



Transmission electron microscopy study of electrodeposited rhenium and rhenium oxides

Alejandro Vargas Uscategui^{a,*}, Edgar Mosquera^b, Luis Cifuentes^a

^a Laboratorio de Electrometalurgia, Departamento de Ingeniería de Minas, Facultad de Ciencias Físicas y Matemáticas, Universidad de Chile, Tupper Avenida 2069, Santiago, Chile

^b Laboratorio de Materiales a Nanoescala, Departamento de Ciencia de los Materiales, Facultad de Ciencias Físicas y Matemáticas, Universidad de Chile, Tupper Avenida. 2069, Santiago, Chile

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ABSTRACT

In this paper we present a study of electrodeposited nanocrystalline rhenium and rhenium oxides by transmission electron microscopy (TEM). The electrodeposition process was carried out using an alkaline aqueous electrolyte consisting of ammonium perrhenate dissolved in sodium hydroxide solution. The electrodeposited material showed a dendritic structure with no evidence of powder formation at the current density imposed on the system. TEM observations showed that metallic rhenium, rhenium (IV) oxide and rhenium (VI) oxide could coexist in the electrodeposited material.

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1. Introduction

Rhenium (Re) is a gray-colored metal, heavy, rare in nature, with some attractive characteristics that have proven useful in petrochemical industry, high temperature alloys, electrodes for fuel cells and military applications, among others [1]. The special features of Re and its compounds in these industries have shown that the production of Re and Re compounds, such as rhenium oxide, is very relevant.

In 2010, about 53% of the world production of rhenium and its compounds — as a byproduct from porphyry copper-molybdenum ores — was obtained in Chile [2]. Generally, the extraction methods of metallic rhenium from the ores comprise the production of perrhenate salts and perrhenic acid [3,4]. A subsequent production of rhenium (VII) oxide (Re₂O₇) involves the oxidation of metallic rhenium in air, while rhenium (VI) oxide (ReO₃) can be formed by reducing rhenium (VII) oxide with carbon monoxide. Rhenium (IV) oxide (ReO₂) is another stable compound that can be obtained as a laboratory reagent. Of these three oxides, ReO₃ is the most important one because of its high electronic conductivity (~10⁴ S/cm) and the possibility of intercalated ions in its crystalline structure [5].

The rhenium oxides can be produced by several synthesis methods, but in the case of electrodeposition process, they can be obtained as intermediate species in the reduction pathway form perrhenate ions toward metallic rhenium in aqueous acidic media [6]. Some recent investigations have focused on producing and characterizing rhenium oxide and mixed molybdenum-

rhenium oxides covering gold, glassy carbon and indium-tin oxide from acidic perrhenate solutions [7,8].

For these reasons, the aim of this study is to generate knowledge about the electrodeposition of rhenium and rhenium oxide on a copper substrate. To our knowledge, the present study is the first one to use transmission electron microscopy to examine nanocrystalline rhenium and rhenium oxides obtained by electrodeposition.

Previously, the authors have carried out research on the spontaneous precipitation and crystallization of Re compounds [9,10].

2. Experimental details

Rhenium and rhenium oxides were prepared by electrodeposition from alkaline perrhenate electrolyte in a standard electrochemical cell. The test solution is described in Table 1. Reagent-grade Ammonium Perrhenate (NH₄ReO₄) was provided by Moly-met S.A. and high purity sodium hydroxide (NaOH, Sharlau) was used. The electrolyte solution was prepared with ultrapure water (Barnstead, nanopure, 18 MΩ cm).

The electrodeposition was carried out in a standard two electrode cell (anode and cathode). Prior to electrodeposition, copper TEM grids, used like substrates, were cleaned by sonication in acetone for 15 min, followed by sonication and rinsing with ultrapure water. A platinum electrode was immersed in a 1:1 sulphonic solution (H₂SO₄ [5M]–HNO₃ [5M]) for 60 s, then immersed in H₂O₂ for 120 s and finally rinsed with ultrapure water. The Cu substrate was the cathode, with an apparent surface area of 13 mm², whereas the Pt electrode was the anode, with an apparent surface area of 1 cm². The anode–cathode

* Corresponding author. Tel.: +56 2 978 4795/4222; fax: +56 2 699 4119.

