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Electrical Discharge Machining of Alumina Using Ni-Cr Coating and SnO Powder-Mixed Dielectric Medium

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Abstract: Aluminum-based ceramics exhibit excellent wear resistance and hot hardness that are suitable for various responsible applications allowing products to work under extreme mechanical and thermal loads (up to 1000 °C). The problem of high-precision forming complex-shaped parts is a known engineering challenge due to the insulating properties of aluminum-containing ceramics and the formation of chemically active carbides in a hydrocarbon medium. The alternative approach for electrical discharge machining non-conductive sintered Al2O3 in the water-based medium using nickel-chrome plasma-vapor-deposited coating of 12 mm, SnO powder suspension (particle diameter of ø10 μm, concentration of 150 g/L), and brass wire-tool is proposed. The productivity was evaluated by calculating the material removal rate and discharge gap for various combinations of pulse frequency and duration. The maximal material removal rate of 0.0014 mm3/s was achieved for a pulse frequency of 30 kHz and pulse duration of 1.7–2.5 μs. The recommended value of the interelectrode gap is 48.0 ± 4.9 μm. The possibility of electrical discharge machining aluminum-containing insulating ceramics without using hydrocarbons, carbon and copper-group assisting measures was proposed and shown for the first time. The chemical content of the debris in the interelectrode gap between components of the materials was thermochemically analyzed.

Keywords: alumina; assisting electrode technique; brass; electrical discharge machining; electrode; erosion; thermochemical analyses

1. Introduction

The well-known drawback of shaping ceramics is related to the excellent properties that allow them to work under extreme mechanical and thermal load conditions [1,2]. Cutting ceramics is prospective cutting tool material for milling nickel based alloys achieving temperatures of 800 °C in the working zone [3]. The specific wear of ceramics shows their typical brittle fracture [4,5]. It makes ceramics unreplaceable for a wide range of applications such as the cutting tool industry, common machinery, and aerospace industry that can be only improved by adding fillers during sintering [6–9] or deposit complex multi-component or nano-structured coatings [10,11]. Some important properties of alumina are given in Table 1 [12]. At the same time, these properties hamper the development of machining technologies and make ceramics extremely difficult-to-machine material [13,14]. Up to now, it is possible to obtain some simple shapes with powder sintering and grinding [15], but more precise shaping is an energy and resource-intensive process [16].

Electrical discharge machining is a known method of machining for hard materials allowing the shaping of conductive materials by electrical erosion [17]. The authors of the method, Lazarenko spouses, mentioned in their works complex nature of the thermochemical dissociation of the electrode materials [18,19] without changing the electrical
properties of the oxide and nitride ceramics by adding fillers [20]. This already classical way of shaping difficult-to-machine materials by electrical discharges (thermal dissociation of the material) [21] does not work in the case of insulating materials [22]. One of the ways to make the alumina able to be subjected to electrical erosion without introducing the conductive particles into its structure and losing optical properties was proposed more than 35 years ago [23]. Ten years later, similar experiments allowed electrical discharge machining Si₃N₄ insulating ceramics in hydrocarbons to a depth of 1.5–2.0 mm [24].

Table 1. Some physical, thermal, optical and electrical properties of alumina.

| Property                     | Value                        |
|------------------------------|------------------------------|
| Density, g/cm³               | 3.8–4.0                      |
| Melting Point, K             | 2345                         |
| Coefficient of Linear Thermal Expansion, α × 10⁶, K⁻¹ (at 20–1000 °C) | 7.0–8.0                      |
| Thermal Conductivity, λ, W/(m·K⁻¹) (at 20–1000 °C) | 22–25                        |
| Spectral Transmission Range, µm | 0.17–5.5                    |
| Permittivity, F/m            | 9.5–10.0                     |

The principle is in the addressing of the electrical discharges on a conductive (assisting) coating that covers the insulating workpiece (Figure 1) [25]. Then the addressed to the coating discharges contribute to the material heating and sublimating, sometimes thermal cracking of the subsurface under layers (dielectric substrate) [20]. It should be noted that many materials (such as carbon in its many forms) do not exist in the liquid phase at elevated heat and under normal pressure [26–29]. Despite this fact, they can be easily subjected to electrical erosion. Several research groups developed the idea with the results presented in Table 2 [30–34]. It can be summarized as follows:

1. Maximum achievable depth is about 5000 µm was achieved in the carbon-containing medium with carbon particles [34];
2. Most of the works were conducted in carbon-containing mediums (hydrocarbons) that can have dramatic consequences for the personnel and equipment and are not applicable on the industrial scale;
3. The material for the primary and assisting electrodes is varied from work to work (mostly copper-group materials);
4. There are no works devoted to electrical discharge machining with a wire tool electrode, meanwhile it can be prospective for the cutting tools and aerospace industry;
5. The main type of the assisting electrode deposition to the dielectric substrate (Al₂O₃ workpiece) is adhesion when other physical and chemical methods of deposition based on material diffusion, as an example, stayed not estimated;
6. In all the considered works related to Al₂O₃ ceramics, the roughness of the obtained surfaces is not provided, but visually the machined surface does not correspond to the basic requirements for the responsible surface of machinery parts: the surface contains visible macrodrops and material agglomerations, ceramics has presence adsorbed carbon-containing components of the medium, Rₐ is more than approximately 3.6–6.3 µm.

