The Passivation Behavior of Sputter-Deposited W-Ti Alloys in 1 M NaOH Solution

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Abstract

The passivation behavior of the sputter-deposited amorphous or nanocrystalline W-Ti alloys is studied in alkaline 1 M NaOH solution at 25°C, open to air using corrosion tests, electrochemical measurements and confocal scanning laser microscopic (CSLM) techniques. The corrosion rates of the W-Ti alloys decreased with increasing titanium content and the corrosion rates of the alloys containing 53 at % (atomic percentage) or more titanium as well as the sputter-deposited titanium metal are nearly two orders of magnitude lower than that of the sputter-deposited tungsten in 1 M NaOH solution. The pitting corrosion is clearly observed in the W-Ti alloys containing 30-53 at % titanium from CSLM studies. The open circuit potentials of all the examined W-Ti alloys are located between those of tungsten and titanium metals.

Introduction

The development of new technologies leads to a growing demand on advanced metallic alloys with improved chemical properties. The growing demand for such optimized materials stimulates the development of novel corrosion-resistant alloys having attractive chemically inert properties. Furthermore, the development of new corrosion-resistant engineering materials is provoked by different reasons and one of them is the improved corrosion resistance properties of the materials. The research activities on amorphous or nanocrystalline alloys produced by sputter deposition technique are recently being of a widespread interest in the field of corrosion science which is motivated by practical importance of such novel materials. It has been reported that the sputter-deposited amorphous or nanocrystalline alloys are chemically more homogeneous structure than conventionally processed crystalline alloys,[1-2] and hence such sputter-deposited alloys are interesting to develop the corrosion-resistant materials. Since homogeneous single-phase amorphous or nanocrystalline alloys possess many superior corrosion resistance properties, a variety of corrosion-resistant titanium-base alloys have been prepared.[3-8] On the other hand, the sputter deposition technique has been recently used as one of the appropriate methods for preparing extremely high corrosion resistance single-phase amorphous or/and nanocrystalline chromium-,[5,9-12] molybdenum-,[13-17] tungsten-[18-28] and manganese-[29] transition metal alloys. Furthermore, one of the present authors had successfully prepared novel sputter-deposited amorphous or / and nanocrystalline binary W-Ni[30-32] and W-Mo[33] alloys in a wide composition range, and reported high corrosion resistance in 12 M HCl, 0.5 M NaCl and 1 M NaOH solutions. In particular, only less than 15 at% of tungsten addition is enough to cause spontaneous passivation of the sputter-deposited amorphous or nanocrystalline W-Ti alloys and the alloys showed about three orders of magnitude lower corrosion rate than that of titanium metal in concentrated hydrochloric acid solutions at 30°C.[18,27,34] Quantitative surface analysis by X-ray photoelectron spectroscopy (XPS) has clarified that the spontaneously passivated films formed on the sputter-deposited amorphous or nanocrystalline W-Ti alloys are composed of new passive double oxyhydroxide films consisting of both tungsten and titanium ions {that is, $(0.67)W^{4.91+}(0.33)Ti^{4+}(2.08)O^{2-}(0.45)OH^{-}$} in concentrated hydrochloric acid solutions at 30°C[35] having pH values less than one in which regions tungsten is passive and titanium is active. It is noteworthy to mention here that tungsten metal generally corrodes in solution having pH 4 or higher whereas titanium metal does not corrode in slightly alkaline oxidizing solutions.[36] Therefore, it is very interesting to study the passivation behavior of the sputter-deposited W-Ti alloys in alkaline 1 M NaOH solution.

Present research work is aimed at studying the passivation behavior of the sputter-deposited amorphous or nanocrystalline W-Ti alloys in 1 M NaOH solution at 25°C, open to air by using corrosion tests, electrochemical measurements and confocal scanning laser microscopic (CSLM) techniques.

Experimental Methods

The binary W-Ti alloys were prepared by direct current (D. C.) magnetron sputtering machine on glass substrate as described elsewhere.[18,37] An electron probe microanalysis was used to determine the composition of the sputter-deposited W-Ti alloys. The sputter-deposited binary W-Ti alloys were confirmed as amorphous or nanocrystalline single-phase solid solution by X-ray diffraction.[18] The composition, structures and apparent grain size of the sputter-deposited W-Ti alloys are summarized in Table 1.

