Evaluation of thickness variation of recast layer formation on nitinol from electrical discharge coatings process

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Abstract. Nitinol is an intermetallic alloy with outstanding properties that suitable as biomaterial. This alloy is capable of recovering to its initial shape after external loading through transformation of the crystalline structure. Unfortunately, excessive exposure of nickel element from this alloy is harmful to human body if released. Thus in this study, the alloy surface was deposited with an oxide layer via electrical discharge coating (EDC) process. The process was performed in deionized water and pure titanium as the electrode. The variation thickness of the recast layer formation was examined by analysing the effects of polarity, gap voltage and erosion depth. Single crater images and electrical waveforms were captured and utilised to elucidate the aforementioned effects. The results exhibited a significant change of layer thickness variation due to different polarity conditions. It was also confirmed that the single crater formation at different polarity was influenced by discharge energy. On other hand, the increase in the open gap voltage can expand the recast layer thickness in lower variation of reverse polarity condition. Finally, erosion depth attributed to a constant layer thickness but in low thickness variation when reverse polarity was employed.

1. Introduction
Nitinol which composed from nearly equi-atomic element of nickel and titanium has a great potential alloy to be biomaterial alloys. This alloy has superior mechanical properties with unique capability of thermal shape memory effect and super-elasticity. This alloy is capable of recovering to its original shape until 8% of tensile strain after external force by heat stimuli [1]. The shape recovering occurs due to the transformation of crystalline structure between martensite and austenite. This unique transformation added to the distinctive advantage of orthodontic and orthopaedic implantation. However, the excessive exposure of nickel element from this alloy is harmful to human body if released due to the corrosion or wear. A number of attempts [2]–[6] have been reported to develop a coating layer on nitinol surface that acts as a barrier to prevent the migration of this chemical element. The techniques used were sol-gel technology, selective oxidation, anodization in acid electrolyte and hydrothermal method. However, the techniques were ineffective due to poor adhesion and bond strength and might failure in corrosive environment under longer loading condition [7]. Another technique was electrical discharge machining (EDM) process that capable in forming suitable surface structure for cell proliferation [8]. Moreover, the process was cost-effective operation compared with other process.

Electrical discharge coatings (EDC) is a new adaption method from electrical discharge machining (EDM) process which utilised repetitive electrical sparks and generate heat energy to erode workpiece...
material. In EDC, the coating material is transferred and composed of the electrode material, elements of the dielectric breakdown and the workpiece material itself. Very often, the hardness of the coatings is much higher than the workpiece but is highly depends on the process conditions [9]. The coating mechanism involves a gradual dilution of melt pool from repetitive sparking event (melt and re-melt the solidified material) on a specific location in order to develop a continuum coatings [10]. However, excessive discharge energy from the EDC process conditions can deteriorate the uniformity of the coatings. With regard to process parameters, Muhammad Hanif et. al [11] reported that polarity contributed to a high material removal rate and surface roughness when EDMing the AISI D2 steel. As for deposition purposes, the amount of material removal should be in the main consideration in order to achieve uniform distribution of recast layer formation. However, A. Gill et al. [12] concluded that positive polarity of tool electrode can encourage higher uniformity of alloying layer. They claimed that large amount of material removal was not an effective way to form a coating layer. Whereas, S. Clijsters et. al [13] reported that the increase of open gap voltage can reduce the material removal rate but too low of the parameter can resulted in short-circuits and instable the process.

Based on the aforementioned review, a complex mechanism existed to deposit a uniform material coating on the nitinol surface. Thus, an experimental investigation is inevitable so as to identify the factors or parameters that contributed to the variation formation of the recast layer thickness. In this paper, an oxide layer was managed to be alloyed on nitinol surface by manipulation of EDC process parameters, namely; polarity, erosion depth and open gap voltage.

2. Materials and procedures
Nitinol alloy (medical grade, ASTM F2035-12) was used as the workpiece material, which was acquired from Baoji Hanzi, China. The workpiece was cut into the size of 70 mm x 70 mm x 5 mm, sequentially grinded with 200, 600, 1000 and 2000 grits of SiC papers, etched with Kroll’s reagent (6 ml of HNO3, 2 ml of HF, and 92 ml of distilled water) and polished with monocrystaline diamond suspension. Pure titanium round bar (99.9% purity) with a size of Ø20 mm x 10 mm was employed as the electrode tool. The bar was attached to a copper rod holder (Ø20 mm x 100 mm) using a copper adhesive foil. Then, the holder was fixed on the EA8 Mitsubishi die sinker machine, which was utilised to accomplish the experimental works. In order to form an oxide layer, deionized water was used as the dielectric medium. For each trial, 200 ml of the fluid was filled up into a special fixture that hold the workpiece sample.

