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Improvement of Ti-Plasma Coating on Ni-Ti Shape Memory Alloy Applying to Implant Materials and its Evaluation

Masaru Okuyama, Jun Endo, Seisho Take, Yasuhiko Itoi, and Satoshi Kambe*

Oyama National College of Technology, 771 Nakaguki, Oyama 323-0806, Japan
**Teikyo University, Faculty of Science and Technology, 1189-4 Nishikitayama, Nagaoka, Utsunomiya, 220-0004, Japan*

Utilizing of Ni-Ti shape memory alloy for implant materials has been world-widely studied. It is, however, known that Ni-Ti alloy is easily attacked by chloride ion contained in body liquid. To prevent Ni dissolution, the authors tried to coat the alloy surface with titanium metal by means of plasma-spray coating method. The plasma coating films resulted in rather accelerating pitting corrosion because of their high porosity. Therefore, sealing of the porous films was required. In order to solve this problem and satisfy prolonged lifetime in the body, the authors tried to use the vacuum evaporation technique of titanium metal. Two types of Ti vacuum evaporation procedures were employed. The one was to cover a thin film on Ni-Ti alloy surface prior to massive Ti plasma spray coating. The other was to first coat plasma spray films on Ni-Ti alloy and then to cover them with vacuum evaporation films of Ti. Protective ability against pitting corrosion was examined by electrochemical polarization measurement in physiological solution and the coating films were characterized by microscopic and SEM observation and EPMA analysis. Vacuum evaporation thin films could not protect Ni-Ti alloy from pitting corrosion. In the case of plasma spray coating over the Ti vacuum evaporation thin film, the substrate Ni-Ti alloy could not be better protected. On the contrary, vacuum evaporation of Ti over the porous plasma spray coating layer remarkably improved corrosion protective performance.

Keywords : *NI-Ti shape memory alloy, implant material, plasma spray coating, vacuum evaporation.*

1. Introduction

Application of Ni-Ti shape memory alloys has been studied to implant materials in human bodies.[1-5] However, they often undergo pitting corrosion due to chloride ions contained in living body liquid. In order to improve their corrosion resistance, the authors have tried to employ a titanium surface coating by using a plasma spraying technique, but it was resulted in rather enhancing pitting corrosion because of high porosity of the plasma spray films.[6] Thus, the authors first tried to seal the pores using organic polymers.[7] The several kinds of biocompatible polymers were tested and their corrosion protection performance was examined. It turned out that a thermoplastic polyamide resin conformed to the purpose. However, the question remained to the prolonged life after implanting them inside the body. For this purpose, metal materials are thought to prefer. In this study, the vacuum evaporation of titanium was employed for sealing of porous plasma-sprayed films and then the corrosion protection performance of the samples was examined by using an electrochemical polarization technique, and SEM and microscopic observation were carried out for their characterization.

2. Experimental

The one end of a 50at% Ei-Ti shape memory alloy rod of 3 mm in diameter and 50mm in length was ground into the shape of a cone as a sample. After sand-blasting of the sample surface, plasma spray of titanium powder was performed on the surface during rotating around its long axis so that the film might become uniform in thickness. For sealing of the porous plasma spray films, vacuum evaporation of Ti was employed. Two ways of Ti vacuum evaporation procedures were taken. The one was that Ti vacuum evaporation was done prior to plasma spray coating but the other was reverse. Thickness of the plasma coating films are controlled 20 to 50 μm and those of vacuum evaporation films 5 to 20 μm. The sealing effect by vacuum evaporation of Ti was evaluated by the electrochemical polarization experiment to judge whether pitting corrosion was controlled or not. The potential- dynamic polarization experiment was conducted using a potentiostat in the electrolyte dearated by passing pure nitrogen gas. The electrolyte was the Hanks' physiological solution at 40 C. After introducing a sample into the electrolytic cell and 5 minute immersion in the electrolyte, the polarization was carried out from -0.30V (SSE) in the anodic direction to 1.5 V or the potentials where anodic current suddenly rose up and, then, the potential sweeping direction was reversed down to the potential where the current reached zero (repassivation potential). The potential-sweeping rate was kept 0.25 V/min. Judgment whether the pitting corrosion broke out or not was made from appearance of a hysteresis of the polarization curves between on potential rising and downing. Characterization of the samples was performed through the observation of a stereomicroscope and SEM, and EPMA analysis.

