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# Electrochemical micromachining of passive electrodes – Application to bulk metallic glasses

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ABSTRACT

Electrochemical micromachining (ECMM) is a method for micro-forming of metallic materials independent of their hardness and without inducing significant heat into the work piece. Thus, it appears to be well suited for micro-shaping of bulk metallic glasses (BMGs). On the example of a Fe-based BMG, $Fe_{65.5}Cr_4Mo_4Ga_4P_{12}C_5B_{5.5}$, the capability of ECMM exploiting the transpassive dissolution regime is discussed. The glassy alloy exhibits spontaneous passivity in aqueous acidic electrolytes. Due to its low Cr content the electrochemical behaviour during the ECMM is not comparable to that of stainless steel and therefore, established experimental conditions are not applicable. The electronic behaviour of the ECMM setup is discussed in relation with the electrochemical reactions during the machining. Resultant, different ways of machining the glassy $Fe_{65.5}Cr_4Mo_4Ga_4P_{12}C_5B_{5.5}$ alloy in an aqueous acidic electrolyte are derived and ways to enhance the electric efficiency are discussed: the addition of an oxidant to the machining electrolyte and the application of a Schottky diode in the electronic setup.



## 1. Introduction

Bulk metallic glasses (BMGs) exhibit outstanding mechanical properties and are therefore very promising materials for the production of load-bearing parts of micro-devices. Due to their high strength and hardness they can be used as structural materials in microelectromechanical systems (MEMS) as shown in Greer and Ma (2007). Fe-based (and Co-based) soft magnetic glassy alloys are furthermore appropriate functional materials, for example for micro-sized yokes in positioning systems (see Inoue and Nishiyama, 2007), or magnetic cores (Roth et al., 2006).

A limitation of the application of BMGs is the challenge of shaping them on microscale. Surface patterning, as for example done by Saotome et al. (2002), and the production of micro-parts (Schroers, 2010) was demonstrated using thermo-mechanical forming processes. However, this route is limited to alloys exhibiting a wide undercooled liquid region at low temperatures such as Pd- or Zr-based bulk metallic glasses. A micro-shaping technique operating at room temperature might open new possibilities for the utilization of glassy alloys.

For crystalline metallic materials, different electrochemical microprocessing methods operating at room temperature were developed, which are collated and discussed in Landolt et al. (2003).

One of these microprocessing methods is the pulsed electrochemical micromachining (ECMM) allowing a submicrometer precision, as can be seen in Bhattacharyya et al. (2004). The ECMM technique was successfully established for the machining of crystalline material surfaces such as Cu (Schuster et al., 2000), Ni (Maurer et al., 2010) and stainless steel (Cagnon et al., 2003). High aspect ratios and complex structures were machined. The applicability of the pulsed ECMM to glassy alloys was firstly proven by Koza et al. (2011) for a Zr-based BMG. In Sueptitz et al. (2012) the principal feasibility of this ECMM method was also demonstrated for the Fe-based glassy alloy $Fe_{65.5}Cr_4Mo_4Ga_4P_{12}C_5B_{5.5}$ (Fe-based BMG) in a non-aqueous electrolyte. A micrometer-sized tool electrode (tool) made from W or Pt is brought in close distance to the metallic glass (work piece) surface. When ultra-short voltage pulses are applied, the voltage across the work piece electrode–electrolyte interface, named $U_{WPE}$, can be described by charging the work piece electrode capacity $C_{wp}$ via the electrolyte resistance $R_s$

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

where $U_{max}$ stands for the maximal available voltage (corresponds to the pulse voltage) and $t$ for the time.

This means that only for small distances between the tool and the work piece electrode (WPE) the capacity of the WPE is

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locally charged sufficiently for a significant anodic dissolution. For larger distances between tool and WPE the resistance through the electrolyte is high and the capacity is not charged sufficiently for a significant dissolution. Micromachining of passive electrodes requires the exploitation of the transpassive dissolution regime. In Sueptitz et al. (2013) it is concluded that in principle such electrodes can be treated as active electrodes with high reaction overpotential. However, the passive layer growth might disturb the machining, as shown in Sueptitz et al. (2012), and furthermore, the capacitive losses are high. These effects can be minimized following different strategies for pre-polarization of the WPE.

Aim of the present study is to evaluate the feasibility of different pre-polarization strategies for the micromachining of a Fe-based BMG with low Cr content. For comparison, the machining of a crystalline 1.4303 stainless steel (X4CrNi18-12; AISI 305/308) will also be investigated. An enhancement of the electronic setup is presented as well as modifications of the electrolyte composition for improving the machining process.

## 2. Experimental

Bulk glassy $Fe_{65.5}Cr_4Mo_4Ga_4P_{12}C_5B_{5.5}$ rods of 1 mm diameter and up to 50 mm length were cast and their microstructure was characterized as described in Stoica et al. (2007). Slices of 5 mm thickness were cut from these rods and embedded in epoxy resin for use as work piece electrode. For the characterization of the electrochemical behaviour of the tool electrode material, a W rod (Goodfellow) of 7 mm diameter was embedded in epoxy resin, too. Furthermore, a sheet of 1.4303 stainless steel was used as reference WPE material. The samples were successively polished with SiC paper up to grit 4000 and cleaned with distilled water and ethanol before electrochemical testing. Electrolytes were prepared from deionized water, analytical grade $Fe_2(SO_4)_3$ and analytical grade $H_2SO_4$ (98%).