As was shown in the literature review, there is only a published work devoted to the experiments with electrical destruction of insulating alumina in a water-based medium [30]. However, the work is dedicated to electrical discharge milling using a steel electrode without reporting the final quality parameters of the obtained surface and the eroded depth in the workpiece material. The rest studies used carbon-containing mediums [31–34] and even carbon-containing assisting materials [34].
Figure 1. Principle of the electrical erosion of insulating material using assisting electrode technique.
Table 2. Reported types of auxiliary electrodes.

| Auxiliary Electrode | Primary Electrode | Dielectric Medium | Technology | Workpiece Material | Machined Epith | Reference |
|---------------------|-------------------|-------------------|------------|--------------------|---------------|-----------|
| Copper | - | Sheet | - | Steel | Water-based emulsion | Electrical discharge milling | Al₂O₃ | - | [30] |
| | - | Foil | Adhesive | - | Kerosene | Electrical discharge machining | Al₂O₃ | - | [31] |
| | 60 µm | Foil | Adhesive | Copper, 5000 μm x 5000 μm | Kerosene | Electrical discharge machining | Al₂O₃ (92% of purity) | Depth of 1500 μm | [32] |
| Silver | 20 µm | Varnish (45% of silver) applied with a paintbrush | Adhesive | WC rod with 6% of cobalt binder, ø115 or 500 μm * | Hydrocarbon (mineral) oil HEDMA-111 | Micro-electrical discharge machining | 10% of Alumina Toughened Zirconia, ZrO₂-Al₂O₃ | Depth of 731 µm x ø120 μm for programmed depth of 500 masμm, 43 min of processing | [33] |
| Carbon | - | Polymer-based material containing carbon powder | Adhesive, heated at 150 °C | Copper pipe of ø3500 μm with a hole of ø3000 μm | Kerosene with graphite powder of ø30 μm average particle size, concentration of 7000–10,000 mg/L | Electrical discharge machining | Al₂O₃ | Depth of ~5000 µm, ~235 min of processing | [34] |

* the authors provide two different values in two paragraphs.

When developing technology of electrical discharge machining (EDM) insulating ceramics using assisting electrode technique, it should be considered that the erosion products (debris) and the near-surface layer of the machined surfaces are formed from the components of the ceramic workpiece, dielectric medium, an assisting electrode in the presence of high heat (over 10,000 °C) [17–19]. As can be seen from the successful results with electrical discharge machining insulating zirconia [34,35], the formation or addition of any conductive debris can assist electrical erosion [36]. Otherwise, the formation of insulating debris hampers further electrical discharge machining [37,38].

It should be emphasized that forming some chemicals in the form of insoluble or pyrotechnically dangerous sediment or gas can have catastrophic consequences for equipment and personnel [39–41]. This fact is often ignored by modern searching works and was brought to attention only a few times before. Firstly, it was mentioned by method creators [18,19]. It was again brought to attention in developing a similar technology (electrical discharge milling) [42]. And later, in researching assisting electrode techniques, there was considered the importance of chemical interactions between elements [35]. The research group of MSUT Stankin has investigated the problem of texturing insulating cutting ceramics with attention to thermochemistry for many years [20,21] and has developed an independent theoretical approach [43] approved by international publications and supported by experiments [44]. That confirms the idea that thermochemical interaction of the material components in the presence of high heat should be considered for further research [45]. Moreover, the chemical composition of the erosion debris can be predicted by pre-calculating such factors as enthalpy and entropy of the reactions [46].

Thus, the formed erosion products may have properties that are incompatible with the concept of safety in engineering, so it is necessary to carefully analyze the composition of all used primary and auxiliary materials before designing the conditions for electrical discharge machining non-standard for the technology materials [43,45].
Aluminum exhibits specific thermochemical properties—a high affinity for oxygen under normal conditions (due to its high electronegativity, $\chi = 3.44$). During the thermal decomposition of the oxide in the presence of hydrocarbons, it forms dielectric compounds $\text{Al}_4\text{C}_3$ or $\text{Al}_2(\text{C}_2)_3$ that exhibit insulating properties as all the methanides and acetylenides. They are unstable to water, oxygen, and hydrogen [47]:

$$2\text{Al}_2\text{O}_3 + 9\text{C} \rightarrow \text{Al}_4\text{C}_3 + 6\text{CO}↑ \quad \text{(over 1800 °C)} \quad (1)$$

$$\text{Al}_4\text{C}_3 + 6\text{O}_2↑ \rightarrow 2\text{Al}_2\text{O}_3 + 3\text{CO}_2↑ \quad \text{(at 650–700 °C)} \quad (2)$$

$$\text{Al}_4\text{C}_3 + 6\text{H}_2↑ \rightarrow 4\text{Al} + 3\text{CH}_4↑ \quad \text{(at 2200 °C)} \quad (3)$$

Thus, to avoid the presence of the carbides in the working area during electrical discharge machining of Al-containing ceramics, it was decided to choose water-based suspension assisted by one of the metal oxides that exhibit semiconductive properties, stable at normal conditions and commercially available on the market. One of the prospective oxides with the band gap $E_g$ of 2.5–3.0 eV at 300 K is SnO (tin monoxide), an $n$-type broadband semiconductor obtained by thermal decomposition of the tin (IV) oxide ($\text{SnO}_2$, $E_g = 3.6$ eV). As less band gap is, as more conductive properties exhibits compound [48,49].

At the same time, the most typical coating for the assisting electrode technique used in the works is copper foil or sheet placed adhesively on the surface of the ceramic workpiece due to its relatively high conductivity and inertness to the medium [30–33]. During decomposition in water, it forms insulating oxides as other elements of the copper group (Ag, Au) that are unstable in the presence of hydrogen (in the case of Cu) [50] or dissociates at elevated temperatures (as Ag-oxides and Au$_2$O) [51,52]. It should be noted that Au$_2$O$_3$ is stable and conductive under normal conditions, but the possibility of its usage on the industrial scale is limited economically [53].

An applied by the plasma vapor deposition method [54,55] Ni-Cr coating was proposed as an alternative to the proven assisting electrode materials. The nickel-chromium was chosen due to the known affinity of nickel for aluminum to form conductive bonds [56,57]. The principle of the chemical compound formation during electrical discharge machining is shown in [43,45].

The current study aims to develop a method of electrical discharge machining alumina using non-carbon-based medium and assisting particles. The current study’s novelty is searching for a way to solve the global problem of alumina machinability based on material destruction under electrical discharge, excluding pyrotechnically dangerous component formation and using alternative commercially available materials for texturing cutting ceramics on the industrial scale. The band gap of tin oxide determines the choice of this $n$-type broadband semiconductor powder to assist electrical discharge machining alumina when the known affinity of aluminum to nickel determines the choice of the coating composition.

