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Effect of WC grain size on the corrosion behavior of WC–Co based hardmetals in alkaline solutions

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ABSTRACT

The corrosion behavior of hardmetals with different grain sizes was investigated in alkaline solutions by electrochemical methods. A clear tendency was observed that the smaller the grain size, the higher the corrosion resistance. Surface analytical characterization of the samples was carried out to obtain insight information on the origin of this behavior. Laterally resolved Auger Electron Spectroscopy revealed that significant amounts of W and C diffuse into the Co binder matrix during the sintering process, and that the W and C concentration in the Co phase increases with decreasing grain size. Moreover, the distribution of W and C in the binder phase is not homogeneous, instead a seam with a higher concentration is observed near the interface to WC. W and C dissolved in Co stabilize the fcc crystal structure of the Co binder, which is otherwise not thermodynamically stable at the room temperature. X-ray diffraction experiments demonstrate that the small-grained hardmetals showed a higher fraction of fcc Co in the structure. The higher corrosion resistance of the small-grained hardmetals may therefore be ascribed to the higher amount of fcc Co, which has a better corrosion behavior than hcp Co due to the higher thermodynamic stability. As Cr₃C₂ and VC additions were used for grain-refining, possible effects of the chemical modifications of the hardmetals on the corrosion behavior are shortly discussed.

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1. Introduction

Hardmetals are composite materials with a wide range of applications. In the hardmetal manufacturing process conventional powder metallurgical techniques are used, such as milling and liquid phase sintering [1–3]. The main feature of the hardmetal composite is the combination of a tough metal binder (mostly Co) with a hard material phase. This arrangement of phases offers an enhanced performance of certain material properties such as an excellent wear resistance [4–7]. As a result hardmetals are used as cutting tools, saw blades, valves and jet nozzles [5,6,8]. Technical applications of hardmetals are, however, limited by their poor corrosion resistance. Regarding the corrosion behavior of the two major alloying components, Co and W have opposite behaviors when considering the influence of environment acidity [9]: in alkaline solutions Co shows stable passivity, whereas W readily dissolves; the situation observed in acidic electrolytes is vice versa. Therefore, hardmetals typically fail by corrosion of the less resistant phase, which is defined by the environment [10]. Moreover, galvanic interactions between the phases of different nobility take place; WC typically is significantly more noble than Co [10]. Additions

of alloying elements such as Cr₃C₂ and Ni in the Co binder phase can generally enhance the corrosion resistance [11–14]. Moreover, small additions of TiC or TaC were found to significantly improve the corrosion performance [2,3,11]. Diffusion of W and C into the binder phase during the sintering procedure [3,11] also affects the corrosion resistance [15,16], due to a different electrochemical activity versus pure WC and Co [5]. Magnetic saturation measurements have been used to determine contents of these elements in the Co matrix [3,5]. By adding small amounts of Cr₃C₂ and VC, which inhibit the growth of the WC grains [1,3,17,18], the mechanical behavior can be further improved. A decrease of the grain size of WC can be expected to show also an influence on the corrosion behavior. A small-grain size increases the surface area of interfaces, and could enhance formation of galvanic couples on the material surface – both these factors could be expected to lead to an impairment of the corrosion behavior. The findings reported in the literature on the influence of grain size on the corrosion behavior, however, give no clear picture: Human and Exner found almost no influence of the grain size on the corrosion behavior in acids [5,19], while Tomlinson reported on an increase of the passive current densities by increasing grain size in acidic solutions [8]. As neither the materials nor the electrolytes are identical in the different studies, it is not possible to draw conclusions on the origin of the different findings.

In most of the hardmetal corrosion literature, the experiments have been carried out in acidic or neutral solutions [12,19–21],

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and only a few authors have reported on the behavior in alkaline media [4,11,22]. The high dissolution rates in acidic and neutral electrolytes may hinder observations on the effects of different microstructural parameters on the corrosion behavior (i.e. small-scale effects are lost in the large average reaction rates). The present investigation hence explores the corrosion behavior of hardmetals of different grain sizes in alkaline solutions, where passivation of the Co binder is possible.

2. Experimental

The hardmetals were manufactured by Tigra GmbH in Germany. The different samples vary in grain size, binder content and alloying elements, for an overview see Table 1. As a reference material, commercially pure Co sample and WC samples (purity 99.9%) were used.

