

An evaluation of the machinability of nitinol shape memory alloy by electrochemical polishing[†]

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(Manuscript Received August 2, 2009; Revised January 13, 2011; Accepted January 29, 2011)

Abstract

Nitinol, a shape memory alloy (SMA), is manufactured from titanium and nickel, and is employed in various fields for use in devices such as micro sensors, ultra-precision devices and satellite wings. It is also highly recommended as a material in medical stents for insertion into the human body because it has excellent organic compatibility. However, because they are intended to be inserted into the human body, products such as medical stents require a high-quality surface. Because nitinol has more of the characteristics of titanium than of nickel, one of its drawbacks is that heat generated in nitinol during machining is not discharged smoothly and inner stress occurs when traditional machining methods are used. To overcome this difficulty, various non-traditional machining methods, including non-contact machining, have been investigated for use with nitinol. To further explore non-traditional machining methods that may be appropriate for use with nitinol, this study investigates the application of electrochemical polishing to the machining of nitinol. Characteristics of the electrochemical polishing (EP), a representative non-traditional machining, for nitinol SMA are studied. Nitinol SMA of the EP machining parameters such as electrolyte composition, applied current, machining time and inter electrode gap (IEG) are researched and the machined surface state is analyzed according to each parameters parameter. So, the most suitable EP machining conditions for nitinol SMA are derived.

Keywords: Electrochemical polishing; Electrochemical machining; Ti-Ni alloy; Nitinol; Shape memory alloy; EP; ECM

1. Introduction

Smart materials are being developed and studied in the manufacturing fields due to increasing requirements for miniaturized components. A smart material is a material with characteristics that change according to specific conditions, such as temperature, pH, stress, electric current and moisture. Smart materials that have been developed include piezoelectric materials, magnetic shape memory alloy, pH-sensitive polymers and shape memory alloys [1, 2].

One of those smart materials, shape memory alloy (SMA), has a special characteristic called the shape memory effect (SME) that is under active research. SME refers to the recovery of a deformed alloy to its original state through the application of temperature or stress to the alloy [3].

With the development of smart materials, non-traditional machining methods, such as laser machining, ER/MR fluid machining and Electro Chemical Machining (ECM), have

been researched for smart materials [4].

Especially, electrochemical polishing (EP), a type of ECM, can machine locally with high precision using electrochemical reactions. EP has thus far been investigated for use in micro scale machining by applying ultra-short pulse current [5]. EP is a particularly useful machining method because, as a non-contact machining method, it produces neither machining heat nor internal stress in the machined materials [5-6].

In this paper, to find the most suitable EP machining condition for nitinol SMA, an EP machining process was conducted on nitinol SMA under a variety of machining conditions and the machining results were analyzed according to each machining condition.

2. Nitinol SMA

Generally, metals that suffer plastic deformation cannot be restored to their initial shape when a force exceeding their elasticity restoration stress is applied. However, an SMA can be restored to a specific memorized shape when a specific stress or temperature is applied, even if the applied force exceeds the elasticity restoration stress. This effect is called SME, and an SMA has not only SME but also super elasticity

[†] This paper was recommended for publication in revised form by Associate Editor In-Ha Sung

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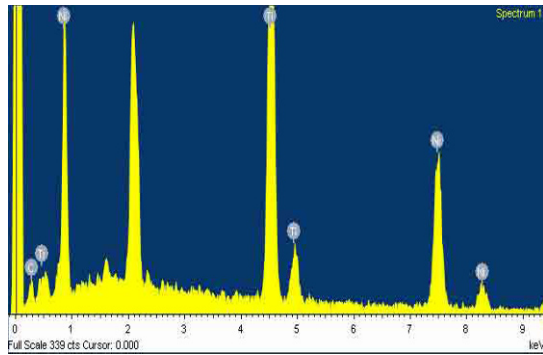


Fig. 1. Chemical composition of nitinol SMA by EDX.

[4].

Nitinol has more tensile strength, greater fatigue limits and higher corrosion resistance than a Cu-based alloy that is also an SMA. Nitinol also has high elongation, caused by its high tensile strength and low yield strength. Moreover, its SME ability is not diminished by more than a million repetitions of a shape restoration test. Nitinol is more widely applied than the Cu-based SMA because of its better shape restoration ability [7]. Fig. 1 shows the chemical composition of nitinol SMA by EDX and Table 1 illustrates the physical and mechanical properties of nitinol SMA.

