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Energy-based Analysis of Material Dissolution Behavior for Laser-Chemical and Electrochemical Machining

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Abstract

Laser-chemical and electrochemical machining (ECM) have the common feature that material removal is based on the chemical dissolution on atomic scale. Although, the mechanisms of dissolution and surface modification are quite similar, physical main active principle and corresponding material loadings differ. During laser-chemical machining the material is heated locally and chemical reactions are enabled by heat going into the reaction. On the other hand in ECM the material is dissolved by an electric field support. For this reason, this paper presents the energy-based analysis and comparison of these two material loadings to process performance and material modifications. The results imply that the stability of an electrochemically evolved oxide layer is strongly depending on the local temperature. Furthermore, the results appear that the chemical reaction and thus the dissolution speed depends on the microstructural composition of the workpiece material.

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1. Introduction

Every manufacturing technology causes several chemical and physical changes in the workpiece material. Mechanical, thermal and chemical effects influence the generation of the new surface and change the material structure in the near surface including stress or a change in microstructure [1].

These properties cannot be predicted for manufacturing technologies reproducible in advance. This lack of predictability shall be solved by a new approach, called process signatures. These process signatures will combine the material loadings forced by the manufacturing process with the change of state variables. To achieve comparability for different processes with same physical working principle, it is necessary to describe the transition from material loadings to the change of material properties in a uniform way [2].

The suggestion to develop process signatures is based on the fundamental assumption that all manufacturing processes are energy driven. Energy dissipation and energy conversion will impact the material and thus determine the final surface and subsurface properties [1].



Fig. 1. Causal sequence regarding the energy conversion, energy dissipation and material modification as a result of different machining processes on the example of electrochemical and laser-chemical machining process (according to [1], modified)

Fig. 1 illustrates, on the example of comparing an electrochemical machining process (ECM) with a laser-chemical machining process (LCM), that this change of properties itself is independent from the chosen

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manufacturing process. The modification of the surface and subsurface properties is a result of changes of one or more state variables such as residual stresses or microstructure [3].

LCM and ECM have quite similar mechanisms of dissolution and surface modification. These processes have the common feature that material removal is based on the chemical dissolution on atomic scale. To describe and compare the process mechanisms of LCM and ECM, an energy based approach is chosen that characterizes the material loadings with respect to process performance and material modifications, especially in the respective working area. A first step for the development of such process signatures and identification of process specific material loadings for LCM and ECM are shown.

2. Process fundamentals

In aqueous solutions the metallic workpiece behaves like an electrode. Metal ions which enter the solution leave the electrode in an electron surplus. A potential difference can be observed due to the formation of an electrolytic double layer at the phase boundary. According to Helmholtz, metal cations near the electrode are attracted and it comes to a formation of a simple double layer (Fig. 2). This is also called a rigid Helmholtz double layer, in contrast with the thereafter forming diffuse Nernst layer, which is followed by the solution. Consequently the charge with increasing distance to the electrode becomes weaker and the concentration of reactants increases [4].



The needed energy to dissolve a specific amount of material is described by Gibbs free energy:

$$|\Delta g_{reac}| = \dot{q} + z \cdot F \cdot |\varepsilon|$$

where z is the absolute number of transmitted electrons/ions and F is the Faraday constant. The electric potential between the two electrodes is described by $|\varepsilon|$, while \dot{q} expressed the dependence of the heat flux density. The sign of the Gibbs free energy depicts if a chemical reaction or a further passivation through the reinforced electro-chemical double layer proceeds. With an appropriate choice of $|\varepsilon|$ and \dot{q} it is possible to control the chemical dissolution. Therefore electrochemical machining takes advantage that the material removal rate is proportional to the applied current. Since with higher currents the heat flux increased, it is necessary to cool the workpiece with higher flow rates to guarantee the chemical dissolution.

For laser-chemical machining the influence of laser radiation causes chemical reactions on the metal surface only starting at average laser intensities in kW/mm² region which are associated with material removal [6]. Selective material removal is possible in all metals which are protected against corrosion at room temperature. Depending on the material-electrolyte pairing this can be realized on the one hand by self-passivation or by means of an applied potential resulting in a thin passivation layer. According to Nernst the electrochemical potential is proportional to the temperature, and therefore to the laser power applied [6].

Another fundamental influence on the processing speed beside the thermal activation of chemical reactions is the mass transport limitation within the electrolyte. Therefore, the processing speed in LCM is diffusion limited [6].

3. Experimental Setup

For the fundamental examination of the electrochemical dissolution mechanisms, potentiostatic measurements were used. These measurements were performed with a classical three electrode arrangement for ECM process.

For the results obtained by LCM process a fiber-laser source with a maximum output power of 300 W was used. Its TEM_{00} cw laser radiation is emitting 1080 nm. The passivation of the workpiece material has been realized with a three electrode arrangement.

As workpiece material the normalized alloyed tempering steel 42CrMo4 and as electrolyte sodium nitrate NaNO₃ at a concentration of 21 wt.% and a temperature of 36°C (for ECM) respectively a temperature of 20 °C (for LCM) were used. Additionally the dissolution rate as a function of current density (for ECM process) was examined for the normalized 42CrMo4 steel. This examination allows an estimation of necessary electrical charge for the specific material removal.

4. Results and Discussion

4.1. Electrochemical machining results

To investigate the electrochemical behavior of 42CrMo4 in NaNO₃ potentiostatic measurements were performed. Fig. 3 depicts the electrochemical reaction of the workpiece based on the variation of the current density I in dependence of the applied electrode potential ε . In the potentiostatic measurements three different phenomena could be examined, first the active dissolution at low anodic potentials, secondly at slightly higher potentials the evolution of an oxide layer. Thereby, the completion of the oxide layer is marked by the sharp descent in electric current, the so called Flade potential. Finally the material dissolves at higher potentials transpassively.

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