### Nomenclature of used symbols

| Symbol | Description | Unit |
|--------|-------------|------|
| $U_o$  | Operational voltage | V    |
| $f$    | Pulse frequency | kHz  |
| $D$    | Pulse duration  | µs   |
| $W_r$  | Rewinding speed | m/min|
| $W_f$  | Feed rate      | mm/min|
| $F_T$  | Wire tension   | N    |
| $\Delta$ | Discharge gap | µm  |
| $d_w$  | Wire diameter  | mm   |
| $r_{w}$ | Wire radius   | µm  |
| $r_{w}^\prime$ | Wire radius taking into account spark gap $\Delta$ | mm  |
| $w$    | Width of kerf  | µm   |
| $h$    | Depth of kerf  | µm   |
| $l$    | Length of kerf | mm   |
Table 14. Calculated enthalpy of formation of some Ni-containing substances.

| Substance | Enthalpy $\Delta H^\circ$, kJ·mol$^{-1}$ |
|-----------|----------------------------------------|
| $\text{NiO (12)}$ | -1675.0 |
| $\text{AlNi (15)}$ | -121.9 |

Table 15. Calculated entropy of some Ni-containing substances and equilibrium temperatures.

| Substance | Entropy $\Delta S^\circ$, J·mol$^{-1}$·K$^{-1}$ |
|-----------|----------------------------------------------|
| $\text{NiO (12)}$ | 4.68 |
| $\text{AlNi (15)}$ | 2.56 |

| Substance | Gibbs energy $\Delta G^\circ$, kJ·mol$^{-1}$ |
|-----------|----------------------------------------------|
| $\text{NiO (12)}$ | 2870.0 |
| $\text{AlNi (15)}$ | 2568.0 |

2. Materials and Methods

2.1. Sintering of the Samples

The following powder was used for producing samples:

- Corundum $\alpha$-Al$_2$O$_3$ A16SG (Alcoa, New York, NY, USA), with an average particle diameter $d_{50} = 0.53$ μm.

Granulometric analysis of powder was carried out on specialized equipment—an optical analyzer of granulometry and particle morphology 500NANO (Occhio, Liege, Belgium). Optical microscopy was carried out on an Olympus BX51M instrument (Ryf AG, Grenchen, Switzerland).

Powder mixtures were prepared and ground in a Turbula multidirectional shaker (Eskens B.V., Alpen aan den Rijn, The Netherlands) in ethanol in a polyethylene container at 150 rpm for 24 h. Suspensions were dried in a FreeZone2.5 lyophilizer (LabConco, Kansas, MI, USA) to increase the density of the poured powders and to avoid accumulation and agglomeration. The collector temperature was set at $-50 \pm 2$ °C, while the sheath temperature was $+23 \pm 2$ °C. During the entire treatment process, the pressure in the chamber was $0.02 \pm 0.01$ mbar.

The prepared powder mixtures were freely poured into specially prepared molds made mechanically of graphite blanks. The standard grade of graphite MPG-6 for special applications with a degraded structure are made on cokes such as shale, pitch, etc. are made by “cold” pressing. Mechanical machining of graphite molds required special measures [58,59]. Machining was carried out from graphite blanks with a particle size of 1 μm on CNC milling equipment in the following modes: 100–300 m/min roughing with a feed of 0.1 mm/tooth; 150–600 m/min finishing with a feed rate of 0.013–0.015 m/min on a CTX beta 1250 TC turning and milling machine (DMG Mori Seiki Co., Ltd., Nagoya, Japan) equipped with a SinumerikCNC system (Siemens AG, Munich, Germany) and vibroacoustic monitoring system (MSUT Stankin, Moscow, Russia) [60] with a carbide tool with a multi-layer combined coating [61,62] deposed by physical vapor deposition [63].

The alumina powder was compacted into molds and sintered on a spark plasma sintering machine KCE FCT-H HP D-25 SD (FCT Systeme GmbH, Rauenstein, Germany) at 1400 °C with a heating rate of 100 °C·min$^{-1}$ at uniaxial pressure 80 MPa in vacuum [64–66]. The final temperature and pressure were maintained for 10 min. The sintered discs with a diameter of 65.5 mm and a thickness of 5.5 mm were labeled.

The resulting samples were examined using scanning electron microscopy (SEM) on VEGA3 equipment (Tescan, Brno, Czech Republic) at the fracture site. The fracture was made mechanically of graphite blanks. The standard grade of graphite MPG-6 for special applications with a degraded structure are made on cokes such as shale, pitch, etc. are made by “cold” pressing. Mechanical machining of graphite molds required special measures [58,59]. Machining was carried out from graphite blanks with a particle size of 1 μm on CNC milling equipment in the following modes: 100–300 m/min roughing with a feed of 0.1 mm/tooth; 150–600 m/min finishing with a feed rate of 0.013–0.015 m/min on a CTX beta 1250 TC turning and milling machine (DMG Mori Seiki Co., Ltd., Nagoya, Japan) equipped with a SinumerikCNC system (Siemens AG, Munich, Germany) and vibroacoustic monitoring system (MSUT Stankin, Moscow, Russia) [60] with a carbide tool with a multi-layer combined coating [61,62] deposed by physical vapor deposition [63].

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The resulting samples were examined using scanning electron microscopy (SEM) on VEGA3 equipment (Tescan, Brno, Czech Republic) at the fracture site. The fracture was
done mechanically, which required the application of significant and repeated efforts. A chemical analysis of the fracture sites was also carried out on the same equipment.

2.2. Electrical Discharge Machining

A two-axis wire electrical discharge machine ARTA 123 Pro (NPK “Delta-Test”, Fryazino, Moscow Oblast, Russia) was used for experiments (Figure 2a). The coated samples are presented in Figure 2b. Figure 2c shows the scheme of the sample fastening at the CNC machine. The main characteristics of the machine are presented in Table 3.

Figure 2. (a) Wire electrical discharge machine ARTA 123 Pro (common view); (b) coated samples; (c) installation of the coated Al₂O₃ sample at working area of the machine, where 1—upper guide, 2—holder, 3—replaceable work tank; 4—a coated workpiece; 5—a rewinding wire tool; 6—a lower guide.

