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Electrochemical Study of Tantalum Plating in LiF–NaF–CaF_2 Melt*

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Abstract

Investigation into electrodeposition of tantalum has been performed in LiF–NaF–CaF_2 melt containing K_2TaF_7. In spite of large content of oxyfluorotantalate ($TaOF_5^{2-}$) in the melt, electrodeposition of compact tantalum coating has been possible. The CaF_2 present in the electrolyte is responsible for removing the oxide ions from the electrode surface if these are released by electro-reduction of $TaOF_5^{2-}$. A conproportionation/disproportionation reaction that interferes with electrodeposition of tantalum has also been discovered in the fluoride melt. However, the conproportionation product is soluble in the melt, and it does not contaminate electrodeposited coating.

INTRODUCTION

Coatings composed of valve metals and their alloys exhibit extremely high corrosion resistance [1–6]. Among valve metals, the highest corrosion resistant element is tantalum. In addition, alpha (bcc) tantalum has high thermal and electric conductivity and excellent fabricability among valve metals.

For preparing valve metal coatings, vapour deposition and molten salt electrolysis are candidate processes. Nevertheless, molten salt electrolysis is the most useful owing to its adaptability for different shapes and dimensions of the object to be coated in addition to low cost. Molten salt electrolysis has been successfully applied for deposition of valve metals [7] and their alloys [8, 9] although a compact coating is usually difficult and often dendritic or powdery deposit is formed [8–10]. The usual problem in preparing coatings in molten salts arises from the presence of oxide ions and the occurrence of disproportionation or conproportionation reactions [10–14].

Due to an increased understanding of preparation of molten salt electrolytes and their properties [15–19], efforts to develop electrodeposited coatings in molten salts may succeed to an extent that these could be employed for engineering purposes similarly to the aqueous electrolytes.

We have been working for developing electrolytic coating of tantalum in molten salt [20–22]. This paper presents the results that show the possibility of good electrolytic tantalum coating in LiF–NaF–CaF_2 melt, in spite of disproportionation reaction and large amount of oxyfluorotantalate in the melt.

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EXPERIMENTAL

Electrochemical measurements were performed by using a tungsten/nickel wire, a graphite rod and a nickel rod as the working, counter and quasi-reference electrodes, respectively. A graphite or nickel crucible was used. The electrolyte consisted of 55 % LiF–35 % NaF–10 % CaF_2 containing 1–2 % K_2TaF_7. (The quantities are given in mol. %.) In the reaction chamber, the mixed salts were dried overnight at 200 °C under vacuum followed by an overnight drying at 450 °C while maintaining argon flow through the chamber. The electrochemical measurements were performed at 700 °C under argon atmosphere. The electrodeposits were characterized by using XRD, SEM and EDX.

RESULTS AND DISCUSSION

Figure 1 shows a typical voltammogram obtained on tungsten in the LiF–NaF–CaF_2 melt containing K_2TaF_7. Although minute cathodic reaction with charge transfer number of 3 also occurs within about −0.25 to −0.3 V *vs.* Ni [20], the major reaction is the electrodeposition of tantalum from TaF_7^{2-} with charge transfer number of 5. This reaction occurs at −0.5 to −0.6 V *vs.* Ni in the melt containing 2 % K_2TaF_7. The deposition of metallic tantalum in this region has been confirmed by EDX analysis and XRD measurements of the electrodeposits.

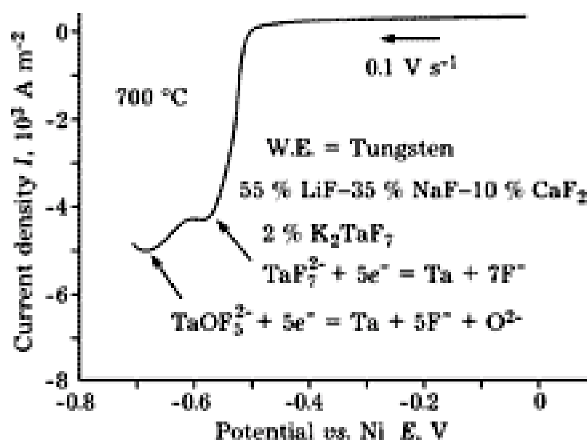

Fig. 1. Cathodic voltammogram, obtained on tungsten, showing two clearly distinct waves related to electroreduction of fluorotantalate and oxyfluorotantalate to form metallic tantalum.

