



Electrochemical reduction of solutions of ReF_6 in fused LiF-NaF-KF eutectic mixture

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Abstract

Electrolyte was prepared by introducing gaseous ReF_6 into the molten LiF-NaF-KF eutectic at 600 °C. The electrochemical properties of the solutions were studied by voltammetric techniques. The reduction of ReF_8^{2-} to Re occurred via a single irreversible step with diffusion controlled mass transfer. The diffusion coefficient of ReF_8^{2-} was $8 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ and the cathodic transfer coefficient was 0.13. Well-crystallized pure rhenium layers, up to 50 μm thick, were obtained on W, Ag, graphite and vitreous carbon substrates and were examined by SEM and X-ray diffraction techniques.

1. Introduction

Rhenium has many interesting properties such as high-temperature strength and wear resistance. It is used in the space and nuclear industries, for high temperature thermocouples and also for cathodic X-ray tubes as a diffusion-barrier and heat-dissipating layer. It is also increasingly used in the oil industry for its catalytic properties.

Rhenium metal is electrowon from aqueous solutions of KReO_4 [1–9], but the amorphous deposits obtained present surface cracks and contain inclusions of rhenium oxides (ReO_2 , ReO_3). Various heat treatments are necessary to crystallize the product. The oxide inclusions have to be reduced by hydrogen at high temperature. In this work an alternative electrolytic process using a molten electrolyte is investigated.

The electrochemistry of rhenium in molten salts has scarcely been studied [10–17], although molten electrolytes are suitable media for the electroplating of refractory metals. Bailey et al. [10] examined the reduction of KReO_4 dissolved in molten LiCl-KCl eutectic at 450 °C. They postulated that lithium cations were first reduced to lithium metal which reacted with perrhenate ions to yield rhenium metal. Baraboshkin et al. [11, 12] claimed that the cathodic reduction in $\text{Na}_2\text{WO}_4\text{-WO}_3\text{-KReO}_4$ molten electrolytes yielded rhenium metal. The mechanism involved a seven-electron exchange process kinetically depending on the acidity of the medium. Affoune et al. [13–15] showed that solutions of KReO_4 in molten LiF-NaF-KF eutectic mixture were stable. Their cathodic reduction involved two electrochemical

steps, yielding Re(VI) and Re(IV) soluble oxocomplexes. These oxocomplexes underwent disproportionation reactions producing rhenium metal via a complex mechanism. The anodic reoxidation of rhenium metal surprisingly occurred at a high potential close to that of the silver electrode oxidation. These authors also showed that solutions of K_2ReCl_6 in the same solvent were unstable [14, 16]. More recently, Kuznetsov et al. [17] investigated the stability of rhenium chloride complexes in the following molten solvents: pure NaCl , NaCl-KCl equimolar, 0.4 NaCl -0.6 KCl , pure KCl and pure CsCl . In the two first melts, Re(III) complexes were the only stable species, whereas in the others Re(IV) species were also present. Studying the effect of fluoride and oxide ions, they observed that rhenium(IV) fluorocomplexes could be reduced to rhenium metal in two steps. The addition of oxide ions to molten CsCl containing Re(IV) species resulted in Re(V) and Re(III) complex species. Re(VI) and Re(VII) oxo or oxofluoro complexes were stabilized in oxofluoride melts depending on the oxygen/rhenium ratio. Rhenium coatings were obtained from these electrolytes. The electroplating of refractory metals from molten fluoride electrolytes was achieved some time ago [18, 19] and processes using molten salts are employed at an industrial level in the case of refractory metals such as tungsten and hafnium. The present authors demonstrated that it was possible to electroplate rhenium from solutions of KReO_4 or K_2ReCl_6 dissolved in the molten LiF-NaF-KF eutectic mixture, but the experimental conditions suitable to the scaling-up of the process proved too difficult. The use of ReF_6 as a solute in the molten LiF-NaF-KF eutectic

mixture has not been considered until now because this very reactive compound is difficult to handle.

The study of the electrochemical behaviour of ReF_6 dissolved in molten LiF-NaF-KF eutectic at 600°C is presented here. The experiments were carried out using transient electrochemical techniques.

2. Experimental techniques

2.1. Preparation of the LiF-NaF-KF solvent

The LiF-NaF-KF eutectic mixture (46.5–11.5–42.0 mol %) was contained in a graphite crucible situated inside an air-tight stainless steel cell. To dehydrate this salt mixture, KHF_2 amounts of 1.5 mol % were added before melting. The salt mixtures were heated to 300°C under vacuum for 6 h; then their temperature was raised up to 600°C at a rate of 100°C h^{-1} under an argon flow [15].

