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Hydrogen evolution on Ni/WC composite coatings

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Abstract

The catalytic activity for the hydrogen evolution reaction (HER) of Ni/WC composites obtained by electrochemical deposition of nickel from a conventional Watt's bath, using two different ways of depositing the WC particles, was investigated. All the composite coatings exhibited electrocatalytic activity for the HER larger than that of pure Ni in both alkaline and acid solution. The activity increased with increasing content of WC in the coating and, in the pulsed current regime, with increasing frequency of pulsation. In addition, coatings with smaller particles incorporated exhibited higher activity than those with larger particles. At a constant potential, an order of magnitude higher current densities were obtained in some cases.

1. Introduction

Considerable attention has been paid to the search for active cathode materials for hydrogen evolution in alkaline and acid solutions. The kinetics of H_2 evolution from bases has been widely investigated at Ni [1–8] and at Ni-based alloys [9–15].

The electrocatalysts used nowadays in industrial electrolysers are composite materials. In spite of the many different concepts which have been developed for considering the electro catalytic properties of composite materials [9, 16–18], predicting their catalytic activity is still difficult. This is because no theory describing all the kinetic, potential and surface effects contributing simultaneously to the electro catalytic properties of materials has yet been developed. As a result, the electro catalytic properties of most materials, including composite materials, have hitherto been determined by measuring their exchange current density and Tafel slope and not by prediction from theory.

A few concepts have been developed which deal with the prediction of electro catalytic properties of composite materials [9, 16–18].

Bearing in mind that Ni-based electrochemical coatings have a better activity for the cathodic evolution of hydrogen compared to pure Ni [12–15] and also the high activity of tungsten carbide, WC, for hydrogen evolution, Ni/WC composite coatings were tested for their catalytic activity for the hydrogen evolution reaction and compared with those of pure Ni, which is usually employed for this purpose.

The high activity of WC for cathodic hydrogen evolution in acid solutions was discovered by Bianchi et al. [19]. In the HER, WC electrodes have an activity which is only one order of magnitude lower than that of Pt and they are extremely stable during the cathodic process [20].

Carbide cathodes based on tungsten have been thoroughly investigated [21–24].

The mechanism of hydrogen evolution on tungsten carbide provokes special interest due to the fact that tungsten carbide also adsorbs hydrogen well [25, 26]. Hydrogen evolution on smooth tungsten carbide in 1 M H_2SO_4 obeys the Tafel equation [27, 28]; a coefficient *b* of 135 mV at 22 °C has been reported [27], whereas the same coefficient was 65 mV at 50 °C [28].

Serious difficulties in establishing the mechanism of electrode processes on carbides arise from the fact that the kinetics depend on the method of preparation of the material and the available data are contradictory.

Sokolsky et al. [21] and Zoltowsky [23] investigated hydrogen evolution on smooth WC disks prepared according to the same technique. However, the values of *i* differed by at least one order of magnitude: within the same region of η, in one study [21] one linear section was obtained with $b = 100–115$ mV/dec, while in the other [23], a section with $b = 65$ mV/dec was obtained at low η with a slow increase in the value of b with increasing overvoltage.

An analysis of literature data [21–28] showed that the differences between the data obtained by different authors could be connected not only with the different methods of preparation and dispersity of the carbides, but also with features of the method used for the measurement of the log $i - \eta$ curves.

The kinetics of the hydrogen evolution reaction on smooth stoichiometric tungsten and chromium carbides were investigated in order to determine the mechanism of the process in the absence of any complicating phenomena such as dispersity, defects in the crystalline lattice, etc. [29]. The authors were of the opinion that the most satisfactory interpretation was that hydrogen evolution proceeded predominantly on metallic atoms, which are much less oxidized in the presence of carbon than on the surface of metallic tungsten (this last assumption has generally been accepted [30]). Taking into account the last observation [29], the activity of Ni/WC composites could be expected to increase with increasing WC content in the coating. The weight percentage of WC in a deposited layer depends on the plating conditions [31–35]. Accordingly, in the present work the HER was investigated on Ni/WC composite coatings containing different amounts of WC, resulting from the different method of preparation. The first type of coating (I) was obtained by electochemical deposition on a RDE using a pulsating current from an electrolyte containing Ni and WC particles, and the second type (II) was obtained using a new technique whereby WC from an aqueous suspension was deposited onto the substrate prior to electrochemical deposition of Ni [31, 32].

