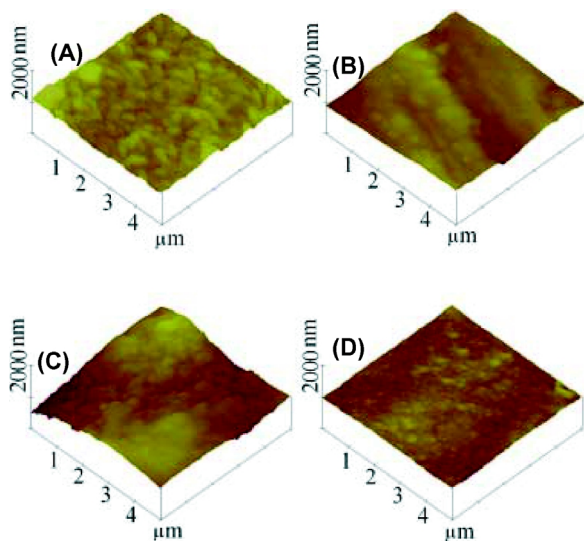


Fig. 6. Atomic force micrographs of the Co-Al alloys electrodeposited on a Cu plate in the ternary molten salts at 40 °C. Electrolyte: $\text{AlCl}_3\text{-BPC-CoCl}_2=70:30\text{-}1.12$ mM. The experimental conditions: Input potential: (A) -0.1 , (B) -0.2 , (C) -0.3 , and (D) -0.4 V; $Q = 10$ C.

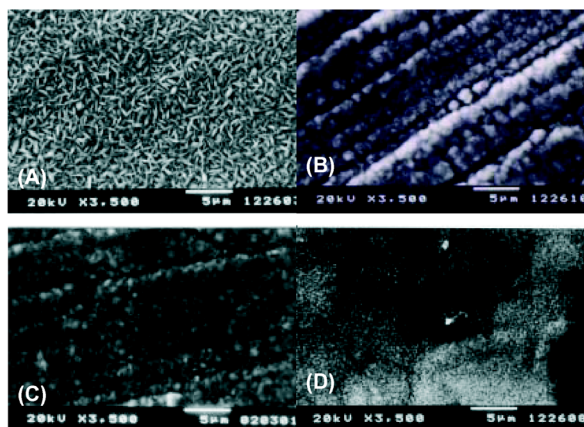


Fig. 7. Scanning electron micrographs of the Co-Al alloys electrodeposited on a Cu plate in the ternary molten salts at 40 °C. Electrolyte: $\text{AlCl}_3\text{-BPC-CoCl}_2=70:30\text{-}1.12$ M. Input potential: (A) -0.1 , (B) -0.2 , (C) -0.3 , and (D) -0.4 V; $Q = 10$ C.

of cobalt are high enough for the analyses of the reactions. The cyclic voltammograms of the basic ($\text{AlCl}_3/\text{BPC} < 1$), neutral ($\text{AlCl}_3/\text{BPC} = 1$), and acidic melts ($\text{AlCl}_3/\text{BPC} > 1$) in the ternary system $\text{AlCl}_3\text{-BPC-CoCl}_2$ are shown in Fig. 5. A tungsten electrode was used at 40 °C, and the scanning rate was 400 mV/s. It was observed that electrochemical window of the acidic melt is high than that of basic and

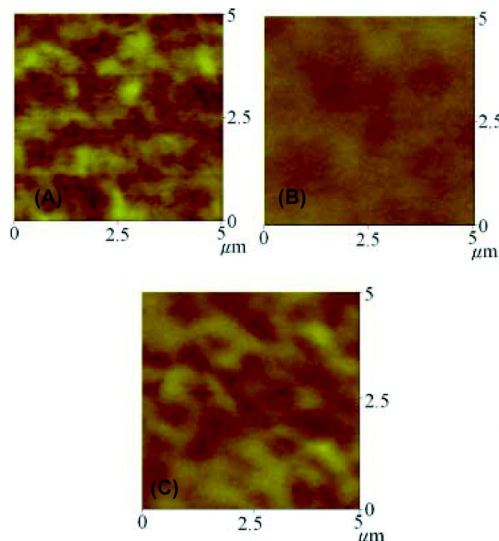


Fig. 8. Magnetic force micrographs of the Co-Al alloys electrodeposited on a Cu plate in the ternary molten salts at 40 °C. Electrolyte: $\text{AlCl}_3\text{-BPC-CoCl}_2=70:30\text{-}1.12$ mM. Input potential: (A) -0.1 , (B) -0.3 , and (C) -0.4 V; $Q = 10$ C.