E-mail addresses: avargasuscat@ing.uchile.cl (A.V. Uscategui),

lucifue@cec.uchile.cl (L. Cifuentes).

Table 1
Composition of the electrolyte solution.

NH ₄ ReO ₄ (mM)	NaOH (mM)	pH	t °(C)
125	10	13.3	25

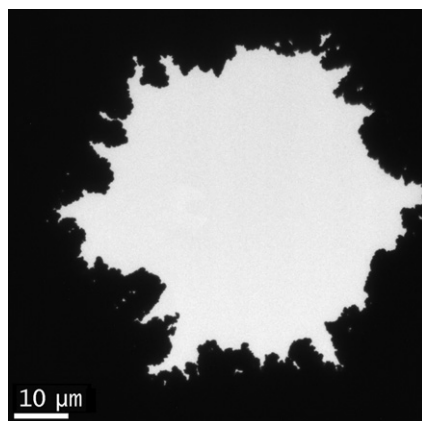


Fig. 1. Morphology of rhenium and rhenium oxide electrodeposits.

separation was 24 mm. The copper substrate was copiously rinsed with ultrapure water after the electrodeposition process.

The galvanostatic electrodeposition was conducted with a 5 A–30 V GW rectifier (model GPC-3030D), which also allowed cell voltage measurement. The latter variable was monitored throughout the experiment and shown to be stable at 3 ± 0.15 V during the electrodeposition experiment. The cell current was about 10 mA and was maintained to a total deposition charge of 36 C. The deposition took place at room temperature (25 ± 0.2 °C) under continuous bubbling of N₂ to eliminate the oxygen in the solution and stirring at 1200 rpm. Transmission electron microscopy (TEM) studies were carried out in a Tecnai F20 FEG-S/TEM operated at 200 kV, equipped with an Energy Dispersive X-ray analysis system (EDS). TEM observations were made on a freshly electrodeposited specimen.

3. Results and discussion

Available reports regarding rhenium and rhenium oxide electrodeposition are related to the use of an aqueous acidic electrolyte (NH₄ReO₄ or HReO₄ dissolved in H₂SO₄) [1,6,11,12], and in some cases preparing an electrolyte by dissolving metallic Re in hydrogen peroxide [7]. In contrast, in this report we show the possibility of obtaining rhenium and rhenium oxide from an alkaline aqueous electrolyte prepared by dissolving NH₄ReO₄ in sodium hydroxide as shown in Fig. 1.

This figure shows a dendritic formation of the electrodeposit, which follows a hexagonal pattern due the honeycomb form of the copper TEM grid. The material exhibited black-color when observed by optical microscopy and a texture consistent with electrodeposition process with a parallel hydrogen reduction reaction. No precipitation of powder material was observed during the process, which took place with concurrent bubbling of hydrogen ($2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$) from the specimen surface.

Fig. 2 shows a blown up image of one of the dendrites observed in Fig. 1. An inset image allows to appreciate hemispherical formations over the dendritic material with a size between 3 nm and 6 nm, corresponding to a covering material on the dendritic surface.

The compositional analysis is obtained using EDS. Fig. 3 shows the EDS spectra of two zones (see Fig. 2) with evident peak at

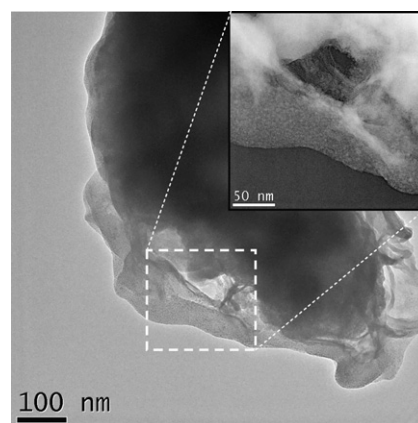


Fig. 2. Low magnification TEM image that shows the dendrite formation of the electrodeposited material. The dotted frame is shown magnified (inset) to reveal a contrast-inversion image of the selected area.

