Technical Paper

Cathode Reaction of Titanium Chloride in Molten LiCl-KCl Eutectic Mixture

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The mechanism of the cathode reaction of titanium chloride in molten LiCl-KCl eutectic mixture at 450°C has been studied by means of the potential sweep voltammetry and the Faradaic impedance measurement. The results, obtained from the detailed analysis of the peak in the potential sweep voltammogram and of the maximum peak in the variation of $1/(\omega C_d)$ with $\omega^{-1/2}$, indicate that the following catalytic reaction (the disproportionation)

occurs in addition to the reversible charge transfer in molten LiCl-KCl eutectic mixture at 450°C.

1 Introduction

The mechanism of titanium metal deposition in molten salts has been investigated actively. Bockris and his coworkers¹⁾ pointed out that the titanium metal deposition occurred as the result of the reduction of titanium metal ion by previously deposited alkali metals, while Reid et al.²⁾ proposed a mechanism of the direct reduction of Ti^{3+} and Ti^{4+} to metal. Recently, Quemper et al.³⁾ have supported the direct reduction of titanium halides. None of these authors, however, have considered the catalytic reactions (the disproportionations) of titanium chlorides in molten salt mixtures.

In gaseous phase, Funaki et al.⁴⁾ measured the vapor pressures of the titanium dichloride and the titanium trichloride, and defined the following equilibria;

No reports concerning the above types of reactions in molten salt mixtures have been published. It is, thus, the purpose of this paper to examine whether the reaction (1) will occur or not in molten salt mixtures by the electrochemical methods.

2 Experimental

The purification of LiCl-KCl eutectic mixture was

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the same as described in the publication⁵⁾. A system with three electrodes, *i. e.*, a reference electrode, a counter electrode and an indicator electrode, was used for all measurements. The reference electrode was the silver-silver chloride electrode, Ag/AgCl (0.1 mole fraction in LiCl-KCl eutectic mixture), the counter electrode was a glassy carbon rod and the indicator electrode was Pt micro electrode which was prepared from Pt rod of 0.8 mm diameter sealed into Pyrex glass. The electrode surface area of Pt micro electrode was 0.2 cm² (cross section+cylindrical surface) for the potential sweep voltammetry and 0.005 cm² (cross section) for the Faradaic impedance measurement, respectively.

The transformer ratio arm bridge was used for the impedance measurement. A schematic diagram is

Fig. 1 Apparatus for the impedance measurement

shown in Fig. 1. The transformer was constructed by "EI" shaped ferrite core for the measurement at

higher frequencies up to 100 kHz. In order to prepare a solution of Ti^{4+} in molten salt mixture, the reagent grade $TiCl_4$ was distilled and bubbled into the molten salt mixture.

3 Results and Discussion

3.1 Potential sweep voltammetry of Ti^{4+}

The triangular wave cyclic voltammogram of Ti^{4+} in molten LiCl-KCl eutectic mixture at 450°C is shown in Fig. 2. According to the result of the

Fig. 2 Potential sweep voltammogram of Ti^{4+} in LiCl-KCl eutectic mixture

potential sweep voltammogram of Ti^{4+} , Ti^{3+} and Ti^{2+} solution by Niki et al.⁶⁾, the assignments of the peaks in cathodic process are as follows;

The peak (a) was not observed in their work. Considering the noble potential of peak (a), we suppose the formation of the titanium oxychlorides due to the trace of moisture in the molten salt mixture.

Let us now consider the peak (b) in detail. If the peak (b) implies the following catalytic reaction in addition to the reversible charge transfer such as the reduction of Ti^{4+} to Ti^{3+} ,

the relation between the current i and the potential E has been given by the equation (5)⁷⁾.

$$i = \frac{C_0 n F A \sqrt{D k_f}}{1 + \exp\left(\frac{n F}{R T} (E - E_{1/2})\right)} \quad (5)$$

where C_0 is the bulk concentration of the oxidized species, n is the number of electron involved in the electrochemical reaction, A is the area of the elect-

rode, D is the diffusion coefficient of the oxidized species (and the reduced species), k_f is the chemical reaction rate constant of the reaction (4) and $E_{1/2}$ is the half wave potential; R , T and F have their usual significance. It is noted that the equation (5) can be applied to the system with the large value of k_f . From the experimental result that the peak (b) in Fig. 2 is independent of the sweep rate, it seems reasonable to consider that the present system has the large value of k_f . With the transformation of the equation (5), we have

$$\exp\left(\frac{n F}{R T} (E - E_{1/2})\right) = \frac{C_0 n F A \sqrt{D k_f}}{i} - 1 \quad (6)$$