Nitinol is applied not only in high-tech industrial applications such as satellite parts and micro sensors, but also in medical devices such as artificial joints, coronary stents and orthodontics, because nitinol has excellent organic compatibility [4].

Despite of its advantages, nitinol is very difficult to machine by traditional machining methods like a milling, drilling and turning. This difficulty arises from the fact that nitinol, which is composed of approximately 45% titanium and 55% nickel, expresses the characteristics of titanium more than those of nickel. So it cannot emit machining heat and it makes internal stress. It has been reported that machining heat and the resultant internal stress affect SME badly. As a result, the application of nontraditional machining methods to nitinol SMA is being widely researched [3, 4].

3. Electrochemical polishing

3.1 Theory of electrochemical polishing

The theoretical removal rate of EP is predicted using Faraday's law and the theoretical process is as follows:

1. The eluted atom of the metal should be confirmed.
2. The metal elution is only from the atom state caused by the electrochemical reaction.
3. The metal elution is the only reaction at both ends.

According to Faraday's law, the necessary quantity of electricity to elute 1g of an element with the atomic value n and the atomic weight M is nF/M coulombs. Therefore, the eluted element quantity W [g] caused by I [A] current during t [s] time is as follows [7].

Table 1. Physical and mechanical property of nitinol SMA.

Melting range (°C)	1240-1310
Density (kg/mm ³)	6450
Mean Coef. Of Thermal Expansion (24~900 °C), per °C10 ⁻⁶	10.4
Electrical Resistivity μΩ/cm	~55
Young's Modulus (MPa)	25000
Tensile Strength (MPa)	1450
Elongation Thickness (%)	60
Hardness (H _{RA})	65~68

$$W = \frac{MIt}{nF} [g], \quad (1)$$

where F is the Faraday constant. When the density of this atom is ρ , the theoretical removal volume V_0 is as follows:

$$V_0 = \frac{MIt}{nF\rho} [mm^3], \quad (2)$$

where $M/nF\rho$ is the specific removal volume V_0 that is the eluted volume per unit quantity of electricity ($I=1A$, $t=1s$), which differs according to metal type.

The electrochemical equivalent of metal element k is as follows:

$$k = \frac{M}{nF}. \quad (3)$$

When the metal to be machined is an alloy, the electrochemical equivalent k' is as follows:

$$k' = \sum \left(\frac{w_i}{k_i} \right), \quad (4)$$

where w_i is each material allocation of alloy and k_i is an electrochemical equivalent of each metal element.

The dissolved quantity and volume can be defined by using an electrochemical equivalent as follows.

$$M = \eta W, \quad (5)$$

$$V = \eta V_0, \quad (6)$$

$$\eta = \frac{\text{realremovalrate}}{\text{theoreticalremovalrate}}. \quad (7)$$

However, the theoretical removal rate of EP is less than the actual value, due to diverse machining conditions, environmental conditions and material properties, etc. Thus, the removal rate of EP can be calculated by multiplying the theoretical value by the current efficiency η [7].

3.2 Mechanism of electrochemical machining

As a finishing machining process, EP uses an electrochemi-

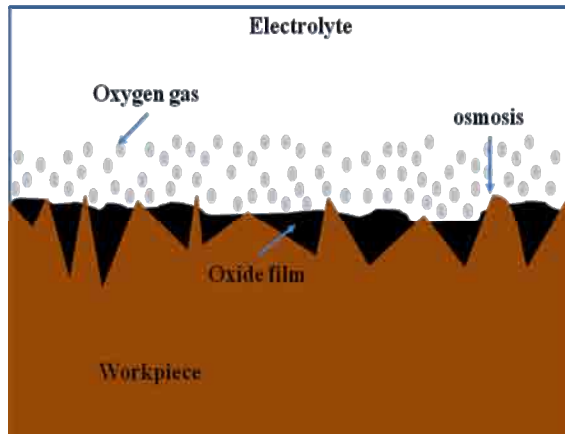


Fig. 2. Schematic of EP mechanism.

cal dissolution process. Through local dissolution of prominent parts on a workpiece surface, EP can be used to obtain various effects such as a smooth surface, brightness, corrosion resistance, removal of hydrogen and removal of micro-burrs [4].