2.2. Preparation of solute and molten electrolyte

Literature data [20] indicated that the reaction of KF and ReF_6 yielded the K_2ReF_8 octofluoride compound. Assuming that the dissolution of rhenium hexafluoride in molten flinak could yield similarly stable rhenium octofluoro complexes, we selected rhenium hexafluoride for the solute. Due to its physical properties (m.p. 18°C , and b.p. 33.4°C), the preparation of ReF_6 solutions by directly introducing the solute into the melt required special care. The experimental set-up is shown in Figure 1. It includes an electrochemical cell previously described [21], the inside of which was protected by a graphite lining.

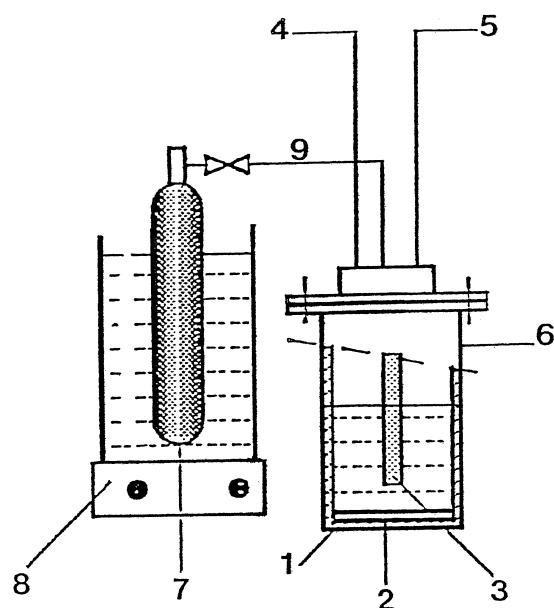


Fig. 1. Experimental set-up. Key: (1) electrochemical cell; (2) graphite crucible; (3) graphite tube; (4) argon input; (5) argon output; (6) connection to vacuum pump; (7) ReF_6 -containing cylinder; (8) bain-marie; (9) monel tube.

After the preparation and purification of the solvent, gaseous rhenium hexafluoride was introduced into the melt through a monel (Ni-Cu alloy) tube with a graphite tube extension which was initially maintained over the melt. The cylinder containing ReF_6 and the monel tube were both heated at 36°C . The cylinder tap was then opened and the ReF_6 gas was allowed to flow over the melt and finally to bubble inside the melt once the graphite tube was dipped into the liquid. Quantities of 10^{-5} to 5×10^{-5} kg of ReF_6 were added to the molten solvents. These quantities were estimated by weighing the cylinder before and after the introduction of ReF_6 . For accurate determinations of the rhenium concentration in the solutions, samples of about 10^{-3} kg of molten electrolyte were taken during the electrochemical measurements using a syringe; they were then frozen and weighed, and sent to the Solaise Analytical Laboratory of the French National Research Center for chemical analysis.

2.3. Electrolysis cell

The molten electrolyte was contained in the graphite crucible previously used for its preparation. The experiments were carried out at 600°C under an argon atmosphere. The working electrodes were either a 3 mm diameter vitreous carbon wire or a 1 mm diameter tungsten wire, both inserted into a graphite holder. The graphite crucible was also used as the counter electrode and a platinum wire as the comparison electrode. Linear sweep voltammetry and chronopotentiometry were applied by means of a potentiostat-galvanostat (PAR EG&G model 273) monitored with a signal generator (PAR 175).

3. Results and discussions

3.1. General features of the voltammograms

Two typical voltammograms obtained at a vitreous carbon electrode and at a tungsten electrode in the pure LiF-NaF-KF solvent are shown in Figure 2. The potentials were measured against that of the platinum

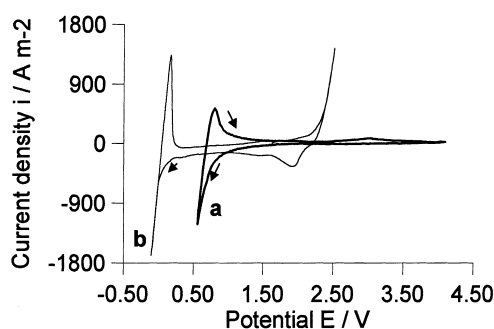


Fig. 2. Electrochemical window of the molten LiF-NaF-KF solvent. Voltammograms obtained at a vitreous carbon electrode (a) and at a tungsten electrode (b). $T = 600^\circ\text{C}$; $\nu = 0.5 \text{ V s}^{-1}$.

