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Zinc nano-powder mixed electrical discharge machining for antibacterial surface modification

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Abstract

Powder mixed electrical discharge machining (PMEDM) using silver nano-powder has proven its capability in modifying implant surfaces to achieve excellent antibacterial properties along with good biocompatibility. However, the widespread of bacterial resistance to silver in clinical has been reported. In addition, for implantable devices, further enhancement of biocompatibility of the modified surface is required. Zinc is known as a strong antibacterial agent and a biocompatible element to the human body. Consequently, in this study, Ti6Al4V surfaces are modified using the PMEDM milling operation process with zinc powder admixed to the hydrocarbon-based dielectric fluid. The powder with nano-sizes from 40 nm to 60 nm and different powder concentrations up to 15 g/L is utilised. Ti6Al4V sheet tool electrodes with a length of 6 mm and different thicknesses of 0.2 mm and 0.12 mm are used, while discharge energy is varied from 10 µJ to 125 µJ. The workpiece is stimulated by an ultrasonic vibration frequency of 22.3 kHz and an amplitude of 2.5 µm. Results show that the deposited zinc content is homogeneously distributed over the modified surface. Powder concentration, discharge energy, and tool thickness significantly affect the zinc deposition and surface roughness. PMEDM using zinc nano-powder shows a promising potential for antibacterial surface modification of the implantable devices.

Keywords: powder mixed EDM, zinc deposition, antibacterial effect, biocompatibility

1. Introduction

The demand for medical implants has been rapidly increasing. The global market was valued at 5.7 billion USD in 2022 and is predicted to reach more than 24.8 billion USD in 2031 [1]. However, implant-associated infections still pose a major challenge for the implantable device industry. For example, the incidence of prosthetic joint infection and failure in the subsequently prosthesis revision is up to 3 %, as reported in [2].

PMEDM using silver nano-powders has been studied for ablative shaping of medical implants and concurrently forming antibacterial layers on the implant surfaces. The surfaces integrated with silver exhibited long-term antibacterial properties both *in vitro* and *in vivo* while optimizing bone ingrowth of endoprosthesis [3]. The content of deposited silver significantly affects the bacterial colonization on the modified surfaces, whereby an increase of the silver content resulted in a reduction of the bacterial number [4]. However, in clinical, the widespread of bacterial resistance to silver has been reported with various kinds of the bacteria, such as *Pseudomonas aeruginosa*, *Acinetobacter baumannii*, *Staphylococcus aureus, Klebsiella pneumonia, Escherichia coli*, and *Enterobacter cloacae*, etc [5]. The use of high silver contents increases the antibacterial effect, nevertheless it leads to toxicity to human cells. In addition, it has been found that silver showed a weaker antibacterial effect on gram-positive bacteria compared to its effect on gram-negative strains [6].

Zinc, a vital element for multiple biochemical functions of the human body, is a strong antibacterial agent. In contradiction to silver, zinc exhibited a higher susceptibility against gram-positive bacteria, whereas its antibacterial effect is reduced on gram-negative bacteria [6]. Additionally, literature showed that, as a biodegradable element, zinc has a better biocompatibility than silver [7]. And it can be realized that until now there was no challenge related to Zn-resistant bacteria in clinical.

Zinc powders were used in the PMEDM process for modifying AZ31 magnesium alloy surfaces. A study using zinc powder concentration in the dielectric medium up to 3 g/L to modify magnesium alloy showed that the corrosion rate of the PMEDM surfaces was significantly lower than the surface modified without powder. And the lowest corrostion rate was obtained at 2 g/L zinc powder concentration [8]. The enhancemences of microhardness and cytocompatibility were found when mixing zinc powder into the dielectric fluid to modify Ti6Al4V surfaces. The formation of zinc oxide was assumed as its reason [9]. Effects of the powder material on machining efficiency were also investigated, whereby zinc, cobalt and molybdenum powders with different concentration were mixed into the hydrocarbon-based dielectric fluid to machine a nickel-based superalloy. It was found that the highest material removal rate was achieved by using zinc powder, whereas molybdenum powder provided the smoothest surface [10].

It can be realized that zinc is a promising potential agent for antibacterial surface of the implantable devices. Consequently, in this study, PMEDM using zinc nano-powder is investigated for antibacterial surface modification of titanium alloy. This study focuses on the content and distribution of deposited zinc on the modified layer, which is very important for antibacterial capability of the implant surface as well as for homogeneous antibacterial properties over its entire surface.