In contrast with traditional machining methods, EP is a non-contact machining process where the machining tool and the workpiece are not in contact with each other. Because the EP machining process does not result in a mechanical load, internal stress and machining heat are eliminated. Thus, EP is not only suitable for polishing thin workpieces and for machining complex shapes, but can also for machine materials that are neither hard nor strong. The EP mechanism has not yet been clearly determined, but it is usually explained as follows [8].

When the voltage is increased, an emulsion with high specific gravity, viscosity and electric resistance is created by the ion, which is eluted from the workpiece as shown in Fig. 2. Then, the emulsion covers the concave parts of the surface due to osmosis and interrupts the dissolution of depressed parts so that prominent parts are preferentially dissolved, resulting in a smooth workpiece surface. Ben Franklin verified the phenomenon where current is concentrated on the edges and irregular or sharp points of a piece of metal [8].

During machining, oxygen is given off at the cathode with the dissolution of the workpiece, and hydrogen is given off at the anode without any dissolution. Thin oxidization films have formed on workpiece surfaces because of the electrochemical reaction of metallic ions (+) and electrolytic ions (-). This thin oxidization film is called differently insulating film, and it disturbs the electrochemical reaction on depressions on the workpiece surfaces. Thus, the EP condition, which is not as likely to produce an oxidization film on depressions on the workpiece surfaces and which requires high machining ability, should be researched [8-10].

Generally, the factors affecting machinability are the composition of the electrolyte, the applied current, the electrolyte temperature, the machining time, and the Inter Electrode Gap. However, the electrolyte and the applied current are the most influential factors affecting electrochemical machining.

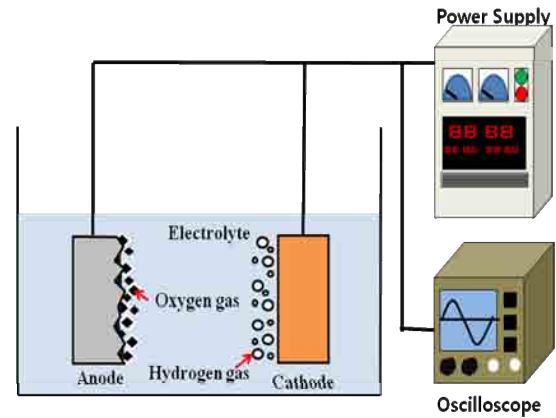


Fig. 3. Schematic of EP experimental system.

4. Experimental setup

Fig. 3 shows the experimental system. The electrode for the cathode is made of copper and is connected to positive (+). The electrode for the anode is nitinol, is fixed by an electrode holder, and is connected to negative (-). The electrode holder is connected to a micro stage and the inter-electrode gap (IEG) is regulated through controlling the micro stage.

The cathode and anode were inundated in an electrolyte bath and electrolyte was circulated by a pump and a sewage filter during machining. The power source used in this experiment can apply a maximum current of 20A as well as a pulse current. The pulse on/off time was set as 800 μ s/200 μ s by the result of the previous experiment, and its frequency was monitored with an oscilloscope.

The initial surface roughness of the 20mm \times 20mm \times 2mm nitinol sample was 2 μ m. The workpiece and cathode electrode were opposite the IEG during machining.

Table 2 describes the experimental conditions. Among the machining factors that affect machinability, the cathode materials, machining temperature, electrolyte temperature and pulse on/off ratio were set up as fixed conditions, and the composition of the electrolyte, the applied current, the IEG and the machining time were set up as the variable conditions.

5. Result and discussion

5.1 Machining characteristics of electrolyte composition

The composition of the electrolyte chosen for the EP process is important because it greatly affects machinability.

The electrolyte has various roles in the general EP process. First, the electrolyte facilitates the flow of current between the electrode and the workpiece. Second, it fluxes the electrochemical products in the IEG. Third, it reduces the heat of the reaction during EP.

The electrolyte applied should be suitable for the material of the workpiece, but the general requirements for an electrolyte can be explained as follows:

- It should not make an insoluble product that adheres to the

Table 2. Experimental setup for electrochemical polishing.