It has already been demonstrated by Polyakova *et al.* [12, 13] and Chamelot *et al.* [14] that the presence of oxyfluorotantalates in the electrolyte gives rise to other cathodic peaks at active potentials than that meant for electrodeposition of tantalum from fluorotantalate. Hence, the peak appearing at potential below −0.6 V *vs.* Ni belongs to reduction of $TaOF_7^{2-}$. The relative heights of the two peaks related to reduction of fluorotantalate and oxyfluorotantalate vary in our experiments depending on the amount of added K_2TaF_7 and, up to some extent, from one melt to another with similar composition depending on the preparation of the electrolyte. It seems that the moisture released from supporting electrolyte or the reaction chamber during drying is partly captured by the K_2TaF_7. In any case, the presence of large amount of oxyfluorotantalate is evident by the high cathodic wave related to reduction of $TaOF_7^{2-}$.

In the melts containing NaF, LiF and KF, Polyakova *et al.* [12, 13] and Chamelot *et al.* [14] have observed re-oxidation reaction related to formation of $TaOF_5^{2-}$, from Ta, O^{2-} and F^- (or TaO and F^-). Hence, the presence of O^{2-} in the vicinity of electrode for reformation of $TaOF_5^{2-}$ was confirmed.

We have not observed the re-oxidation wave for the formation of $TaOF_5^{2-}$, as shown in Fig. 2. This shows that O^{2-} liberated by $TaOF_5^{2-}$ during reduction to form metallic tantalum does not remain available to form $TaOF_5^{2-}$ during oxidation or dissolution of metallic tantalum. There are two candidate oxide getters in the melt, *i. e.*, TaF_7^{2-} and Ca^{2+}. The TaF_7^{2-} does not remain available in the vicinity of the electrode surface in reasonable concentration at the active potentials during reduction of $TaOF_5^{2-}$. Accordingly, the O^{2-} ions are removed from the surface by Ca^{2+}. (The chemical or physical nature of the species containing Ca^{2+} and O^{2-} is not clear yet.) This reveals the beneficial role of CaF_2 in the fluoride melt if the presence of oxyfluorotantalate in the melt cannot be avoided.

Another interesting aspect of Fig. 2 is the presence of two oxidation peaks in spite of

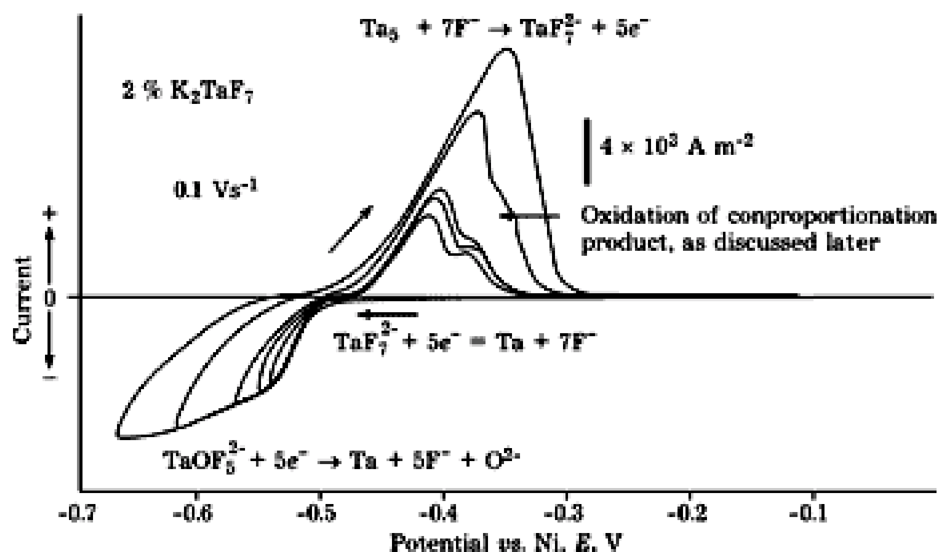

Fig. 2. Cyclic voltammograms obtained on tungsten. The absence of reformation to $TaOF_5^{2-}$ during anodic scan can be noticed. The reactions related with conproportionation are explained in Fig. 3.

reversing the scan direction from a single wave of electroreduction of TaF_7^{2-} to form metallic tantalum. Same is the case of reverse chronopotentiograms, as typically shown in Fig. 3. When the direction of current is reversed after electrodeposition of tantalum at the plateau R, two anodic plateaus are observed.

