Unconventional processes of ceramic and composite materials shaping
Niekonwencjonalne procesy kształtowania materiałów ceramicznych i kompozytowych

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In order to reach the high quality parts of machines or tools very often ceramic or composite materials on metallic or ceramic base are being applied. Efficient shaping above mentioned materials using cutting or classical grinding is difficult because of their high mechanical properties. Rational solution is application of unconventional machining methods as: electrochemical, electrodischarge or electrochemical – electrodischarge (ECDM) in case when machined materials are at least partly conductive of electrical current. In case of shaping ceramic materials unconductive for electrical current the rational solution can be application of Spark Assisted Chemical Engraving (SACE) process – the special kind of ECDM process.

KEYWORDS: unconventional machining processes, ceramic materials, composite materials

Ceramic, metallic-frame of ceramic-frame composite materials at properly designed composition have very good mechanical properties (high hardness, strength, fatigue strength, wear resistance, etc.). Such properties make it difficult and even impossible to process using mechanical methods (machining, grinding).

The scheme of composite materials machining is shown in fig. 1. Metallic-matrix materials (e.g., Al, Al-Mg, Al-Li, Mg, Ti, Ni, Co, Cr and their alloys) are reinforced with ceramic particles (e.g. SiC, PCD, Al2O3, ZrO2, Si3N4, WC TiC, TaC, TiB2, B4C) and cermet are ceramic matrix materials (eg Al2O3, Zr [SiO4], TiC, Si3N4, ZrO2, B4C) mixed with metal powders (W, Co, Ni, Fe, Cu [1]. These materials usually retain very good mechanical properties even at high temperatures. There are still a number of materials that are widely used in the manufacture of MEMS (micro-electromechanical systems); are different types of glass, quartz, silicon and its compounds (silicon oxide, silicon nitride, PZT (lead zirconate-titanate)). They are used to make microelements forming a part of the MEMS. It is often necessary to make micro-holes in these materials to create electrical connections between layers [1-3]. These materials - due to their very good mechanical properties: high strength and hardness (e.g. Al2O3), high hardness and brittleness (e.g. glass) or small dimensions (dimensions of micronutrients in MEMS << 1 mm) should be shaped using processes, in which removal of the allowance does not depend significantly on the mechanical properties of the workpiece.

Fig. 1. Machining the workpiece made of composite material. A - matrix material (metal or ceramic material), B - reinforcement phase particles (metal or ceramic grain), ER - working electrode

This condition is fulfilled by electrochemical machining (ECM), electro-discharge machining (EDM) and electrochemical-discharge machining (ECDM), which coincides with electrochemical reactions and electrical discharge.

Characterization of machining of hard-to-machine materials using ECM, EDM and ECDM processes

During ECM processing, the workpiece material (anode) is removed by ionizing the atoms and then diffusing into the interelectrode gap where they enter into further reactions and form - usually insoluble - hydroxides. If there are non-metallic grains in the material, after the solution of the surrounding metallic phase they are flushed out by the electrolyte flowing through the gap and the work area remains empty. For this reason, the use of
ECM for the treatment of composite materials with non-metallic phase is limited by grain dimensions of this phase. If the non-metallic grain is not rinsed, the thickness of the inter-electrode gap is reduced in its surroundings, the concentration of hydrogen emitted at the cathode locally increases, which can lead to electrical discharges damaging the electrode and the workpiece. Therefore, electrochemical treatment can be used primarily for the formation of homogeneous metallic materials or metallic matrix with fine (micro, nano) reinforcing phase grains [1-3].

In electro-discharge machining (EDM), the treated material is removed by electrical discharge. Their surroundings give off heat, and the temperature locally reaches 6,000 ÷ 12,000 K. Therefore, the material (metallic and non-metallic phases) melts, partially evaporates and forms craters on the work surface. Because EDM (drilling or cutting) can only be efficiently processed with conductive materials, a conductive phase is often added to the materials. Percentage of such phase has a significant influence on the course and results of EDM processing [1-3].