Conditions	
Composition of electrolyte	A : H_2SO_4 (17.8M)+ H_3PO_4 (14.6M)+ H_2O B : NaNO_2 (1.5M) + $\text{Na}_2\text{C}_4\text{H}_4\text{O}_6$ (0.1M)
Workpiece	Nitinol
Electrode	Copper (99%)
Surface roughness tester	Taylor Hobson Surtronic 3+
Pulse On/Off Time	on time 800, off time 200 (μs)
Applied Current	3A, 6A, 9A, 12A, 18A
Inter Electrode Gap	0.3, 0.5, 1, 2 (mm)

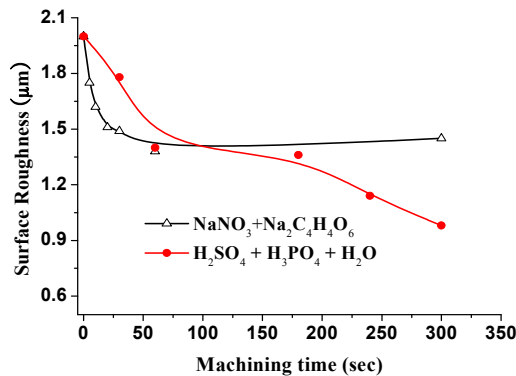


Fig. 4. The machining characteristic of acid electrolyte and neutral electrolyte according to variation of machining time.

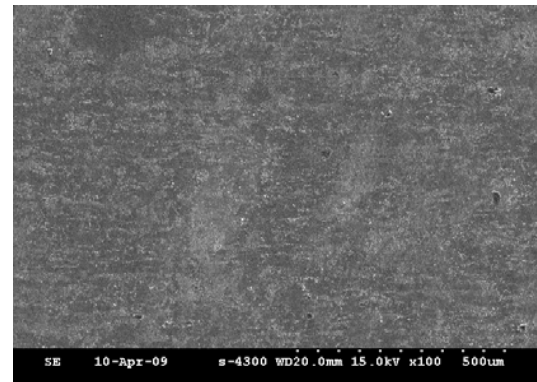
workpiece surface.

- It should not cause positive ions to be electrodeposited to the cathode surface.
- It should have high electric conductivity and low viscosity
- It should not corrode the workpiece, and should be a non-poisonous solution.

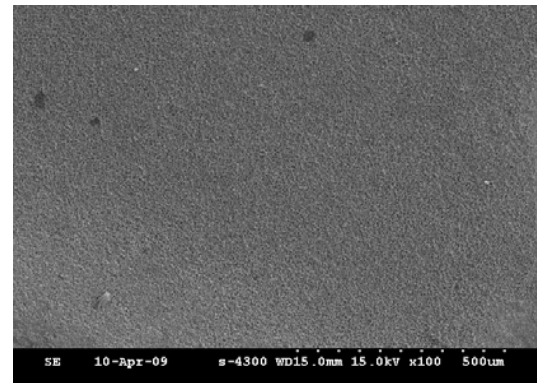
To find a suitable electrolyte for nitinol, an acid electrolyte made of sulfuric acid (17.8M of H_3PO_4), phosphoric acid (14.6M of H_2SO_4) and distilled water (H_2O) was compared with a neutral electrolyte made of sodium nitrite (1.5M of NaNO_2) and sodium tartaric (0.1M of $\text{Na}_2\text{C}_4\text{H}_4\text{O}_6$). Applied current was 12A and the IEG was 1mm [10–11].

The machining results showed that using the neutral electrolyte in the EP process is faster than using the acid electrolyte, as illustrated in Fig. 4. When the acid electrolyte was applied in the EP process, surface roughness improved to $0.98 \mu\text{m}$ after 300sec of machining time. However, when the neutral electrolyte was applied in the EP process, the surface roughness dropped precipitously, and was $1.38 \mu\text{m}$ after 60sec of machining time. But surface roughness increased again to $1.45 \mu\text{m}$ with 300sec of machining time while using the neutral electrolyte.

Especially, when machining time was 300sec, the weight of the nitinol machined using the neutral electrolyte was reduced by about 0.05g, but the weight of the nitinol machined using the acid electrolyte was reduced by about 0.4g. This means



(a) After EP using acid electrolyte



(b) After EP using neutral electrolyte

Fig. 5. A scanning electron microscope (SEM) image of the nitinol surface after electrochemical polishing.

