

## THE EFFECT OF METHOD OF PREPARATION ON THE CORROSION RESISTANCE AND CATALYTIC ACTIVITY DURING CORROSION OF TUNGSTEN CARBIDE

### II. CHANGES IN THE CATALYTIC ACTIVITY OF TUNGSTEN CARBIDES DURING THE CORROSION PROCESS

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(Received October 15, 1979; in revised form February 11, 1980)

#### Summary

Sedimented electrodes were used for the investigation of the changes in the catalytic activity during corrosion in 4.5 and 9.9N  $H_2SO_4$  of tungsten carbides synthesized under different conditions. It is shown that during corrosion the specific activity of all the samples studied reaches a maximum after a certain exposure time. The same phenomenon is observed also during the periodic contact of the corroding samples with hydrogen. The catalytic activity decreases with increase in the quantity of tungsten oxides formed during corrosion. In 4.5N  $H_2SO_4$  the specific activity of the tested samples is subjected to more pronounced changes. Corrosion processes lead to some exceptions in the general rule that carbides synthesized from  $WO_3$  display a higher specific activity than those synthesized from  $H_2WO_4$  (w).

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#### Introduction

The alteration of the catalytic activity of tungsten carbide during partial oxidation at high anodic potentials [1, 2] or in very aggressive medium [3] has been reported recently, but the authors have focused their attention only on the reasons leading to the increase of the catalytic activity as a result of a single corrosion attack. At the present time different explanations of this phenomenon have been advanced. Böhm and Fleischman attribute the increased activity of WC after corrosion in highly oxidising medium (dichromate, hydrogen peroxide, and concentrated  $H_2SO_4$ ) to the formation of new active centers on the surface of the catalyst as a result of the inclusion of oxygen in the crystal lattice of the carbide. The results of Palanker *et al.* [2] show that during corrosion in  $H_2SO_4$  at high anodic potentials in the presence of hydrogen the specific activity of tungsten carbide remains unchanged. The

observed increase of the activity per gram of catalyst is due to the increase of the specific surface of the catalyst during corrosion.

The present paper is aimed at the systematic study of the changes in the catalytic activity of tungsten carbide, synthesized under different conditions, during corrosion in 4.5 and 9.9N  $\text{H}_2\text{SO}_4$ .

## Experimental

The catalytic activities of 4 types of tungsten carbide ( $\text{WC}_{(1)}$  and  $\text{WC}_{(2)}$  synthesized from  $\text{H}_2\text{WO}_4$  (w);  $\text{WC}_{(3)}$  and  $\text{WC}_{(4)}$  synthesized from  $\text{WO}_3$ ) were measured after different exposure times to corrosion in 4.5 and 9.9N  $\text{H}_2\text{SO}_4$ . The selection of the catalysts and the corrosion test conditions are described in Part I of the present paper [4].

The electrochemical investigations were carried out with sedimented tungsten carbide electrodes [5] prepared from the tested carbides. The catalytic activity toward the oxidation of hydrogen was determined from the voltage-current characteristics of these electrodes in the respective electrolytes at 20 °C by a method previously described [5]. The potentials were determined *vs.* a standard hydrogen electrode in the same electrolyte. Catalytic activity was compared at a potential of +200 mV. During these studies the surface of the electrodes cannot be determined from the charging curves, since this method is applicable only if the catalyst surface is oxide-free. Therefore, the current density was evaluated per unit surface area of the respective sample determined by BET measurements. This method for the measurement of the area of sedimented electrodes is not very accurate, since, if the catalyst is present in substantial quantities, part of it will not react electrochemically due to the screening of the particles. The measurements show that for sedimented electrodes with weights up to 0.8 mg ( $\text{WC}_{(2)}$  and  $\text{WC}_{(4)}$ ) and 1.1 mg ( $\text{WC}_{(1)}$  and  $\text{WC}_{(3)}$ ) the agreement between electrode surfaces determined by means of charging curves and those measured by BET is quite acceptable (differences less than 7 - 8%).

