273

THE EFFECT OF METHOD OF PREPARATION ON THE CORROSION RESISTANCE AND CATALYTIC ACTIVITY DURING CORROSION OF TUNGSTEN CARBIDE
I. CORROSION RESISTANCE OF TUNGSTEN CARBIDE IN SULFURIC ACID

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Summary

The corrosion resistance in 4.5N and 9.9N H_2SO_4 of tungsten carbide synthesized under different conditions has been investigated. The amount of oxides in both electrolytes increases linearly with time, suggesting that during the corrosion process the catalyst surface is not passivated. The corrosion rate depends on the method of preparation of the tungsten carbide. Under identical preparation conditions, carbides synthesized from H_2WO_4 displayed the lower corrosion resistance. The corrosion resistance of carbides synthesized from identical starting materials depends on the carburation temperature: carbides synthesized at elevated temperatures display higher corrosion resistance. The different corrosion rates are explained by the variations in the specific surfaces, the grain size, and the different extent of segregation of the tungsten carbide particles, respectively. It is shown that the corrosion rate in 4.5N H_2SO_4 is twice that in 9.9N H_2SO_4. This observation is discussed in terms of differences in the rate of the anodic process and the lower solubility of the corrosion process depolarizer (oxygen) in highly concentrated solutions.

Introduction

One of the basic characteristics of any catalyst is its corrosion resistance in the working medium and the alteration of its catalytic activity due to corrosion. No data are given in the literature up to now on the changes which occur with tungsten carbide catalysts during exposure to H_2SO_4 solutions in the absence of hydrogen, *i.e.*, when the fuel cells are idling.

The purpose of the present paper is to investigate the corrosion resistance of tungsten carbides synthesized under different conditions during operation in 4.5N and 9.9N H_2SO_4 solutions. The choice of these concentra-

tions was determined by the fact that up to the present our studies with WC-catalyzed gas diffusion electrodes were carried out in 4.5N H_2SO_4 [1], and in the future we intend to use 9.9N H_2SO_4 (sp. gravity 1.28) in our experiments.

Experimental

Preparation and selection of tungsten carbides

Our experiments were carried out with tungsten carbides synthesized from WO_3 (S_{BET} = 17 m^2/g, d* = 2 - 5 μm) and H_2WO_4 (white mod.) (S_{BET} = 30 m^2/g, d = 1 - 3 μm) in a CO + H_2 atmosphere according to a previously described [2] method. These two starting materials were selected, since our previous investigations [2, 3] confirmed that carbides synthesized from them display a different catalytic activity with regard to the evolution and oxidation of hydrogen. From all the tungsten carbides prepared from both initial raw materials, two of each, synthesized at different temperatures, were selected in an effort to investigate the effect of this parameter on the synthesis. The four carbides were selected so as to keep constant the other parameters which could affect the corrosion rate (quantity of carbon bound in the crystal lattice ($C_{c.l.}$) and free carbon ($C_{f.}$). Table 1 shows the different synthesis conditions and the parameters of the investigated samples.

TABLE 1

Preparation conditions and surface area (BET), grain size, carbon content in the crystal lattice, and free carbon content of the tungsten carbides investigated and their corrosion potentials after τ = 1 h

Preparation conditions		WC						
Starting materials	Temp. (°C)	No	Surface area (m^2/g)	Grain size (μm)	$C_{c.l.}$ (%)	$C_{f.}$ (%)	φ corr. in 4.5N H_2SO_4 (mV)	φ corr. in 9.9N H_2SO_4 (mV)
$H_2WO_{4(w)}$	850	1	3.74	2 - 8	4.72	0.13	+455	+423
$H_2WO_{4(w)}$	750	2	10.02	1 - 5	4.77	0.15	+571	+534
WO_3	850	3	4.26	3 - 10	4.82	0.15	+444	+432
WO_3	750	4	10.38	2 - 6	4.73	0.1	+535	+500

The surface was determined by low temperature nitrogen adsorption by the BET method, while the method of determination of $C_{c.l.}$ and $C_{f.}$ was described in a previous paper [2]. The particle size distribution was determined by a Sartorius sedimentation balance [4].

