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Electrochemical corrosion behaviors of straight WC–Co alloys: Exclusive variation in grain sizes and aggressive media

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ABSTRACT

The electrochemical corrosion behaviors of straight WC–10Co cemented carbides with grain sizes of 1.2, 2.6, 6.1 and 8.2 μm, were comparatively investigated in the solutions of NaOH (pH = 13), Na_2SO_4 (pH = 7) and H_2SO_4 (pH = 1) respectively. To insure a sole variable of WC grain sizes, specific magnetic saturation values of the alloys are adjusted to be identical. The results show a good linear dependence for R_{ct} (charge transfer resistance) and I_{corr} (corrosion current density) against the grain sizes. A high sensitivity of the grain sizes to both R_{ct} and I_{corr} are identified in NaOH and H_2SO_4. In the solutions of NaOH and Na_2SO_4, the alloys with smaller WC grain sizes exhibit better corrosion resistances, while the alloys with larger WC grain sizes exhibit better corrosion resistances in H_2SO_4. Additionally, in terms of the corrosiveness, NaOH is the weakest and H_2SO_4 is the most aggressive for all the alloys. The corrosion mechanisms were discussed in light of the SEM surface observation, X-ray photoelectron spectroscope analysis and the electrical equivalent circuits for electrochemical impedance spectroscopy.

1. Introduction

Cemented carbides are susceptible to oxidation, chemical corrosion and erosion in industrial applications [1–4]. Once corroded, the surface properties and wear resistance deteriorate, which shortens the lifetime of the tools in service [5,6]. Therefore, improving the physical and corrosive wear resistance properties and selecting the right material are highly valued for a tool in complex working environments.

There are reports on the effect of WC grain sizes on the electrochemical corrosion resistance of cemented carbides. Human et al. [6] reported that there was no significant difference between the polarization curves with a change in the average WC grain size from 1 to 5 μm for straight WC–10Co alloys in the solution of 1 N H_2SO_4. However, Tomlinson et al. [7] reported that an increase in grain size (1.4 vs. 3.0 μm) increased the passive current density of straight WC–6Co alloys in acidic solutions. One of the reasons for the contradictory results is that neither the materials nor the solutions are identical in different studies. Limitation of the monotonous evaluation means, i.e. sole polarization curves is also responsible for the inconformity.

Kellner et al. [8] investigated the effect of WC grain size on the corrosion behavior of WC–Co based alloys in 1 M NaOH solution. Nevertheless, the compositions of the five investigated alloys were quite different. Kellner et al. [8] indicated that the grain size effect due to the fcc Co phase stabilization played a dominant role in the corrosion behavior; the chemical modifications of the alloys certainly had also an effect on the electrochemical behavior, but in this case seemed to play a secondary role. As VC and Cr_3C_2 additions are commonly used for grain refining, the chemical modifications of the alloys can influence the electrochemical behaviors [9,10]. Therefore, investigation of the effect of grain sizes on the corrosion behaviors should be carried out in the condition that only the WC grain size is modified to the alloys. Up to now, limited information is documented on the effect of WC grain sizes on the corrosion behaviors of straight cemented carbide system. Nevertheless, the effect of grain sizes on corrosion behaviors in other material system has been intensively investigated by a number of researchers [11–14].

The aim of this work is to perform a systematic investigation on the effect of WC grain sizes and aggressive media on the electrochemical corrosion behaviors of straight WC–Co cemented carbides. Potentiodynamic polarization curve and electrochemical impedance spectroscopy (EIS) techniques are employed to investigate the electrochemical behaviors in H_2SO_4 (pH = 1), Na_2SO_4 (pH = 7) and NaOH (pH = 13) solutions at room temperature.

2. Experimental details

2.1. Alloy preparation

Commercial WC powders and $CoCl_2 \cdot 6H_2O$ were used as the raw materials. A hydrazine-reduction chemical route [15–18] was chosen to prepare Co coated WC powders, followed by a treatment under H_2 atmosphere at 500 °C for 40 min and wet-milling with paraffin wax in

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Table 1
Fisher subsieve sizer (FSSS) particle sizes of WC raw materials, WC grain sizes and specific magnetic saturation values (*Ms*/Co) of WC–10Co alloys.

Alloy	FSSS of WC powder μm	WC grain size of alloy μm	*Ms*/Co %
1#	3.4	1.2	96.3
2#	8.0	2.6	96.1
3#	10.0	6.1	96.0
4#	30.8	8.2	96.8

cyclohexane for the preparation of the four WC–10Co alloys with different WC grain sizes. Dewaxing and sintering of the pressed specimens were performed in a sinter-HIP furnace. The sintering parameters were as follows: temperature: 1430 °C; Ar pressure: 5.6 MPa; and residence time: 90 min. The Fisher subsieve sizer (FSSS) particle sizes of WC raw materials, WC grain sizes and the specific magnetic saturation values (*Ms*/Co) of the alloys are listed in Table 1. As is reported that the tungsten and carbon contents in cobalt influence the corrosion behavior [19,20], to insure a sole variable of WC grain size in this investigation, the values of Ms/Co of the alloys are adjusted to be identical through the adjusting of the carbon content in the alloys, as shown in Table 1. The microstructures of the polished sections of the four alloys are shown in Fig. 1. A commonly used linear intercept method was used to determine the WC grain size. According to the standard proposed by Sandvik Hard Materials [21], alloys 1#–4# belong to fine, medium coarse, extra coarse and S-grade, respectively.