Table 3. Main characteristics of wire electrical discharge machine ARTA 123 Pro.

| Specification                          | Value and Description |
|----------------------------------------|-----------------------|
| Max axis motions along the axes X × Y × Z, mm | 125 × 200 × 80         |
| Accuracy of positioning along the axes, µm | ±1                    |
| Achievable roughness parameter Ra, µm  | 0.6                   |
| Dielectric medium                      | Any                   |
| Max power consumption, kW              | <6                    |

Water-based suspension of SnO with various concentration (7, 14, 21, 35, 50, 100, 150 g/L) was used as dielectric medium. The following powder was used for producing suspension:

- tin (II) oxide SnO ChDA GOST 22516-77 (OOO “PKF Cvet”, Yekaterinburg, Sverdlovskaya obl., Russia), with an average particle diameter d₅₀ = 164 µm.

The powder was subjected to granulometric analysis and optical microscopy. During preparing the suspension, an EL104 (Mettler Toledo, Columbus, OH, USA) laboratory balance with a measurement range of 0.0001–120 g with an error of 0.0001 g was used. According to the previously published data by different research groups [67–70], the smallest size of suspended particles led to the highest rate of volumetric material removal and to the lowest wear of the primary tool electrode.

The pre-sieved powders were mixed into suspension before each experiment. It was constantly stirred during it, since the powder particles are specifically heavy, and their weight favored their settling to the bottom of the working tank. After processing, the samples were cleaned with alkali.
The CNC program was prepared manually as a single approach to the coated workpiece; the path offsets were not considered. The technology factors in equivalent units of the machine chosen following the recommendations [71] are presented in Table 4. The classical tool electrode was a brass wire \( d_w \) of 0.25 mm in diameter made of CuZn35 (Cu—65%; Zn—35%) due to its conductivity, inertness to the media, and availability in industrial conditions. Pretesting experiments with each SnO-concentrations were conducted 3 times for 9 sets of the factors depending on the obtained results and is about 200 experiments. More than 150 experiments were conducted (five repeats for each factor-set).

Table 4. The factors chosen for wire electrical discharge machining in the water-based suspension.

| Factor                  | Value                      |
|------------------------|----------------------------|
| Operational voltage, \( U_o \) | 108 V                      |
| Pulse frequency, \( f \)     | 10, 15, 20, 25, 30 kHz     |
| Pulse duration, \( D \)      | 1, 1.5, 1.7, 2, 2.35, 2.7 \( \mu s \) |
| Rewinding speed, \( W_s \)  | 3.4 m/min                  |
| Feed rate, \( W_f \)        | 0.1 mm/min                 |
| Wire tension, \( F_T \)      | 0.25 N                     |

The parameters of the kerf were controlled by optical microscopy. Here and below, the optical measurement error was calculated by the formula [72,73]:

\[
\delta_l = \pm \frac{L}{30} + \frac{gL}{4000}, \quad (4)
\]

\[
\delta_t = \pm \frac{L}{50} + \frac{gL}{2500}, \quad (5)
\]

where \( \delta_l \) is the longitudinal measurement error, \( \mu m \); \( \delta_t \) is the transversal measurement error, \( \mu m \); \( L \) is the measured length, mm; \( g \) is the product height above microscope table glass (taken equal to zero), mm.

The spark gap \( \Delta \) was calculated using the following formula [74]:

\[
\Delta = \frac{h}{2} + \frac{w^2}{8h} - r_w, \quad (6)
\]

where \( w \) is the width of slot (kerf), \( \mu m \); \( h \) is the depth of slot (kerf), \( \mu m \); \( r_w \) is the tool electrode radius (125 \( \mu m \)), \( \mu m \).

The volumetric material removal rate was calculated through the feed rate of the primary electrode into the processing area and the volume of removed material [75,76]:

\[
A = \frac{1}{2} r_w^2 \left( \alpha - \sin \alpha \right), \quad (7)
\]

where \( A \) is the kerf area in the plan, mm\(^2\); \( r_w' \) is the radius of the electrode-tool, taking into account the spark gap, mm; \( \alpha \) is the angle of the cutting segment in the plan, rad. The volume of removed material is calculated using the formula:

\[
V = A \cdot l, \quad (8)
\]

where \( l \) is the length of slot (kerf), mm. Then the material removal rate is [77]:

\[
MRR = \frac{V}{t}, \quad (9)
\]

where \( t \) is the machining time calculated from the feed rate of the electrode-tool, s.
2.3. Ceramic Workpiece Coating

The chosen thickness of the coating was 12 μm to provide the conductive layer; the thickness was controlled optically [78]. The coating was deposited at a STANKIN-APP technological unit prototype (MSUT Stankin, Moscow, Russia) [54,55]. KhN771YuR (NiCr20TiAl) chrome-nickel alloy was chosen as the target [79], where Ni is responsible for thermal resistivity, and Cr hampers oxidation [80]. Before coating, the ceramic samples were placed in an ultrasonic tank and were cleaned using a soap solution at a temperature of 60 °C for 20 min and in alcohol for 5 min.

A Fischer Sigmascope SMF10 instrument (Helmut Fischer GmbH, Sindelfingen, Germany) controlled the specific electrical resistance ρ of the deposited coating. The device measures the electric conductance in Siemens and the percentage of the control sample’s electrical conductance produced from annealed bronze in the range of 1–112%.

Approbating the coated sample was conducted without SnO powder in a water medium.

2.4. Thermochemical Analyses

To assess the chemical composition of formed debris in the conditions of the elevated temperatures, the authors proposed an original estimation technique based on the main thermochemical parameters—enthalpy (ΔHf, kJ mol⁻¹) and entropy (ΔSf, J mol⁻¹ K⁻¹), Gibbs energy (ΔGf, kJ mol⁻¹), and calculating the equilibrium temperature (T, K) of the proposed systems [81]:

\[ \Delta G_f = \Delta H_f - T \cdot \Delta S_f \]  

The focus is on the interaction of nickel of the chosen coating with oxygen, zinc of the wire tool electrode, and aluminum of the workpiece. The chemical reactions with Ni of the coating with water medium can be presented as [43,82,83] when NiO was taken as the most likely compound of nickel with oxygen:

\[ Ni^2+ + H_2O \xrightarrow{T} NiO + H_2 \]  

(11)