ECM processing can be used both for conductive and non-conductive materials. In the case of treatment of electrically conductive materials in the material removal area, the electrochemical dissolution and electrical discharge processes coincide. As a result of the electrochemical reactions of the anode, the atom of the anode is removed - the metallic phase of the workpiece - which ultimately forms the hydroxides. On the surface of the cathode, as the reaction equivalent to the evolution of hydrogen in places where its concentration exceeds 70%, there is an electrical discharge. As a result of high temperature in the discharge area (about 6,000 ÷ 12,000 K), evaporating and melting of the workpiece and working electrode (tools), electrolyte evaporation, digestion, etc. intensify the heterogeneity of the electrolyte mixture-treatment products and, under appropriately chosen conditions, ECM and EDM processes [1-3].

The concept of using electrochemical-electro-discharge hybrid process (ECDM) to shape hard-working materials has been and is being strongly developed [4-6]. Testing of metallic materials (e.g. 1Cr18Ni9Ti stainless steel) has shown that ECDM machining yields can be many times greater (50 times) than electrochemical processes and surface quality is much better than EDM. Also the wear of the working electrode is much smaller than in the classical EDM process. The research also concerned metallic composite materials (e.g. aluminum 6061 with Al2O3 grains at amounts of 10 ÷ 20%) [1, 4]. The results of ECDM processing of such materials are also promising, although they have been implemented in very few cases. The ECDM process has also been used with a positive effect during treatment of Nd-Fe-Ba alloy and composite material on the ceramic matrix ZrB2-Cu.

An additional anode (e.g. made of Pt) should be used to maintain the machining process for low conductivity or non-conductive material. The current flows between the additional anode and cathode, on which hydrogen is released, and electrical discharges occur between the cathode and the electrolyte. As a result of these discharges, material is removed from the workpiece (by melting, evaporation, crushing and additionally thermal digestion). This variant of the ECDM process is called in literature the spark-assisted chemical engraving (SACE). It has been used successfully to treat Al2O3, glass or ZrO2 [4, 7].

All ECDM process studies - both for metals and their alloys, metallic and ceramic composite materials and non-conductive ceramics - show the advantages of high efficiency, good surface quality and low electrode wear - Matched processing conditions. Nevertheless, this process has not yet been widely applied in industrial practice due to, among others, poor popularization of the research results. For this reason, the purpose of this article is to demonstrate the practical uses of EDM and ECDM (also in the SACE variant).

Electro-discharge machining of composite materials on ceramic matrix

Among ceramic materials (e.g. Si3N4, Al2O3, B2C), ZrO2 has very good durability (~12 GPa) but moderate hardness. It can be increased by adding a conductive phase. This improves the electrical conductivity and allows electro-discharge machining of such material [8]. In order to improve mechanical properties and enable more efficient EDM processing, WC, TiCN or TiC in the form of nano, micro powders or mixtures were added to ZrO2-based ceramics. By changing the percentage of these phases (40 ÷ 60%) and grain size in the conductive phase, the cutting speed can be adjusted in the range of 3 ÷ 10 mm/min. At the same time, Re changes in the range of 9 ÷ 20 μm. Cutting tests were performed on a Charmilles Robofil 240C. A bronze wire with a diameter of 250 μm was used, and the process was carried out in deionized water with a conductivity of 5 μS/cm. Studies have shown that by properly selecting the type and granularity of the conductive phase of ceramic materials based on ZrO2, it is possible to significantly influence on the cutting speed and roughness of the machined surface, which decreases as the cutting speed decreases [8].

Electrochemical-electro-discharge machining of composite materials on metallic matrix

Metallic-matrix composite materials can be processed both by EDM and ECDM.

![Fig. 2. Typical voltage pulse waveform in ECDM; Phase I - increase of inter-electrode voltage with simultaneous electrochemical phase of electrochemical dissolution and hydrogen secretion up to the attenuation voltage φ2 and spark initiation. At the start of the discharge the voltage drops to φ - Phase II, where the arc discharge lasts until the end of the voltage pulse; Phase III, as a result of the capacitive effect, the voltage gradually decreases to zero [9]](image-url)
ECDM process studies were performed for aluminum composite 359 composite material containing 20% SiC (reinforcing phase). The size of the strengthening phase grain was 10 μm. NaNO₃ concentrations of 1 to 1.6% were used as the electrolyte. The electrolyte was pumped through the nozzle into the treatment area.