The chemical analysis of the four investigated carbides proved that no oxides were present prior to contact with the corrosion media.

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*d — equivalent Stokes diameter.

Corrosion test conditions

250 mg samples of all the types of tungsten carbide studied were treated with 80 ml of sulfuric acid (4.5 or 9.9N) in 100 ml beakers. The different samples were kept in contact with the acid for 24, 48, 100, 300, 500, 700, 1 200, 1 500 and 2 000 h, respectively, at 20 °C under free aeration conditions. After the required time (τ) had elapsed, the acid was removed by centrifuging, the samples were rinsed with water until the rinsings showed pH = 7 (litmus test) and dried at 120 °C. The processed samples were subjected to studies aimed at the determination of the changes due to corrosion.

Methods for the determination of the changes in the test samples

X-ray diffractograms were used for the approximate determination of the composition of the samples. Accurate analysis of the oxide content was carried out by checking the weights. A 200 mg sample was treated with 20% KOH soln. for 15 min, heating simultaneously to 60 °C. During this treatment the oxides are dissolved [5]. After spinning, rinsing to neutrality, and drying, the weight loss is used for the evaluation of the quantity of oxides. The accuracy of the method is 1 - 2%.

In addition to the composition of the samples after corrosion, the alteration of the specific surfaces was also monitored by BET tests, and by checking the crystal habits of the particles by SEM photographs using a JEOL type SEM 100 B electron microscope.

Electrochemical measurements

Current–potential curves at high anodic potentials were measured in both electrolytes in an effort to elucidate the causes of the different corrosion resistance of the carbides. A cell as described in ref. 2 was used. The electrodes for these test runs were prepared in the following manner: a filter paper disc was fixed on a fritted glass holder and 30 mg of the WC sample were placed upon it. The sample was covered with another paper disc, and the electrode so formed was pressed with a golden spring which ensured the electric contact. Preliminary experiments proved that under the experimental conditions the currents on the gold filament are negligible (up to 1 μA) by comparison with the currents on the carbides (30 - 280 μA).

The corrosion current–potential curves were measured under potentiostatic conditions at 20 °C in 4.5 and 9.9N H_2SO_4 electrolytes using an OH 405 Radelkis (Hungary) potentiostat with a JR compensator. Potentials were changed in steps of 50 mV and compared with the potential of a standard hydrogen electrode in the same electrolyte. Current values were checked 10 minutes after setting the potential. This interval is adequate for charging the double layer of the highly expanded surface of the electrode, so that charging will not interfere with the current values. The current density is referenced to unit real surface area determined from the charging curves [2].

Results and discussion

Corrosion resistance in 4.5 and 9.9N H$_2$SO$_4$

The X-ray diffractograms of carbides subjected to corrosion show that, initially, WO$_2$ is formed, while the higher oxide WO$_3$ appears after τ = 1 000 h in 4.5N H$_2$SO$_4$ and τ = 1 500 h in 9.9N H$_2$SO$_4$.

Figures 1 and 2 show the increments of the weight percentage of oxide in the investigated samples during corrosion tests in both electrolytes as a
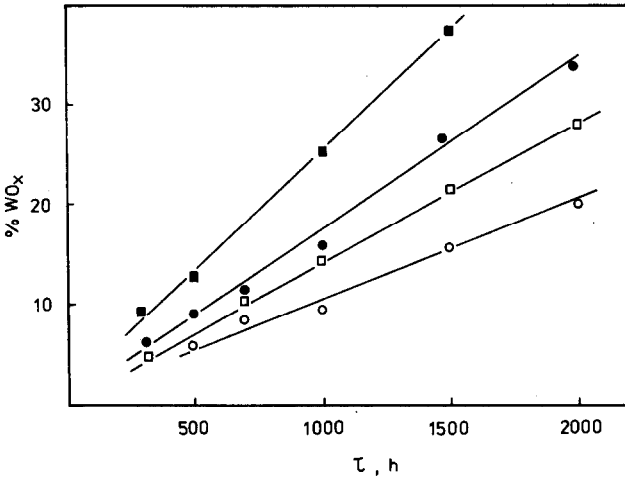