Knowing the peculiarity of nickel to form intermetallic compounds with some metals, we will consider the possibility of forming a NiZn₃ intermetallic compound (γ-phase, evidenced by the constancy of the entropy factor) [84] as a more prevalent chemical reaction (reverse corrosion process):

\[ Ni^2+ + 2Zn^{2+} \rightarrow NiZn + \frac{1}{3}Zn^{4+} \rightarrow NiZn_3 + \frac{1}{2}Zn^{4+} \rightarrow Ni_5Zn_{21} \text{(metastable phase)} \rightarrow \frac{1}{5}Ni^2 + 21Zn^{2+} \rightarrow Ni_5Zn_{21} \]  

(12)

According to the state diagram [85–87], five compounds are formed in the alloys of the Al-Ni system: Al₃Ni, Al₃Ni₂, AlNi (β’), AlNi₅ (α’), Al₃Ni₅. The Al₂Ni compound has a constant composition. The other compounds have significant areas of homogeneity. The AlNi compound melts congruently, while Al₃Ni₂, AlNi, and AlNi₅ melt according to peritectic reactions. Thus, as AlNi intermetallic compound was taken as a more prevalent chemical reaction:  

\[ 2Al_2O_3 + 4Ni^{2+} \xrightarrow{T} 4AlNi + 3O_2 \]  

(14)

Table 5 presents standard enthalpy and molar entropy for some substances. In considered reaction, it was accepted that Ni is already dissociated in the form of an ion from the coating at elevated temperatures when Al₂O₃ workpiece dissociation has not yet begun (melting point Tₘ of Al₂O₃ is 2345 K, of KhN771YuR chrome-nickel alloy is ~1670 K). The main objective is to create conditions for thermochemical dissociation of Al₂O₃ when the material of electrodes and assisting means demonstrate lower erosion wear and transform into the compounds that improve conducting conditions in the interelectrode gap. In other words, creating denser discharges between electrodes addressed to the conducting or
semiconducting debris. At the same time, it should not be too much debris to avoid short circuit conditions.

Table 5. Enthalpy and molar entropy for some substances at 298 K [88].

| Substance      | Standard Enthalpy of Formation $\Delta H_{298}^{\circ}$, kJ mol$^{-1}$ | Standard Molar Entropy $\Delta S_{298}^{\circ}$, J mol$^{-1}$ K$^{-1}$ |
|----------------|--------------------------------------------------------------------------|---------------------------------------------------------------------|
| Al (c)         | 0                                                                       | 28.31                                                               |
| Al$_2$O$_3$ (c) [89] | $-1675.0$                                                              | 50.94                                                               |
| AlNi (c) [90,91] | $-118.407$                                                              | 11.47                                                               |
| H$_2$ (g)      | 0                                                                       | 130.52                                                              |
| H$_2$O (l)     | $-285.84$                                                               | 69.96                                                               |
| Ni (c)         | 0                                                                       | 29.86                                                               |
| NiO (c) [92,93] | $-239.7$                                                                | 37.99                                                               |
| O$_2$ (g)      | 0                                                                       | 205.03                                                              |
| Zn (c)         | 0                                                                       | 41.63                                                               |
| ZnO (c) [94]   | $-350.8$                                                                | 43.5                                                                |

3. Results and Discussion

3.1. Characterization of Al$_2$O$_3$ and SnO Powders

Granulometric analysis of Al$_2$O$_3$ powder showed that it has a predominantly favorable spherical shape of granules, which contribute to dense compaction of the powder into molds and positively affect the porosity of the samples (Figure 3, Table 6). The variety of powder sizes should have a positive effect on the mechanical characteristics of sintered samples and increase their impact strength; the powder does not have pronounced peaks along the inner diameter.

Figure 3. Granulometric analysis of the composition of aluminum oxide powder.
Table 6. Granulometry of aluminum oxide powder.

| Inner Diameter Range, µm | Volume, % | Cumulative Volume, % |
|--------------------------|-----------|----------------------|
| 1.00–10.00               | 8.17      | 8.17                 |
| 10.00–16.00              | 14.57     | 22.74                |
| 16.00–20.00              | 7.50      | 30.24                |
| 20.00–25.00              | 8.62      | 38.87                |
| 25.00–32.00              | 12.09     | 50.95                |
| 32.00–38.00              | 9.25      | 60.20                |
| 38.00–45.00              | 9.55      | 69.75                |
| 45.00–53.00              | 8.86      | 78.61                |
| 53.00–63.00              | 8.45      | 87.05                |
| 63.00–75.00              | 6.47      | 93.52                |
| 75.00–90.00              | 3.55      | 97.07                |
| 90.00–106.00             | 1.93      | 99.00                |
| 106.00–125.00            | 1.00      | 100.00               |

Granulometric analysis (Figure 4, Table 7) of SnO powder showed that the powder sample had an average inner diameter of 63.79 µm and 33.46 µm for 50% of the particles. The average circularity of the tin oxide powder is about 0.597 µm and about 0.625 µm for 50% of the particles.

Figure 4. Granulometric analysis of the composition of tin oxide powder.
### Table 7. Granulometry of tin oxide powder.

| Inner Diameter Range, \(\mu m\) | Volume, % | Cumulative Volume, % |
|---------------------------------|-----------|----------------------|
| 1.00–10.00                      | 6.81      | 6.81                 |
| 10.00–16.00                     | 9.13      | 15.94                |
| 16.00–20.00                     | 5.85      | 21.79                |
| 20.00–25.00                     | 6.57      | 28.35                |
| 25.00–32.00                     | 8.18      | 36.54                |
| 32.00–38.00                     | 7.52      | 42.25                |
| 38.00–45.00                     | 5.79      | 48.04                |
| 45.00–53.00                     | 7.34      | 55.38                |
| 53.00–63.00                     | 7.36      | 62.74                |
| 63.00–75.00                     | 6.81      | 69.55                |
| 75.00–100.00                    | 6.69      | 76.24                |
| 90.00–106.00                    | 3.09      | 79.33                |
| 106.00–125.00                   | 3.01      | 82.35                |
| 125.00–150.00                   | 3.12      | 85.47                |
| 150.00–180.00                   | 1.70      | 87.17                |
| 250.00–300.00                   | 12.84     | 100.00               |

#### 3.2. Sintered Samples (SEM and Chemical Analyses)

An analysis of the SEM images of the sintered samples’ fracture shows that a fine-grained structure was obtained during sintering, which, as a rule, should have a positive effect on the mechanical properties (Figure 5a). The grain size is in the range of 50–250 nm (Figure 5b). The place of mechanical failure of the sample is characterized by the uniformity of destruction and the passage of a bulk crack (Figure 5a), which can indirectly confirm stronger intergranular bonds and better mechanical characteristics such as strength and impact strength, and hence wear resistance, which is a parameter related to impact strength and depends on the intergranular adhesion of the samples. Analysis of the alumina sample (Figure 5b) showed scattered isthmuses, which may be due to the low electrical conductivity of alumina in the presence of heat.