2. Methodology

In order to provide the homogeneous distribution of deposited zinc over the surface, the homogeneous distribution of zinc nano-particles in the spark gap is vital [3,4]. Additionally, the narrow spark gap, from approx. 5 µm to approx. 10 µm, leads to challenges for transporting the suspended powders through the gap. In this study, thin Ti6Al4V sheets were therefore used as tool electrodes for modifying the Ti6Al4V surfaces.

To reduce the spattering of materials on the modified surface and support the transportation of zinc powder though the machining gap, the workpiece was stimulated by a Hielscher UIP250 ultrasonic vibration system, which was integrated with a PMEDM circulation system as shown in Figure 1.

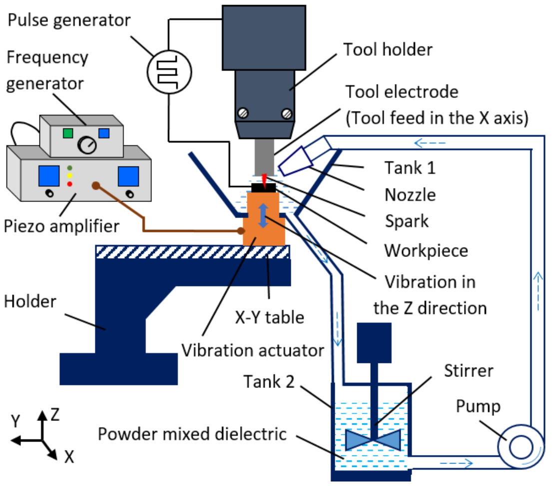

Figure 1. Schematic showing the experimental setup.

The vibration frequency and amplitude were measured by a Polytec OFV-505 Laser Vibrometer and a Polytec OFV-5000 controller. The applied experimental conditions are given in Table 1.

Table 1 Experimental conditions

Parameter	**Value**
Machine	Sarix T1T4 µ-EDM machine
Workpiece	Material: Ti6Al4V
Tool electrodes	- Length: 6.0 mm - Thickness: 0.2 mm and 0.12 mm - Material: Ti6Al4V
Dielectric fluid	HEDMA111 oil
Discharge energy	10 µJ, 55 µJ and 125 µJ
Polarity	Negative tool electrode
Zinc powder	- Size: 40-60 nm - Concentration in dielectric: 5 g/L and 15 g/L
Ultrasonic vibration	- Frequency: 22.3 kHz - Amplitude (a_{p-p}): 2.5 µm

For each machining condition, three samples were prepared, whereby a (5 x 6) mm² area with a depth of 45 µm was machined on each one as shown in Figure 2. After machining, an ethanol filled ultrasonic bath was used to clean each sample. The elemental composition of the modified surfaces was analysed using energy dispersive X-ray spectroscopy (EDS), whereby a spectrum of approx. (3 x 3) mm² was analysed at the center of each surface to analyse the average deposited zinc content in the modified layer. To evaluate the distribution of zinc contents over the modified surface, 10 smaller EDS spectra numbered from 1 to 10 were analysed perpendicularly to the tool feed direction as represented in Figure 2. Scanning electron microscopy (SEM) was used to analyse the surface topography. In addition, the modified surfaces were scanned by a Keyence VK9700 confocal 3D laser-scanning-microscope, then MountainsMap 7.4 scanning topography software was utilised to analyse the roughness values.

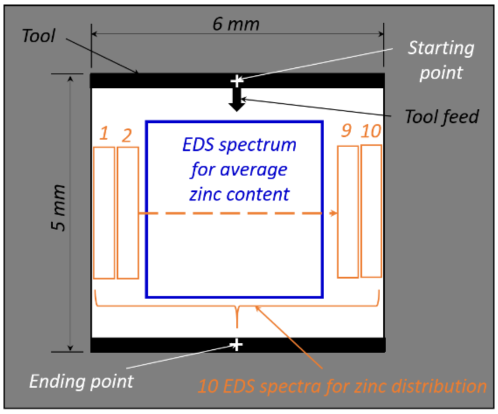

Figure 2. Schematic showing the geometry of the modified area and EDS spectra for analyses of the zinc content and zinc distribution

3. Results and discussions

In this section, the content and distribution of deposited zinc as well as roughness of the modified surface will be represented and discussed. It focuses on effects of powder concentration, discharge energy and tool thickness when applying the PMEDM process using sheet tool electrode on the targeted results.

3.1. Averaged content of the deposited zinc

Figure 3 shows the content of deposited zinc dependent on the concentration of zinc nano-powders mixed in the dielectric fluid and the thickness of tool electrode.