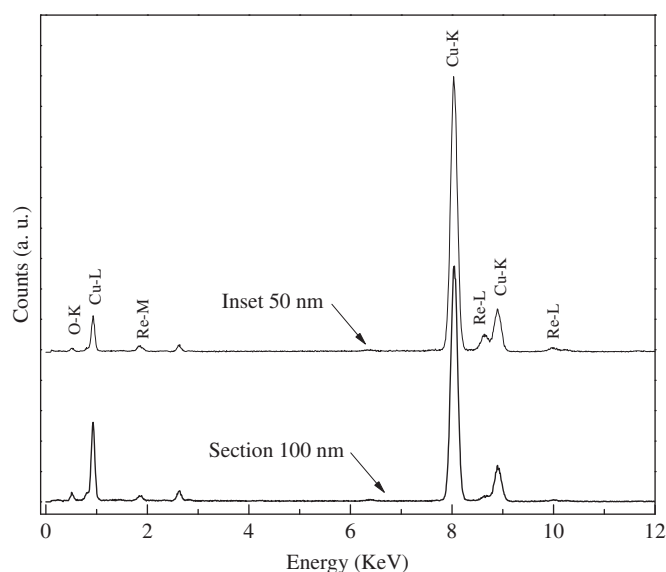


Fig. 3. EDS spectra of the electrodeposited material shown in Fig. 2. Section 100 nm refers to the EDS spectra of the image with 100 nm scale bar, while the inset 50 nm refers to the EDS spectra of the image with 50 nm scale bar.

8.046 keV corresponding to Cu-K α energy from the substrate material. Also, the EDS spectra shows the presence of O-K α (0.525 keV), Cu-L α (0.928 keV), Re-M α (1.843 keV), Re-L α (8.625 keV), Cu-K β (8.905 keV), and Re-L β (10.010 keV) with atomic percent of 97 wt% Re and 3 wt% O, section with scale-bar of 100 nm, without considering Cu peaks, while the section with scale-bar of 50 nm contains 77 wt% Re and 23 wt% O. These data suggest that the electrodeposited material corresponds to a mixture of rhenium and mixed-valence rhenium oxides, for example Re₂O₇ (77% wt Re–23% wt O), ReO₃ (80% wt Re–20% wt O) or ReO₂ (85% wt Re–25% wt O).

Fig. 4 shows a bright field (BF) TEM image of one dendrite of the electrodeposited material, which allows the observation of a crystalline formation. This zone was used to obtain the corresponding selected-area electron diffraction pattern (SAED) and to analyze the corresponding spots of major intensity. The analysis was carried out with the help of CaRIne Crystallography v. 3.1 software after reconstruction of the cell structure of Re (hexagonal structure–ICSD 43590), ReO₂ (orthorhombic structure–ICSD 24060) and ReO₃ (hexagonal structure–ICSD 202338). The analysis of the SAED pattern shows that the three considered structures could co-exist in the