![Figure 5. Microstructure of the Al₂O₃ sintered sample at the fracture at 10,000 × (a), at 66,700 × (b).](image-url)
The chemical analysis of the sample (Table 8) at the fracture corresponded to the declared chemical composition of the powder without additional inclusions and impurities, which should have a positive effect on the physical and mechanical properties in volume.

| Chemical Elements | Atomic Ratio, at. % | Weight Ratio, wt. % |
|-------------------|---------------------|---------------------|
| Al                | 37.41               | 50.2                |
| O                 | 62.59               | 49.8                |

3.3. Conductive Coating (Assisting Electrode)

The coating showed visually good adhesion (did not peel off after deposition), uniformity (optically uniform thickness in the range of 10–15 µm), and controlled electrical properties. The controlled and calculated electrical properties of the developed PVD coating are shown in Table 9. Values for Al₂O₃ are provided for reference. The coating was not studied tribologically due to the absence of the required mechanical load resistance in the working area of the EDM machine.

| Material          | Electrical Conductivity γ₁, Sm·cm⁻¹ | Electrical Conductivity γ₂, Sm·m⁻¹ | Specific Resistivity R₁, Ω·mm²·m⁻¹ | Specific Resistivity R₂, Ω·m |
|-------------------|-------------------------------------|-----------------------------------|------------------------------------|----------------------------|
| Chrome-nickel alloy KhN77TYuR | 0.008019 ± 0.000001¹ | 0.8019 × 10⁶ | 1.247 | 1.247 × 10⁻⁶ |
| Al₂O₃             | 0.0000001 ± 0.0000005³ | 0.0000474 × 10⁶ | 210,985.2 | 2.11 × 10⁻¹ |

¹ experimental values; ² calculated values; ³ for reference.

3.4. Electrical Discharge Machining (Optical and Scanning Electron Microscopy)

Approbating a sample of alumina ceramics using a Ni-Cr coating showed satisfactory processing results in a deionized water medium. The pre-testing results are planned to be improved using assisting powders. The coating can be considered as prospective, despite the relative difficulty in removing it after processing. The most pronounced (the deepest kerf) electrical discharge machining results using SnO suspension were obtained for the following groups of factors: concentration of 150 g/L, frequency f = 10 kHz, pulse duration D = 2 µs, and D = 2.7 µs. The general view of the working area and results of the optical microscopy for the machined kerf are shown in Figure 6.

Figure 6. The obtained slot (kerf) with a depth of 68.99 µm at pulse duration D = 2 µs, optical microscopy, general view (a), top view (b).
SEM-image and its chemical mapping are presented in Figure 7. The kerf has a classical view of the surfaces subjected to the electrical erosion of the material: the presence of the pronounced borders of the subjected area, deposed material in the form of drops, wells, and pores (Figure 7a). The chemical mapping shows that the ceramic sample under the coating was subjected mainly to thermal destruction. The surface of the kerf chemically corresponds to the chemical composition of the ceramic workpiece (Figure 7b,c). The kerf has traces of the coating: deposed Ni and Cr (Figure 7d,e). The kerf boarders have the presence of the adsorbed tin (Figure 7f). The presence of wire tool components (Cu, Zn) was detected visually but not quantitatively. The detailed spectra are shown in Table 10.

![SEM-image of the machined kerf of the coated Al₂O₃ sample, 10,000× (a), chemical mapping of the observed area by elements, aluminum (b), oxygen (c), nickel (d), chrome (e), tin (f).](image)

**Figure 7.** SEM-image of the machined kerf of the coated Al₂O₃ sample, 10,000× (a), chemical mapping of the observed area by elements, aluminum (b), oxygen (c), nickel (d), chrome (e), tin (f).

**Table 10.** Chemical analysis of machined sample at the machined kerf.

| Spectrum Number | Chemical Elements, wt. % |
|----------------|--------------------------|
|                | Al | O | Ni | Cr | Sn |
| 1              | 37.53 | 48.7 | 4.89 | 2.65 | 1.61 |
| 2              | 36.57 | 48.14 | 5.3 | 2.57 | 1.67 |
| 3              | 39.89 | 48.77 | 4.93 | 2.11 | -   |
3.5. Spark Gap and Material Removal Rate

The measured values of the kerf parameters and the calculated values of the spark gap are shown in Table 11. The spark gap for further calculations was taken as an average that has no more than 20% of the range of scattering values $40 \leq \Delta \leq 60$ that were previously re-searched for the materials with the threshold conductivity [21,71]. Thus, the recommended value of the interelectrode gap is 48.0 ± 4.9 µm.

Table 11. The average measured kerf parameters for each factor-set and discharge gap of the machined alumina using a 12 µm thick Ni-Cr coating and SnO-suspension (150 g/L).

| Number | Pulse Frequency $f$, kHz | Pulse Duration $D$, µs | Kerf Width $w$, µm | Kerf Depth $h$, µm | Kerf Length $l$, µm | Spark Gap $\Delta$, µm |
|--------|--------------------------|------------------------|-------------------|-------------------|---------------------|------------------------|
| 1      | 10                       | 1                      | 310.74 ± 3.01     | 68.99 ± 3.00      | 2000 ± 3.06         | 84.44 ± 4.88           |
| 2      | 10                       | 2.35                   | 318.76 ± 3.01     | 66.32 ± 3.00      | 3600 ± 3.12         | 99.67 ± 4.88           |
| 3      | 20                       | 2.5                    | 269.02 ± 3.00     | 67.99 ± 3.00      | 2000 ± 3.06         | 42.05 ± 4.88           |
| 4      | 25                       | 2.5                    | 257.79 ± 3.00     | 95.20 ± 3.00      | 3000 ± 3.10         | 9.86 ± 4.88            |
| 5      | 30                       | 2.5                    | 320.37 ± 3.01     | 49.74 ± 3.00      | 4000 ± 3.13         | 157.80 ± 4.88          |
| 6      | 10                       | 2.7                    | 254.05 ± 3.00     | 50.81 ± 3.00      | 2000 ± 3.06         | 59.19 ± 4.88           |

The material removal rate is shown in Table 12. A graphical presentation of the results, which shows the relationship between material removal rate and experiment factors (pulse frequency and duration) for the concentration of SnO-suspension of 150 g/L is shown in Figure 8. The optimized values of the factors of electrical discharge machining alumina ceramics using a nickel-chromium coating of 12 µm in thickness with SnO-suspension (150 g/L) were: pulse frequency of 30 kHz, pulse duration of 1.7–2.5 µs.