2.2. Electrochemical measurements

To test the consistency of the results, we carried out both potentiodynamic polarization analysis and EIS analysis, which were realized by using a CHI 660E electrochemical workstation with a typical three-electrode configuration at the temperature of 25 ± 1.5 °C. The test specimens as working electrode were placed in a Teflon holder and the exposed surface area to the corrosive medium was 1 cm^2. A saturated calomel electrode (SCE) and a platinum sheet were used as the reference electrode and counter electrode, respectively. All potentials were reported vs. the SCE. NaOH (pH = 13), Na_2SO_4 (pH = 7) and H_2SO_4 (pH = 1) solutions were selected as electrolytes in open air. Prior to the measurements, the specimens were immersed in the corresponding electrolyte for 30 min to establish the open circuit potential (E_{oc}).

The EIS measurements were carried out at a steady-state E_{oc} using a frequency range from 10 mHz to 100 kHz (10^{-2}–10^5 Hz) with amplitude of sinusoidal wave of 5 mV and auto-sensitivity. Based on an appropriate electrical equivalent circuit (EEC), the Nyquist plots obtained from the EIS measurements were fitted by ZSimpWin software to calculate the corresponding parameters. The potentiodynamic polarization measurements were conducted after a steady-state E_{oc} test and were carried out with a scanning range from an initial potential of −200 mV vs. the E_{oc} to a final potential of +1500 mV. The scan rate was 5 mV/s and auto-sensitivity was chosen.

Both potentiodynamic polarization analysis and EIS analysis need special precautions for their results to be valid. The main complications in performing the measurements can be summarized in the following

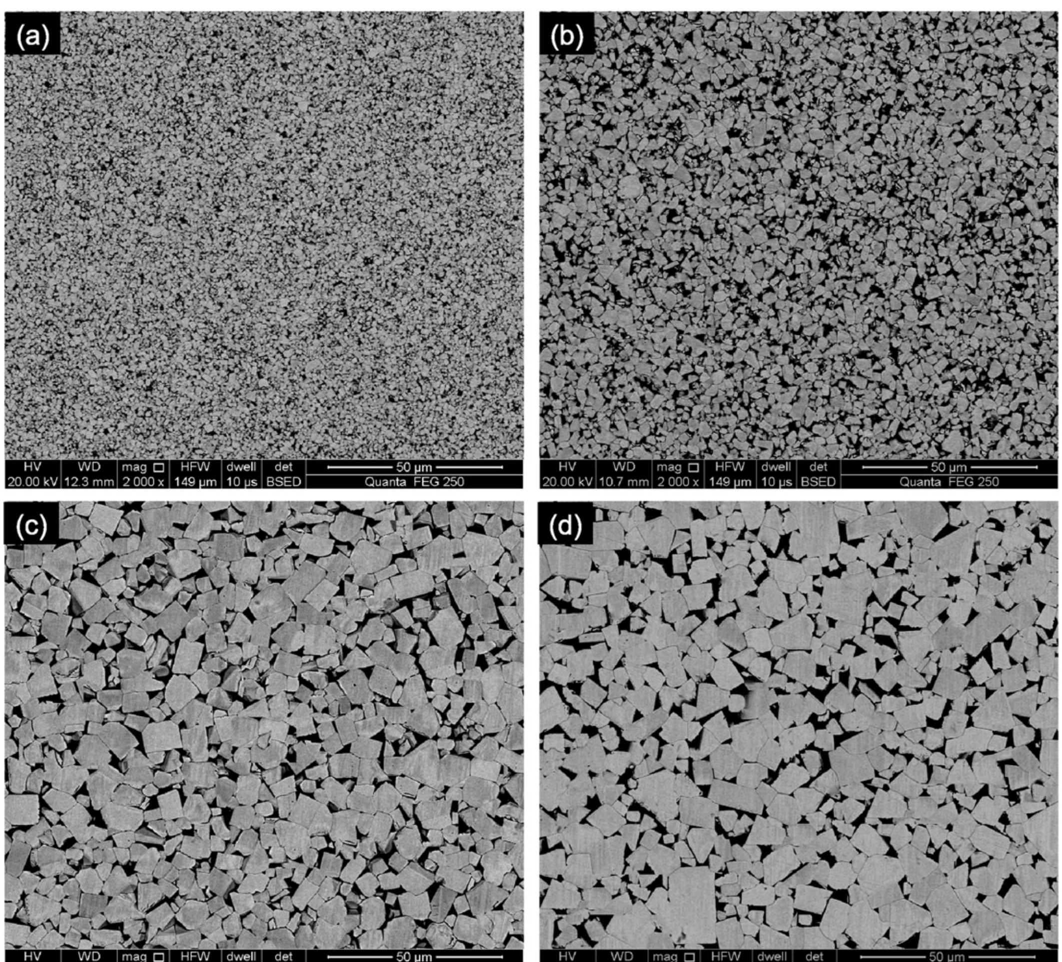

Fig. 1. SEM images of polished sections of WC–10Co alloys, (a)–(d): alloys 1#–4#.