Electrochimica Acta 109 (2013) 562–569

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Electrochemical micromachining of passive electrodes

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ARTICLE INFO

Article history:
Received 21 February 2013
Received in revised form 17 July 2013
Accepted 17 July 2013
Available online xxx

Keywords:
Electrochemical micromachining
Numerical simulation
Passive electrode
Stainless steel

ABSTRACT

The electronic model describing the electrochemical micromachining (ECMM) of passive electrodes utilizing the transpassive dissolution is discussed. Numerical simulations are performed on a machining model circuit using measured electrochemical properties of the model system which consisted of a tungsten tool electrode, a 1 M H_2SO_4 electrolyte and a stainless steel work piece electrode. The results of these simulations were verified by performing machining experiments applying the same model system. For a passive stainless steel electrode it is shown that it can be treated like an actively dissolving electrode with high reaction overpotential. The efficiency of the machining process can be enhanced by polarizing the steel work piece electrode close to the transpassive potential region. Three different ways of achieving this polarization are discussed: by polarizing the work piece electrode only, by polarizing both electrodes and by adding oxidizing species to the electrolyte solution.

1. Introduction

Electrochemical micromachining (ECMM) is a method to micro-structure metallic materials and it exhibits some unique advantages over other methods [1]. A sub-micrometre precision can be achieved when ultra-short voltage pulses are used. Thus, tool wear and induction of heat or stress into the work piece are omitted and the material removal is independent of the microstructure and of the hardness of the work piece material [1]. These benefits make the ECMM a promising technique for manufacturing micro-parts, e.g. microelectromechanical systems (MEMS). A potential application of this method, which is the subject of recent and ongoing investigations, is the shaping of bulk metallic glasses (BMGs) [2,3]. This class of materials exhibits outstanding mechanical properties, such as high hardness and strength at room temperature, but shaping is still challenging. A recent trend is to produce micro-parts from BMGs by thermo-mechanical processing [4]. However, this method is not applicable to high strength Fe-based BMGs and therefore, alternative methods like ECMM are mandatory. ECMM of BMGs is quite complicated due to the multi-component alloy nature and the unusual reactivity of the metastable phase. Therefore, fundamental studies on the machining process need to be performed on simpler and well understood work piece materials.

The method of ECMM of crystalline materials was impressively demonstrated by Schuster et al. [5] for Cu and p-Si. It was shown for Ni electrodes that a sub-μm precision can be achieved [6]. Maurer et al. succeeded in micro-machining the Ni-based Hastelloy B-2 [7] and a NiTi shape memory alloy [8]. High precision and small structures with sub-μm dimensions can be achieved when the machining process is conducted using an atomic force microscope (AFM) setup with the cantilever tip acting as tool electrode [9,10]. The principle of operation of the ECMM method is shown schematically in Fig. 1a for an actively dissolving work piece electrode. Inside an electrolyte an electrochemical double layer (DL) establishes at the metal surface which can be regarded as a capacity (C_{wp}). In the electrolyte, a micro tool electrode is brought into very close distance to a work piece electrode. When ultra-short voltage pulses are applied between these electrodes, the voltage of the work piece DL capacity C_{wp} as a function of time is given by

$$U_{C_{wp}} = U_{max}\,(1 - e^{-t/RC_{wp}}) \qquad (1)$$

U_{max}: maximum voltage (corresponding to pulse voltage), t: time, R: resistance (see text).

Thus, the voltage across the DL is strongly dependent on the electrolyte resistance $R_{electrolyte}$ between the electrodes. Furthermore, for an actively dissolving electrode exhibiting a Tafel behaviour (purely charge transfer controlled reaction mechanism), the dissolution current density increases exponentially with increasing voltage. This means only for short distances between the electrodes ($R_{electrolyte\ short}$ in Fig. 1) the work piece electrode DL is charged sufficiently for a significant metal dissolution. This mechanism can be described analytically and the shape evolution during the machining process was modelled and simulated successfully [10–12].

Micromachining of passive electrodes requires the exploitation of the transpassive dissolution regime, i.e. the dissolution at high anodic polarization. This appears to be more difficult. According to Schuster [13] and Kock [14] an additional resistance, the resistance

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http://dx.doi.org/10.1016/j.electacta.2013.07.139