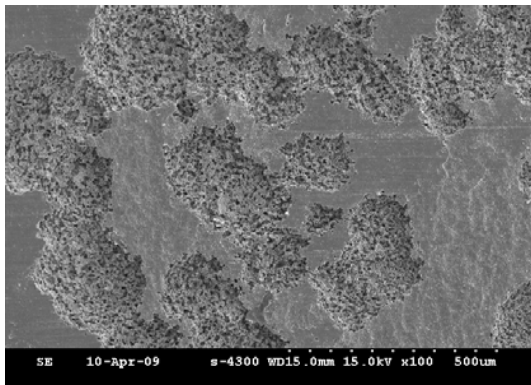
that the electrochemical dissolution is faster and more extensive when using the neutral electrolyte than when using the acid electrolyte.

An unusual effect occurred on the surface of the nitinol electrochemically machined with neutral electrolyte. In general, polishing techniques, including EP using an acid electrolyte, not only improve surface roughness but also brighten the surface. However, while EP using a neutral electrolyte did improve the surface roughness, it also blackened the surface.

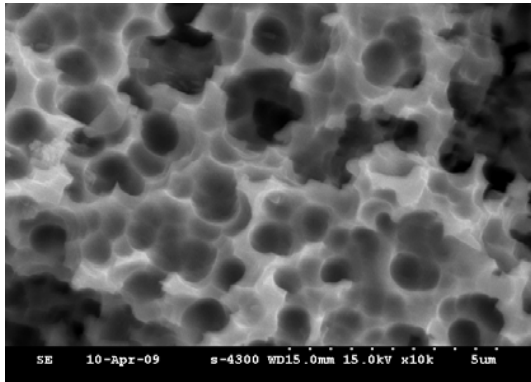
The nitinol surface was captured using scanning electron microscopy (SEM) after EP as shown in Fig. 5, with the EP result where acid electrolyte was used shown in Fig. 5(a) and the EP result where neutral electrolyte was used shown in Fig. 5(b). The nitinol surface shows dense patterns after EP treatment using the neutral electrolyte, but not after treatment with the acid electrolyte. This means that electrochemical dissolution is dependent upon the composition of the electrolyte involved.

To analyze this machining result, the EP process was conducted under minimal machining conditions, which required use of a neutral electrolyte, a pulse on/off time of $1 \mu\text{s}/999 \mu\text{s}$, an applied current of 1A and a machining time of 3sec, and machining results were captured using SEM as shown Fig. 6.

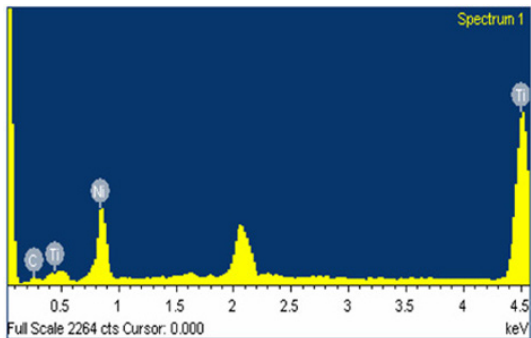
Fig. 6(a) shows the partially machined surface after EP using the minimal machining conditions. Fig. 6(b) shows an



(a) The Partially machined surface



(b) Ultra-microscopic holes on the machined surface



(c) Chemical composition of nitinol shape memory alloy by EDX (Wt.%)

Fig. 6. SEM image of workpiece surface after EP using minimal machining conditions (pulse on/off time is set $1 \mu\text{s}/999 \mu\text{s}$, applied current is 1A and machining time is 3sec).

enlargement of ultra-microscopic holes on the machined surface. There are innumerable ultra-microscopic holes on the surface. Because of the holes, improvement of the surface roughness was limited during EP using the neutral electrolyte.

When EP was conducted using the neutral electrolyte, innumerable ultra-microscopic holes appeared. The differences in machining characteristics according to the composition of the electrolyte involved can be explained in two ways.

First, the nitinol is dissolved more quickly and thoroughly when using the neutral electrolyte than when using the acid electrolyte because nitinol has an affinity to the neutral electrolyte.