The effect of discharge current, pulse time, pause time, and electrolyte concentration on ECDM [9] was investigated. There was also a randomized EDM process. The treatment was carried out for 3 min. Breakdown voltage was 26 ÷ 30 V for ECDM and 110 V for EDM. The productivity of both processes was comparable. Because of the low concentration and conductivity of the electrolyte, the ECM share in the removal of the metallic phase (allowance) was small. Performance numbers are not given.

Fig. 3 shows selected large and irregular processing products. Their dimensions and shape indicate that, as in the EDM, the basic mechanism of ECDM overrun removal is the crushing caused by thermal stresses. Surface analysis after ECDM and EDM shows that there is also a process of re-solidification of molten or evaporated material. Thus, melting and evaporation are further main mechanisms of removing allowance. The similarity between EDM and ECDM products demonstrates that arc discharges occur in both processes. The average dimensions of the largest (percentage) ECDM products vary between 23 ÷ 80 μm. In the EDM process the product dimensions are 35 ÷ 100 μm. Although products below 5 μm can also be found.

Electrochemical-electro-discharge machining of non-conductive materials

Glass, silicon and polymers are popular materials used in the manufacture of MEMS. The hardness and fragility of glass impedes its processing. Previous methods of micro hardworking and brittle materials have not been satisfactory. USM can be used to process glass and ceramics, but its range is limited by high sonotrode wear and mechanical cracks on the surface and inside the workpiece. Lithographic methods provide very good surface quality and edge sharpness, but in this case, the amount of material is limited. LBM laser processing enables most materials to be formed, but its use for forming reflective and transparent materials is hampered. In ECDM, the material is removed by electrical discharges accompanied by heat release and temperature increase (6,000 ÷ 12,000 K), which causes the material to melt and evaporate, and sometimes tear due to internal thermal stresses [10]. The workpiece is immersed in an electrolyte (usually aqueous NaOH or KOH). The voltage is applied to the additional electrode (the anode - most often made of Pt) and the tool (cathode) near the workpiece of the non-conducting electric current.

The anode reaction: 4OH⁻ → O₂ + 4e⁻, while the cathode reaction is following: 2H₂O + 2e⁻ → 2OH⁻ + H₂

When the voltage reaches a critical value, the hydrogen bubbles form a layer adjacent the cathode and over-discharge (penetration of the layer). Since the electrode (cathode) is close to the workpiece, during the discharge the material from its surface is removed by melting and evaporation.

Fig. 3. ECDM erosion products in 359 aluminum alloy reinforced with SiC (voltage amplitude U = 110 V, pulse time 40 μs, NaNO₃ electrolyte concentration 1%, current amplitude 5 A, treatment time 3 min, gap between electrodes s = 5 microns). The average size of the largest (percentage) ECDM products varies between 23 ÷ 80 μm [9]

Fig. 4. Typical surface view after ECDM treatment (Al 359 + 20% SiC grains of 10 μm) - reusable metallic phase and reinforcing phases and microcracks are visible again [9]
Presented research was aimed at the production of holes (drilling) and structures smaller than 100 μm and good surface quality (milling) in glass (Pyrex Glass). The effect of the type of electrolyte, its concentration, and the time of the voltage pulse and the time interval for the results of the process were analyzed.

By changing the type of electrolyte (KOH 20 ÷ 40% and NaOH 20 ÷ 30%), the voltage amplitude (30 ÷ 40 V) and the interval between voltage pulses (0 ÷ 3 ms), the opening diameter of the electrode can be varied within 70 ÷ 110 μm. The exit hole diameter for the above parameters varies between 50 ÷ 70 μm. The time of execution of through holes in a 150 μm plate varied with the given variation ranges of parameters in the range 500 ÷ 2000 s. The execution time of the hole decreased significantly as the electrolyte concentration increased.