The bulk concentration of the oxidized species, Ti^{4+} , in LiCl-KCl eutectic mixture is 5.9×10^{-2} mole/cm³, being almost equal to the saturated concentration of $TiCl_4$ in this melt at 450°C. Plotting $\exp\left(\frac{n F}{R T} (E - E_{1/2})\right)$ against $1/i$, we have a straight line passing -1 at $1/i=0$ as shown in Fig. 3, which indicates

Fig. 3 Relation between $1/i$ and $\exp\left(\frac{n F}{R T} (E - E_{1/2})\right)$ at peak (b)

the presence of the catalytic reaction. Since the $\exp\left(\frac{n F}{R T} (E - E_{1/2})\right)$ increases linearly with $1/i$, we can calculate the value of 0.84 (cm²/sec²) for $D k_f$ from the slope of the line.

3.2 Faradaic impedance measurement

The conventional models of the equivalent circuit for the electrode (including the Faradaic impedance separated from double layer capacity) and of circuit for measurement proposed by Laitinen et al.⁸⁾ are used for this study, as shown in Fig. 4. The double-layer capacity C_{dl} and the solution resistance R_{soln} are obtained by extrapolating the plotted curves of the measured values of the resistance R_m and of the capacity C_m against the inverse square root of the frequency, $\omega^{-1/2}$, to the infinite frequency. The

typical example of the variation of R_m and C_m with $\omega^{-1/2}$ at 450°C is shown in Fig. 5. Since no special relationship between R_m and $\omega^{-1/2}$ seems to exist, the extrapolation of R_m is achieved easily.

Fig. 4 Model of the equivalent of impedance

(a) : For electrode
(b) : For measurement

Fig. 5 Estimation of C_{dl} and R_{soln} by the extrapolation of C_m and R_m to $\omega \rightarrow \infty$

Fig. 6 Relation between R_s , $1/(\omega C_s)$ and $1/\sqrt{\omega}$

The relation between the Faradaic impedance and $\omega^{-1/2}$ is shown in Fig. 6. At lower frequencies, the obtained curves agree with that expected under the diffusion control because of the linear variation of the Faradaic impedance, such as R_s and $1/(\omega C_s)$, with $\omega^{-1/2}$. At higher frequencies, however, an unexpected and the very remarkable maximum peak is observed in $1/(\omega C_s)$ against $\omega^{-1/2}$. Such a maximum may be attributed to the presence of the catalytic reaction (an homogeneous reaction) at the surface of the electrode due to the disproportionation of titanium chloride^{*1}. According to the results concerning the general Faradaic impedance of the catalytic reaction rate-control by Vetter⁹⁾, the following equation is derived;

$$\omega_{\max} = \sqrt{3}k \quad (7)$$

where k is the reaction rate constant of the catalytic reaction (the homogeneous reaction due to the disproportionation). Since the value of $\omega_{\max}$ is 4.9×10^4 (sec^{-1}) as shown in Fig. 6, we can calculate the value of k as 2.9×10^4 (sec^{-1}) from the equation (7). It is found that the value of k agrees well with the value of k_f obtained by the potential sweep voltammogram described above if the diffusion coefficient of Ti^{4+} is equal to the value of Ti^{3+} ($=3.0 \times 10^{-5} \text{ cm}^2/\text{sec}$)¹⁰⁾.

4 Conclusion

From the the two kinds of experiments, the potential sweep voltammetric method and the Faradaic impedance method, it is suggested that the catalytic reaction is occurred in molten LiCl-KCl eutectic mixture containing Ti^{4+} at 450°C.