The measurement of the catalytic activity after continuous corrosion of the carbides is shown as experimental conditions I in the Figures.

Long term electrochemical measurements of the activity of the catalyst during intermittent operation were carried out with sedimented electrodes. The measurement techniques (shown in Fig. 5 as experimental conditions II) were as follows: the electrode was polarized for 4 h daily at +200 mV in the presence of hydrogen, while during the rest of the time the electrode remained immersed in the electrolyte without external polarization and in the absence of hydrogen. Under these conditions the carbide electrode acquires a corrosion potential and corrosion processes proceed. After 1 500 h under these conditions, the extent of corrosion can be evaluated by comparing the ratio of the areas of the peaks of  $\text{WO}_2$  and WC in the X-ray diffractograms with the same data for samples in which the  $\text{WO}_2$  content has been determined by chemical analysis.

## Results and discussion

Figure 1 shows the changes in the activity of 1 g of all 4 investigated catalyst types with corrosion exposure time ( $\tau$ ) in 4.5N  $\text{H}_2\text{SO}_4$ . It can be seen that carbides synthesized from  $\text{WO}_3$  display a distinct maximum at  $\tau = 24 - 48$  h. With the two other carbides the maximum is rather diffuse. These differences are eliminated if the current is referred to the catalyst area (current density) (Fig. 2). As can be seen, this mode of representing the experimental data gives distinctly shaped current maximum for all  $i/\tau$  curves. A behaviour inherent to all samples is that after the rapid decrease of the specific activity (from  $\tau = 48$  h to 500 h), a period of slow decrease follows. In all cases, after a sufficiently long exposure (1 500 - 2 000 h) the decrease of specific activity, as compared with the data for samples not subjected to corrosion, is substantial: between 40% for  $\text{WC}_{(3)}$  ( $\tau = 2\,000$  h) and 66% for  $\text{WC}_{(2)}$  (1 500 h). The initial ratio between the activities of both types of carbides, however, is retained, and catalysts synthesized from  $\text{WO}_3$  are more active than those prepared from  $\text{H}_2\text{WO}_4$  (w).

Curves with similar shapes are observed after corrosion in 9.9N  $\text{H}_2\text{SO}_4$  (Figs. 3 and 4). In this case the maximum current densities are reached after longer (100 - 300 h) exposures to corrosion. After 2 000 h corrosion, a substantial decrease of the specific activity as compared with the initial figures is observed only for sample types  $\text{WC}_{(2)}$  and  $\text{WC}_{(4)}$ . The initial ratio between