Fig. 1. Relation between the amount of tungsten oxides (wt.%) in tungsten carbides: □, WC$_{(1)}$; ■, WC$_{(2)}$; ○, WC$_{(3)}$; ●, WC$_{(4)}$ and corrosion time in 4.5N H$_2$SO$_4$, in air; T = 20 °C. Rate constants (WO$_x$ wt.% for τ = 100 h): □, 1.5; ■, 2.5; ○, 1; ●, 1.75.
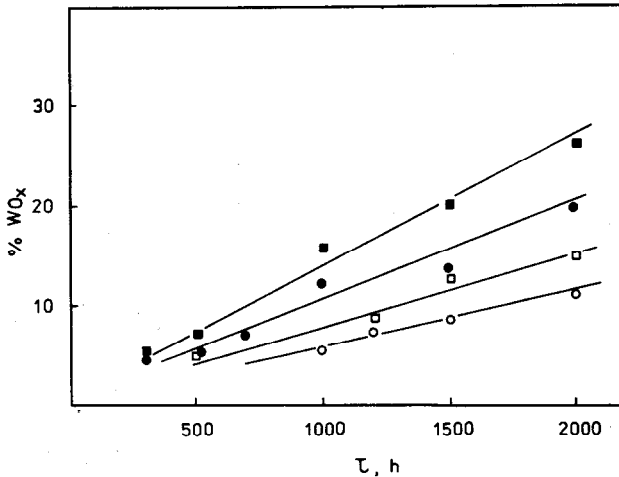
Fig. 2. Relation between the amount of tungsten oxides (wt.%) in tungsten carbides: □, WC$_{(1)}$; ■, WC$_{(2)}$; ○, WC$_{(3)}$; ●, WC$_{(4)}$ and corrosion time in 9.9N H$_2$SO$_4$, in air, T = 20 °C. Rate constants (WO$_x$ wt.% for τ = 100 h): □, 0.8; ■, 1.45; ○, 0.65; ●, 1.

function of time. The oxides WO_2 and WO_3 are given as WO_x, since there are no analytical methods to determine them separately.

The Figures show that in all cases the quantity of oxides increases linearly with time. This proves that the WO_2 layer formed on the WC particle surface does not protect the catalyst against further oxidation. The linear increase of the qu   tity of oxides with time offers the possibility of evaluating the corrosion ....e in different electrolytes. If there were no oxides on the surface of the catalyst initially, the relation between the quantity of oxide "g" and time is given by the equation:

$$g = \tau k$$

where "k" is the rate constant of the process. The values of k (weight percent. WO_x for $\tau = 100$ h) for the samples investigated are given in the captions to Figs. 1 and 2. Their values and the Figures show that the carbides differ with regard to their corrosion resistance. A comparison between the corrosion rate of the catalysts in both electrolytes shows that corrosion is faster in 4.5N H_2SO_4.

Causes of the different corrosion resistance of the carbides studied

The different corrosion resistance of solid solutions such as tungsten carbide can be due to: (i) inclusion of different impurities in the WC during synthesis; (ii) different bound carbon contents in the crystal lattice; (iii) structural peculiarities — anisotropy of the crystal surface with respect to corrosion resistance, dislocations and other crystal defects, segregation between separate crystals, different size of the particles. Since the impurities in the four initial raw materials are approximately equal in quantity [2], and the investigated carbides are selected so as to contain equal amounts of bound carbon in the crystal lattice, causes (i) and (ii) may be eliminated, and obviously the causes must be sought in the different structural peculiarities inherent in the preparation conditions.

In Table 1 are juxtaposed the surfaces of the catalysts, determined by BET tests, with the respective corrosion potentials reached in both electrolytes after one hour.

Table 1 shows that samples with a highly developed specific surface ($WC_{(2)}$ and $WC_{(4)}$) have a higher initial corrosion potential, and from Figs. 1 and 2 it follows that the quantity of oxides in the same samples is higher. This suggests that the surface plays a decisive role in the corrosion resistance of tungsten carbides if they differ substantially in terms of surface (compare $WC_{(1)}$ and $WC_{(3)}$ with $WC_{(2)}$ and $WC_{(4)}$).