comparison electrode, and then referred to the equilibrium potential of the K^+/K couple, the cathodic limit of the solvent. This procedure was necessary since no stable reference electrode was available for molten flinak, or more generally for molten fluoride mixtures [22]. The potential of the platinum wire dipped into the melt varied when ReF_6 was added to the pure flinak mixture, but it remained stable in a given melt provided that the platinum wire had not been polarized. In these conditions, a platinum wire dipped into the pure flinak mixture or in solutions of ReF_6 in molten flinak could be used as a comparison electrode. We used Paillère's results [23] to refer the potential of potassium intercalation against that of potassium metal when the working electrode was made of vitreous carbon.

The electrochemical window of the pure solvent was limited on the cathodic side by the reduction of potassium ions, which was depolarized (about 600 mV) in the case of vitreous carbon because of potassium intercalation. On the vitreous carbon electrode, the anodic peak observed at 2.8 V could be attributed to CO_2 formation due to a small content of oxide ions dissolved in the melt, or to the formation of carbon-fluoride compounds. In the case of the tungsten electrode, the oxidation of tungsten, occurring at 2.2 V, limited the electrochemical window on the anodic side.

The addition of ReF_6 to the melt produced one new cathodic and one new anodic peaks as illustrated in Figure 3. Successive voltammograms obtained at various times, at the same electrode in the same solution, using the same sweep rate, did not show any significant variation. The solutions of ReF_6 were therefore considered as stable. The nature of the rhenium species present in the solutions could theoretically be determined by spectroscopic techniques but unfortunately in the case of fluoride melts, *in situ* spectroscopic studies are extremely difficult. We assumed that ReF_8^{2-} species, which have been characterized in the K_2ReF_8 octofluoride compound obtained through the reaction of ReF_6 with KF [20], were formed when ReF_6 was dissolved in the molten flinak due to the high complexing power of the fluoride ions and to the chemical stability of the higher oxidation states of rhenium. A deposit obtained at a vitreous carbon electrode surface by potentiostatic

electrolysis at 2.2 V was proved to be rhenium metal by means of an X-ray diffraction analysis. Thus, the cathodic peak observed at about 2.2 V was assigned to the formation of rhenium metal, which was reoxidized, along the reverse scan, with the stripping peak observed at 3.6 V.

3.2. Kinetic study of the ReF_8^{2-} cathodic reduction

Voltammograms obtained on fresh vitreous carbon electrodes (Figure 4) show a crossover of the direct and reverse parts of the curves. This suggests the occurrence of a nucleation step prior to bulk metal electrodeposition. These first nuclei are probably not stable, which explains why no rhenium reoxidation peak is seen. These phenomena disappeared after a few potential cycles (Figure 3). A large difference between the cathodic and the anodic peak potentials (about 1.55 V, Figure 3) is also seen, which is characteristic of an irreversible charge transfer.

A current-reversal chronopotentiogram related to the reduction/reoxidation of rhenium ions is presented in Figure 5. The equality of direct and reverse transition times strongly suggests the electrodeposition/dissolution of an insoluble product.

Voltammograms at a vitreous carbon electrode for various sweep rates are presented in Figure 6. The

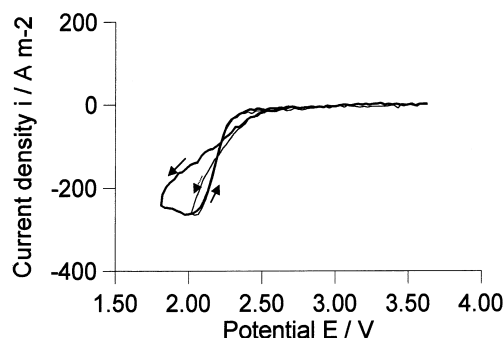


Fig. 4. Voltammetric study of molten LiF-NaK-KF- ReF_6 mixtures. Evidence for rhenium electrocrystallization phenomena. Working electrode: vitreous carbon; ReF_6 concentration: 26 mol m^{-3} ; $T = 600 \text{ }^\circ\text{C}$, $v = 0.5 \text{ V s}^{-1}$.

