Anodic Dissolution Property and Structure of Passive Films on Equiatomic TiNi Intermetallic Compound

Jeong-Ja Lee, Won-Seog Yang, and Woon-Suk Hwang[†]

School of Materials Science and Engineering, Inha University, Incheon 402-751, Korea

The anodic polarization behavior of equiatomic TiNi shape memory alloy with pure titanium as a reference material was investigated by means of open circuit potential measurement and potentiodynamic polarization technique. And the structure of passive films on TiNi intermetallic compounds was also conducted using AES and ESCA. While the dissolved Ni(II) ion did not affect the dissolution rate and passivation of TiNi alloy, the dissolved Ti(III) ion was oxidated to Ti(IV) ion on passivated TiNi surface at passivation potential. It has also been found that the Ti(IV) ion increases the steady state potential, and passivates TiNi alloy at a limited concentration of Ti(IV) ion. The analysis by AES showed that passive film of TiNi alloy was composed of titanium oxide and nickel oxide, and the content of titanium was three times higher than that of nickel in outer side of passive film. According to the ESCA analysis, the passive film was composed of TiO_2 and NiO. It seems reasonable to suppose that NiO could act as unstabilizer to the oxide film and could be dissolved preferentially. Therefore, nickel oxide contained in the passive film may promote the dissolution of the film, and it could be explained the reason of higher pitting susceptibility of TiNi alloy than pure Ti.

***Keywords** : TiNi, polarization, passive film, pitting*

1. Introduction

The equiatomic TiNi intermetallic compounds are well known as Nitiol or TiNi shape memory alloys(SMA). The TiNi alloys have been widely used for biomedical implant materials on account of their excellent shape memory properties, good biocompatibilities, high strength, and good formability among intermetallic compounds.[1] It is also well known that TiNi alloy has an excellent corrosion resistance in solutions of human body fluids.[2]

Corrosion resistance properties of TiNi alloy relies on the presence of a passive film on the surface. As long as the passive film is sound, no general corrosion problems are to be foreseen. However, breakdown of the passive film can occur both during surgery and in service life.[1,2]

Especially, conflicting results have been reported on the localized corrosion such as pitting and crevice corrosion. Shabalovskaya[3] remarked that any corrosion attack was not observed on the TiNi alloy implants for a decade of in vivo investigations. On the contrary, Edie et. al.[4] reported that pitting corrosion resistance of TiNi alloy was inferior to other titanium alloys. And Nakayama et. al.[5]

indicated instability of passive film and scattering of pitting potential. Dutta et. al.[6] also reported that intermetallic phases in TiNi alloys may provide preferential sites for pit initiation in Hank's simulated physiological solution.

There have been some reports on the passive oxide composition of TiNi alloy. Takahashi et. al.[7] reported that passive film of TiNi alloy was composed of TiO_2 and NiO in 0.5 M H_2SO_4 solutions. However, Oshida and Miyazaki[8] reported that air-formed oxide film on TiNi alloy under 300℃ for 10 minutes is TiO_2 containing some $NiTiO_3$. And, Han et. al.[9] reported that it is composed of TiO and TiO_2.

In general, pitting starts with the breakdown of the passive film. Therefore, the stability of passive film is the most important factor to the occurrence of pitting. Such environmental factors as pH, Cl⁻ concentration and temperature may be significant to this passive film stability, but its own structural property is also important.

Thus, in this study, the structure of passive films on TiNi intermetallic compounds was analyzed by AES, ESCA, and ellipsometry. The polarization behavior of equiatomic TiNi shape memory alloy with pure titanium as a reference material was also investigated by means of open circuit potential measurement and potentiody-

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[†] Corresponding author: wnshwang@inha.ac.kr

namic polarization technique. And, the reason for the occurrence of localized corrosion like pitting was discussed based on these results.

2. Experiments

Nearly equiatomic TiNi alloy sheet has been used in the present study, M_s and A_f transformation temperatures were -34℃ and 33℃, respectively, and there were no change of microstructures in the TiNi alloy during the experiments. The chemical compositions and the other properties of the specimens are given in Table 1. The specimens, which were cut from sheet, had an exposed area of 1.1 cm². Prior to the test, the specimens were mechanically polished up to 2000 grit abrasive paper, and then were degreased with acetone and washed in distilled water. A Teflon holder was used in order to prevent the effect of crevice corrosion and to insure the uniformity of exposed surface area.