The electrochemical investigations were carried out in aerated 1 M NaOH solution at the room temperature, using a three electrode cell, placed in a Faraday cage. A platinum gauze served as a counter electrode and an Ag/AgCl electrode in 3 M KCl with a potential of +207 mV versus SHE was the reference electrode. At first the WC–Co samples were polished with diamond/plastic coated discs (120 and 220 grit) from Struers and then diamond polished down from 6 to 1 μm with felt discs from Struers. Between each polishing step the samples were cleaned with ethanol in an ultrasonic bath. Electrochemical Impedance Spectroscopy (EIS), potentiostatic and potentiodynamic polarization techniques were used for characterization. The frequency range for the EIS was between 100 kHz and 10 mHz, and the amplitude of the signal was ± 10 mV. After immersion in the cell, the samples were let to reach equilibrium at the open-circuit potential for 2 h. Subsequently, EIS investigations were performed with a Zahner IM6 set-up. Next, potentiodynamic polarization curves were measured from -1.5 to 2 V with a scan rate of 5 mV/s. Auger Electron Spectroscopy (AES) was employed to detect the content and distribution of dissolved W and C particles in the Co binder. For this a Physical Electronics (PHI) 670 instrument with a 10 kV electron beam operating at 10 nA and with a tilt of 30° of normal was used. Sensitivity factors were used as provided by the instrument manufacturer. The lateral resolution of the Auger instrument was approximately 50 nm. X-ray diffractometry was performed with a X'Pert MPD PW 3040 instrument. The angle of incidence was 10°. Microstructural changes during corrosion were examined by a Hitachi FE-SEM 4800 instrument, with a voltage of 10 kV and a current of 11 μA .

3. Results

3.1. Electrochemical behavior

Fig. 1 shows the impedance spectra measured at the open-circuit potential for the different hardmetal samples in 1 M NaOH (for the values of the open-circuit potential see Table 2). Both the impedance values as well as the phase angle behavior indicate a clear grain size dependency of the electrochemical behavior: the polarization resistance R_p increases significantly with decreasing grain size and the broadening of the phase angle corresponds to

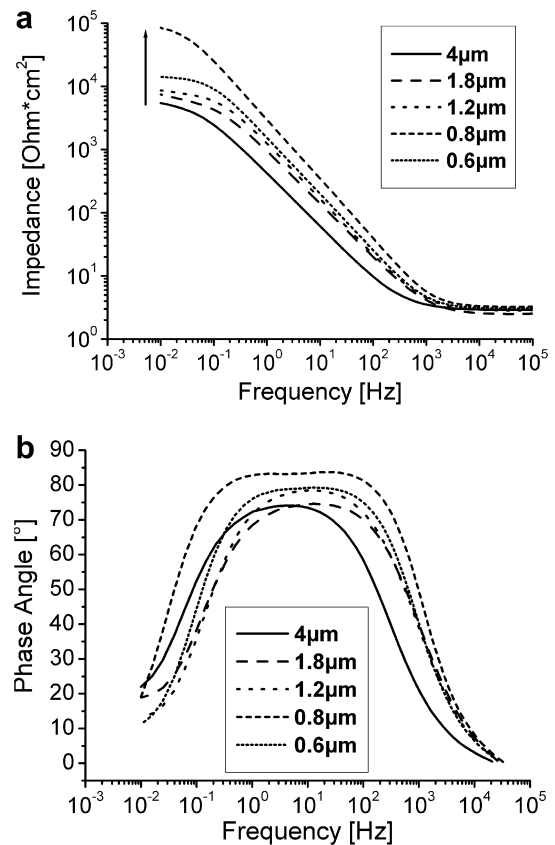


Fig. 1. Electrochemical impedance spectra of hardmetals with different grain sizes in 1 M NaOH measured at the open-circuit potential (a: impedance, b: phase angle).

an increase of the corrosion resistance. A positive effect of the small grain size is also seen in the potentiodynamic measurements (Fig. 2). Similar to the behavior of pure Co, an active/passive-transition is observed for the WC–Co samples, whereas pure WC shows active dissolution starting from a significantly more noble potential than pure Co or the hardmetal samples. An exception to this is the sample with a grain size of 0.8 μm , which shows a behavior similar to the pure WC sample. As indicated in Table 1, this sample contains only 3.2 wt% of the Co binder (instead of ≈ 6 wt% as in the other hardmetal samples). Moreover, the sample contains Ni in the Co binder. Seemingly this leads to an electrochemical behavior similar to pure WC, illustrating that the small areas of the Co/Ni-binder are spontaneously passivated in this case, and hence Co-type active/passive-transition is not observed for this sample.

For the other hardmetal samples, smaller grain size reduces the critical current density i_{crit} , the passive current density i_{pass} and the corrosion current density i_{corr} (see Fig. 2 and Table 2). In comparison to the behavior of pure Co, the passive range of the hardmetals is limited by the onset of WC dissolution at relatively low potentials. Contrary to the behavior in 1 N H_2SO_4 as studied for example by Sutthiruangwong, Mori and Human et al. [3,11,16], in 1 M NaOH hardmetals show a true passive behavior (even if of limited poten-

Table 1
Grain sizes and composition of the hardmetals from Tigra.

Material	Co-content [wt%]	Grain size [μm]	Cr_3C_2 -content [wt%]	VC-content [wt%]	Ni-content [wt%]	Mo_2C -content [wt%]
WCCo6	6	4.0	–	–	–	–
WCCo6.5Cr ₃ C ₂ 0.2	6.5	1.8	0.2	–	–	–
WCCo6Cr ₃ C ₂ 0.2VC0.05	6	1.2	0.2	0.05	–	–
WCCo3.2Ni1.1	3.2	0.8	0.35	–	1.1	0.1
WCCo6Cr ₃ C ₂ 0.9	6	0.6	0.9	–	–	–

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