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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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the reaction. The dissolution current thus obtained is given in the third column.

3.2 Corrosion rate by polarization measurements

Steady state polarization curves of tungsten carbide are shown in Fig. 1 for the case of the solution 0.3 N NaOH + 0.7 N Na₂SO₄. Polarization curves in other

Fig. 1 Current-potential curve of tungsten carbide in 0.3 N NaOH + 0.7 N Na₂SO₄ solution containing dissolved air

three kinds of solution closely resembled to that shown in Fig. 1, that is, "Tafel slope" was observed in the anodic polarization curve and a curve indicating diffusion limiting current was obtained in the cathodic branch.

Fig. 2 gives electrode potential of tungsten carbide in 1N NaOH containing dissolved air as a function of immersion time, and shows that the electrode potential reaches a steady state value after immersion for 20 hr. The corrosion potential, determined by extrapolation of the anodic and cathodic curves, accorded fairly well with the steady state electrode potential shown in

Fig. 2 Change of open circuit potential of tungsten carbide electrode with dipping time in 1N NaOH containing dissolved air

Fig. 2. Hence, one can obtain the corrosion current from Fig. 1 as well as the corrosion potential. The values of the corrosion potential and current determined by such an extrapolation method are shown in

Table 2. The apparent αn values of the anodic process are given in the fourth column of the table.

To make sure of the corrosion rate, the analysis by the polarization resistance method was also tried. The electrode was polarized within ± 8 mV from the steady state corrosion potential. As had been found for various metal electrodes, I - V curves showed a linear relation: the ratio of the increment of the potential to that of the current ($\Delta V/\Delta I$), however, was found to decrease with increasing alkalinity. These curves were analyzed to determine the corrosion rate on the basis of the theory of the polarization resistance for the case when the cathodic reaction is diffusion limiting¹⁰. Thus determined corrosion rates as well as $\Delta V/\Delta I$ values are shown in Table 3. The corrosion rates determined by three different methods, which are shown in Tables 1, 2, and 3, surprisingly accorded with one another.

Table 1 Corrosion rate of tungsten carbide in various alkaline solutions

Solution	Dissolved tungsten mole/hr·cm ²	Corrosion current μ A/cm ²
1N NaOH	7.7×10^{-8}	16.5
0.3 N NaOH + 0.7 N Na ₂ SO ₄	3.7×10^{-8}	8.0
0.1 N NaOH + 0.9 N Na ₂ SO ₄	3.1×10^{-8}	6.7
0.03N NaOH + 0.97N Na ₂ SO ₄	2.6×10^{-8}	5.8

Table 2 Corrosion rate and potential determined as an intersecting point by extrapolation of the anodic and cathodic polarization curves

Solution	Corrosion potential V vs. SHE	Corrosion current μ A/cm ²	αn of anode process
1N NaOH	-0.13	17.8	0.37
0.3 N NaOH + 0.7 N Na ₂ SO ₄	-0.10	8.9	0.51
0.1 N NaOH + 0.9 N Na ₂ SO ₄	-0.07	6.5	0.45
0.03N NaOH + 0.97N Na ₂ SO ₄	-0.08	5.2	0.49

Table 3 Corrosion rate determined by polarization resistance method

Solution	$\Delta V/\Delta I$ V/A	Corrosion current μ A/cm ²
1N NaOH	4.5×10^3	15.4
0.3 N NaOH + 0.7 N Na ₂ SO ₄	5.2×10^3	9.7
0.1 N NaOH + 0.9 N Na ₂ SO ₄	6.6×10^3	8.6
0.03 N NaOH + 0.97 N Na ₂ SO ₄	8.8×10^3	5.9

3.3 Thermodynamic considerations

When nitrogen gas was bubbled through the solutions, the corrosion potential shifted towards cathodic direction by 200-300 mV. This suggests that the main

cathodic reaction was the reduction of dissolved oxygen:

$$E(\text{SHE}) = 1.24 - 0.059 \text{ pH}$$

As Fig. 1 shows, the dissolved oxygen seems to have been reduced under the diffusion limiting condition at the corrosion potential, by about 600 mV more cathodic than the thermodynamic equilibrium potential of oxygen reduction. The diffusion limiting current indicates that tungsten carbide has an electrocatalytic activity enough to reduce oxygen of the order of the amount dissolved with polarization of 0.6 V. The electrocatalytic activity for reduction of oxygen has sometimes an important role in corrosion of carbides, for in the case of corrosion of titanium carbide, for example, dissolved oxygen was reduced under an "activation controlled process" at a by far low rate at its corrosion potential by as large as 1.2 V more cathodic than the thermodynamic equilibrium potential of oxygen reduction, and as a consequence, the corrosion rate was very low¹¹.

The anodic reaction was considered to be the anodic dissolution of tungsten carbide. As was reported previously⁹, the equilibrium potential is given;

$$E(\text{SHE}) = -0.717 + 0.0074 \log p_{\text{CO}} + 0.0074 \log a_{\text{WO}_4^{2-}} - 0.074 \text{ pH}$$

This equation was derived from the anodic polarization at fairly large current density. In order to make sure, quantities of dissolved tungsten and evolved gas were analyzed after the anodic polarization at $20 \mu\text{A}/\text{cm}^2$ in 1N NaOH under nitrogen atmosphere. The current value chosen was comparable to the corrosion current as Tables 1, 2, and 3 show. In conclusion, the validity of equation (2) was confirmed again.

For this reason, the corrosion of tungsten carbide in alkaline solutions was found to proceed according to the following equation as a whole,

4 Summary

The following results were obtained in this study.

- 1) Rate of corrosion of tungsten carbide becomes high with increasing alkalinity of a solution.
- 2) Rates of corrosion determined by three different methods, chemical analysis by colorimetry, extrapolation method of polarization curves to the corrosion potential, and the polarization resistance method, accorded fairly well.
- 3) The corrosion in alkaline solution proceeds via the local cell process and the overall reaction was identified as

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