All test solutions were prepared from distilled and deionized water. The solutions were deoxygenated with nitrogen gas for 1 hour prior to the start of the test, and subsequent electrochemical studies were conducted under a nitrogen atmosphere.

Prior to anodic polarization, a strong cathodic polarization of 1 mA/cm² for 60s was used to remove preformed oxide film and to activate the surface of TiNi alloy.

Polarization studies were performed using EG&G potentiostat 273A and a saturated Ag/AgCl electrode was used as the reference electrode. The pitting susceptibility was investigated by potentiodynamic polarization measurements. In case of the occurrence of pitting corrosion on potentiodynamic anodic polarization, the scan was reversed when a current density of 1 mA/cm² was reached.

In order to investigate the effects of Ti^{4+} ion on the pitting behavior of TiNi alloy, $Ti(SO_4)_2$ was added to the simulated physiological solutions, and the concentrations of the Ti^{4+} ion were varied from 0.1 mM to 0.4 mM. The thickness of the passive film on TiNi surface was measured by ellipsometry and AES depth profiling with sputtering rate of 50 Å/min., and the composition was investigated by ESCA.

Table 1. Chemical composition and transformation temperature of the specimen

Chemical Composition [wt.%]		Transformation Temperature			
Ni	55.96	M_s	239K,	M_f	206.5K
C	0.052	A_s	279K,	A_f	306K

3. Results and discussion

Anodic polarization curves of TiNi shape memory alloy and pure Ti in 1 M sulphuric acid solution at 40℃ were measured. The open circuit potential of Ti showed active state, and active dissolution peak existed during the anodic polarization. But, in case of TiNi alloy, it showed passive state at open circuit state, and maintained the passive state during the anodic polarization. The anodic polarization curve of TiNi alloy showed a curve with an active/passive transition type like Ti at 70℃, during which its limiting current density for passivation showed 10-times higher than that of Ti at the same temperature. Anodic polarization curve of TiNi alloy shows that, if electrode potential reaches 1.5 V, current density increases sharply and oxygen is generated. While there is no oxygen evolution in Ti because it is a valve metal where its passive film blocks the electricity, like Ni the oxygen evolution in TiNi shows that the composition and property of passive film on TiNi is different from that of Ti's.

Therefore, in order to confirm the structure and composition of passive film on TiNi alloy, a specimen which was passivated in a 1 M H_2SO_4 solution at 0.5 V for 3,600s was analyzed by AES. Fig. 1 shows the relation between energy intensity and sputtering time of each element. The film thickness estimated from sputtering speed is more than 100 Å, and the Figure shows that it is thicker than passive film of Ti.[10]

Fig. 2 is the summary of the elemental ratio of Ti / Ni from the results of Fig. 2. The content of Ti was three times higher than that of Ni in outer side. It also showed that the content of Ni increased with its approach to the base material, and reached the equivalent value to Ti content at inner side of film. These results showed that the
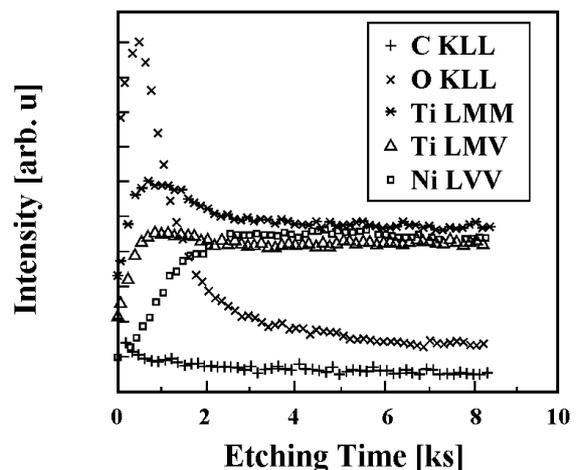