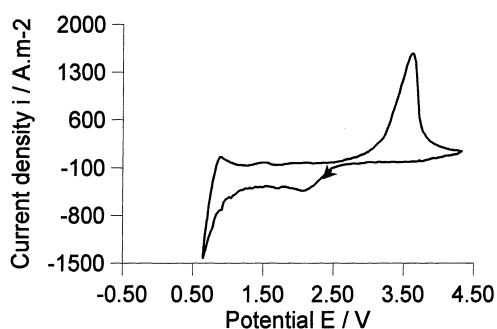


Fig. 3. Voltammetric study of molten LiF-NaK-KF- ReF_6 mixtures. Working electrode: vitreous carbon; ReF_6 concentration: 26 mol m^{-3} ; $T = 600 \text{ }^\circ\text{C}$; $v = 0.5 \text{ V s}^{-1}$.

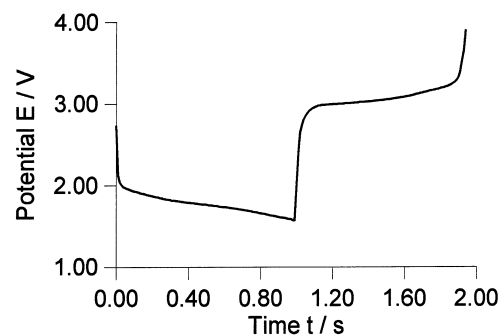


Fig. 5. Current reversal chronopotentiogram of molten LiF-NaK-KF- ReF_6 mixtures. Working electrode: vitreous carbon, ReF_6 concentration: 26 mol m^{-3} , $T = 600 \text{ }^\circ\text{C}$, $i = -1650 \text{ A m}^{-2}$.

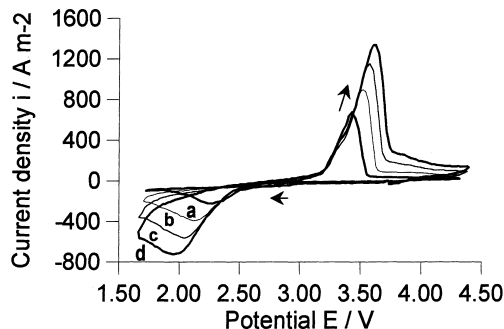


Fig. 6. Voltammogram study of molten LiF–NaK–KF–ReF₆ mixtures for various sweep rates. Working electrode: vitreous carbon, ReF₆ concentration: 26 mol m⁻³, T = 600 °C. Sweep rate, v: (a) 0.05, (b) 0.2, (c) 0.5 and (d) 1.0 V s⁻¹.

influence of the ohmic drop on the voltammograms was not taken into account because of the high conductivity of the electrolyte ($\sigma = 131 \text{ S m}^{-1}$ [24]). The cathodic peak currents were proportional to the square root of the potential sweep rate. The mass transfer was therefore limited by diffusion under the conditions of the experiment. The difference, $E_p - E_{p/2}$, between the cathodic peak and the half peak potentials, which remained practically constant when the sweep rate varied (Figure 6), was 0.2 V. Using the theoretical relation $E_p - E_{p/2} = 0.14/\alpha n$ at 600 °C for an irreversible exchange, we found $\alpha n = 0.8$. In Section 3.1, it was stated that the stable rhenium species in the LiF–NaF–KF–ReF₆ melts, ReF₈²⁻, was reduced to rhenium metal in one step (i.e., via a six-electron exchange). According to these conclusions, the calculated value for α was 0.13. Besson [25] reported that such a low value of α can be accounted for by an electrochemical process involving a complex mechanism with successive electrochemical steps, the slowest of them limiting the kinetics of the overall electrochemical reaction.

The voltammograms were alternatively analysed with the semi-integral method, which is not sensitive to the interference of the ohmic drop as far as the applied signal is concerned, in contrast to conventional voltammetry. A typical voltammogram with the corresponding semi-integral curve is presented in Figure 7. The semi-

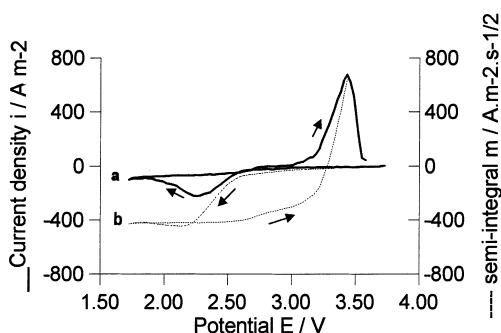


Fig. 7. Voltammogram study of molten LiF–NaK–KF–ReF₆ mixtures. Working electrode: vitreous carbon, ReF₆ concentration: 26 mol m⁻³, T = 600 °C, v = 0.05 V s⁻¹ (a) Voltammogram (b) semi-integral.

integral values tend towards a limit, m^* , because the mass transfer is limited by diffusion. The diffusion coefficient $D_{\text{ReF}_8^{2-}}$, calculated from this limiting value using the relation $m^* = nFCD^{1/2}$ taking $n = 6$, equalled $8 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$.