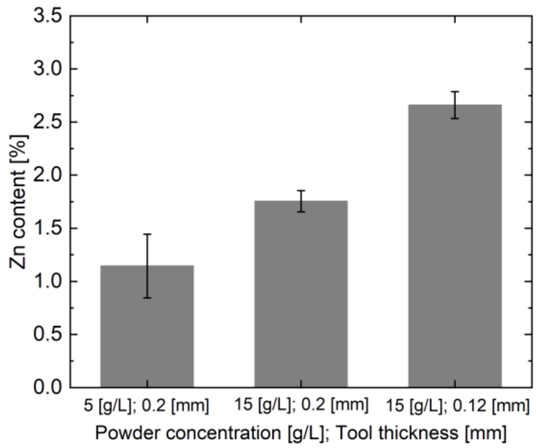

Figure 3. Effects of powder concentration and thickness of the sheet tool electrode on the averaged zinc content (55 µJ discharge energy)

It is clear that an increase of powder concentration increases the deposited zinc content. The addition of more powder to 15 g/L results in a slight improvement of the deposited zinc content to approx. 1.8 % from approx. 1.2 % when using 5 g/L powder. However, zinc nano-powders seem to still face challenges to flow through the spark gap, when applying a 0.2 mm tool thickness and side flushing with ultrasonic vibration assistance. The zinc deposition was also investigated when using a 0.2 mm tool thickness, 5 g/L powder and without vibration assiatance. EDS results show that the content of deposited zinc is reduced to approx. 0.84 $^{\pm 0.3}$ %. Therefore, the assistance of ultrasonic vibration also significantly increases the amount of zinc particles in the gap. However, it can be realised that the efficiency of the PMEDM process on transferring zinc to the modified layer is still low in comparison to the transfer of silver [3]. The reason is not understood well. Nevertheless, low melting and boiling points of zinc are assumed to be a main reason.

The utilisation of a thinner tool electrode with thickness of 0.12 mm can solve the challenge for powder transportation through the machining gap, whereby the content of deposited zinc is remarkably increased to approx. 2.7 % with mixing 15 g/L powder into the dielectric fluid. However, It can be realised that delivering powder particles into the machining gap still faces difficulties when utilising side flushing. Therefore, other flushing stratergies should be investigated in further studies.

Influence of discharge energy on the deposited zinc content is shown in Figure 4.

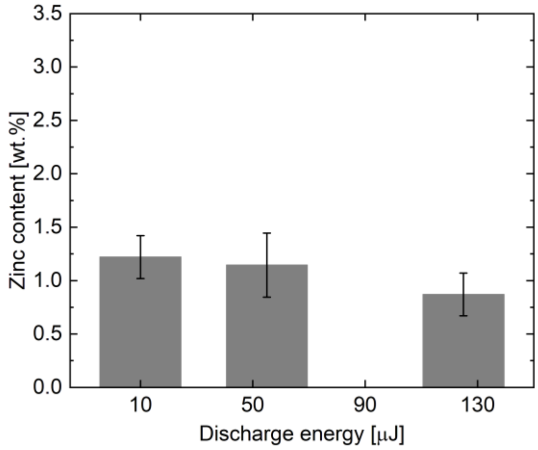

Figure 4. The deposited zinc content on workpiece surfaces for different discharge energies (5 g/L powder, 0.2 mm tool thickness)

Results show that the application of a higher discharge energy leads to a reduction of the deposited zinc. The increase of discharge energy leads to a higher heat, which causes a stronger evaporation of zinc. Therefore, it decreases the amount of zinc re-solidified into and onto the modified layer.

3.2. Distribution of the deposited zinc

Since the content of antibacterial agent plays a vital role in the antibacterial property, therefore a homogeneous deposition over the modified surface is a very important prerequisite for the homogeneous antibacterial effect of the surface. Providing a uniform distribution of zinc powder over the machining gap, which significantly affects the homogeneous deposition of zinc, is the aim of using sheet tool electrodes. Results from Figure 5 indicate that the deposited zinc is quite uniformly distributed over the modified surface in all cases. Especially when using a 0.12 mm tool thickness, the zinc content distributes in a range of 2.7 $\pm^{0.17}$ %. This result shows a potential of applying the sheet tool electrode for providing the homogeneous distribution of the antibacterial agent over the big surfaces by the PMEDM process.