Fig. 1. Auger spectra depth profile of TiNi alloy passivated in a 1M H_2SO_4 solution at 0.5V for 3,600s.
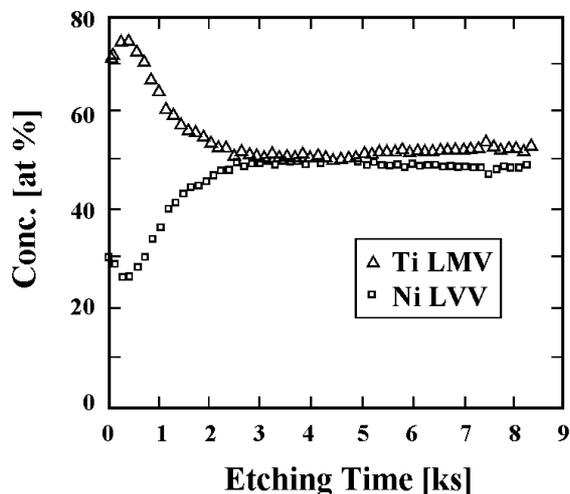
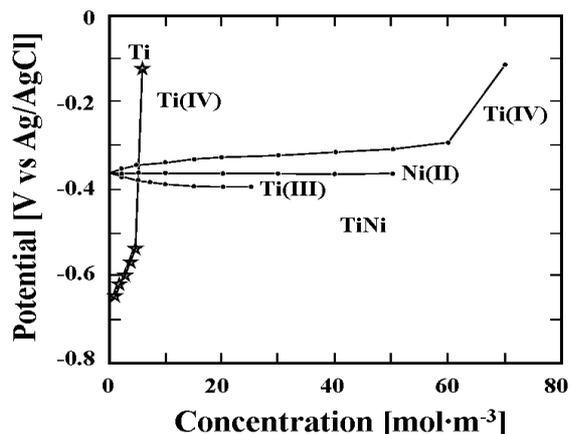**Fig. 2.** Concentration profiles of TiNi alloy passivated in a 1M H_2SO_4 solution at 0.5V for 3,600s.

Fig. 3. Effects of Ni(II), Ti(III), and Ti(IV) ions on the open circuit potential of activated TiNi alloy in 0.5M H_2SO_4 solution at 60℃.

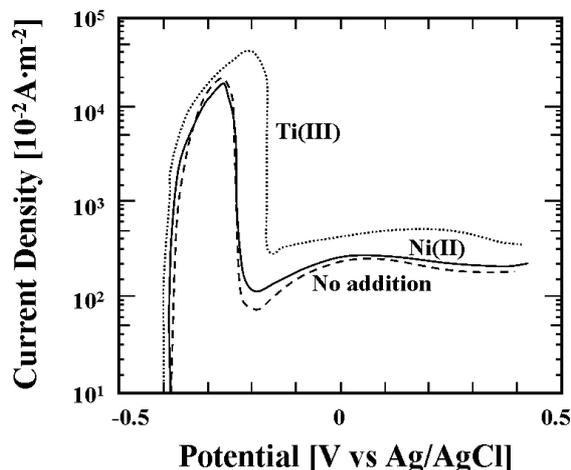**Fig. 4.** Effects of Ni(II) and Ti(III) ions on the potentiodynamic anodic polarization curves of activated TiNi alloy in 1M H_2SO_4 solution at 60℃.

passive film of TiNi alloy is not formed as an unified composition of TiNi oxide film, but its composition and property vary depending upon the change of film thickness.

Fig. 3 shows the results of the investigation into the effects of Ti(Ⅲ), Ti(Ⅳ) and Ni(Ⅱ) ion concentrations on TiNi open circuit potential in a 0.5 M H_2SO_4 solution. It can be learned that there is no change in the potential by the addition of Ni(II), the existence of Ni(II) does not affect open circuit potential. It shows a trend that, as the Ti(III) concentration increases, the open circuit potential decreases.

As Ti(IV) in the solution increases, the potential goes up and becomes passivated at over 60×10^{-3} mol. Compared with 6×10^{-3} mol, which is the Ti(IV) concentration

necessary for passivation of pure Ti, this value is 10 times larger, and it can be seen that the limiting current density for passivation of TiNi alloy, which was described earlier, is 10 times larger than that of Ti.