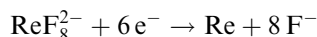
The direct and reverse semi-integral curves show a significant hysteresis within a large potential domain. This confirms that the electron transfer must be considered as irreversible. For an irreversible process involving a soluble oxidized species and an insoluble reduced species, the potential/semi-integral relationship can be written as follows:

$$E = E^\circ + \left(\frac{RT}{\alpha nF}\right) \ln\left(\frac{k^\circ}{\sqrt{D}}\right) + \left(\frac{RT}{\alpha nF}\right) \ln\left(\frac{m^* - m}{i}\right)$$

where k° is the intrinsic electron transfer rate constant.

The analysis of the semi-integral curve according to this equation is presented in Figure 8. The slope of the straight line yields the value $\alpha n = 0.78$ which is in keeping with the value of 0.8 previously obtained from the difference between the peak and half peak potentials.

The semi-integral method again leads to an estimated value of 0.13 for transfer coefficient α corresponding to the irreversible six-electron exchange reaction:



3.3. Electrochemical oxidation of rhenium metal

A typical voltammogram, with an anodic start, at a rhenium working electrode in the LiF–NaF–KF eutectic mixture at 600 °C is shown in Figure 9 (curve (a)). The oxidation of rhenium metal starts from 2.8 V, and the corresponding redeposition peak occurs at 2.2 V. These values are in good agreement with those observed in the case of the ReF₆ solutions (Figures 3 and 6). We can therefore conclude that anodic oxidation of rhenium metal yields the same species as that produced by the dissolution of ReF₆, which we described as ReF₈²⁻. Similar observations, as far as the behaviour of rhenium

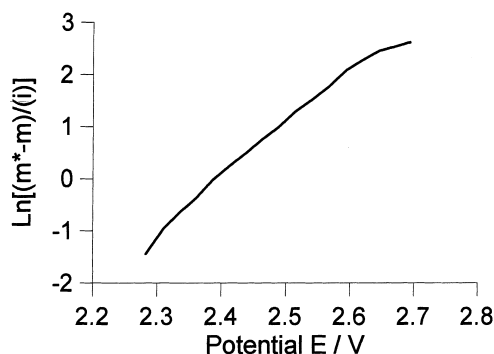


Fig. 8. Voltammogram study of a molten LiF–NaK–KF–ReF₆ mixture. Logarithmic analysis of curve (b) in Figure 7.

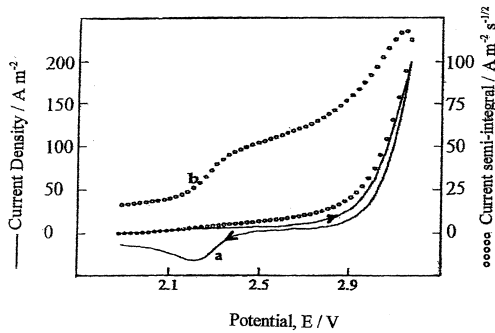


Fig. 9. Voltammetric study of the anodic oxidation and reverse reduction of rhenium in the molten LiF–NaK–KF eutectic. $T = 600\text{ }^{\circ}\text{C}$. (a) Voltammogram, (b) semi-integral of curve (a), $v = 0.5\text{ V s}^{-1}$.

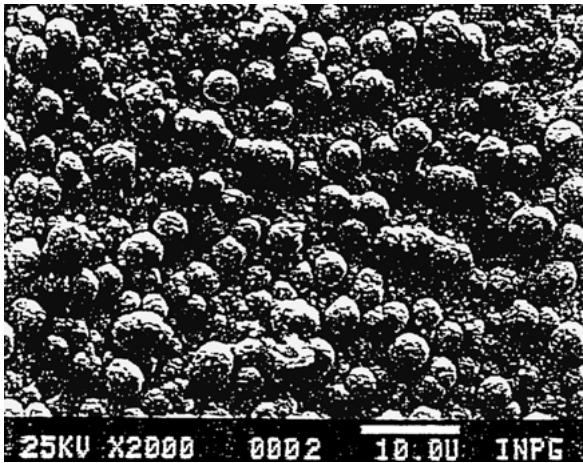


Fig. 10. SEM picture of a rhenium deposit obtained at a vitreous carbon substrate by direct current electrolysis. Electrolyte: solution of ReF_6 (26 mol m^{-3}) in the molten LiF–NaK–KF eutectic, $T = 600\text{ }^{\circ}\text{C}$, $i = -450\text{ A m}^{-2}$, $t = 14\text{ }400\text{ s}$.

metal is concerned, have been reported in the case of solutions of KReO_4 in molten LiF–NaF–KF eutectic [15].