2. Experimental details

The HER in NaOH solutions was investigated on pure Ni and Ni/WC composite coatings obtained in two ways: (a) by the simultaneous electochemical deposition of Ni with a pulsating current on the rotating disc electrode (RDE) from a conventional Watt's bath containing suspended WC particles whereby the WC particles were mechanical trapped (occluded) by the depositing metal; and (b) by deposition of WC onto the substrate from an aqueous suspension followed by electochemical deposition of Ni from a pure Ni-bath.

The catalytic activity for the HER was investigated in 1 M NaOH solution and 0.5 M H_2SO_4. All experiments were carried out in a classical 3-electrode electrochemical cell. A Pt wire encased in a compartment separated by a porous glass disc served as the counter-electrode. A SCE connected to the investigated electrodes via a Luggin capillary served as the reference electrode.

Two sets of samples were investigated with respect to their catalytic activity for the HER. In the first set, composite coatings were obtained by the electrochemical deposition from a Watt's bath containing WC particles using a pulsating current. The average current density was $j_{av} = 2.5$ mA cm^{-2}, the duration of on- and off-periods was the same, $p = 1$, and the frequencies were $\nu = 20$, 50 and 100 Hz. In the second case, a steel disk electrode was electroplated from a Watt's electrolyte until a 5 μm thick Ni coating had been formed. Then a suspension of 0.4 or 0.7 μm WC particles in water was dropped on to it using a micropipette. After drying and covering with a Nafion solution, a 0.2 or 0.4 μm thick layer of Ni was electrodeposited over the 0.4 μm WC particles, that is a 0.2, 0.4 or 0.6 μm thick layer of Ni over the 0.7 μm WC particles.

Polarization curves for the HER were recorded using the galvanostatic technique. Steady-state values of the potential recorded at each current density were taken after 100 s. All the values were corrected for the ohmic drop, which was assessed from galvanostatic pulse readings.

The Ni and Ni/WC coatings were electrochemically characterized using cyclic voltammetry.

A potentiostat/galvanostat Stonehart BC 1200 with a function generator PAR 175, a NICOLET oscilloscope and a PHILIPS PM 8143X-Y recorder were used for all the experiments.

All solutions were deaerated with purified nitrogen before recording the cyclic voltammograms and the steady-state investigations. Measurements were made at room temperature (23 ± 1 °C).

All the solutions were prepared from analytical grade reagents and high purity Millipore (18 M Ωcm) water. The aqueous solution of Nafion used for covering the WC layer was made from a commercial 5% (w/w) alcohol solution of Nafion (1100 E.W. Aldrich).

3. Results and discussion

In order to establish the effects of introducing WC into the deposits, cyclic voltammograms were first recorded for both pure Ni and the Ni/WC composites (Fig. 1). The current values in the passive region for pure Ni and Ni/WC composites, which reflect the surface capacitance, were found to be similar for all the composites obtained by electrochemical deposition (procedure I), as well as for the Ni/WC composites obtained by the second procedure (II) with 0.7 μm WC particles. On the other hand, the current values in the passive region for the coatings with 0.4 μm WC particles obtained by the second procedure were three times smaller. As all the condition were the same, it could be concluded that the active surface was much smaller in the second case, indicating a more compact and smoother (less porous) surface than in the first case. The morphologies of the deposits were presented in previous papers [31, 32].