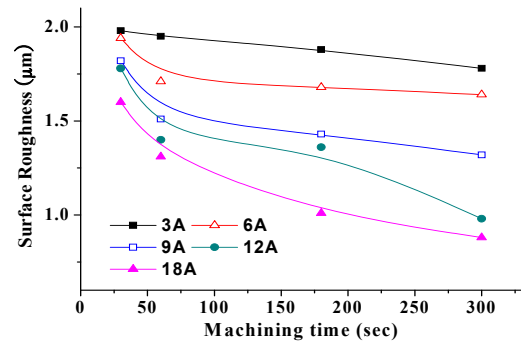


Fig. 7. The machining characteristic of applied current according to variation of machining time.

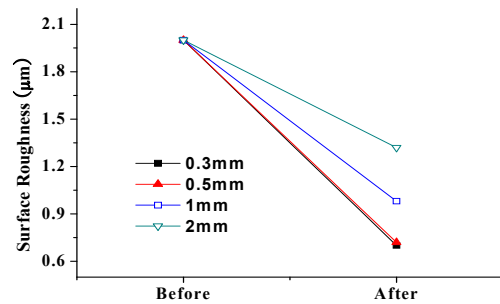


Fig. 8. Machining characteristics according to IEG.

The second explanation comes from EDX analysis. The quantity of oxygen on the nitinol surface after EP using the neutral electrolyte is more than is present before EP and more than is present after EP using the acid electrolyte. It is thought that the acid electrolyte might make an oxide film on the nitinol surface during electrochemical dissolution. Because of the oxide film, electrochemical dissolution does not occur excessively, unlike EP when using the neutral electrolyte and polishing is conducted efficiently, as the prominent parts are preferentially dissolved.

Thus, using the acid electrolyte is suitable for polishing and using the neutral electrolyte is more suitable for ECM than for polishing. In terms of traditional machining, using the neutral electrolyte is similar to rough grinding and using the acid electrolyte is similar to the finishing process of machining.

5.2 Characteristics of applied current

Fig. 7 shows machining characteristics according to applied current. In this experiment, an acid electrolyte composed of sulfuric acid, phosphoric acid and distilled water was used. The IEG was 1mm and machining time was 300sec.

When the applied current is increased, the surface roughness is improved. However, when excessive current is applied, the machining state becomes unstable. Further, there is little difference in the result achieved at 12A, a surface roughness of $0.98 \mu\text{m}$, and the result at 18A, a surface roughness of $0.9 \mu\text{m}$. Also, if the applied current is over 18A, machining control is too difficult and excessive nitinol is removed. This means that the process is no longer a polishing process, but a machining

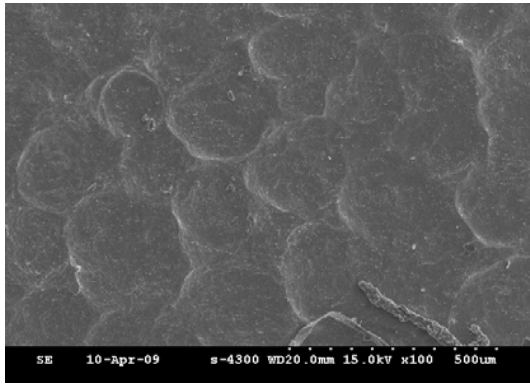


Fig. 9. SEM image of bubble mark on nitinol.

process.

5.3 Machining characteristics of inter-electrode gap (IEG)

Fig. 8 shows the machining characteristics according to IEG. In this experiment, the acid electrolyte was used. The applied current was 12A and machining time was 300 sec.

Generally, a smaller IEG is better, as it results in better surface roughness. However, similar results were achieved with an IEG of 0.3mm as with an IEG of 0.5mm, and it was found that an IEG that is too tight causes unstable machining and results in bubble marks on the nitinol surface, as shown in Fig. 9.

These bubble marks can be explained as damage to the nitinol from hydrogen gas. As mentioned above, hydrogen gas appears in the form of bubbles on the cathode during EP. During electrochemical dissolution, this bubble form of hydrogen gas does not affect machining due to the continual formation and explosion of the hydrogen bubbles. However, when the IEG is too tight, this process of formation and explosion is discontinued, because the nitinol is machined while hydrogen bubbles are attached to the cathode and the nitinol. The nitinol is partially interrupted by the attached hydrogen bubbles, and partial bubble marks are created on the nitinol. Therefore, a suitable IEG is required for effective machining.