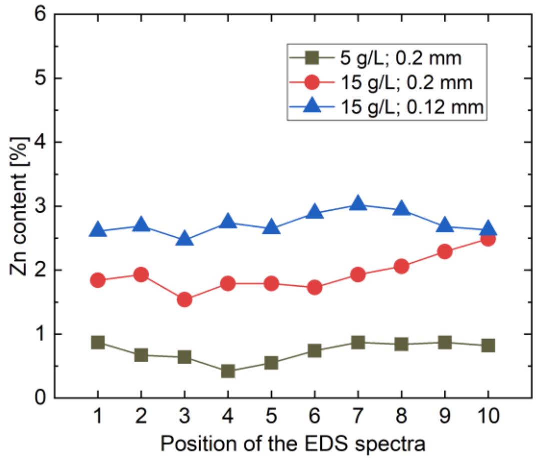

Figure 5. Distribution of deposited zinc over the modified surfaces when using different powder concentrations (g/L) and tool thicknesses (mm) at a discharge energy of 55 µJ

SEM images of the surfaces modified using different machining conditions are represent in Figure 6. It can be obsverved that the modified surface is formed by overlapping craters. The crater size is mainly affected by discharge energy as can be seen in Figure 6(a-c). The crater sizes are approx. 10 µm, 15 µm, and 40 µm with applying 10 µJ, 55 µJ and 125 µJ discharge energies, respectively. By visualizing backscattered electrons in the SEM analysis, spattered materials containing a large amount of zinc are depicted as a bright color on the surface due to the strong interaction. The use of a higher energy leads to a reduction of the spattered material. This is also one of the reasons for decreasing the deposited zinc content when applying a high energy. However, micro-cracks can be observed with using discharge energy of 55 µJ and especially at 125 µJ.

The amount of spattered materials is remarkably increased with adding more powder into the dielectric fluid as can be seen in Figure 6(d-e). This is due to the fact that a higher powder concentration facilitates the formation of more molten

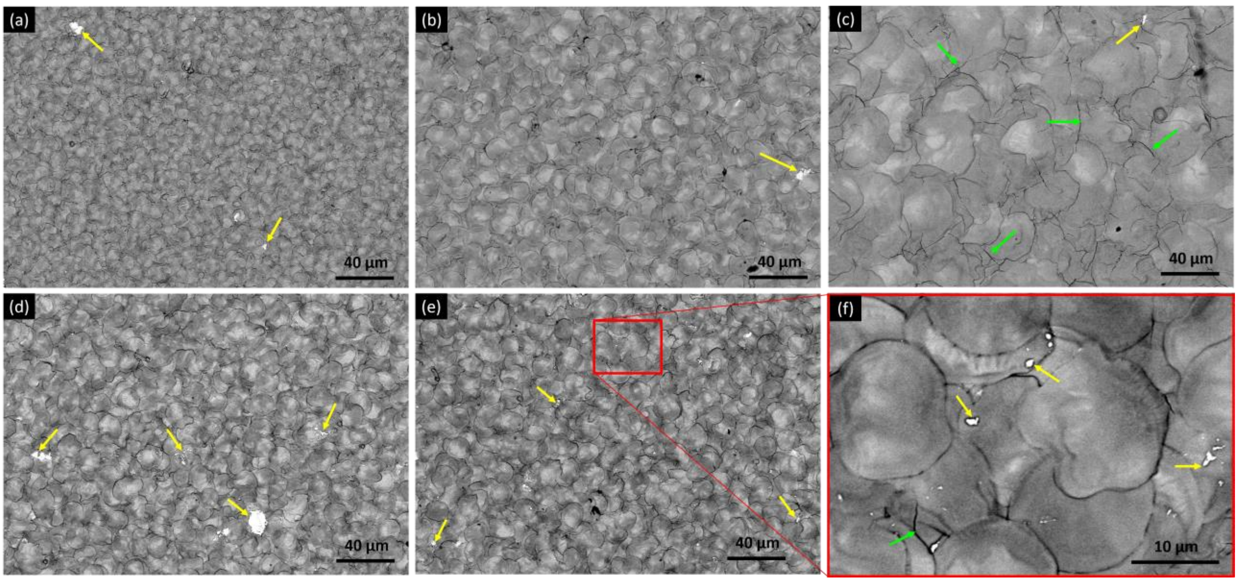

Figure 6. Backscattered electron images of the surfaces modified by the PMEDM process using: (a-d) 0.2 mm tool thickness with (a) 5 g/L, 10 µJ; (b) 5 g/L, 55 µJ; (c) 5 g/L, 125 µJ; (d) 15 g/L, 55 µJ; (e-f) 0.12 mm tool thickness and 15 g/L powder concentration (orrange arrows point on spattered material, green arrows point on micro-cracks)

materials. Additionally, the zinc powders seem to be agglomerated when utilising the 0.2 mm tool electrode (Figure 6(d)), whereby big spattered particles can be found on the surface.