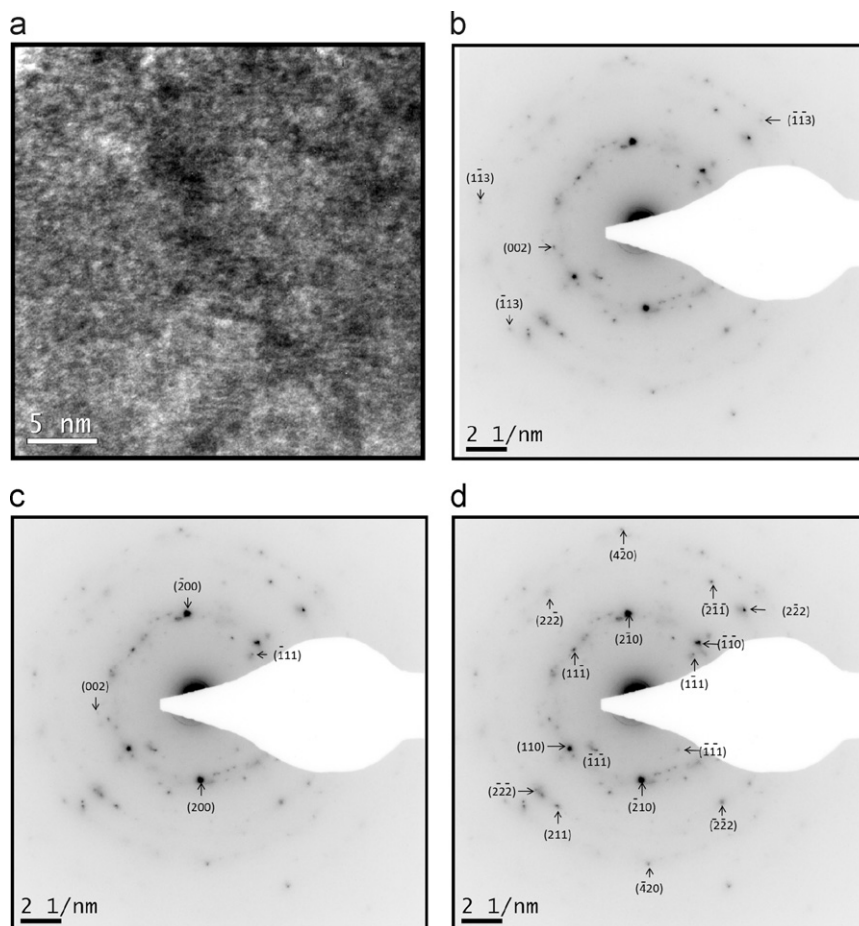


Fig. 4. (a) BF-TEM image of the electrodeposited material; and SAED pattern analysis considering (b) Re (hexagonal structure), (c) ReO_2 (orthorhombic structure) and (d) ReO_2 (hexagonal structure).

electrodeposited material. Every condition of diffraction was examined with the consideration that the amount of misorientated crystals such that could produce rings in the SAED pattern was not enough, so that the electron beam only reach the Bragg condition with some crystals of the three materials in low symmetry zone axis. There was not enough evidence in the SAED pattern or in other observations to establish the presence of Re_2O_7 in the electrodeposited material.

According to the TEM observations on the zone near the edge of the dendrite of the electrodeposited material, it is possible to ascertain that the mechanism of electrocrystallization involves the reduction of Re (7+) from the ReO_4^- ions to metallic Re (0) throughout the successive reduction of ReO_3 (6+) to ReO_2 (4+) [13]. An overview of the electrodeposition mechanism is undergoing investigation and will be shown in future publications which will take in to account various electrochemical analyses.

4. Conclusions

It is possible to electrodeposit rhenium and rhenium oxides from alkaline aqueous electrolyte without evident formation of powdery deposits. Despite the parallel hydrogen reduction reaction present during the electrodeposition, the electrodeposited material has shown a crystalline structure near the edge of the dendritic formation. It was possible to study the possible co-existing structures in the material through the use of transmission electron microscopy observations.

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References

- [1] Zerbino JO, Castro Luna AM, Zinola CF, Méndez E, Martins ME. *J Electroanal Chem* 2002;521:168–74.
- [2] Polyak D. *U.S. Geological Survey* 2012;62.1–5.
- [3] Kholmogorov A, Kononova O. *Hydrometallurgy* 2005;76:37–54.
- [4] Amer A. *JOM* 2008;60:52–4.
- [5] Cazzanelli E, et al. *J Appl Phys* 2009;105:114904.
- [6] Méndez E, Cerdá MF, Castro Luna AM, Zinola CF, Kremer C, Martins ME. *J Colloid Interface Sci* 2003;263:119–32.
- [7] Hahn BP, May RA, Stevenson KJ. *Langmuir* 2007;23:10837–45.
- [8] Hahn BP, Stevenson KJ. *Electrochim Acta* 2010;55:6917–25.
- [9] Cifuentes L, Crisóstomo G, Casas JM. *Miner Process Extr Metall* 2011;120:97–101.
- [10] Casas JM, Sepúlveda E, Bravo L, Cifuentes L. *Hydrometallurgy* 2012;113–114:192–4.
- [11] Horányi G, Bakos I. *J Electroanal Chem* 1994;378:143–8.
- [12] Schrebler R, Cury P, Orellana M, Gómez H, Córdova R, Dalchiele EA. *Electrochim Acta* 2001;46:4309–18.
- [13] Schrebler R, et al. *Thin Solid Films* 2005;483:50–9.