In milling operations, the allowance was removed layer by layer to the depth required. Removing the material with thin layers prevents the random mechanical contact of the electrode (cathode) during its infiltration of the workpiece, and thus the formation of cracks on the workpiece. It also favors better flushing of the gap between the cathode and the workpiece and thus the material is more easily removed. Unfortunately, as the layer thickness decreases, the processing time increases. A stable process was observed for the removal layer with a thickness of ~ 30 μm. Increasing this thickness to 40 μm caused the cathode to hit the workpiece and microcracks at the same time. For safety, further material was removed with 25 μm thick layers.

At more than 3 μm/s, the feed rates make microcracks, and over 5 μm/s, the tool breaks.

The WECDM, also known as Wire Spark Assisted Chemical Engraving (WSACE), can be used for slicing non-conductive materials with high hardness, brittleness
or strength. As a result of electrochemical reactions, a thin layer of hydrogen forms on the cathode. If the voltage reaches a critical value, there is a continuous discharge, and the material from the workpiece is removed by electrical erosion and chemical etching. In the case of the wire cut process as a result of lightning and wire vibrations at usually thin slit thickness, the cut quality is not satisfactory. In order to maintain the proper thickness of the slit, a mixture of SiC abrasive grains was used.

Adding the abrasive to the electrolyte causes the grains to be also located in the machining area and prevent the accumulation of hydrogen bubbles in one place. Thanks to that, the hydrogen layer is fairly uniform. This causes the critical voltage to increase, thereby decreasing the energy of the discharge, thus reducing the fracture of the fracture gap (Fig. 10). Adding abrasive reduces surface roughness. Abrasive grains participate in the allowance removal process, helping to reduce microcracks and melted areas that result from discharges. The use of smaller grains is conducive to reducing $R_s$.

![Fig. 10. Width of cutting slit in SACE (Pyrex Glass): $R_s = 0.84$ μm, breakage of 0.024 mm, KOH electrolyte with SiC grain size (average particle size 57 μm) with a concentration of 300 g/l [11]](image)

When using SACE machining to holes with greater depths, Al$_2$O$_3$ exhibits a distinct deterioration in the hole quality (cracks due to temperature shock). To reduce this effect, a metal-based grinding wheel (instead of a cylindrical metal cathode) was used (fig. 11).

![Fig. 11. Schematic diagram of Al$_2$O$_3$ element machining with SACE electrodes with abrasive grains [12]](image)

The use of the abrasive tool makes it possible to make deeper holes with better performance and better surface quality. The maximum depth is 1.5 mm, the revolutions range from 275 to 631 rpm, and the voltage pulse amplitude is 50 ÷ 120 V. Special voltage pulse generator ($U$ to 300 V), current pulse up to 15 A, pulse $t = 0.25 \div 1000$ μs, feedrate 0.002 ÷ 1.980 mm/min, speed 0.1 ÷ 99 rpm. Depending on the amplitude of the current, pulse duration and voltage amplitude, the output varied between 5 ÷ 30 mm$^2$/min.

**Conclusions**

In order to achieve high durability of machine elements or tooling, ceramics and composite materials are increasingly used in their manufacture. The dynamically developing MEMS applications require the processing of microparts (<1 mm) from special materials such as silicon and its compounds, quartz or various types of glass (e.g. Pyrex Glass). Effective shaping of these materials by conventional machining or conventional grinding and ultrasonic machining is very difficult or impossible due to their mechanical properties or small dimensions of MEMS components. Also the use of laser treatment is limited due to the fracture of the material. Rational solution to these problems is the use of unconventional methods - electrochemical, electro-discharge or electrochemical-discharge machining (ECDM) for at least partially conductive materials. Nonconductive ceramics can be shaped using an ECDM variant called spark assisted chemical engraving (SACE).

The article presents basic possibilities and problems associated with shaping these special materials on the example of:

- EDM cutting of ZrO$_2$ material with conductive phases: WC, TiCN or TiC in the form of nano, micro powders or mixtures,
- ECDM composite treatment based on aluminum alloy 359 containing 20% SiC (reinforcing phase),
- drilling and milling microelements made of Pyrex Glass applying SACE,
- Pyrex Glass wire cut in a mixture of electrolyte with abrasive grains,
- drilling holes in Al$_2$O$_3$ with a grinding wheel on a metallic matrix by means of SACE.

**REFERENCES**