The large difference between the rhenium oxidation potential and the redeposition potential of the soluble rhenium species formed confirms the previous observation that the Re(VI)/Re(0) couple was quasi-reversible or irreversible. The analysis of the anodic part of the voltammogram through semi-integration, as reported in Figure 9 (curve (b)), shows that the direct and reverse semi-integral curves do not superimpose, which is an additional proof that the electronic exchange is slow [26].

Numerical simulations of voltammograms for the oxidation and redeposition of a metal for reversible, irreversible and quasi-reversible transfer processes have been made by one of the present authors [14]. Application to the case of rhenium is under progress [27].

3.4. Rhenium metal electrowinning

The galvanostatic deposition of rhenium was carried out at $600\text{ }^{\circ}\text{C}$ on tungsten, silver, graphite and vitreous carbon substrates. Thin rhenium layers, to $50\text{ }\mu\text{m}$ in thickness, were obtained. For current densities lower than 800 A m^{-2} , the deposits were dense, coherent and adherent. Since the frozen electrolyte sticking to the surface of the rhenium deposits could not be eliminated by washing the samples in hot acidic aqueous solutions, the samples had to be cleaned by heating at $800\text{ }^{\circ}\text{C}$ under vacuum for 4 h. Scanning electronic microscopy (Figure 10) showed fine crystallization with hemispherical outgrowths over the dense rhenium layer and a surface free from cracks. The dimensions of the grains varied from 1 to $7\text{ }\mu\text{m}$ according to the current density. X-ray diffraction analysis (Figure 11) showed that the deposit was pure rhenium.

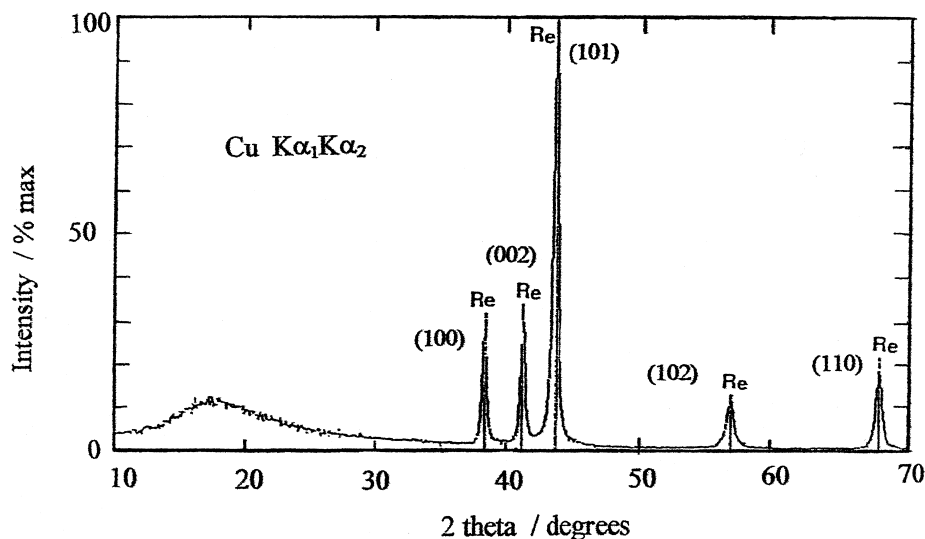


Fig. 11. X-Ray diffraction analysis of the deposit presented in Figure 10.

4. Conclusion

Solutions of rhenium hexafluoride in molten LiF–NaF–KF eutectic mixture at 600 °C yielded stable ReF_8^{2-} species which were cathodically reduced via a six-electron irreversible charge transfer step. Pure well-crystallized rhenium metal layers were obtained. The reduction mechanism was simpler than that of KReO_4 or K_2ReCl_6 solutes in the same molten solvent. Furthermore, due to the absence of surface cracks and oxide inclusions, this process offers major improvements in comparison with electrolysis in aqueous solutions as far as the quality of the deposits is concerned.

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