3. Results and discussion

3.1 The corrosion protection effect of the Ti coating films formed by vacuum evaporation on Ni-Ti alloy

In order to examine how much corrosion-protective the Ti vacuum evaporation film was, the Ni-Ti alloy samples was directly coated by vacuum evaporation and the corrosion test of the samples was carried out in the physiological solution at 40 C. The polarization curve of the sample covered with 10 μm vacuum evaporation films was shown in Fig. 1. A distinct hysteresis can be observed between up-rising and downing curves, showing that the former current is much larger than the latter. This suggests breakout of pitting corrosion. Fig. 2 shows the surface photographs of the sample before and after the polarization

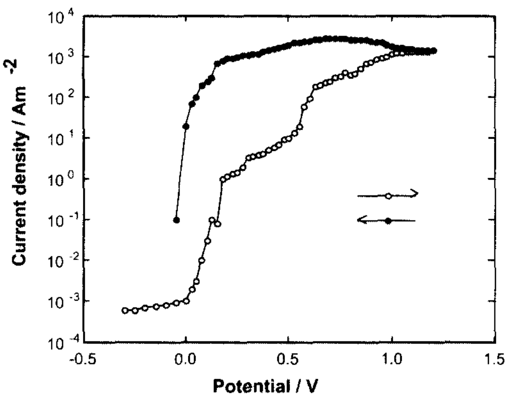


Fig. 1. Polarization curves of Ni-Ti alloy coated with Ti vacuum evaporation of 20mm in physiological solution at 40 ℃.

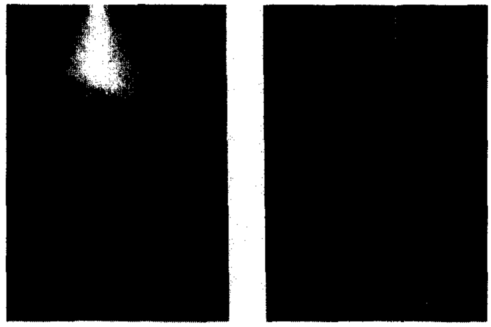


Fig. 2. Microscopic photograph of sample used in Fig. 1 before (left) and after (right) polarization experiment.

experiment. Exfoliation of a vacuum evaporation film can be evidently observed for the sample after the polarization experiment. From the whole experiments for the samples of this type, it could be mentioned that the thicker the vacuum evaporation film was, the more effective the corrosion protection was.

Nevertheless, since adhesion of the vacuum evaporation film to the substrate Ni-Ti alloy seemed to be weak, complete prevention from pitting corrosion was not expected only for this surface treatment.

The effect of vacuum-evaporation Ti undercoating on corrosion protection performance of Ti plasma-sprayed Ni-Ti alloy.

Hysteresis can be seen on the potential-current curves and that the current density of the backward curve is larger than that of the forward one. Therefore, this evidently indicates that pitting corrosion has happened. Fig. 4 shows a microphotograph of the sample after the polarization experiment. Destruction of a surface layer can be seen. As already mentioned, the Ti vacuum evaporation film lost the adhesion to the Ni-Ti alloy substrate. Moreover, plasma spraying heated the substrate surface up to several 1000 ℃ momentarily so that the inner vacuum evaporation film was destroyed by thermal stress, or it exfoliated during rapid cooling to the room temperature. As a result, it can be concluded that the method for coating of Ti vacuum evaporation film beneath plasma spray coating film is disqualified.