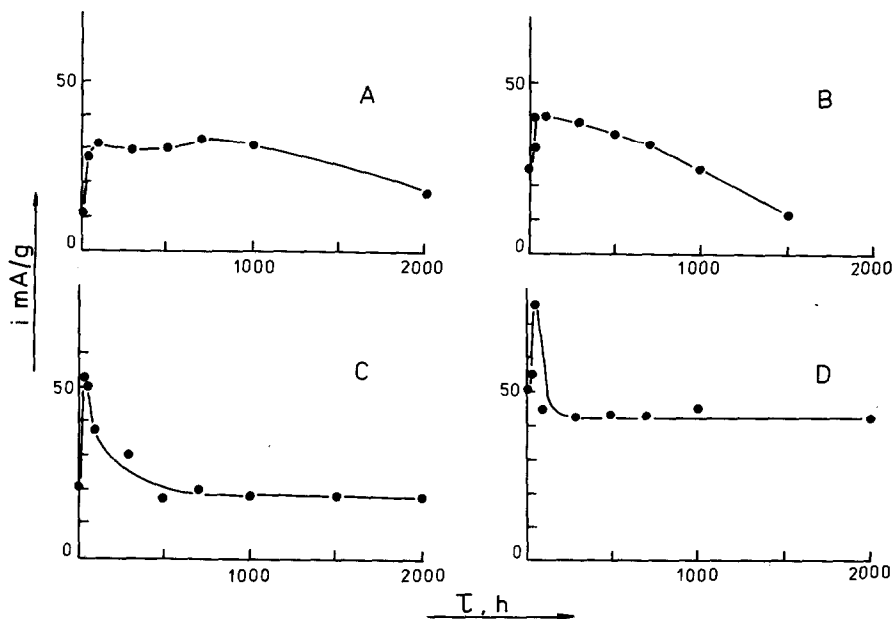


Fig. 1. Catalytic activity (mA/g at  $\varphi = +200$  mV) measured with sedimented WC electrodes: A,  $\text{WC}_{(1)}$ ; B,  $\text{WC}_{(2)}$ ; C,  $\text{WC}_{(3)}$ ; D,  $\text{WC}_{(4)}$  experimental conditions I, after different corrosion times in 4.5N  $\text{H}_2\text{SO}_4$ ;  $T = 20^\circ\text{C}$ .

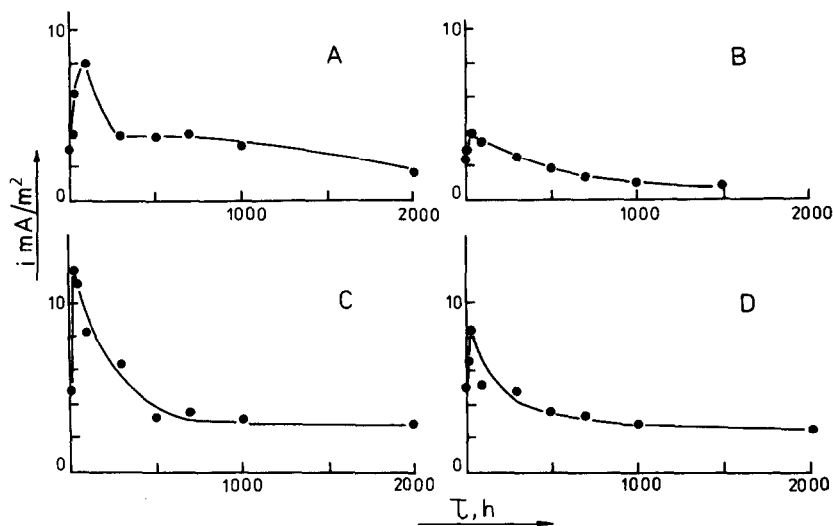


Fig. 2. Specific catalytic activity (mA/m<sup>2</sup> at  $\varphi = +200$  mV) measured with sedimented WC electrodes: A, WC<sub>(1)</sub>; B, WC<sub>(2)</sub>; C, WC<sub>(3)</sub>; D, WC<sub>(4)</sub> experimental conditions I, after different corrosion times in 4.5N H<sub>2</sub>SO<sub>4</sub>;  $T = 20$  °C.

