

Electrochemical Machining of cemented carbides

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ARTICLE INFO

Article history:

Received 3 April 2014

Accepted 4 June 2014

Available online 20 June 2014

Keywords:

Anodic dissolution

Electrochemical Machining (ECM)

Tungsten carbide cobalt

Cemented carbides

ABSTRACT

The present work is focused on the electrochemical behavior of tungsten carbide cobalt in alkaline ammonia electrolytes under near-ECM conditions. Potentiodynamic measurements were carried out in an electrolyte mixture of sodium nitrate and ammonia. It could be shown that a homogenous dissolution of both phases, the hard phase tungsten carbide and the binder phase cobalt, is possible with this electrolyte mixture. Additionally, galvanostatic pulse experiments coupled with polarographic analysis of the waste electrolyte were carried out to investigate the current efficiency of the machining process. Current efficiencies between 70 and 100% can be achieved under the chosen conditions dependent on the current density.

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Introduction

Electrochemical Machining (ECM) was firstly developed in the 1920s in the former Soviet Union [1,2]. Nowadays ECM is well-established for shaping metals, both ferrous and non-ferrous. Not least because of the negligible tool wear occurring at this process. Main fields of application are the aircraft (e.g. turbine blades [3]) and automobile manufacturing (e.g. injection nozzle [4]) as well as the consumer industry (e.g. shaving heads [5]).

The basic principle of ECM is a specific anodic dissolution of materials. The process is illustrated schematically in Fig. 1. Thereby the work piece is connected as anode and the work tool as cathode. A highly conductive electrolyte is pumped through the gap between the electrodes with high speed (> 10 m/s). The electrode gap is at the order of $100\ \mu\text{m}$ [6] during the machining process (state II) and the material of the work piece dissolves anodically. Finally, the inverse shape of the tool is generated in the work piece (state III). Common electrolytes are aqueous solutions of sodium nitrate or sodium chloride. Current densities in the range of 5 and $100\ \text{A}/\text{cm}^2$ are applied [7].

ECM has a number of advantages [6,8]:

- No impact of mechanical stress
- A priori no thermal impact
- High surface quality
- Independence of material hardness and brittleness
- No process related tool wear
- Design flexibility even for complex shape.

ECM of metallic materials based on Fe or Cu is often described over the last decades [4,9–33]. In contrast, ECM of metal ceramic compounds is still scarcely investigated. Cemented carbides, widespread used as indexable inserts, are near net shaped produced by powder metallurgical processes. However, the finishing processes associated by high tool wear as well as mechanical and thermal stress impact into the work piece. Therefore, ECM could be an interesting alternative machining method for these extremely hard and heat-resistant materials. First publications regarding the ECM of cemented carbides were done by Russian scientists in the 1970s [34–37]. However, their work was commonly focused on technical aspects and limitations of the process. Unfortunately, the evaluation of relevance and success of these early works is complicated by a lack of macro- or micrographs in the publications. The fact that ECM of cemented carbides is not yet commercially applied, indicates that a homogeneous removal of material and surface finish have not been sufficiently realized up to now.

Recently, Shibuya et al. [38] reported about the fabrication of micro-pins with ECM in sodium nitrate. Alas the authors did not specify the material exactly. The binder phase is not clearly named in this publication. Moreover, the described machining process is indeed a hybrid technique. The obviously formed solid reaction products were removed by a so-called ultrasonic washing after the ECM. Another approach is reported by Korean scientists [39]. The authors described the successful machining of micro grooves and holes in a WC–Co alloy using a sulfuric/nitric acid electrolyte and ultra-short voltage pulses (100 ns at 9 V). Under such condition the cobalt binder easily dissolves but the tungsten carbide phase forms a passive film. The authors explain that this problem is solved applying negative potential during the pulse pauses which led to an alkalization in front of the work piece and chemical dissolution of the passive layer on the tungsten carbide phase.

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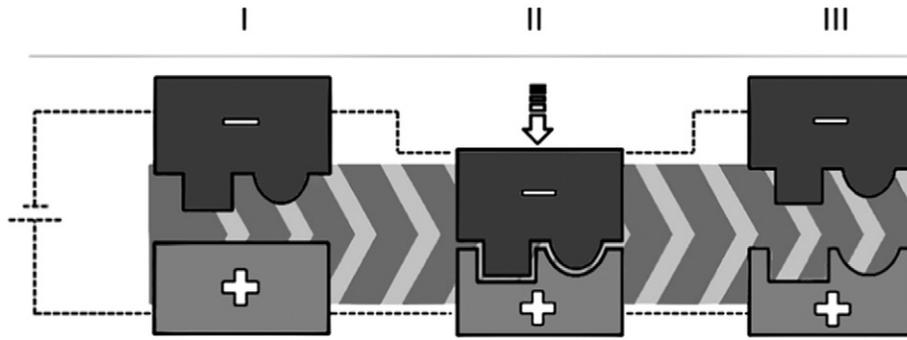


Fig. 1. Schematic illustration of ECM. I—initial state, II—state of machining process III—final state.