In all cases the effect of the initial raw material, particularly the crystal habit of the particles [2], is demonstrated by the different corrosion resistance of carbides with almost identical specific surfaces, but synthesized from different raw materials ($WC_{(1)}$–$WC_{(3)}$ and $WC_{(2)}$–$WC_{(4)}$). The investigations proved that in this case also, after exposure for $\tau = 300$ h in 4.5N H_2SO_4 and $\tau = 500$ h in 9.9N H_2SO_4, the problem is reduced to the different changes of the specific surface during corrosion. Table 2 shows that the

TABLE 2

Surface area (m^2/g) (BET) of tungsten carbides after different corrosion exposure times (τ)

(a) In 4.5N H_2SO_4.

WC No	τ (h)								
	0	48	100	300	500	700	1 000	2 000	2 000*
1	3.74	–	3.85	7.45	7.93	8.50	9.73	11.38	10
2	10.02	–	–	14.1	17	17.64	17.9	18.7	17.1
3	4.36	–	4.72	4.90	5.52	5.93	5.88	6.16	5.63
4	10.38	9.28	–	9.06	11.73	12.64	12.88	12.33	11.93

*Surface area (m^2/g) (S_{BET}) of carbides $(\tau = 2\ 000$ h), after oxides removed by dissolution in 20% NaOH.

(b) in 9.9N H_2SO_4.

WC No	τ (h)				
	0	300	500	1 000	2 000
1	3.74	4.10	5.23	6.51	9.77
2	10.02	11.69	12	–	17.43
3	4.36	–	4.88	–	5.85
4	10.38	–	9.27	10.54	11.63

surface of all samples increases with increase in exposure time. This alteration is more pronounced with samples synthesized from the acid ($WC_{(1)}$ and $WC_{(2)}$). Among samples synthesized from identical starting materials, more pronounced changes occur to catalysts with a smaller surface (juxtapose $WC_{(1)}$ with $WC_{(2)}$ and $WC_{(3)}$ with $WC_{(4)}$).

The measurements of the specific surface, after the oxides are dissolved in hydroxide solutions, of the samples subjected to corrosion tests in 4.5N H_2SO_4 (the last column in Table 2(a)) show that the surface slightly decreases after this treatment, but still remains substantially higher than that of samples not subjected to corrosion. This proves that during the corrosion process the carbide surface really increases.

The SEM photographs of samples after different corrosion times give information about the processes which are involved in the increase of the surface. These processes are more distinctly revealed in samples synthesized from H_2WO_4 (w).

Figure 3 gives, at rather low magnification, the general appearance of sample 1 prior to corrosion (a), and after 1 000 h exposure to corrosion (b). It can be noted that the crystal habit of the particles in both cases differs substantially. The distinct contours of the catalyst grains in (a) have disappeared and a porous structure with no distinctly visible particle boundaries is seen in (b). Figure 4 at a tenfold higher magnification traces the alterations
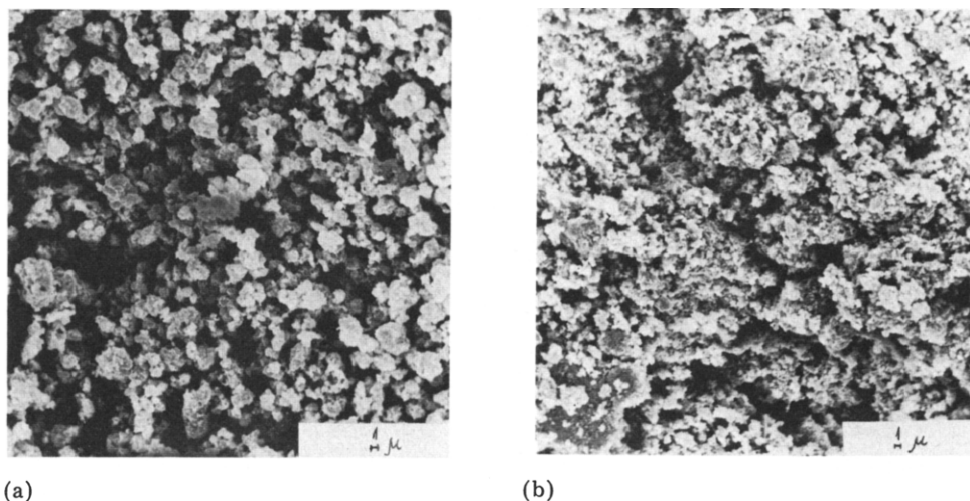
(a)   (b)