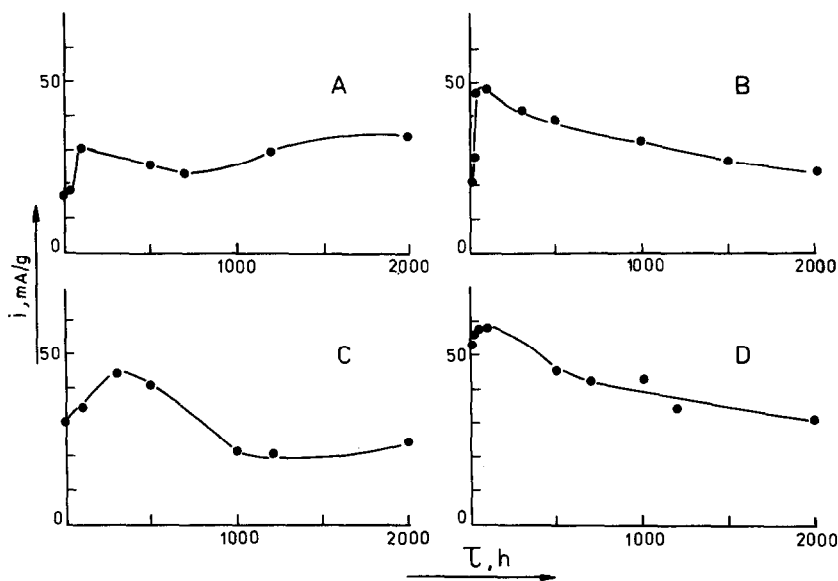


Fig. 3. Catalytic activity (mA/g at  $\varphi = +200$  mV) measured with sedimented WC electrodes: A, WC<sub>(1)</sub>; B, WC<sub>(2)</sub>; C, WC<sub>(3)</sub>; D, WC<sub>(4)</sub> experimental conditions I, after different corrosion times in 9.9N H<sub>2</sub>SO<sub>4</sub>;  $T = 20$  °C.

the activities of the two types of carbides is no longer retained — the activity of WC<sub>(1)</sub> is higher than that of WC<sub>(4)</sub>. If Fig. 4 is compared with Fig. 2 it can be seen that the specific activity of the samples after 2000 h exposure to

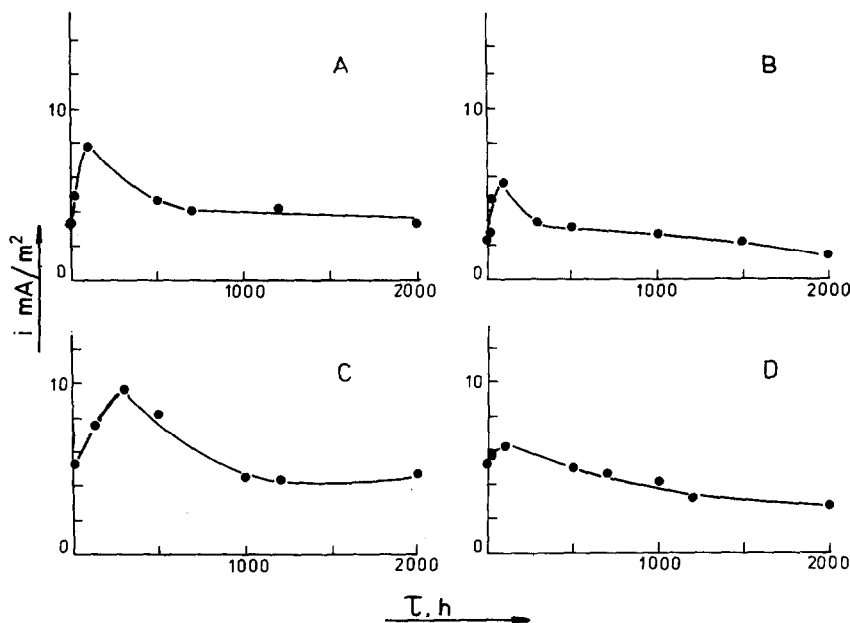


Fig. 4. Specific catalytic activity ( $\text{mA}/\text{m}^2$  at  $\varphi = +200$  mV) measured with sedimented WC electrodes; A,  $\text{WC}_{(1)}$ ; B,  $\text{WC}_{(2)}$ ; C,  $\text{WC}_{(3)}$ ; D,  $\text{WC}_{(4)}$  experimental conditions I, after different corrosion times in  $9.9\text{N H}_2\text{SO}_4$ ;  $T = 20^\circ\text{C}$ .

corrosion in  $9.9\text{N H}_2\text{SO}_4$  is equal to that of samples in  $4.5\text{N H}_2\text{SO}_4$  after 1 000 hours.

