The mechanism of anodic dissolution of cobalt in neutral and alkaline electrolyte at high current density

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ABSTRACT

The anodic dissolution of cobalt is investigated in neutral and alkaline electrolytes at high current densities. Beside electrochemical measurements, the amount of dissolved cobalt is investigated by UV–vis-spectroscopy. The measurements are completed by optical measurements of the metal removing. It is shown that cobalt can be anodically dissolved in alkaline solutions by using a complexing agent. In this case the current efficiency is approximately 91%. The continuous anodic dissolution of cobalt starts in the transpassive range.

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1. Introduction

Cobalt is the most important binder material for cemented carbides (90–94% WC, 6–10% Co), which are commonly used for tools such as in replaceable cutting inserts [1,2]. Cemented carbides are characterized by enhanced hardness and wear resistance. Due to these properties cemented carbides are commonly sintered near-net-shaped to avoid high tool wear by extensive finishing. Tool wear is negligible in electrochemical machining (ECM). Therefore, ECM is a promising option to shape cemented carbides without tool wear. ECM is known to avoid mechanical stress and thermal impact to the work piece and provides the opportunity of shaping even complex forms of materials with a high surface quality, independent of the hardness of the material [3,4]. The principle of the ECM process is shown in Fig. 1. The gap between anode (work piece) and cathode (tool) is approximately 0.1–1 mm. The current density amounts typically to 10–300 A/cm^2 and the electrolyte flow speed varies between 5 and 50 m/s [5,6].

Investigating the mechanism of ECM and evaluating the suitability of parameters for machining metal-ceramic-compounds is the objective of this work. Considering the contrary nature of electrochemical behavior of hard phase (WC) and binder phase (Co), the electrochemical machining of a composite material such as WCCo is a challenge. A homogenous dissolution process of both phases is required to retain the material properties and to get high surface quality. Therefore, it is necessary to dissolve either the hard phase or the binder phase in the transpassive state. As is well known from the pH-potential-diagram WC can be dissolved electrochemically in an alkaline solution and thus forms a passive layer in neutral and acidic electrolytes. On the other hand, Co forms passive layers in an alkaline solution and can be machined in the neutral and acidic electrolyte [7]. Due to the fact that tungsten carbide is the main component of cemented carbides and forms non reducible ion conducting oxides in acidic and neutral electrolyte, alkaline electrolytes for ECM would be preferable. The challenge is to enable dissolution of Co in an alkaline electrolyte. A possible achievement of this aim could be the usage of a complexing agent for cobalt, which avoids the passive film formation or the degrading of existing passive layers. In the 1970s Vu et al. investigated the leaching behavior of cobalt and cobalt oxides in ammoniacal solution and calculated a pH-potential-diagram for the system Co–H$_2$O–NH$_3$ [8,9]. Thus ammonia could be a promising chemical for ECM of cobalt. A special feature is that ammonia acts as a base itself and no further chemicals for adjustment of the pH value are necessary. With this background the authors investigated the electrochemical behavior of cobalt in an ammoniacal electrolyte and compared the dissolution mechanism at different pH values. The work is focused on pH 6 (NaNO$_3$), pH 12 (NH$_3$ + NaNO$_3$) and pH 14 (NaOH).

2. Experimental

Electrochemical measurements were carried out with a capillary flow-through cell (so called Θ-cell). Such a cell concept was

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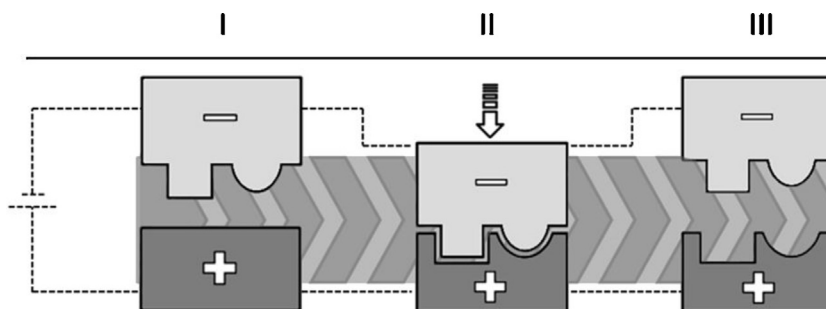E-mail address: Michael.Schneider@ikts.fraunhofer.de (M. Schneider).

Fig. 1. Basic concept of electrochemical machining (ECM). State I: (initial state) closed electric circuit of power supply, cathode (tool), electrolyte flow and anode (work piece),state II: lowering the cathode, specific electrochemical dissolution at the anode, state III: (final state) anode with negative shape of the cathode.
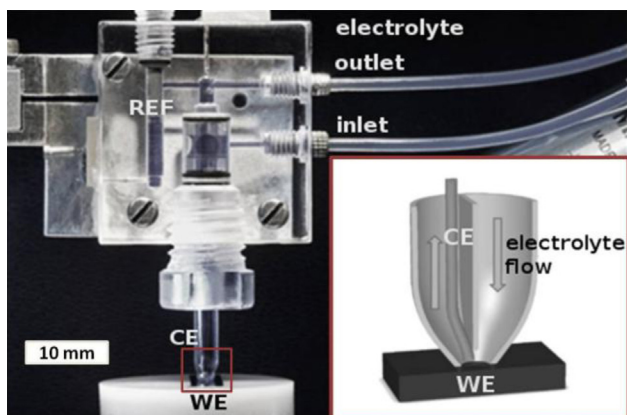

Fig. 2. Photo of the capillary flow-through-cell and enlarged scheme of the framed section of the capillary.

introduced by A. Moehring at first [10,11]. Fig. 2 shows a photo of the Θ-cell used in the present work. It is mounted on a force sensor.