Fig. 4 is the potentiodynamic polarization curves when Ni(II) and Ti(III) were added to 1 M H_2SO_4 solution respectively. In case of Ni(II), like the result of the open circuit potential, there is no change in polarization curve by the addition. In a solution adding Ti(III), it shows a trend that apparent current densities of anodic dissolution and passivation increase, and the more Ti(III) solution is added, the higher current goes.

As shown from the above results, the effects of Ti(III) and Ti(IV) on the potentiodynamic polarization curves are identical with the results at Ti.[11),12)] It is thought that Ti(III) ions in the solution become oxidated in the electrode surface to Ti(IV) at passivation potential, and Ti (IV) becomes to Ti(III) by reduction on the active alloy surface. Therefore, the reduction on Ti(IV) occurs on the electrode surface, and if its cathodic current density becomes larger than limiting current density for passivation, the alloy becomes passivated.

Followed by the case of the sulphuric acid solution described previously, this study examined the composition and structure of the passive film to be formed under the condition of chloride. First of all, the passive film on the TiNi surface was investigated by ellipsometry, and the thickness of passive film was obtained as 40-50 Å under the conditions of potentiodynamically polarized to 0.2 V in a physiological solution for 1 hour. This result is consistent with the data reported previously in 3% NaCl solutions by Takahashi et. al.[8]. The results of AES analysis
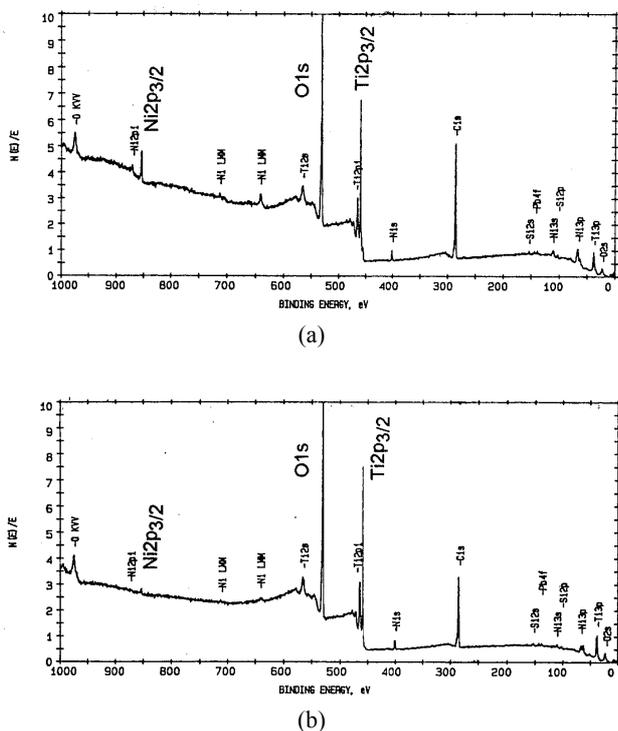
(a)

(b)

Fig. 5. ESCA analysis on the surface of TiNi alloy passivated in a simulated physiological solution. (a) afer 1 hour at open circuit condition (b) after pitting occured
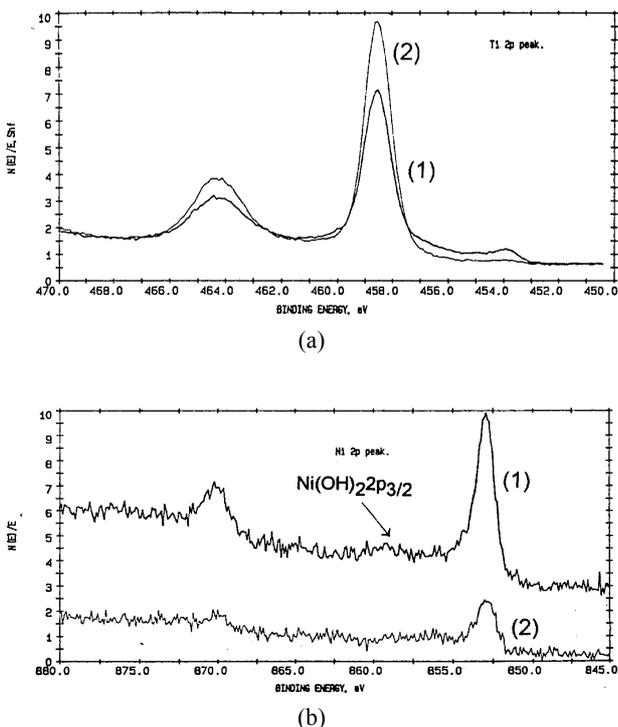