For characterizing the polarization behaviour of the Fe-based glass, the stainless steel and the W electrode potentiodynamic polarization experiments were conducted in the machining electrolyte 0.1 M $H_2SO_4$ using a conventional three electrode Teflon cell with a Pt mesh as counter electrode and a $Hg/Hg_2SO_4/SO_4^{2-}$ reference electrode (MSE; $E$(SHE) = 640 mV). Prior to the polarization experiments the open circuit potential (OCP) was monitored for 30 min. Afterwards, the polarization studies were performed starting from (OCP + 200 mV) in cathodic direction up to −2 V vs. MSE for the W electrode and from (OCP − 200 mV) in anodic direction to 2 V vs. MSE for the Fe-based glass and the stainless steel electrodes. In all measurements a potential scan rate of 5 mV $s^{-1}$ was used.

The micro tool electrodes used for the machining experiments were made of W-wire material with various diameters, which were embedded in glass tubes except a 100 μm long tip. During the processing the tip of the employed micro tool electrode is brought into close distance (~5 μm) to the WPE, i.e. the glassy alloy, and was moved incremental towards the work piece during the pulsing process. The voltage pulses are applied in two ways: (i) by applying the voltage pulse (100 ns length, 1 μs period) directly by connecting the pulse generator (Agilent 81101A) to the tool and WPE and (ii) by a setup composed of the mentioned pulse generator, a wide band transformer, a capacitor and a DC voltage source, which is described in detail in Koza et al. (2011) and discussed in Sueptitz et al. (2013). This second method allows a DC-polarization of the WPE and will be discussed in detail in the next section.

## 3. Results and discussion

Recently, Sueptitz et al. (2013) investigated the principal mechanism of ECMM exploiting the transpassive dissolution by means of numerical simulations and experimental validation. For passive materials it was found to be necessary for the ECMM to reduce the passive layer growth during the voltage pulse. This can be achieved by three ways. Firstly, by using pulses of high amplitude which are able to drive high currents with a low raise time. The electrode might get rapidly into the transpassive state without a significant passive layer growth. This approach was not successful in our studies and will be therefore not discussed.

Secondly, an electrolyte free of water or with low water content can be used. Since for the passive layer growth commonly water is necessary, the growth can be suppressed significantly. Thus, the machining of a Fe-based BMG succeeded in methanolic 2 M $H_2SO_4$ solution (Sueptitz et al., 2012). However, the capacitive losses are high because the WPE needs to be polarized up to the onset of transpassivity before a material removal starts.

The third way is to polarize the WPE to a potential close to the onset of transpassivity as it was demonstrated by machining a stainless steel electrode in aqueous 0.1 M $H_2SO_4$ solution (Sueptitz et al., 2013). Since 0.1 M $H_2SO_4$ is easier to handle, cheaper and more environmentally friendly than methanolic 2 M $H_2SO_4$, it would be a favourable electrolyte for machining the Fe-based BMG. But without applying a bias potential the machining of this alloy was not possible in aqueous $H_2SO_4$ solution (Sueptitz et al., 2012). As discussed theoretically in Sueptitz et al. (2013), the most efficient way of DC-polarization is to choose a suitable voltage for the pulse off time because this way, capacitive losses are minimized. Fig. 1 shows the potentiodynamic polarization curves, anodic for the glassy $Fe_{65.5}Cr_4Mo_4Ga_4P_{12}C_5B_{5.5}$ WPE and cathodic for the W tool in 0.1 M $H_2SO_4$ solution. When a DC voltage is applied to the electrodes in an ECMM process, the WPE is polarized anodically and the tool cathodically to potentials at which the magnitude of the cathodic current is equal to the magnitude of the anodic current as indicated by the vertical lines in Fig. 1. During the voltage pulses the electrodes are polarized as indicated by the arrows in Fig. 1. It is obvious that pulses of low magnitude should be sufficient for a polarization in the transpassive region leading to a material removal at the WPE. However, electrochemical micromachining was not successful in this setup. Experiments were performed using pulse voltages of 2 V to 9 V and pulse off voltages from −0.4 V to 1.6 V. For low pulse off voltages in general no material removal was achieved, for high

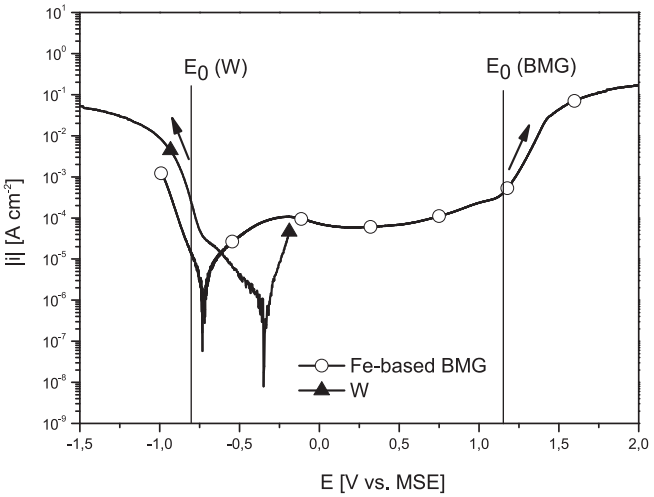


**Fig. 1.** Potentiodynamic polarization curves of W and the Fe-based BMG $Fe_{65.5}Cr_4Mo_4Ga_4P_{12}C_5B_{5.5}$ recorded in 0.1 M $H_2SO_4$ with a scan rate of 5 mV $s^{-1}$. $E_0$ indicates schematically the potential establishing when the pulse off voltage is applied between both electrodes. The arrows indicate the polarization during the voltage pulses.