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References :

- 1) J. O'M. Bockris, G. J. Hills, I. A. Menzies, L. Young, *Nature* **178**, 654 (1956).
- 2) W. E. Reid, *J. Electrochem. Soc.* **108**, 393 (1957).
- 3) F. Quemper, D. Derou, N. Rigaud, *ibid.* **119**, 1353 (1972).
- 4) K. Funaki, K. Uchimura, *Kogyo Kagaku Zasshi* **59**, 14

*1 It has been known that the homogeneous reaction rate-control is recognized when the curves R_s and $1/(\omega C_s)$ against $\omega^{-1/2}$ are parallel straight lines for very high frequencies and, on the other hand, the heterogeneous reaction rate-control is recognized when the capacitive component of reaction $1/(\omega C_r)$ has a linear dependence on ω^{-1} at high frequencies⁸⁾ where C_r is the reaction capacity. Because of the lack of the data at high frequencies, we can not determine conclusively which type of the reaction rate-control is predominant for this molten salt mixture. However, it is reasonable to consider that the homogeneous reaction rate-control is predominant because of the more noble potential of the homogeneous reaction of (b) peak than that of the heterogeneous reaction of (d) peak as shown in Fig. 2.

- (1956).
- 5) H. A. Laitinen, R. P. Tischer, D. K. Roe, *J. Electrochem. Soc.* **107**, 546 (1960).
 - 6) N. Ogawa, K. Niki, T. Tomonari, "The 36th Electrochemical Soc. Meeting", Preprint p. D105 (1969), June, Yokohama.
 - 7) R. S. Nicholson, I. Sain, *Anal. Chem.* **36**, 706 (1964).
 - 8) H. A. Laitinen, H. C. Gaur, *J. Electrochem. Soc.* **104**, 730 (1957).
 - 9) K. J. Vetter, "Electrochemical Kinetic", p. 445 (1967), Academic Press, New York.
 - 10) D. L. Hills, G. J. Hills, L. Young, J. O'M. Bockris, *J. Electroanal. Chem.* **1**, 79 (1959).

Technical Paper

Corrosion of Tungsten Carbide in Aqueous Alkaline Solutions Containing Dissolved Air

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Corrosion of tungsten carbide in alkaline aqueous solutions containing dissolved air was studied by chemical as well as by electrochemical analyses. The rate of corrosion was high for the solution of high alkalinity. Corrosion was found to proceed via the local cell process, that is, anodic dissolution of tungsten carbide and cathodic reduction of dissolved oxygen. The overall corrosion reaction was identified as

1 Introduction

Tungsten carbide (WC) has high electrocatalytic activities for combustion of fuels such as hydrogen, oxygen, and hydrazine^{1)~7)}. Recently, tungsten carbide was investigated as a catalyst for liquid phase heterogeneous catalytic hydrogenation⁸⁾ on account of its high electrocatalytic activities. Some electrochemical properties of tungsten carbide were reported by the authors⁹⁾ in connection with those of tungsten metal, and tungsten carbide was found to corrode anodically as is the case of tungsten. In spite of various investigations on the catalytic activities of tungsten carbide, very few studies had been conducted on the corrosion of this material in aqueous media. Therefore, one has yet no concrete information on the rate and mechanism of corrosion of tungsten carbide. This study has been intended to acquire information on corrosion of tungsten carbide.

2 Experimental

Tungsten carbide electrode was prepared in the same way as was reported previously⁹⁾. Before various measurements, the electrode was polarized anodically and cathodically twice at 0.1 mA/cm² in 1N NaOH for 3 min, and finally anodically at the same current

density for 3 min again. Then, it was dipped in conc. HNO₃ for 5 min, followed by immersion in 1N NaOH at 50°C for 15 min, and washed thoroughly with de-ionized water to finish the pretreatment. Polarization measurements were made by using a commercial potentiostat (Hokuto Denko Co., model PS-250), and long time electrolysis was carried out with a constant current power supply which had been fabricated by special order and could feed constant current of 0.5 μA or above. Open circuit electrode potential of tungsten carbide was measured by an electrometer (Hokuto Denko Co., model EM-1). The other details of the experimental procedures were reported in the previous paper⁹⁾. All the measurements were made in solutions under a static condition.

3 Results and Discussion

3.1 Corrosion rate by chemical analysis

After tungsten carbide had been immersed in an alkaline aqueous solution of four kinds containing dissolved air for 100–150 hr, the dissolved tungsten was analyzed colorimetrically by the dithiol method. Table 1 gives the average rate of dissolution in each solution. It was found that tungsten carbide corroded more readily in highly alkaline solutions. The amounts of dissolved tungsten, shown in the second column, were converted to the unit of current density on the assumption that eight electrons participated in

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