In our experiments, the ratio between T_c and T_{diss} varies with the concentration of K_2TaF_7 in the melt and current density. Particularly, T_{diss} increases and T_c decreases with increase in current density. The plateau almost disappears at high current densities exceeding

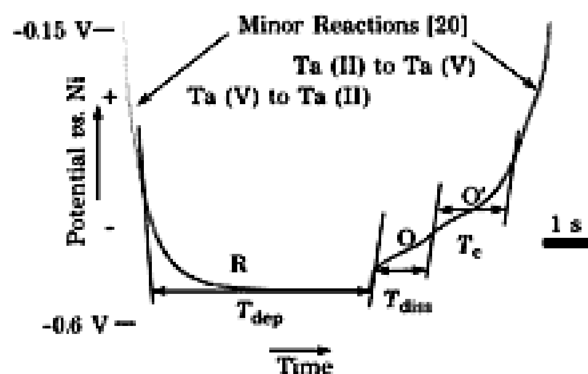

Fig. 3. Part of reverse chronopotentiogram obtained on tungsten at 20 mA cm^{-2} in a melt containing 1 % K_2TaF_7. R = Formation of tantalum by electrodeposition: Ta(V) + 5e^- = Ta(0) (confirmed by XRD); (Plus) Conproportionation reaction: $[5/(n - 1)]$Ta(0) + Ta(V) = $(5/n)$ Ta(n); O = Anodic dissolution of tantalum: Ta(V) + 5e^- = Ta(0); O' = Oxidation of the species formed by conproportionation reaction: Ta(n) + $(5 - n)e^-$ = Ta(V).

100 mA cm^{-2} in the melt containing 2 % K_2TaF_7. Hence, the two waves O and O' do not correspond to two reactions in series. Knowing the tendency of disproportionation reactions in the molten salts, we believe that a conproportionation (disproportionation) reaction occurs during electrodeposition of metallic tantalum. The plateau O corresponds to the electrodissolution of metallic tantalum that survives from conproportionation reaction and the plateau O' corresponds to the electrooxidation of conproportionation product. As can be noticed in Fig. 2, no other significant reaction occurs at nobler potentials than required for oxidation of conproportionation product. Hence, the conproportionation product completely oxidizes to Ta(V) in a single step. In Fig. 3, the conproportionation product has been mentioned as Ta(n). However, we know that Ta(II) is stable up to nobler potential than that of the plateau O' [20]. Hence, the conproportionation product appears to be Ta(I).

The occurrence of disproportionation is known for the chloride melts during electrodeposition of tantalum. However, its existence in the fluoride melt has not been reported before. This may possibly be due to lack of sufficient evidence and different choice of experimental parameters, *e.g.*, current density, potential for scan reversal, *etc.* We have found one similar result in a paper of Taxil *et al.* [23] showing two anodic waves in voltammograms

obtained on inert molybdenum electrode after a single cathodic wave for electrodeposition of metallic tantalum.

We have analyzed chronopotentiograms at different current densities in a melt containing 2 % K_2TaF_7.

Consider the reverse chronopotentiogram and associated reactions in Fig. 3. It can be shown that the amount (number of moles) of tantalum deposited at R is $(1/5)FIT_{dep}$. The amount of Ta(0) that dissolves at plateau O is $(1/5)FIT_{diss}$. The difference between these two, *i. e.*, $(1/5)FI(T_{dep} - T_{diss})$, is the amount of Ta(0) that undergoes conproportionation reaction. In turn, the amount of Ta(n) that is formed by conproportionation reaction should be

$$[(1/(5 - n)]FI(T_{dep} - T_{diss})$$

where n is the oxidation number of conproportionation product, F is Faraday constant, I is current, T_{dep}, T_{diss}, and T_c have been defined in Fig. 3.

If the conproportionation product is insoluble and oxidizes to Ta(V) completely at the plateau O', the associated charge should be $I(T_{dep} - T_{diss})$. If it is soluble and only a fraction, assume $1/q$, is available for reoxidation at O', the associated charge should be $I(T_{dep} - T_{diss})/q$.

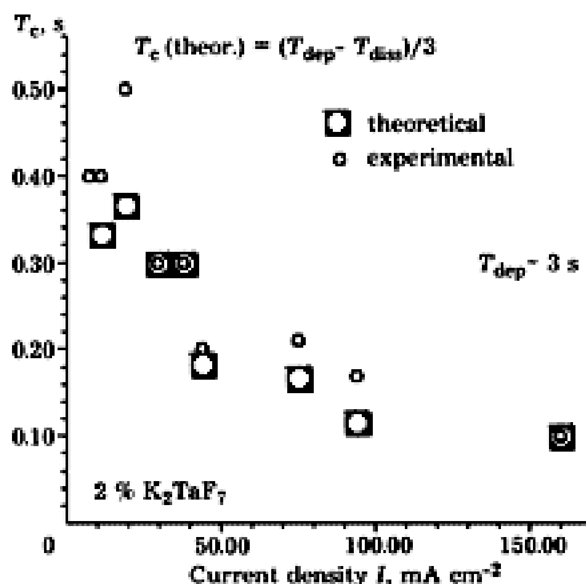

Fig. 4. Comparison of the experimental values of T_c with the theoretical one based on a model that conproportionation product is soluble and only one-third returns to the electrode for electrooxidation at O'.