3.2 The effect of vacuum-evaporation Ti stacking on corrosion protection performance of Ti plasma-sprayed Ni-Ti alloy.

The plasma spray porous films of good adhesive nature to the Ni-Ti alloy substrate were first coated and on them Ti was deposited by means of the vacuum evaporation. This case is considered with the implications of sealing of pores in the plasma spray films rather than formation of uniform films on them by the vacuum evaporation. Changing both the thickness of plasma spray films and

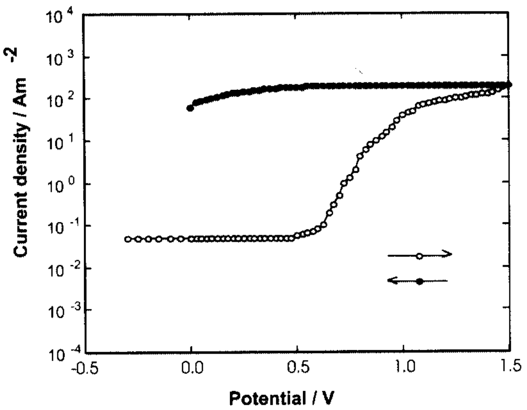


Fig. 3. Polarization curves of Ni-Ti alloy coat-ed with 20 mm Ti vacuum evaporation undercoat and 35.5 mm plasma spray topcoat in physiological solution at 40 C.

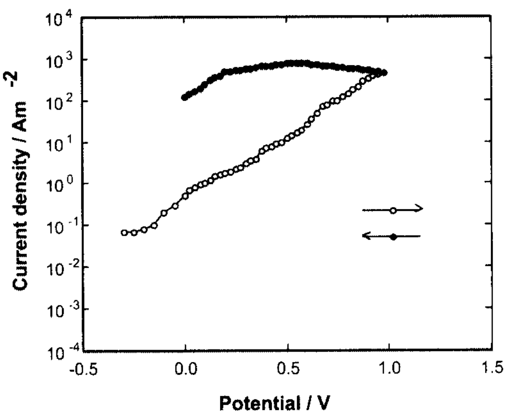


Fig. 5. Polarization experiment of Ni-Ti alloy coated with 17 mm Ti plasma spray undercoat and 10 mm Ti vac-uum evaporation topcoat in physio-logical solution at 40 C.

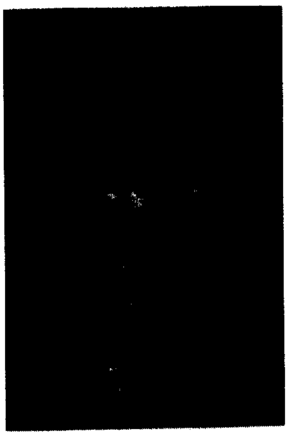


Fig. 4. Microscopic photograph of sample used in Fig.3 after polarization experiment in physiological solution at 40 C.

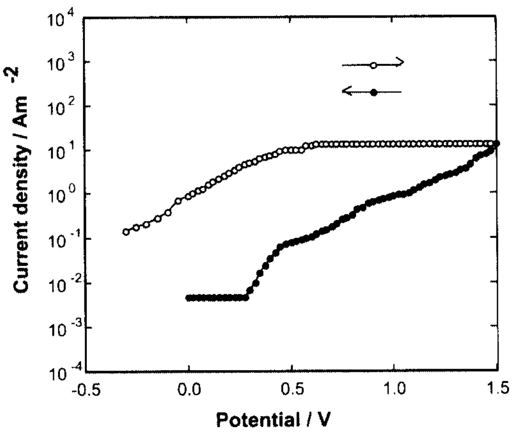
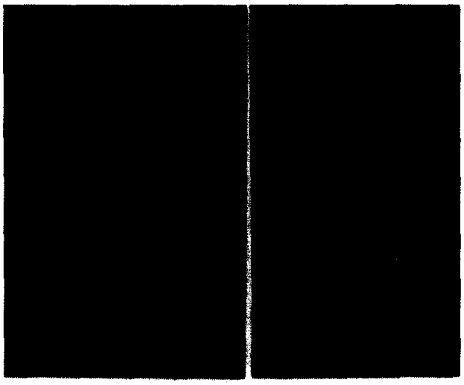