Fig. 3. S.e.m. photographs of $WC_{(1)}$. (a) Before corrosion; (b) after corrosion in 4.5N H_2SO_4, $\tau = 1\ 000$ h.

to which the catalyst grains are subjected during the corrosion process. It can be seen clearly how, with increase in corrosion time, the coarse carbide grains disintegrate into smaller particles. Probably, in this case, intergranular corrosion occurs between the small crystals forming the large crystallites, and, as a result, the coarse particles are broken (intercrystallite corrosion).

A plausible explanation of the alterations observed in the specific surface may be the different extent of segregation of the carbide particles. WC samples synthesized from H_2WO_4 display a higher degree of segregation due to the higher values of specific surface, that is smaller grain size. Among carbides synthesized from identical starting materials, the lower the specific surface values, the more pronounced is the degree of segregation. This explains the experimental fact that the surface of carbides synthesized from tungstic acid undergoes more pronounced alteration, while in the case of carbides synthesized from identical starting materials these changes are more distinct with catalysts characterized by a smaller surface.

A plausible cause for the different corrosion resistance in the two electrolytes may be the different rate of the anodic reaction of the corrosion process and/or the different concentration of the depolarizer in the two electrolytes.

The role of the depolarizer may be played by oxygen, whose potential under the experimental conditions is more positive than that of the carbide. This is proved by the following experiment: the least corrosion resistant sample $WC_{(2)}$ after $\tau = 500$ h in 4.5N H_2SO_4 and an Ar atmosphere showed no presence of oxides. Parallel tests in an oxygen atmosphere under identical conditions showed an oxide content above 10% (Fig. 1).
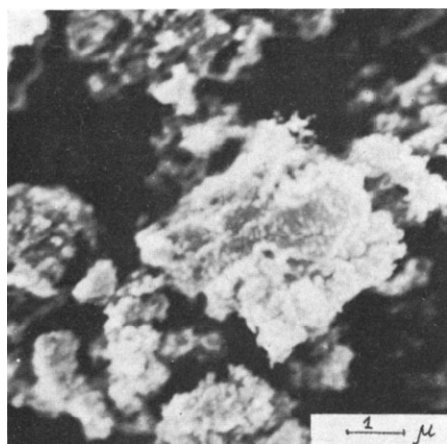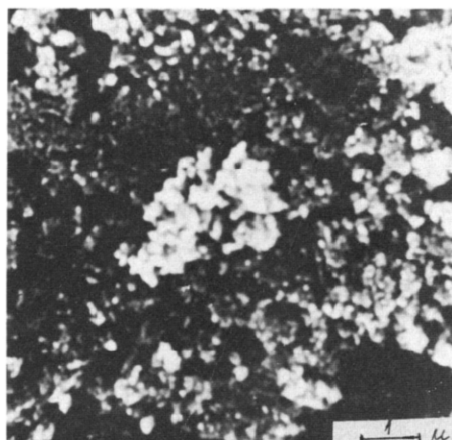
(a)
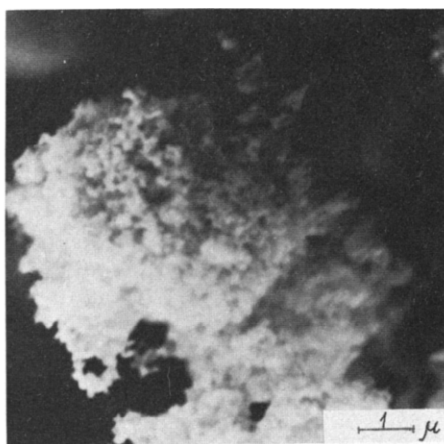
(b)
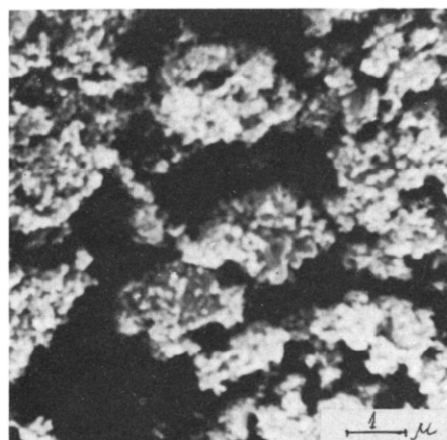
(c)