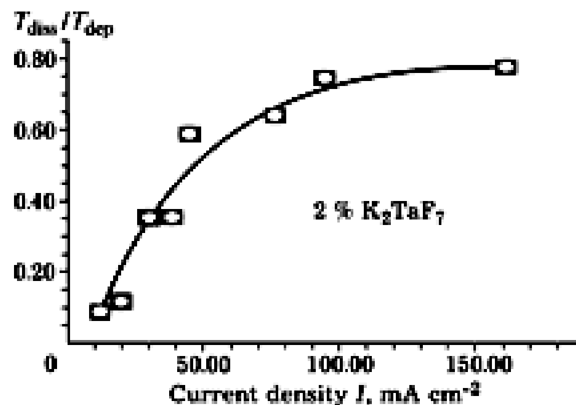

Fig. 5. Effect of current density for deposition on apparent current efficiency obtained from chronopotentiograms after deposition for ~3 s.

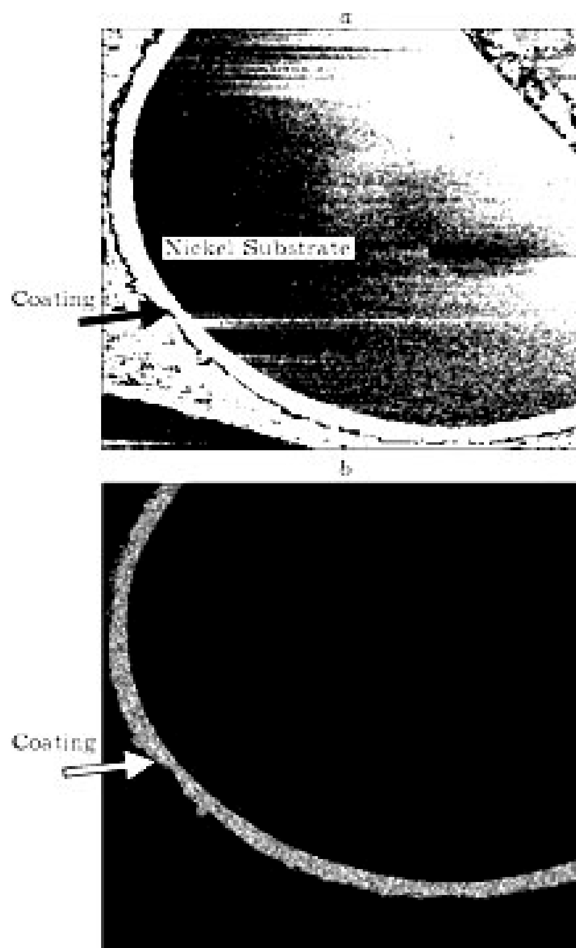

Fig. 6. Cross-sectional view of tantalum coating on 1-mm diameter nickel wire. The coating was prepared in $LiF-NaF-CaF_2$ melt containing K_2TaF_7: *a* – SEM; *b* – characteristic X-ray map of Ta.