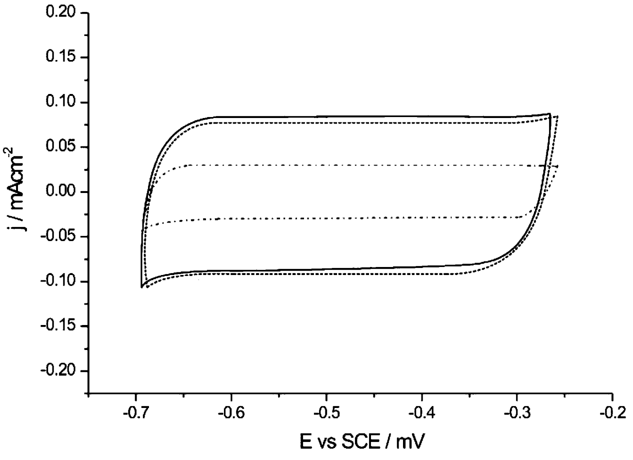

Fig. 1. Cyclic voltammograms obtained in 1 M NaOH solution on pure Ni (——) and on the Ni/WC composites containing WC particles of 0.4 μm and 0.7 μm (– – –) deposited using pulsating currents of different frequencies (at j_{av} = 2.5 mA cm^{-2}, p = 1, rpm 3000) and Ni/WC composites containing 0.7 μm WC particles obtained using a Nafion solution, as well as those obtained on the Ni/WC composites obtained using a Nafion solution (–•–•–) but containing 0.4 μm WC particles.

When recording the kinetics of the HER, linear Tafel lines with slopes of about 120 mV/dec were obtained for all the investigated substrates.

Figure 2 shows the Tafel plots obtained in 1 M NaOH solutions for pure Ni and for the composites deposited electrochemically using a pulsating current at different frequencies of pulsation with 0.4μm (Figure 2a) and 0.7 μm (Figure 2b) WC particles. As can be seen, Tafel plots with slopes of about 120 mV/dec were obtained over three orders of magnitude of the current density. It can be observed that the Tafel lines shift to higher current densities with increasing frequency of current density pulsation.

The influence of the size of the WC particles built into the composite coatings on the HER in 1 M NaOH is presented in Figure 3. As can be seen, linear Tafel plots with a slope of 120 mV/dec were again obtained. The composite coatings containing the smaller WC particles exhibited higher activities for the HER.

Similarly, the Ni/WC composite coatings obtained using the Nafion solution exhibit good activities for the HER. As can be seen in Figure 4, the composite coating with 0.4 μm WC particles, in which the WC particles were only partially, half-covered by Ni (a 0.2 μm Ni layer covering the 0.4 μm large particles), were much more active than the coatings where the WC was completely covered by Ni (0.4 μm Ni deposited onto a layer of WC particles). However, in both cases, the rate of the HER at the same potential was larger than that on pure Ni. It should be mentioned that the current densities for the Ni/WC composite coatings with 0.4 μm WC particles were calculated for the real, rather than for the geometric surface. Ni/WC composite coatings with 0.7 μm WC particles, obtained in a similar manner, exhibited smaller activities for the HER than the coatings containing 0.4 μm WC particles.

It was reported earlier [31, 32] that both the particle size and the frequency of current pulsation affect the WC content in electrochemically deposited coatings. The smaller the size of the particles and the larger the frequency of pulsation, the greater is the content of WC particles in the coating. Using these data, as well as the results of Figures 2–4, the current densities of the HER at a potential of -1.3 V as a function of the content of WC particles in the coatings for both methods of coating preparation is shown in Figure 5.

Increasing content of WC in the coating leads, in all cases, to a significant increase in the activity for the HER. This is reasonable bearing in mind the high activity of tungsten carbide, WC, with respect to hydrogen evolution [19, 20]. In accordance with the opinion of a group of authors [29], hydrogen evolution on WC proceeds predominantly on metallic atoms, which are much less oxidized in the presence of carbon