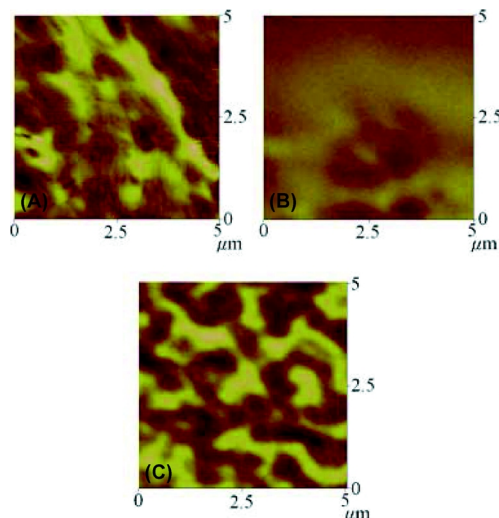
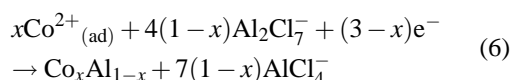
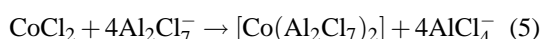
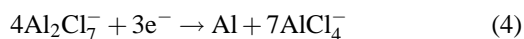


Fig. 9. Magnetic force micrographs of the Co-Al alloys electrodeposited on a Cu plate in the ternary molten salts at 40 °C. Electrolyte: $\text{AlCl}_3\text{-BPC-CoCl}_2=70:30\text{-}1.12$ mM. Input potential: (A) -0.1 , (B) -0.3 , and (C) -0.4 V; $Q = 30$ C.

neutral melts. In the acidic melt the oxidation peaks due to aluminum (peak of A1) and cobalt (peak of A2) exhibit higher current densities. As the component BPC is increased, the processes (peaks of A' and A'') due to the polymerization of pyridine (BP^+) become more clear, as shown in Figs. 5 (A) and (B). Reduction

of pyridine's cation is attributed to limiting of the negative potential in the basic melts, and limiting of positive potential is caused by oxidation of Cl^- ion and polymerization of pyridine's oxidation product [11]. As the AlCl_3 content increases, polymerization of pyridine decreases, and therefore the acidic melts would be more suitable. Fig. 5 (C) shows the peaks due to the reduction of cobalt (peak of C1) and aluminum (peaks of C2 and C3), which suggests that electrodeposition of Co/Al layers occurs through the following steps:



Eq. (4) means that the reaction of Al_2Cl_7^- ion will directly electrodeposit aluminum metal. It has been demonstrated that in acidic melts Al metal is electrodeposited from Al_2Cl_7^- complex ion [13], which will also combine with CoCl_2 to form $[\text{Co}(\text{Al}_2\text{Cl}_7)_2]$ species (eq. (5)). Osteryoung *et al.* [19–23] have found that the complex ions in the anhydrous systems are different from those in the hydrous systems, and that the diffusion mechanisms usually are different. It is expected that coordination by the ligands in the complexes is stronger in molten systems than in aqueous systems. Hussey *et al.* [24–25] have indicated that the formation of the complex ion influences the electrodeposition, and that the acidic melts in the anhydrous systems can be utilized, as these are favorable for electrodeposition of Co/Al layers (eq. (6)).

Analyses of surface morphology

As applied potentials are expected to change the electrode reactions and therefore the composition of the layers electrodeposited, these were deposited at -0.1 , -0.2 , -0.3 , and -0.4 V.