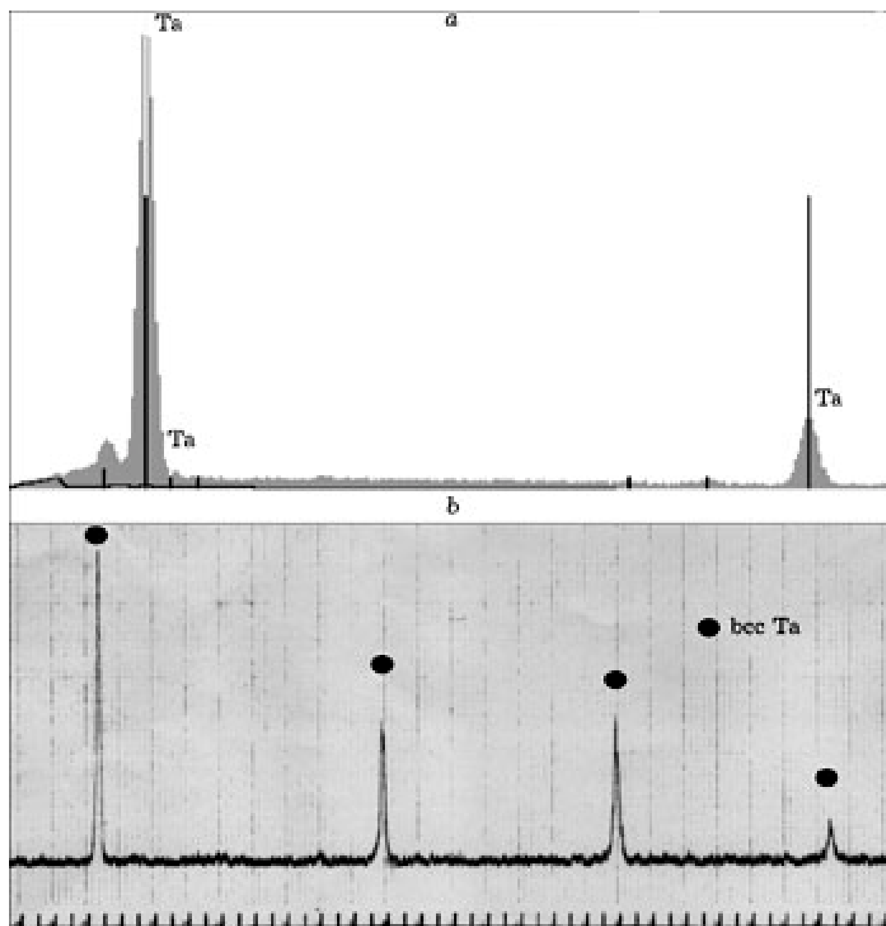

Fig. 7. Typical X-ray spectrum (*a*) and XRD pattern (*b*) obtained from a tantalum coating prepared in LiF–NaF–CaF_2 melt containing K_2TaF_7.

Hence, the T_c based on this assumption should be $(T_{dep} - T_{diss})/q$. As shown in Fig. 4, the experimental values of T_c are close to $(T_{dep} - T_{diss})/3$ in a wide range of current densities. This shows that only about one-third of the conproportionation product becomes available for oxidation at the plateau O', and the rest of the conproportionation product diffuses away into the electrolyte. This suggests the soluble nature of the conproportionation product in the fluoride melt. Accordingly, the conproportionation product may not tend to contaminate the electrodeposits as far as the smooth growth front is maintained and the soluble species are allowed to diffuse into the electrolyte.

We have also found some powdery metallic tantalum at the electrolyte surface, in spite of formation of smooth electrodeposits. It seems that the conproportionation product (Ta(I)) is unstable in the melt away from the metallic tantalum. Hence, it undergoes disproportionation to form powdery metallic tantalum and TaF_7^{2-}. The powdery metallic tantalum tends to segregate out of the electrolyte, *i. e.*, partly at the salt surface.

The conproportionation reaction is responsible for decrease in current density. Figure 5 shows change in apparent current efficiency (T_{diss}/T_{dep}) with the current density, as estimated by chronopotentiometry. It can be noticed that high current density is necessary for good efficiency.

The quality of the coating was also studied after electrodeposition in the said melt. Figure 6 shows a typical SEM image and corresponding characteristic map of tantalum obtained from a cross section of tantalum electrodeposited on 1-mm nickel wire. The formation of compact tantalum coating is evident from the images. Figure 7, *a* shows a typical X-ray spectrum obtained from electrodeposited tantalum. Formation of pure tantalum coating is evident

from X-ray spectrum. Figure 7, *b* shows a typical XRD pattern obtained from a deposit formed at 20 mA cm^{-2} in the melt containing 1 % K_2TaF_7. The structure of electrodeposit is alpha (bcc) tantalum. No non-metallic inclusions were found in the electrodeposit as revealed by XRD.

CONCLUSIONS

1) Electrochemical study has been performed on electrodeposition of tantalum in LiF–NaF–CaF_2 melt containing K_2TaF_7.

2) CaF_2 in the melt is responsible for removing O^{2-} ions, generated by reduction of oxyfluorotantalate, from the electrode surface.

3) A disproportionation/conproportionation reaction also occurs. The conproportionation product is soluble in the melt. Therefore, it dissolves away and does not contaminate the deposit.

4) Hence, in spite of occurrence of disproportionation reaction and presence of large amount of oxyfluorotantalate, compact tantalum coating has been possible in this melt.

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