ELECTROCHEMICAL REDUCTION OF SOLUTIONS OF REF$_6$ IN THE FUSED LIF-NAF-KF EUTECTIC MIXTURE

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Rhenium has many interesting properties such as high-temperature strength and wear resistance. It is used in 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 $KReO_4$ [1-5], 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 electrochemistry of rhenium in molten salts has scarcely been studied [6-11]. Bailey et al. [6] 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. Affoune *et al.* [9-10] showed that solutions of $KReO_4$ in the 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. More recently Kuznetsov et al. [11] observed that 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.

An alternative electrolytic process using a molten electrolyte was investigated. The electrolyte was prepared by introducing gaseous ReF_6 into the molten LiF-NaF-KF eutectic at 600 °C. After preparing and purifying 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 heated at 36 °C. The cylinder tap was then opened and the ReF_6 gas allowed to flow and then to bubble inside the melt by dipping the graphite tube in it.

The electrochemical properties of the solutions were studied by linear sweep voltametry and Chronopotentiometry techniques. The addition of ReF_6 to the melt produces a new cathodic peak and a new anodic one as illustrated in Fig.1. The cathodic peak at about 2.2 V is assigned to the formation of rhenium metal, which gets re-oxidized, during the reverse scan, with the stripping peak observed at 3.6 V. One can also notice a large difference between the cathodic and the anodic peak potentials (about 1.55 V, see Fig.1) which is characteristic of an irreversible charge transfer. A current-reversal chronopotentiogram related to the reduction/re-oxidation of rhenium(VI) ions is presented in Fig.2. The equality of direct and reverse transition times strongly evidences the electrodeposition/dissolution of an insoluble product.

The reduction of ReF_8^{2-} to Re occurred via a single irreversible step with mass transfer controlled by diffusion. The diffusion coefficient of ReF_8^{2-} was 8.10^{-10} $m^2. s^{-1}$ and the cathodic transfer coefficient equalled 0.13. Well-crystallized pure rhenium layers, up to 50 µm thick, were obtained on W, Ag, graphite and vitreous carbon substrates and examined by SEM and X-ray techniques. Due to the absence of surface cracks and oxide inclusions, this process is a major improvement on electrolysis in aqueous solutions.

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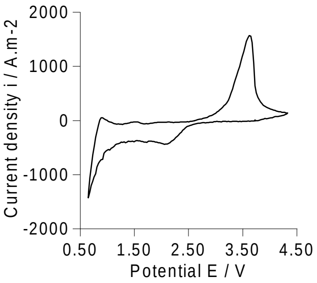

Fig. 1. Voltammetric study of molten LiF-NaK-KF-ReF_6 mixtures. Working electrode : vitreous carbon ; ReF_6 concentration : 26 $mol.m^{-3}$; T = 600 °C ; v = 0.5 $V.s^{-1}$.

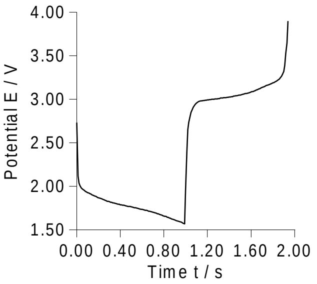

Fig. 2. Current reversal chronopotentiogram.of molten LiF-NaK-KF-ReF_6 mixtures. Working electrode : vitreous carbon ; ReF_6 concentration : 26 $mol.m^{-3}$; T = 600 °C ; $|i|$ = 1650 A. m^{-2}.