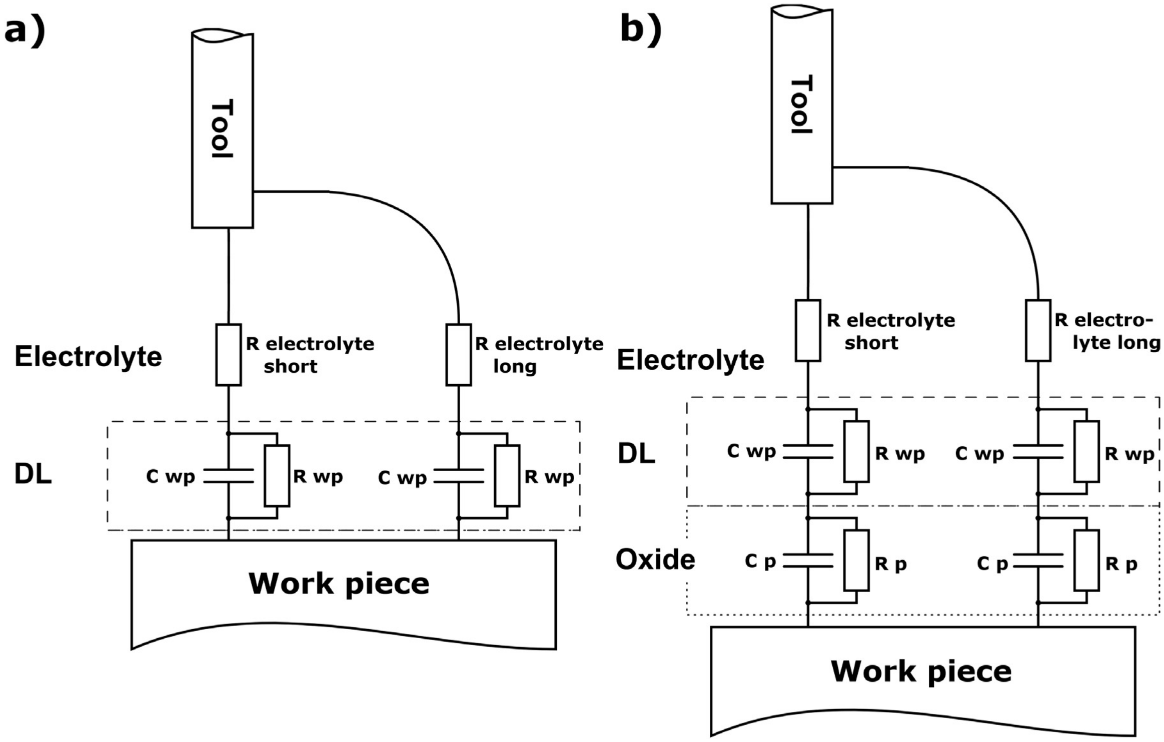

Fig. 1. Principle of operation of the ECMM method for (a) an actively dissolving electrode and (b) for a passive electrode. For better visibility the double layer capacity and charge transfer resistance of the tool electrode are not shown here.

of the passive layer R_p, acts in series with the DL capacity as shown schematically in Fig. 1b. In consequence, R in (1) becomes the sum of $R_{electrolyte}(R_e)$ and $R_{passive\ layer}(R_p)$. If this resistance of the passive layer exceeds the electrolyte resistance in the machining gap, it governs the charge of the DL and therefore, the localization of the process vanishes [13,14]. Kock [14] discussed three successful ways of micromachining passive steel electrodes. Firstly, the work piece electrode can be forced into an active state, either by utilization of an aggressive electrolyte (for example HCl–HF mixtures) or by cathodic polarization. Secondly, the passive layer can be locally reduced by a cathodic voltage pulse. This passive layer reducing pulse is then followed by an anodic pulse for an enhanced dissolution. The third way is the use of electrolytes with low conductivity, such as 1 M acetic acid. Since acetic acid dissociates only partially, a high electrolyte resistance is achieved. However, all these methods also exhibit some disadvantages. For work safety, the use of highly aggressive media, especially hydrofluoric acid, should be avoided if possible. Furthermore, in multi-phase alloy systems selective corrosion phenomena may occur when the work piece electrode is in the active state. Passive layers which are more stable than the layers grown on steels might not be reducible. The use of low conductive media enhances the impact of mass transfer in the electrolyte during the machining process. Due to dissolved metal ions the electrolyte resistance decreases in the machining region during the machining process.

Despite the above critical theoretical considerations, recently the electrochemical micromachining of passive electrodes has been successful. Sjöström and Su [15] machined titanium and elsewhere other researchers succeeded in machining stainless steel [16–20]. Koza et al. [3] micromachined a passive Zr-based BMG and in a previous study we succeeded in micromachining a passive Fe-based BMG [2]. There is obviously a gap between experimental results and theoretical understanding of the micromachining process. The aim of the present study is therefore, to fundamentally investigate the mechanism of the electrochemical micromachining of passive electrodes. The electrochemical parameters of the tool electrode and the work piece electrode are determined for the model system W tool electrode–H_2SO_4 solution–stainless steel work piece electrode. These data are then employed for the numerical simulation of the equivalent circuits for the micromachining system. Afterwards, the predictions of the simulations are tested experimentally in our micromachining setup.

2. Experimental

Specimens used as electrodes for obtaining the material parameters for simulations were a W wire of 99.5% purity and a diameter of 1.5 mm embedded in epoxy resin and a sheet of 1.4303 stainless steel (X4CrNi18-12; AISI 305/308) with a diameter of 7 mm. They were ground with abrasive paper up to 4000 grade and cleaned with water and ethanol. For electrochemical investigations, a cylindrical Teflon cell was used. The electrode under investigation was mounted on the bottom of the cell facing upwards. It was surrounded axial symmetrically by a Pt net which served as counter electrode. A $Hg/Hg_2SO_4/K_2SO_{4(sat.)}$ electrode ($E = 640$ mV vs. standard hydrogen electrode (SHE)) was used as reference electrode. The electrolytes were prepared from analytical grade chemicals and deionised water. For potential control and electrochemical impedance measurements a SI 1287 electrochemical interface was employed in connection with a SI 1260 frequency response analyzer (Solartron). Prior to polarization experiments the open circuit potential (OCP) of the electrode under investigation was recorded for one hour. Potentiodynamic polarization experiments were conducted for the tungsten electrode (in the machining process the cathodic tool electrode) starting at 100 mV vs. OCP and scanning with a potential scan rate of 20 mV s^{-1} to −1500 mV vs. OCP. For the stainless steel electrode (in the machining process the anodic work piece electrode) the potential scans were performed from −200 mV vs. OCP to 1500 mV vs. OCP with a potential scan rate of 20 mV s^{-1}. Electrochemical impedance spectroscopy (EIS)