All cases considered up to now (Figs. 1 - 4) were obtained under experimental conditions I. Figures 1 and 3 give information on the practical applicability of the different types of tungsten carbides. It will be seen that the catalyst with a large surface, synthesized from  $\text{H}_2\text{WO}_4$  (w), is characterized by a rapid loss of activity in both electrolytes. Better performance in  $4.5\text{N H}_2\text{SO}_4$  is displayed by  $\text{WC}_{(4)}$ , while  $\text{WC}_{(1)}$  and  $\text{WC}_{(4)}$  are satisfactory for operation in  $9.9\text{N H}_2\text{SO}_4$ . It should be noted also that all catalysts perform better in  $9.9\text{N H}_2\text{SO}_4$ .

The changes in the activity found under intermittent operation (experimental conditions II) revealed similar relations between the current density and the duration of exposure to corrosion. In Fig. 5 the curves traced under different operating conditions for  $\text{WC}_{(2)}$  are compared. Both curves have a similar shape, but the curve traced under intermittent operating conditions displays a substantially higher maximum. An approximate evaluation, carried out after the test run was over, using X-ray diffractograms, showed that the amount of oxides after 1 300 h operation under periodic conditions is almost equal to the quantity checked after 1 000 h continuous corrosion (experimental conditions I). This proves that the distinctly defined oxides formed during the corrosion process are not reduced by hydrogen. The same conclusion can be drawn from the X-ray diffractograms of carbides subjected to corrosion whose voltage-current curves have been obtained in the presence

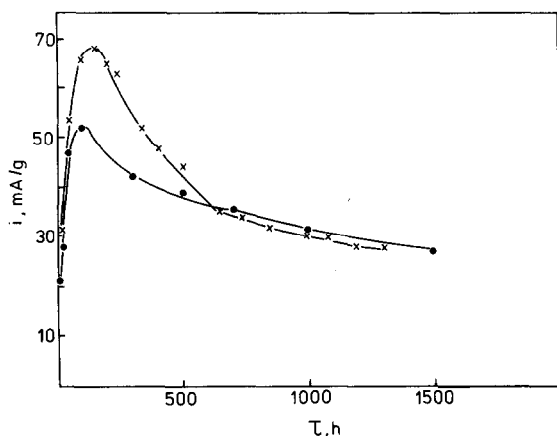


Fig. 5. Catalytic activity (mA/g at  $\varphi = +200$  mV) measured with sedimented WC electrodes: ●, WC<sub>(2)</sub>, experimental conditions I; ×, WC<sub>(2)</sub>, experimental conditions II, after different corrosion times in 9.9N H<sub>2</sub>SO<sub>4</sub>;  $T = 20$  °C.

of hydrogen. The ratio between the areas of the WO<sub>2</sub> and WC peaks in these diffractograms is equal to the same ratio prior to determining the voltage-current curves.

As previously mentioned, the specific activity of all tested samples displays a maximum during the corrosion process. This means that the increase of the activity per gram of catalyst in the initial hours of corrosion is not due to the increase of the specific surface, as established by Palanker [2]. The maximum is reached after different durations in the two electrolytes. In 4.5N H<sub>2</sub>SO<sub>4</sub>, where the corrosion rate is faster, typical figures are about 48 h, whereas in 9.9N H<sub>2</sub>SO<sub>4</sub> this state is reached after 100 - 300 h. These facts support the supposition that this alteration reflects the changes due to the partial corrosion of the surface. Whether this effect is due to the presence of the definite oxide WO<sub>2</sub>, or to some other alteration of the surface must be determined. In an effort to clarify this point, the catalytic activity of WC<sub>(2)</sub> subjected to corrosion for 500 h in 9.9N H<sub>2</sub>SO<sub>4</sub> and then treated with 20% NaOH soln. was determined. During this treatment WO<sub>2</sub> is dissolved. Figure 6 compares the voltage-current curves of the treated carbide with the characteristics of WC<sub>(2)</sub> not subjected to corrosion and WC<sub>(2)</sub> exposed to 500 h corrosion in 9.9N H<sub>2</sub>SO<sub>4</sub>. This Figure proves that when the oxides are removed, activity is increased in comparison with samples before and after corrosion. All these facts give support to the presumption that the presence of definite oxides on the tungsten carbide surface leads to a passivation with regard to the oxidation of hydrogen, while the increase of the catalytic activity after corrosion is due to other changes occurring on the surface. Most probably they comprise the creation of new active centers by the inclusion of oxygen, which partially substitutes carbon in the crystal lattice of the carbide, as proposed by Böhm [3]. Therefore both these factors (formation of WO<sub>2</sub> and creation of new active centers) will affect the

