Anodic Oxide Film Formed on Shape Memory NiTi Alloy

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Shape memory alloys (SMA) show unique thermo-mechanical properties like shape memory effects and pseudoelasticity, which are related to the temperature-dependent austenite-to-martensite phase transformation. Upon phase transformation from a martensite to an austenite for the one-way shape memory effect, starins of up to 10% is recovered, which are accompanied by generation of large work outputs. Therefore SMA is promising materials for actuator and orthodontic devices in various fields. The equiatomic Ni and Ti-based ally is one of SMA which has been widely employed in medical and dental fields such as vascular stents and orthodontic arch wires. Preferable biomedical materials should release no or less toxic products after implantation in the body. It is generally reviewed that NiTi has a good biocompatibility due to the formation of titanium oxide-based film. The oxide film on NiTi seems to protect the bulk material from corrosion and to be a barrier against toxic Ni dissolution. Thus, it is important to know details of behavior during anodic oxidation of SMA, especially, the stability of anodic oxide film under the shape memory performance.

50.62at.%-Ni 49.38at.%-Ti alloy disk with 10 mm diameter and 2 mm thickness was employed as a specimen electrode. The specimen was heated at 337 K for 900 s to trans-phase to austenite. After mechanical polishing to mirror-like surface with diamond slurry, the specimen surface was electropolished in the mixture of glacial acetic acid and perchloric acid to remove a bibly layer. Electrolyte used were pH 6.5 and 8.4 borate solution containing 0.15 mod dm^{-3} borate ion totally, 0.1 mol dm^{-3} HCl, and 0.1 mol dm^{-3} H_2SO_4, which were prepared from analytical-grade regent and de-ionized distilled water. The solution was deaerated with pure argon gas. The electrode potential measured in reference to an Ag/AgCl electrode at 3 mol dm^{-3} KCl solution and converted to a potential scale versus the reversible hydrogen electrode (RHE) at the same solution of $a(H_2)$ = 1. The experimental temperature was controlled at 298 K.

Computer-controlled potentiostat and FRA (Solartorn 1287 and 1255B) were employed for the anodic oxidation of NiTi surface and its electrochemistry. For the anodic oxidation, the potential was raised from a open circuit potential to 7 V by a potential sweep at 5 mV s^{-1}. Electrochemical AC impedance spectroscopy following the anodic oxidation was carried out over the frequency range of 10 m to 10 kHz. The amplitude of applied voltage was 10 mV.

Fig. 1 shows anodic polarization curves of NiTi in various electrolyte solutions. No active dissolution but the passivation is observed in a potential range from 0.1 to 1.7 V (RHE) in whole solutions. It seems to be two-step passivations while it is one step in H_2SO_4 solution after polarization at -0.54 V (RHE) for 600 s. An air-formed oxide film might influence to the first step. Independent of pre-cathodic polarization, in H_2SO_4 solution, the passivation current is two or three times higher than in any other solutions. This means that the oxide film is less protective and removable in H_2SO_4 solution. Oxygen evolution overlaps passivation and mainly take places at potentials more than 1.7 V (RHE). The oxygen evolution current depends on conductivity of solution. From ICP-AES analysis of the electrolyte solution, in which NiTi sample was polarized up to 7 V, NiTi released Ni species ten times more than one of Ti into pH 8.4 borate solution, suggesting the formation of titanium-rich oxide film by anodic polarization. In HCl solution, white corrosion precipitates and pitting corrosion was observed while surfaces were colored slightly gray and brown with metallic luster in pH 6.5 borate and H_2SO_4 solutions and pH 8.4 borate solution, respectively. Details of electrochemistry including AC impedance spectroscopy depending on thermo-elasticity of NiTi will be discussed at the meeting.

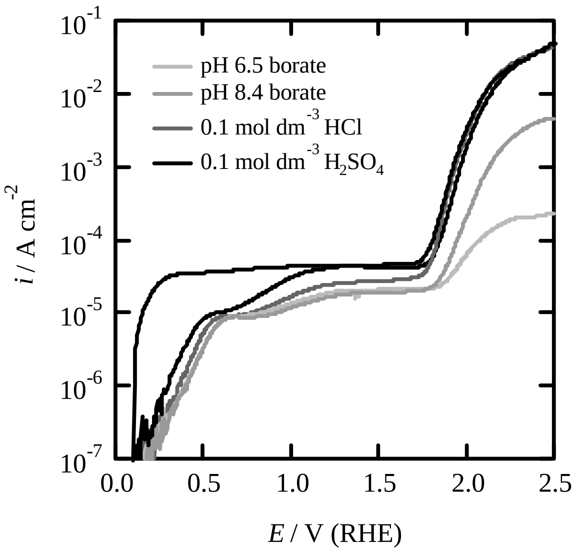

Fig. 1 Anodic current density as a function of electrode potential of NiTi in pH 6.5 and 8.4 borate, 0.1 mol dm^{-3} HCl, and 0.1 mol dm^{-3} H_2SO_4 solutions at 298 K. The potential sweep rate was 5 mV s^{-1}. A dotted line was obtained after polarization at -0.54 V (RHE) in H_2SO_4 solution.