The capillary was positioned on the sample and limits the area of the working electrode to approximately 0.22 mm². As the schematically enlarged section of the capillary in Fig. 2 shows, an inner glass wall separates two channels inside the capillary. A gap was prepared between the channels at the capillary tip. By using one channel as the electrolyte inlet and one as the outlet a continuous electrolyte exchange in front of the working electrode was guaranteed. A gold wire was positioned in the outlet channel. The electrode gap was approximately 0.6 mm. A silver/silver chloride reference electrode was also implemented in the cell. This complete 3-electrode-setup allows measurements with high current density typical for ECM by using commercial potentiostat systems. A computer-controlled PGU 20 V–2 A potentiostat (IPS Ing.-Büro P.Schrems) was used. Samples of a cobalt foil with a purity of 99.95% (Fa. MaTeck) were used. Table 1 shows typical analytical results of this cobalt foil [12]. The samples were grinded with SiC up to P1200-paper and polished with diamond suspension (particle size: 6 μm, 3 μm and 1 μm) and finally SiO₂ suspension (0.04 μm), followed by an etching process with a mixture of 100 mL CH₃OH (99.8%) and 6 mL HNO₃ (65%).

All electrochemical experiments were carried out in the electrolytes listed in Table 2.

The electrochemical behavior of cobalt was investigated by cyclic voltammetry using a potential range of $-0.8\,V_{SHE}$ to

10.2 V_{SHE} ($dE/dt = 500\,mV\,s^{-1}$). Additionally, linear sweep voltammograms focused on the early state of cobalt dissolution performed in a limited potential range between $-0.8\,V_{SHE}$ and $1.2\,V_{SHE}$ ($dE/dt = 100\,mV\,s^{-1}$).

Further on, the current efficiency of the dissolution process of cobalt in different electrolytes was estimated. Therefore, current controlled pulse experiments were conducted (5 pulses, $t_{on} = 1\,s$, $t_{off} = 1\,s$, $i_{on} = 25\,A\,cm^{-2}$). By using a current controlled procedure an equal amount of charge was applied evenly in different electrolytes. This procedure enhances the comparability of the analytical results. The used electrolyte of each experiment was collected in a beaker. The authors investigated the amount of dissolved cobalt ions in this electrolyte by UV–vis-spectroscopy (*StellarNet EPP2000*) using Nitroso-R-salt ($C_{10}H_5NNa_2O_8S_2$) as complexing agent, which leads to the formation of a red cobalt complex in aqueous solutions [13–15]. The absorption intensity of this complex was evaluated at 504 nm as recommended by Shipman et al. [13] and Ghasemi et al. [15]. The standard addition method was used. A linear relation between absorbance and concentration of the cobalt ion complex was observed in the chosen concentration range of 0.3 to 2.0 mg/L Co. Additionally, the removal of cobalt was optically determined using a digital 3D-microscope (*Keyence VH-Z50L/VHX-500S*). The microscope allows a quantitative geometric measuring of the removed material volume. Furthermore, the machined samples were investigated by SEM and EDX with an NVision 40 (*Carl Zeiss SMT GmbH*).

3. Results and discussion

Electrochemical behavior in neutral pH range (NaNO₃, pH 6)
Fig. 3a shows the potentiodynamic polarization curve of cobalt in sodium nitrate electrolyte at pH 6. The potential range was between $-0.8\,V_{SHE}$ and $1.2\,V_{SHE}$ ($dE/dt = 100\,mV\,s^{-1}$).

Due to the Pourbaix-diagram of the system cobalt–water an active dissolution can be expected according to Eq. (1) [7]. A corrosion potential at $-0.25\,V_{SHE}$ was observed in NaNO₃ as shown in Fig. 3a. This corresponds to the standard potential of active cobalt dissolution.

$$Co \rightarrow Co^{2+} + 2e^-, E^0 = -0.277\,V_{SHE} \qquad (1)$$
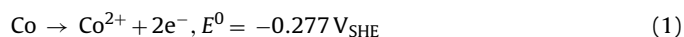
The cyclic voltammogram (Fig. 3b) between $-0.8\,V_{SHE}$ and $10.2\,V_{SHE}$ exhibits a linear increasing current density of up to

Table 1
Typical analytical results of a cobalt foil (MaTeck) with a purity of 99.95%.

Element	Fe	Cu	S
Mass fraction (ppm)	100	10	100

Table 2
Electrolyte characterization.

Electrolyte	Ionic concentration mol L⁻¹	Conductivity mS cm⁻¹	pH value
NaNO₃	2.9	159	6
NaNO₃/NH₃	2.9/2	158	12
NaOH	1	182	14