(d)

Fig. 4. S.e.m. photographs of $WC_{(1)}$. (a) Before corrosion; (b), (c), (d) after corrosion in 4.5N H_2SO_4, $\tau = 300$ h; $\tau = 500$ h; $\tau = 1\,000$ h, respectively.

According to literature data [6], the solubility of oxygen is lower in the more concentrated solution ($\alpha_{4.5N\ H_2SO_4} = 0.020$, $\alpha_{10N\ H_2SO_4} = 0.014$)*. Hence, the cathodic reaction of the corrosion process will proceed more slowly in the more concentrated electrolyte.

In all cases the rates of the anodic reaction in the presence of oxygen can be compared on the basis of the potentiostatic anodic polarization curves shown in Fig. 5. It is shown that the curve traced in the Ar atmosphere in 9.9N H_2SO_4 shifted in the anodic direction as compared with that traced in

*— Bunsen coefficient: gas volume (reduced to 0 °C, 760 mmHg) dissolved in unit volume of liquid at partial gas pressure 760 mmHg.
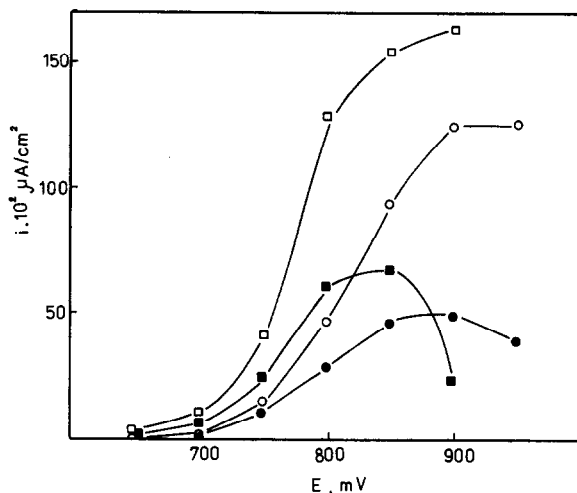
Fig. 5. Potentiostatic current density potential curves for $WC_{(2)}$, 10 min intervals between points. □, ○, in air in 4.5N H_2SO_4 and 9.9N H_2SO_4, respectively; ■, ●, in Ar in 4.5N H_2SO_4 and 9.9N H_2SO_4, respectively.

4.5N H_2SO_4. This reflects the fact that the anodic process slows down in the more concentrated solution. The presence of oxygen increases the current densities and the differences become more pronounced (Fig. 5), which is probably due to the lower solubility of oxygen in 9.9N H_2SO_4.

The experimental results suggest strongly that the higher corrosion resistance of the investigated carbides in 9.9N H_2SO_4 is due to the combined effect of both factors: the lower solubility of oxygen, and the slower rate of the anodic reaction in it.

Conclusions

The corrosion resistance of tungsten carbide depends on the method of preparation. Under identical carburation temperatures and corrosion test conditions, carbides synthesized from the white modification of tungstic acid are less corrosion resistant than those prepared from WO_3. Of two carbides synthesized from identical starting material, but at different temperatures, the one prepared at higher carburation temperature, which also has smaller specific surface, displays an increased corrosion resistance. Corrosion rates of tungsten carbides increase in diluted sulfuric acid solutions.

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