Table 12. The material removal rate of electrical discharge machining alumina ceramics using a 12 µm thick Ni-Cr coating and SnO-suspension (150 g/L).

| Number | Kerf Area in the Plan $A$, mm² | Volume of Removed Material $V$, mm³ | Estimated Machining Time $t$, s | Volumetric Material Removal Rate, mm³/s |
|--------|--------------------------------|-----------------------------------|---------------------------------|----------------------------------------|
| 1      | 0.0148 ± 0.0000921             | 0.03                              | 41.39                           | 0.0005                                 |
| 2      | 0.0146 ± 0.0000939             | 0.05                              | 39.79                           | 0.0010                                 |
| 3      | 0.0128 ± 0.0000918             | 0.03                              | 40.79                           | 0.0005                                 |
| 4      | 0.0180 ± 0.0000930             | 0.05                              | 57.10                           | 0.0006                                 |
| 5      | 0.0108 ± 0.0000942             | 0.04                              | 29.84                           | 0.0010                                 |
| 6      | 0.0089 ± 0.0000919             | 0.02                              | 30.48                           | 0.0004                                 |

Figure 8. The performance of electrical discharge machining alumina using Ni-Cr coating and SnO-suspension.
3.6. Comparison with Literature

A comparison of the performance achieved by using different methods of electrical discharge machining alumina was carried out for the current study’s data and data obtained by other authors in relation to alumina ceramics (Table 13). The results of the present study were compared with methods in which hydrocarbons were used as a working fluid, machining was carried out using a copper profiled tool such as a prism and tube in combination with an assisting electrode of the copper foil 6 µm thick and a polymer-based carbon tape assisted by graphite particles with a diameter of 30 µm, correspondingly. The data indicate that the developed method is not superior to its closest analogs but has some features that allow considering it as a prospect in texturing cutting ceramics without using carbons. Machining was carried out for a continuously rewinding tool electrode, which has a smaller processing surface area but allows the formation of complex ruled surfaces in contrast to profiled electrodes such as a prism, tube, etc.

Table 13. Comparison of performance parameter of electrical discharge machining alumina based on the use of assistive tools.

| Primary Tool | Assisting Tool | Assisting Powder | Working Medium | Volumetric Material Removal Rate, mm³/s | Reference |
|--------------|----------------|------------------|----------------|----------------------------------------|-----------|
| Brass wire, ø0.25 mm | Ni-Cr PVD coating, 12 µm | SnO particles, ø10 µm, 150 g/L | Deionized water | 0.0014 | Current study |
| Copper prism, 5 × 5 mm | Copper foil, 6 µm | - | Mineral oil (hydrocarbons) | 0.0051 | [32] |
| Copper tube, ø3.5 mm (inner—ø3.0) | Resin-based carbon tape | Graphite particles, ø50 µm, 7–10 g/L | Kerosene (hydrocarbons) | 0.0213 | [34] |

3.7. Thermochemistry Analyses

The entropy, enthalpy, and Gibbs energy of the Ni₃Zn₂₁ intermetallic compound in the crystalline form was previously estimated in [46]. The entropy of the intermetallic compound formation is by the Boltzmann equation taking into account the Stirling theory and the corollary of Hess’s law [95]:

\[
\Delta f S_{298}^{\circ} (Ni₃Zn₂₁) = -359.00 \left[ \frac{J}{mol\cdot K} \right]
\]

Then

\[
\Delta f H_{298}^{\circ} (Ni₃Zn₂₁) = -225.96 \left[ \frac{kJ}{mol} \right]
\]

Gibbs energy is:

\[
\Delta f G_{298}^{\circ} (Ni₃Zn₂₁) = -118.98 \left[ \frac{kJ}{mol} \right]
\]

When \( \Delta f G_{298}^{\circ} < 0 \) the reaction at 298 K is possible in the forward direction from sublimated ions of metals, the presence of high heat in the discharge channel (as any other source of high heat such as laser beam or bombarding by fast atoms [54,96]) can only accelerate Ni₃Zn₂₁ (γ-phase) solidification. The oxide film formed on the transition metals can prevent the direct reaction at 298 K. The formation of Ni₃Zn₂₁ intermetallic compound at temperatures above 1000 °C has an explosive character and accompanies by a series of sparks in the interelectrode gap [19,77] that can be vibroacoustically recorded [21,97]. It should be noted that the enthalpy of the formation of ionic and metallic compounds can be estimated by the empirical value of electronegativities with an accuracy of 13.8–20.4% for intermetallics. The calculated values are provided in Table 14.
Table 14. Calculated enthalpy of formation of some Ni-containing substances.

| Chemical Reaction | Chemical Composition of Debris | Amount of Substance \(n\), mol | Enthalpy of Substances \(\Delta H_{298}^{\ominus}\), kJ mol\(^{-1}\) | Enthalpy of Reaction \(\Delta_r H_{T}^{\ominus}\), kJ |
|-------------------|---------------------------------|-------------------------------|--------------------------------|---------------------------------|
| (12)              | NiO                             | \(1 + 1 \xrightarrow{T} 1 + 1\) | \(-285.8\) \(\xrightarrow{T} -239.7 + 0\) | \([1\cdot(-239.7) + 1\cdot0] - [1.0 + 1\cdot(-285.8)] = 46.1\) |
| (14)              | Ni\(_5\)Zn\(_2\)\(_3\)          | \(5 + 21 \xrightarrow{T} 1\)   | \(0 + 0\) \(\xrightarrow{T} -225.96\) | \([1\cdot(-225.96)] - [5\cdot0 + 21\cdot0] = -225.96\) |
| (15)              | AlNi                            | \(2 + 4 \xrightarrow{T} 4 + 3\) | \(-1675.0 + 0\) \(\xrightarrow{T} -118.4 + 0\) | \([4\cdot(-118.4) + 3\cdot0] - [2\cdot(-1675.0) + 4\cdot0] = 2870.0\) |