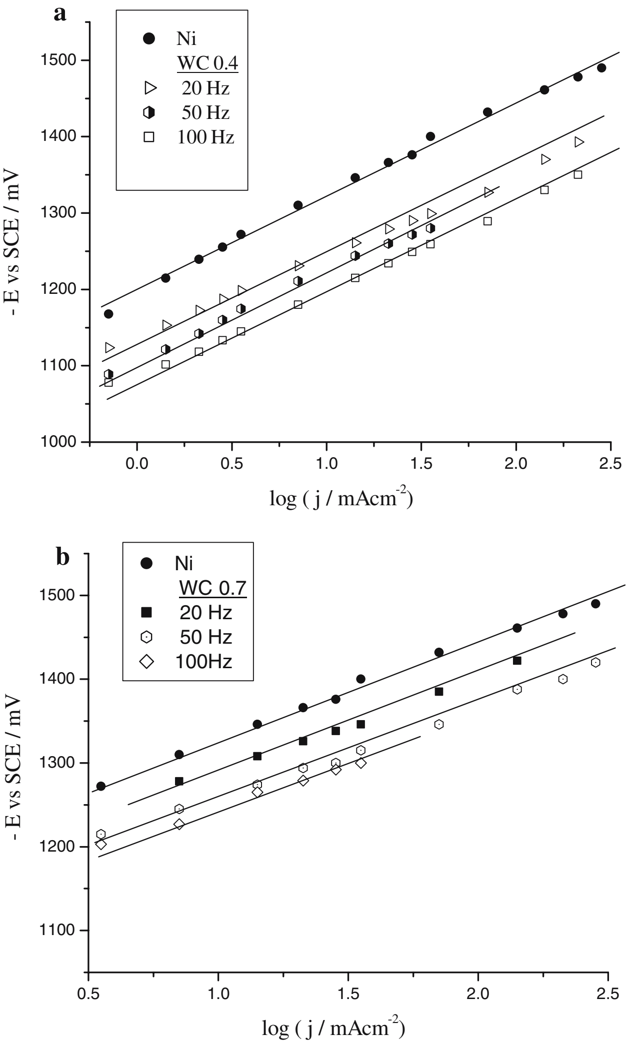

Fig. 2. (a) Tafel plots obtained in 1 M NaOH for electrodes of pure Ni and of Ni/WC composites containing 0.4 μm WC particles, deposited using pulsating currents of different frequencies (at j_{av} = 2.5 mA cm^{-2}, p = 1, rpm 3000). (b) Tafel plots obtained in 1 M NaOH for electrodes of pure Ni and of Ni/WC composites containing 0.7 μm WC particles, deposited using pulsating currents of different frequencies (at j_{av} = 2.5 mA cm^{-2}, p = 1, rpm 3000).

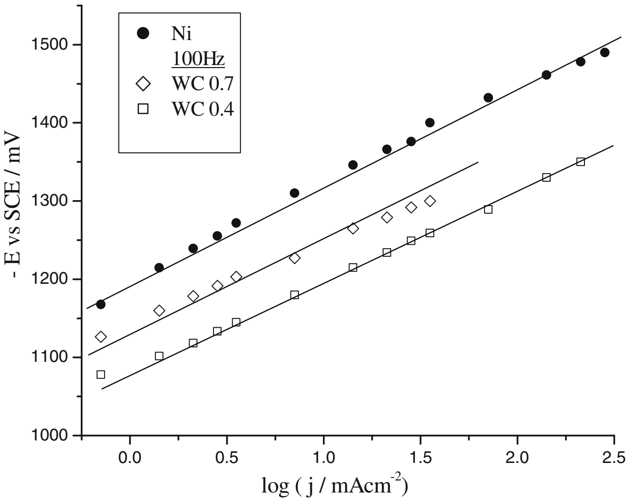

Fig. 3. Tafel plots obtained in 1 M NaOH for electrodes of pure Ni and of Ni/WC composites with 0.4 and 0.7 μm WC particles, deposited using a current pulsating at a frequency of 100 Hz (at $j_{av} = 2.5$ mA cm^{-2}, $p = 1$, rpm 3000).

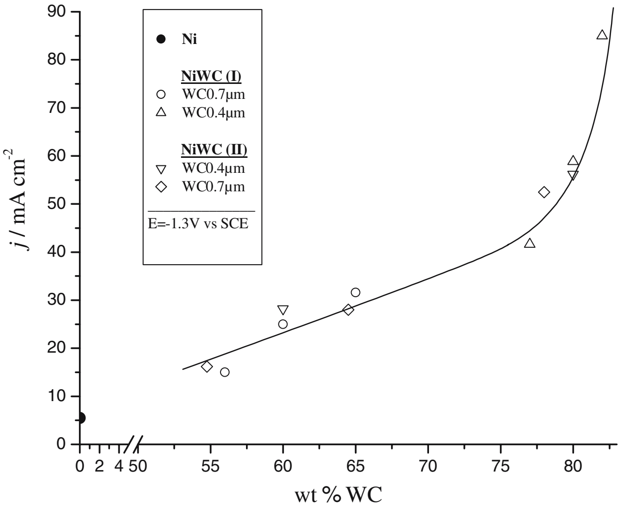

Fig. 5. Current density for the HER on Ni/WC composites at a constant potential of -1.3 V vs. SCE as a function of the WC content in the deposits obtained in the two different ways (I and II).

than those on the surface of plain metallic tungsten. Taking into account this observation [29], it is to be expected that the activity of Ni/WC composites would increase with increasing WC content in the coating. The increase in the activity for the HER with increasing content of WC in the coating, which was observed in all the cases examined in this study, could also be explained in terms of the larger contact surface of the WC particles and Ni.