Three process parameters were varied as shown in Table 1. Other parameters such as discharge duration, pulse interval and currents were kept constant. The varied parameters were selected based on the possibility to influence the recast layer formation, instead of choosing electrical parameters which were directly control the discharge energy. During the experimental trials, Rohde & Schwarz oscilloscope (model: RTO1014, 1 Ghz Bandwidth, 10 Gsample/s of acquisition) was used to acquire the waveform images of electrical pulses. Xoptron 80 series of optical microscopy was utilised to capture and measure single crater images and the recast layer thickness at 500 of optical magnification. The thickness measurements were collected from 40 locations of the cross-sectioned samples.

| No | Material / parameter | Type/ condition |
|----|---------------------|----------------|
| 1  | Workpiece           | Nitinol |
| 2  | Electrode           | Pure titanium |
| 3  | Dielectric fluid    | Deionized water |
| 4  | Polarity            | Straight (-), reverse (+) |
| 5  | Erosion depth, mm   | 0.15, 0.30 |
| 6  | Gap voltage, volt   | 70, 160 |
| 7  | Discharge duration, µs | 295 |
| 8  | Pulse interval, ms  | 7 |
3. Results and discussion

3.1 Electrical waveforms and single crater formation

Electrical pulses play an important role in developing a sequence of sparking events. Each pulse generates a single spark and forms a single crater on the workpiece surface. Figure 1 represents two different patterns of voltage waveforms from different settings of open gap voltage at straight polarity. The waveform pattern was also similar at reverse polarity. The figure indicated a constant discharge voltage of approximately 25 volts for all variation conditions in this experimental trials. The voltage was uncontrolled and relied on the material of electrode, workpiece, and the machining conditions [14]. Open gap voltage was turned on during the ignition delay time when the ionisation of dielectric fluid initiated. Ignition started when the voltage exceeded the dielectric resistivity and generated more free ions and electrons. The waveforms also indicated the variation of ignition delay time during a working condition. This is attributed to the different gap condition over pulses, which caused by the gap distance and different dielectric breakdown strength (resistivity) [15]. Long ignition delay time reflects toward a high gap width that ionised a high volume of dielectric fluid.

![Figure 1. Voltage waveforms of different open gap voltages at straight polarity, (a) open gap voltage = 80 volts (b) open gap voltage = 150 volts.](image)

Figure 2 depicts single crater formation at different polarity settings under low gap voltage. Under the straight polarity, the crater diameter was twice larger compared to that of the reverse polarity. It is apparent that the crater had almost the same height at the inner diameter with the adjacent surface. Due to larger size of the crater, mostly of the molten material (molten workpiece and migration molten from electrode) tends to re-solidify during the end of the pulse. Compared with reverse polarity, it formed a bowl-shape crater with a deeper inner diameter. The inner molten might be ejected into the gap or deposited on the crater wall.
Figure 2. Optical images of single crater formation at low working condition under (a) straight polarity, with crater diameter = 84.8µm, and (b) reverse polarity, with crater diameter = 45.2µm.

3.2 Recast layer thickness
Figure 3 represents the presence of recast layer formation on the nitinol surface resulted from the EDC process. Furthermore, oxide element existed on the recast layer as indicated in the chemical mapping of the energy-dispersive X-ray spectroscopy. Meanwhile, the box plot from Figure 4(a) indicated the layer thickness variation between straight polarity and reverse polarity. Even though a high measurement data was recorded from the EDCed substrate at straight polarity, the variation was substantial. It is important to mention that the formation of the coating layer on the surface was uneven compared to the reverse polarity setting. Theoretically, current flow is generated by the movement of electrons and ions. The electrons and negative ions accelerate to the positive electrode and conversely to the positive ions. Negative ions and electrons have smaller mass but higher number in the gap than positive ions. Thus, a highly pronounced impact and heat generation are produced on the surface of the positive electrode. Consequently, a higher amount of material was melted, evaporated and ejected into the dielectric or re-solidified on the substrate. In the meantime, the negative electrode experienced lesser erosion due to the minor impact of massive positive ions. It results into a more uniformity of recast layer thickness attributed to the less erosion of material. However, this phenomenon only occurred at a low discharge energy condition. During the higher open gap voltage, the strength of electrical field had increased. It allowed a larger number of ions and electrons generation due to the dielectric breakdown and increased drastically the discharge energy.

Figure 4(b) and (c) depicted the influence of increasing erosion depth and gap voltage from different polarity conditions. It disclosed that the thickness variation was consistent over the conditions during straight polarity. However, the variation was trivial at reverse polarity due to the effect of erosion level. Moreover, the reduction of recast layer thickness was recorded when the erosion depth increased during straight polarity but less effect at reverse polarity. Increment in the erosion depth can decrease the resistivity of dielectric fluids due to a higher amount of debris suspended in the sparking gap. Thus, it influenced the machining stability and retarded the material deposition. As for the other side, the gap voltage influenced greater formation of recast layer thickness from both polarities. However, higher recast layer thickness and larger variation of measurement data were observed during the straight polarity as shown in Figure 4(b).
Figure 3. Recast layer formation on nitinol and the chemical mapping of the layer

Figure 4 Box plot of the recast layer thickness (a) Effect of different polarity, (b) Effect of erosion depth and gap voltage at straight polarity, (c) Effect of erosion depth and gap voltage at reverse polarity.
4. Concluding remarks
In conclusion, the EDC polarity and gap voltage influenced the variation thickness of recast layer on nitinol. Both parameters affected the material erosion which being the main basis to increase the material deposition on the nitinol surface. Different geometrical shapes of single crater were observed under different polarity conditions. Larger diameter of crater was developed by the straight polarity as to that of the reverse polarity. Minimal variation of recast layer thickness can be achieved under the reverse polarity due to the influence of discharge energy of the EDC process.

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