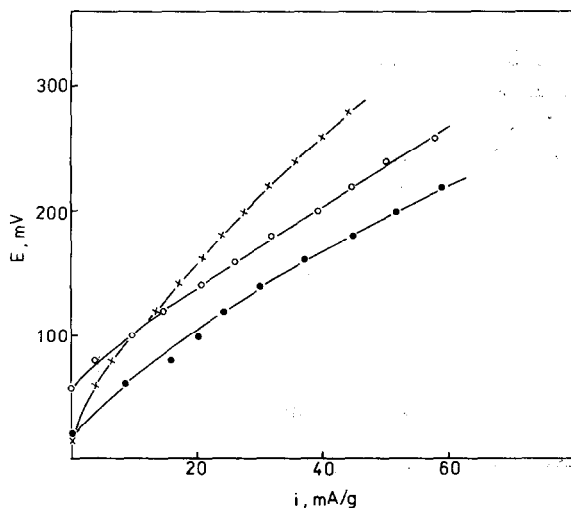


Fig. 6. Current-potential curves of sedimented WC electrodes in 9.9N  $H_2SO_4$ ;  $T = 20^\circ C$ ;  $P_{H_2} = 20 \text{ mmHg}$ ;  $\times$ ,  $WC_{(2)}$  before corrosion;  $\circ$ ,  $WC_{(2)}$  after 500 h corrosion;  $\bullet$ ,  $WC_{(2)}$  after 500 h corrosion and removal of the oxides by dissolution in 20% NaOH solution.

activity of the partially corroded samples. The changes that occur during corrosion in all the catalysts investigated are not strictly identical, and this may lead in some cases to changes in the ratios between the specific activities of the samples and their initial values prior to corrosion, which are determined by the type of starting material [5]. As an example, the specific activity of  $WC_{(1)}$  synthesized from  $H_2WO_4$  (w) reaches that of  $WC_{(4)}$  prepared from  $WO_3$ .

The electrochemical inactivity and passivating action of  $WO_2$  with regard to the oxidation of hydrogen explains the decrease of WC activity when the amount of  $WO_2$  increases (Figs. 1 - 4).

The curves for activity-corrosion time show that after the pronounced initial decrease of activity after 100 - 300 h of corrosion, a period follows when specific activity decreases very slowly. Within the same time interval the quantity of oxides increases linearly [4]. A comparison of these results shows that the specific activity does not decrease in proportion to the amount of oxides formed. A possible explanation of this fact is offered by the results obtained by Böhm [3], who advances the hypothesis that when oxidation starts on a WC particle the process proceeds also in the bulk. Thus the overall amount of oxides in the sample is increased without affecting new catalyst particles.

## Conclusions

The effect of the initial materials used for the synthesis of WC upon the specific activity of the catalyst may be masked in some cases by corrosion

processes. As a general rule, after a certain corrosion time in  $\text{H}_2\text{SO}_4$  solutions, carbides synthesized from  $\text{WO}_3$  display a higher activity than those prepared from  $\text{H}_2\text{WO}_4$  (w), although some exceptions are observed. Carbides synthesized at higher temperature, which have smaller specific surfaces, retain their catalytic activity ( $i$  mA/g) for longer periods in  $\text{H}_2\text{SO}_4$  solutions. If a long retention of the catalytic activity of WC-catalyzed electrodes is required the use of higher acid concentrations and the avoidance of long, idle (open-circuit) periods is recommended.

## References

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