Figures 6 and 7 show the surface morphology of the electrodeposited Co/Al alloys observed by AFM and SEM analyses, respectively. The Co/Al layers were obtained by cyclic voltammetry at the deposition potentials of -0.1 , -0.2 , -0.3 , and -0.4 V and with the quantity of electricity of 10 C. The Co/Al layer deposited at -0.4 V shows morphology of compact and granular particles of about 200 nm in diameter, as seen from the AFM in Fig. 6(D) and from the SEM in

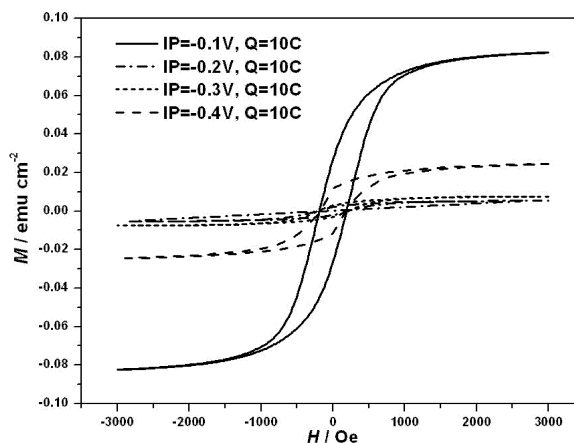


Fig. 10. Hysteresis loops for Co-Al alloy electrodeposited on a Cu plate in the ternary molten salts.

Fig. 7(D). At the deposition potential of -0.1 V layers of high cobalt content have been obtained, as analyzed by energy dispersive X-ray spectroscopy (EDS), as small needle-like crystals (Fig. 7(A)). The mean roughness is 30.667, 39.512, 100.28, and 20.236 nm at the deposition potentials of -0.1 , -0.2 , -0.3 , and -0.4 V, respectively. The roughness at -0.4 V is the smallest.

Analyses of magnetic properties

In Figs. 8(A), (B), and (C) $5 \times 5 \mu\text{m}^2$ scopes of the MFM images at the deposition potentials of -0.1 , -0.3 , and -0.4 V, respectively, under the electricity of 10 C are shown. The scopes in quite similar cases with the exception of the quantity of electricity at 30 C are shown in Figs. 9(A), (B), and (C), respectively. The images of the surfaces obtained at -0.4 V are uniform, and the surfaces do not appear to contain domains, as seen from Figs. 8(C) and 9(C).

The layer under -0.1 V exhibits unclear and irregular domain boundaries. Comparing the magnetic domain with the surface morphology, we can see that the uniform domain is related with the composition and structure.

Saturation magnetizations (M_s), remanent magnetizations (M_r), and coercive forces (H_c) are expected to be correlated with the deposition potentials, as seen from Fig. 10. The thin film sample of $1 \times 1 \text{ cm}^2$ was placed perpendicular to the magnetic fields for the measurement. The thin films obtained at -0.1 and -0.4 V have exhibited high hysteresis losses. These re-

sults well correspond to the AFM and SEM data. As for the coercive field, the dependence of H_c on the deposition potentials is not clear and it approximately ranges between 177 and 212 Oe.

Conclusions

Complex formation by the added solute species in molten electrolytes influence considerably the electrolytic conductivity, especially in the present acid-base molten salt electrolytes. These properties have been used to adjust various parameters. In AlCl_3 -BPC melts, AlCl_4^- and Al_2Cl_7^- anions can coexist, while two AlCl_4^- ionic species lead to one Al_2Cl_7^- with increasing concentration of AlCl_3 . Wide electrochemical windows are obtained for the present layer electrodeposited from the molten mixture owing to the useful complexing property in the acidic melts, which may

be regarded as one of the ideal molten electrolytes for electrodeposition.

Due to the surface morphological analyses *via* both AFM and SEM, the products electrodeposited at -0.4 V from the molten electrolytes were smooth Co/Al thin films consisting of spherical crystals, while the products at -0.1 V were needle-like Co/Al crystals.

As for the magnetic properties, the Co/Al film electrodeposited at -0.1 V possesses irregular domain boundaries and high magnetization. The film deposited at -0.4 V shows a uniform MFM image, which may be attributed to a regular arrangement of the atoms and, in turn, of the layers.

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