Fig. 6. Polarization experiment of Ni-Ti alloy coated with 35.5 mm Ti plasma spray undercoat and 8 mm Ti vac uum evaporation topcoat in physio-logical solution at 40 C.

the vacuum evaporation films, the pitting corrosion-proof performance was examined by

polarization experiments. In the case that the plasma spray films were thin, good results could not be obtained even if vacuum evaporation films were thick. Fig. 5 shows the polarization curves for the sample coated with a 17 μm plasma spray film and a 10 μm-corresponding vacuum evaporation film. Since hysteresis appears on the anode polarization curves, prevention from pitting corrosion cannot be recognized. The microscopic photograph of the sample after the polarization experiment is shown in Fig. 7 (A). The surface looks coarse and defects are presumed to exist partially inside the film. If plasma spray undercoating films are thin, there are many places where the vacuum evaporation film contacts directly with the alloy substrate. As the case of the single vacuum evaporation film deposited on Ni-Ti alloy substrate as mentioned in 3.1, it is thought that the defects were caused by less adhesion force. On the contrary, when plasma spray film was thickened, corrosion resistant was remarkably improved. Fig. 6 shows the anodic polarization curves of the sample coated with a 33.5 μm plasma spray film and a 8 μm-corresponding vacuum evaporation film. A hysteresis likely appears, but the anodic current of the backward curve is rather smaller than that of the forward one and all the currents give small values. This reasonably means that pitting corrosion was completely prevented. In Fig. 7 (B), the surface photograph of the sample after the polarization experiment shows that its surface is considerably coarse, but looks uniform as a whole. Since vacuum-evaporated atoms are stacked and sealed in the holes, tracing the rough surface of the porous sprayed film unlike the case that the spray films are thin. Therefore, good adhesion contact among Ti metals both in plasma spray coating film and the upper vacuum evaporation one can be maintained and thus defects do not arise. Table 1 repre



(A) (B)

Fig. 7. Microscopic photograph of sample used in Fig. 6 (A) and Fig. 7 (B) after polarization experiment.

Table 1. List of coated films on Ni-Ti alloy substrate and result of polarization experiment for the samples

Type of sample	Thickness(um) of		Result of Polarization
	undercoat	topcoat	
PVD/NI-TI		10	Pitting
		20	Pitting
		40	Pitting
Plasma/ PVD/Ni-Ti	10		Pitting
	20		Pitting
PVD/ Plasma/ Ni-Ti	17		Pitting
	18		Pitting
	25		Pitting
	33.5		No
	50		No

sents the summary of the qualitative results of the corrosion prevention test for the surface treated Ni-Ti alloy samples examined.

4. Conclusion

Sealing of the porous plasma spray Ti films coated on Ni-Ti shape memory alloy was tried by means of a vacuum evaporation method. Two ways for Ti vacuum evaporation sealing were adopted. The one was that uniform Ti vacuum vaporization film was first deposited on the substrate alloy and then plasma spray Ti layer was covered. The other was reverse. The pitting corrosion preventive performance of the surface-treated samples were tested using the electrochemical polarization technique and discussed. The results are as follows.

1) For Ni-Ti alloys coated with Ti by the vacuum evaporation, pitting corrosion broke out. It seemed to be attributed to weak adhesion force between the vacuum evaporation film and the alloy substrate.

2) In the case that Ti vacuum evaporation films were deposited as an undercoat and the plasma spray film formed on them, good result could not obtained. This is probably because destruction of the undercoating vacuum evaporation films took place, induced by thermal stress during rapid cooling of plasma spray films.

3) In the case that coating of the plasma spray film was carried out to the alloy substrate and vacuum evaporation of Ti was performed on it, pitting corrosion occurred for thin plasma spray films. However, if spray film was thickened, adhesion nature was improved, and. as a result of good sealing performance, it turns out that pitting corrosion could be completely prevented.

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