Unfortunately, the shown micrographs do not allow a detailed evaluation of the microstructure.

Anyway, ECM of cemented carbides is still a subject of basic research until now. A new approach using electrolytes containing complex agents will be presented in this work.

Material and methods

Materials

The material used was commercially available CTM12a (WCCo6) produced by Ceratizit [40].

All samples were prepared by grinding with SiC paper (up to P1200) and polishing to a mirror-like surface using diamond suspension.

Reference measurements were carried out on pure cobalt (99.9%; commercially available by MaTeck) as well as on pure tungsten carbide (in-house produced).

The used electrolyte is a mixture consisting of ammonia and sodium nitrate (Table 1).

Methods

The electrochemical experiments were carried out using a microcapillary flow through cell. The cell enables experiments under near-ECM conditions using common potentiostates and laboratory conditions [18,19,41–43]. Fig. 2 shows a schematically enlarged image of the tip of the glass capillary on the left and a photo image of the whole cell on the right.

The cell consists of a PMMA body with electrolyte inlet and outlet and the mounted glass capillary. The capillary is positioned at the anode (sample material) and limits the working area to approximately 0.5 mm². By using a potentiostat with 1A current in maximum a current density up to 200 A/cm² can be realized. As shown in Fig. 2 (left), the glass capillary of the cell is divided into two channels by a thin glass wall. At the tip a gap between the two channels is prepared. The electrolyte flow is realized by a special micro gear pump (HNP Mikrosysteme mrz7205). In the electrolyte outlet channel the counter electrode, a thin gold wire, is positioned close to the working electrode. A 3 M Ag/AgCl reference electrode is positioned in the PMMA body. The used potentiostates were a PGU 20 V-2 A (IPS Ingenieurbüro P. Schrems) and IMP 88 PC-200 V (Jaisle). Cyclic voltammetry was carried out in a potential range of –0.90 V to 1 V with a polarization rate of 0.05 V/s. A polarization rate of 1 V/s was used to investigate an extended

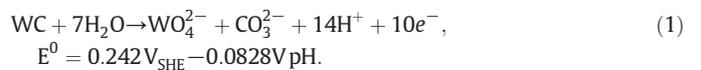
potential range of –0.90 V to 20 V. Additionally, SEM and EDX analyses of the sample surface after ECM were carried out with a scanning electron microscope (NVision 40 CarlZeiss SMT GmbH). Galvanostatic experiments at different current densities were carried out and coupled with analysis of the removed material volume and the reaction products in the electrolyte. The analysis of the removed material volume was carried out with a 3D-microscope (Keyence VHX-500F/VH-Z50L).

The analysis of the reaction products in the waste electrolyte was carried out by polarography with a VA 797 Computrace (Metrohm). The content of dissolved tungsten and cobalt was analyzed by adsorptive stripping voltammetry with ferron [44] and dimethylglyoxime [45] respectively as complexing agents.

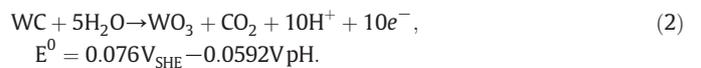
Theory

In this paragraph the authors would like briefly introduce into the special problem of the homogeneous anodic dissolution of cemented carbides from the thermodynamic point of view. WCCo6 is a composite, which mainly consists of a hard phase (WC) enclosed in a binder phase (Co). The electrochemical behavior of both is completely different and complicates a homogenous dissolution process of the material. As shown in Fig. 3 tungsten carbide dissolves to a soluble product only at pH > 7 whereas soluble cobalt species are stable at pH < 6 (Fig. 4) [46].

Due to Fig. 3 the anodic dissolution of tungsten carbide can be assumed to:



In neutral and acidic solutions tungsten carbide forms stable passive layers according to:



Cobalt dissolves in neutral and acidic electrolyte according to Eq. (3), but forms a hydroxide layer in the alkaline pH range (Eq. (4)):



However, since ECM requires a homogeneous dissolution of both phases the authors had to find an electrolyte which overcomes the passivity of each phases for the given situation. The novel approach is the use of an alkaline electrolyte added with complex agents, which suppresses the passivity of cobalt. It is well known, that cobalt easily forms complexes with ammonia [47]. Consequently, ammonia seems to be a suitable additive to suppress the passivation of cobalt.

Table 1
Characterization of the used electrolytes.

Electrolyte	Concentration mol L ⁻¹	Conductivity mS cm ⁻¹	pH value
NH ₃ /NaNO ₃	2.0/2.9	151	12

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