The enthalpy of the formation for reactions NiO (12) and AlNi (15) is less than zero; thus, these reactions spontaneously take place with the release of heat in contrast to another reaction. Table 15 shows the calculated entropy, Gibbs energy, and equilibrium temperature. In NiO (12) and AlNi (15) reactions, the entropy is above zero, corresponding to an increase in the degree of chaos (gases of H\(_2\) and O\(_2\)). When entropy is less than zero in the formation Ni\(_5\)Zn\(_2\)\(_3\) (14), reactions occur with a decrease in the degree of chaos (compound solidification). The calculated Gibbs energy for reaction with Ni\(_5\)Zn\(_2\)\(_3\) (14) is less than zero when Gibbs energies for reactions with NiO (12) and AlNi (15) are above zero. It means that the reaction under normal conditions can only pass in the reverse direction: the formation of NiO (12) and AlNi (15) occurs with heat absorption when equilibrium temperatures (672.8 K and 3253.0 K, correspondingly) are achieved. Thus, the reaction of Ni and Zn is more likely with the presence of nickel-containing coating and brass wire since it does not require heat adsorption (Figure 9). As can be seen, the superior role in the formation of conductive debris in the interelectrode gap may play the chemical composition of the primary electrode (zinc of brass) in combination with the Ni-coating of the alumina workpiece machined in a water medium.

Table 15. Calculated entropy of some Ni-containing substances and equilibrium temperatures.

| Chemical Reaction | Chemical Composition of Debris | Entropy of Substances \(\Delta S_{298}^{\ominus}\), J mol\(^{-1}\) | Entropy of Reaction \(\Delta_r S_{T}^{\ominus}\), J | Gibbs Energy of Reaction \(\Delta_r G_{T}^{\ominus}\), kJ mol\(^{-1}\) | Equilibrium Temperature of Reaction \(T_{r}\), K |
|-------------------|---------------------------------|--------------------------------|---------------------------------|---------------------------------|---------------------------------|
| (12)              | NiO                             | 29.9 + 70.1 \(\xrightarrow{T} 38.0 + 130.52\) | \([1\cdot38.0 + 1\cdot130.52] - [1\cdot29.9 + 1\cdot70.1] = 68.52\) | 46.1 - 298\cdot0.06852 = 25.68 \([46.1 \div 0.06852] = 672.80\) |
| (14)              | Ni\(_5\)Zn\(_2\)\(_3\)          | 29.86 + 41.63 \(\xrightarrow{T} 359.0\) | \([1\cdot359.0] - [5\cdot29.86 + 21\cdot41.63] = -664.53\) | 298\cdot(-0.66453) = -27.93 \([225.96 \div 0.66453] = 340.03\) |
| (15)              | AlNi                            | 50.94 + 29.86 \(\xrightarrow{T} 11.47 + 205.03\) | \([4\cdot11.5 + 3\cdot205.0] - [2\cdot50.9 + 4\cdot29.0] = 882.3\) | 298\cdot0.8823 = 2607.0 \([2870.0 \div 0.8823] = 3253.0\) |
4. Conclusions

The conducted study has shown that:

1. The stable electrical discharge machining with the uniform density of electric discharges was achieved for aluminum-containing ceramics with a pulse frequency of 30 kHz and pulse duration of 1.7–2.5 µs;
2. The optimum concentration of the SnO suspension for electrical discharge machining Al₂O₃ ceramic sample using assisting Ni-Cr coating electrode with a thickness of 10–15 µm and brass wire-tool was 150 g/L for SnO granules of ø10 µm;
3. Thermal dissociation of the insulating material under discharge pulses was proven by the results of the chemical analysis of the eroded kerf;
4. Thermal dissociation of the insulating material has proved once again that the materials under discharge impulses are subjecting sublimation—direct transition of a material from a solid to a vapor state;
5. The maximum achievable material removal rate was 0.001 mm³/s which is less than for similar works that used carbon-containing working fluid and copper-group assisting measures but excluded the formation of insulating and chemically active carbides such as Al₃C₄ or Al₂(C₂)₃ that intent to interact with water at normal conditions (+20 °C), oxygen or hydrogen at elevated temperatures (650–700 °C and 2200 °C correspondingly) and can hampers erosion process, lead to the formation of extremely rough product surfaces, destruction of machine fluid filtration systems and equipment, pose a threat to personnel;
6. The recommended value of the interelectrode gap for rough electrical discharge machining was 48.0 ± 4.9 µm;

Figure 9. Thermochemical parameters of chemical reactions of nickel with some components of water medium (oxygen), brass wire tool (zinc) and dielectric workpiece (alumina).
(7) the developed approach is original from the previously developed ones due to the usage of non-carbon-containing working fluid, non-copper-group assisting measures, and rewinding type of the primary electrode (wire electrical discharge machining);
(8) the developed approach of electrical discharge machining aluminum containing ceramics is suitable for texturing cutting ceramics, aerospace optics, exploratory research of creating a new type of materials such as optically white or transparent conductive oxide ceramics that stayed an industry demand for decades;
(9) the superior role in the formation of conductive debris (intermetallic compounds) in the interelectrode gap may play the chemical composition of the primary electrode (Zn of brass wire tool electrode) in combination with the Ni-Cr coating of the alumina workpiece machined in a water medium;
(10) further research is in the field of properly thermochemically adjusted components of the materials in the working zone, such as insulating workpiece—assisting electrode—assisting powder—working fluid—primary electrode; development of the approach can contribute to developing electrical discharge machining for hard and super hard insulating material to obtain more sophisticated linear surfaces and accelerate the transition to the sixth technology paradigm associated with Kondratieff’s waves.

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