5.4 Machining characteristics of initial surface roughness of anode

Fig. 10 shows the machining characteristics according to initial anode surface roughness. In this experiment, the acid electrolyte was used, the applied current was 12A, the IEG was 1mm and the machining time was 300sec. For this experiment, a nitinol sample with $2\ \mu\text{m}$ of initial surface roughness was machined to a roughness of $0.97\ \mu\text{m}$ by the polishing machine.

The workpiece with $2\ \mu\text{m}$ of initial surface roughness improved gradually, and $0.98\ \mu\text{m}$ of surface roughness was acquired after 300sec. However, after 300 sec of machining time, the surface roughness did not continue to improve significantly. The other workpiece, which had $1\ \mu\text{m}$ of initial surface roughness, improved rapidly until 50sec, but after 50sec of

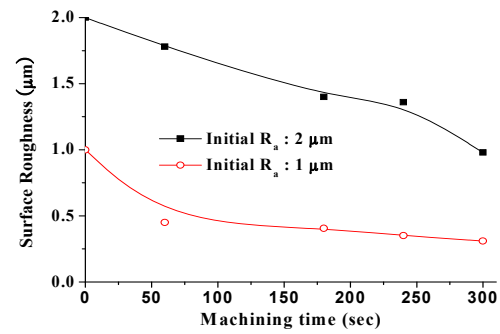


Fig. 10. Characteristics of initial anode surface roughness according to variation of machining time.



(a) Before EP process

(b) After EP process

Fig. 11. The effect of EP machining under the most suitable conditions.

machining time, the surface roughness did not significantly improve.

This result shows that the EP effect has limitations. Therefore, for fast and effective machining, the surface should be initially machined using a polishing machine, and then EP should be conducted.

Fig. 11 shows successful results of EP machining. Fig. 11(a) shows the nitinol surface before the EP process, and Fig. 11(b) shows the nitinol surface after the EP process using the most suitable machining conditions, where the initial surface roughness of the nitinol was $1\ \mu\text{m}$, the electrolyte used was an acid electrolyte, the applied current was 18A, the pulse on/off time was $800\ \mu\text{s} / 200\ \mu\text{s}$, the IEG was 0.5mm and the machining time was 300sec. The resulting surface roughness obtained was $0.31\ \mu\text{m}$.

6. Conclusions

To determine a stable EP process for nitinol SMA, machining factors and machining conditions were researched by experiment, and the resulting machining phenomena were analyzed according to machining conditions.

Experimental results led to the following conclusions:

(1) The effects of using an acid electrolyte and of using a neutral electrolyte were compared. First, performing EP using a neutral electrolyte causes innumerable ultra-microscopic holes on the nitinol surface and does not result in a precision outcome. However, the process is fast, so using a neutral electrolyte is suitable for machining in which metal removal is the primary goal. Second, EP using an acid electrolyte is more

appropriate for slow machining than is using a neutral electrolyte. EP using an acid electrolyte is also more suitable for precision machining.

(2) Final surface roughness is generally better when a higher current is applied, although the machining process state becomes unstable when too much current is applied.

(3) Although surface roughness is generally better when the IEG is small, an excessively tight IEG causes an unstable machining state and results in bubble marks on the nitinol.

(4) Machinability by EP should be evaluated according to initial surface roughness, and it is proposed that initial surface machining should be conducted using a polishing machine for very rough surfaces before EP is conducted as a finishing technique.

(5) A nitinol surface was successfully polished to a surface roughness of $0.31\ \mu\text{m}$ under the most suitable conditions, where the initial surface roughness of the nitinol was $1\ \mu\text{m}$, the electrolyte used was an acid electrolyte, the applied current was 18A, the pulse on/off time was $800\ \mu\text{s} / 200\ \mu\text{s}$, the IEG was 0.5mm and the machining time was 300sec. The final surface roughness obtained was $0.31\ \mu\text{m}$.

Acknowledgment

This work was supported by INHA University Research grant.

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