(a)

(b)

Fig. 6. Quantitative ESCA analysis on the surface of TiNi alloy ((1) afer 1 hour at open circuit condition (2) after pitting occurred). (a) ESCA data for Ti$2p_{3/2}$ peak (b) ESCA data for Ni$p_{3/2}$ peak

showed that Ti composition is higher than that of Ni, like the case of the sulphuric acid solution.

The composition of passive film formed under anodic polarized conditions was investigated by ESCA. Fig. 5(a) shows the results of ESCA on the oxide films formed at open circuit state in a physiological solution for 1 hour. And, Fig. 5(b) shows the results of ESCA on the oxide films after pitting by potentiodynamic polarization. Ti, Ni, O and C were detected under both of these two conditions, and the quantitative analysis on passive film was done by the value of combined energy of Ti and Ni's $2p_{3/2}$ electron.

The compositions of passive film were analyzed by the $2p_{3/2}$ electron binding energy peaks of Ti and Ni. The strong peak at the binding energy of 458.5 eV is corresponding to the state of Ti^{4+} in Fig. 6(a). In Fig. 6(b), binding energy peak of Ni $2P_{3/2}$ at 852.1 eV and the very weak peak at 855.4 eV correspond to the atomic state Ni and Ni^{2+} ion, respectively. It is obvious that the atomic state nickel peak was detected from the matrix through the passive film.

Therefore, it could be concluded that the passive oxide film of TiNi alloy consist of TiO$_2$ including small amount of NiO(or Ni(OH)$_2$). It seems reasonable to suppose that NiO could act as unstabilizer to the oxide film, because NiO is electrochemically unstable than TiO$_2$ in simulated physiological solutions and NiO could be dissolved preferentially. Therefore, small amount of nickel oxide contained in the passive film of TiNi alloy may promote the dissolution of the film, and it could be thought as one of the reason of higher pitting susceptibility of TiNi alloy than pure Ti. And, it is also concluded that the pitting susceptibility will increase as the composition of NiO on passive film goes up.

4. Conclusion

The structure and composition of passive film and electrochemical behavior of TiNi shape memory alloy in sulphuric acid solutions and a physiological solution were analyzed through potentiodynamic polarization, AES and ESCA, and studied in comparison with the case of Ti.

As a result, it can be learned that TiNi alloy is more difficult to activation than Ti, shows higher corrosion resistance, but once activated, dissolution rate of the alloy elements is so fast. The activities of Ti(III)m Ti(IV) and Ni(II) were also investigated when they co-existed in the solution. Ni(II) in the solution did not affect anodic dissolution rate of TiNi alloy and electrodic reactions including passivation. On the contrary, Ti(Ⅲ) and Ti(Ⅳ) showed the same electrochemical behavior as Ti. Ti(III) became

oxidated on the passivated TiNi alloy surface, Ti(IV) became to Ti(III) by reduction on the activated alloy surface. And, Ti(IV) contributed to the passivation of TiNi alloy through the increase of steady state potential.

The results of AES and ESCA analyses showed that the passive film of TiNi alloy consist of TiO_2 including small amount of NiO. It seems reasonable to suppose that NiO could act as unstabilizer to the oxide film and could be dissolved preferentially. Therefore, small amount of nickel oxide contained in the passive film may promote the dissolution of the film, and it could be explained the reason of higher pitting susceptibility of TiNi alloy than pure Ti. And, it is thought that the pitting susceptibility will increase as the composition of NiO on passive film goes up.

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