In acid solution (0.5 M H_2SO_4), the Ni/WC composite coatings also exhibited a similar electrocatalytic activity for the HER. As can be observed immediately from Figure 6, at a constant potential, the current densities obtained for Ni/WC composite coatings were more than one order of magnitude higher than those obtained with pure Ni. If the results for the HER on Ni/WC are compared with those published earlier [21] for pure WC, it can be seen that the Ni/WC coatings exhibited activities for the HER similar to that of pure WC.

Considering the fact that the maximum content of WC in the composites was 80%, lower activities of the Ni/WC composites for the HER as compared to pure WC could be expected. The expected decrease in the activity due to the smaller amount of WC may be compensated by an increase in the number of active sites for the HER at the interfaces between the WC particles and Ni.

4. Conclusions

All the investigated Ni/WC composite coatings exhibited a larger electrocatalytic activity for the HER than

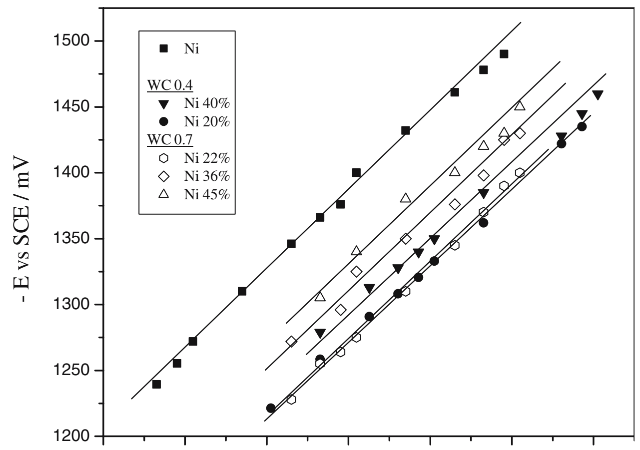

Fig. 4. Tafel plots for the HER in 1 M NaOH on pure Ni and on Ni/WC electrodes containing of 0.4 and 0.7 μm WC particles, obtained using a Nafion solution.

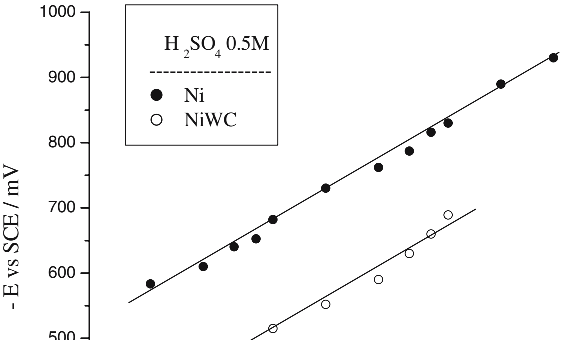

Fig. 6. Tafel plots obtained in 0.5 M H_2SO_4 for electrodes of pure Ni and the Ni/WC composite containing 0.4 μm WC particles, deposited using a current pulsating at 100 Hz (at $j_{av} = 2.5$ mA cm^{-2}, $p = 1$, rpm 3000).

that of pure Ni, both in alkaline and acid solutions. The activity depended on the method of preparation of the composite material, as well as on the conditions of its electrodeposition, which had an impact on the content of WC particles in the coatings.

The activity for the HER increased with increasing WC content in the coating and, in the pulsating current regime, with increasing frequency of pulsation. Coatings containing smaller particles exhibited higher activity than those containing larger particles. In some cases, current densities larger by an order of magnitude were obtained at constant potential. Deposits obtained by electochemical deposition of Ni using pulsating current from an electrolyte containing Ni ions and WC particles, exhibited higher activities than those obtained by depositing WC particles from an aqueous suspension onto the substrate prior to electrochemical deposition of Ni.

The increase in the activity for the HER with increasing WC content in the coating is expected considering the high basic activity of WC with respect to hydrogen evolution. Also, a higher specific content of WC in the coating resulted in an increase in the number of active sites for the HER at the interfaces between the WC particles and Ni.

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