3.3. Surface quality

Figure 7 displays roughness values of the surfaces modified by EDM without powder and with different powder concentration.

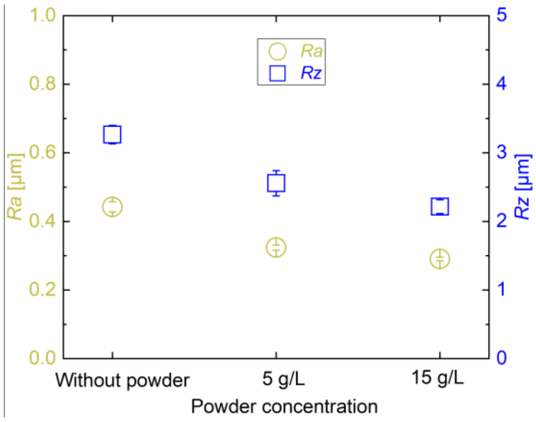

Figure 7. Influence of powder concentration on surface roughness (55 µJ discharge energy)

It can be realised that powder concentration plays a very important role on surface roughness. The addition of powder into the dielectric fluid significantly reduces the roughness of modified surface. Simultaneously, an increase of powder concentration leads to generate a smoother surface. Topography of the surface was also analysed by MountainsMap 7.4 scanning topography software, as shown in Figure 8.

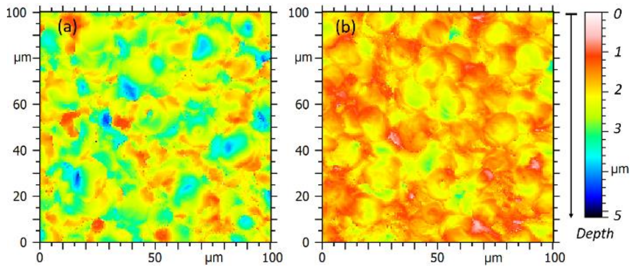

Figure 8. Topography of the surfaces modified by EDM (a) without powder and (b) with 15 g/L powder (55 µJ discharge energy)

It can be observed that shallower craters are formed by EDM with powder addition. An enlargement of the spark gap is assumed as a main reason.

Discharge energy also affects the surface roughness remarkably, which is illustrated in Figure 9. This is clear due to the significant increase of the crater size as illustrated in Figure 6.

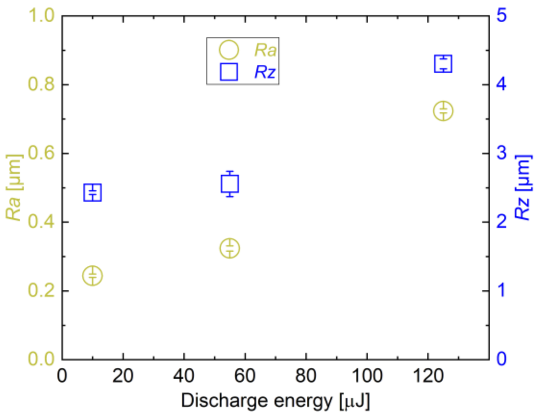

Figure 9. Roughness values of the surfaces modified by PMEDM with 5 g/L powder and different discharge energies

4. Conclusion

In this study, zinc nano-powder has been mixed into the hydrocarbon-based dielectric fluid to modify Ti6Al4V surfaces. Sheet tool electrodes were used, while powder concentration, discharge energy, and tool thickness are varied. Additionally, ultrasonic vibration has been introduced to the Ti6Al4V workpiece during the machining process. From the results, the following conclusions can be drawn:

- Powder concentration, discharge energy and tool thickness significantly affect the integrity of modified surface.
- The content of deposited zinc is increased by adding more powder into the dielectric fluid, reducing the tool thickness, or introducing ultrasonic vibration to the workpiece. However, it is decreased by using a higher discharge energy.
- By utilising the sheet tool, the deposited zinc over the surface is homogeneous, especially when applying a 0.12 mm tool thickness.
- Mixing zinc nano-powder into the dielectric results in smoother surfaces due to the generation of shallower craters.
- PMEDM with zinc nano-powder shows a promising potential for antibacterial surface modification of the implantable devices.

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