Prior to the corrosion tests, electrochemical measurements and surface morphological studies, the sputter-deposited amorphous or nanocrystalline W-Ti alloy specimens were mechanically polished with a silicon carbide paper up to grit number 1500 in cyclohexane, degreased by acetone and dried in air. The corrosion rate was estimated from the weight loss after immersion for 180 h in 1 M NaOH solution at 25°C, open to air. The weight loss measurement for each alloy specimen was done two times or more and the average corrosion rate of individual alloy was estimated. The time dependence of the corrosion rate of the W-Ti alloys including titanium metal was also estimated at various time intervals ranging from 2 to 180 hours.

Table 1: Composition, structure and apparent grain size of the sputter-deposited W-Ti alloys.[18-37]

Name of alloys	Tungsten content (at %)	Titanium content (at %)	Structure	Apparent grain size (nm)
W metal	100	0	Nanocrystal	20.0
W-30Ti	70	30	Amorphous	2.0
W-53Ti	47	53	Amorphous	1.5
W-90Ti	10	90	Nanocrystal	14.0
Ti metal	0	100	Nanocrystal	16.0

The open circuit potentials were measured after immersion for 2 hours in 1 M NaOH solution at 25°C, open to air. A platinum mesh and saturated calomel electrode were used as counter and reference electrodes, respectively. The alloy specimen was used as a working electrode. All the potentials given in this paper are relative to saturated calomel electrode (SCE).

The change in surface morphology of the sputter-deposited amorphous or nanocrystalline W-Ti alloys before and after immersion for 24 hours in 1 M NaOH solution at 25°C was observed using confocal scanning laser microscope (CSLM). The laser source used was He-Ne having wavelength of 633 nm. The scan rates for the samples were ranged from 1 to 16 per second.

Results and Discussion

Changes in corrosion rates of the sputter-deposited amorphous or nanocrystalline W-Ti alloys after immersion for 180 h in 1 M NaOH solution at 25°C, open to air are shown in figure 1. The corrosion rates of the sputter-deposited tungsten and titanium are also shown for comparison. The corrosion rates of tungsten and titanium are about 3.5×10^{-1} and 6.5×10^{-3} mm.y^{-1}, respectively. The corrosion rate of the W-Ti alloys decreased sharply with increasing titanium content and becomes almost constant when the alloys contain 53 at% or more titanium. Furthermore, the corrosion rates of the amorphous or nanocrystalline W-Ti alloys containing 53 at% or more titanium are nearly two orders of magnitude lower than that of tungsten and cannot exceed than that of titanium metal in 1 M NaOH solution at 25°C.

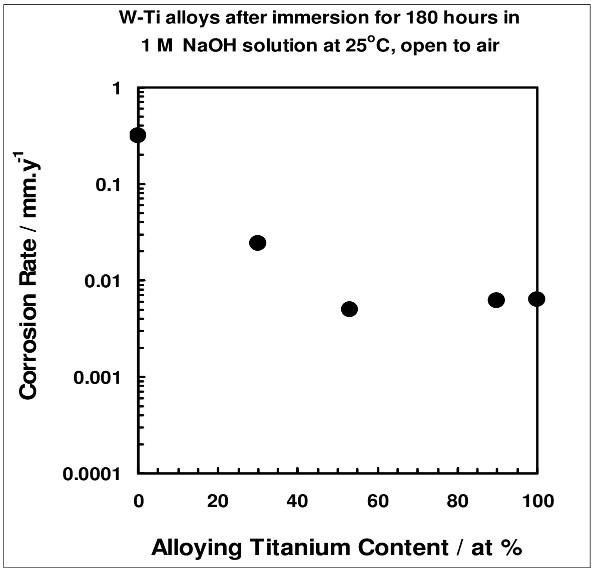

Figure 1: Changes in corrosion rates of the sputter-deposited W-Ti alloys including the sputter-deposited tungsten and titanium metals in 1 M NaOH solution at 25°C, open to air as a function of titanium content in the alloys.

In order to clarify the time dependence of the corrosion rate of the W-Ti alloys, the corrosion rates of the alloys were estimated after immersion for various time intervals. Figure 2 shows the changes in corrosion rates of the sputter-deposited W-Ti alloys including titanium metal in 1 M NaOH solution, as a function of immersion time. The corrosion rates of the W-Ti alloys containing 53 at% or more titanium and titanium metal are generally high at initial period of immersion (that is, 2 h). The corrosion rates of the alloys become almost steady after immersion for about 36 h. Accordingly, initially faster dissolution of the W-Ti alloys results in faster passivation by forming a more protective passive films on the surface of the alloys in 1 M NaOH solution.

The change in the surface morphology of the alloys gives important information about the dissolution process in nano-scales to study the passivation behavior of the alloys. Figures 3(a) and 3(b) show CSLM images of the W-Ti alloys before and after immersion for 24 h in 1 M NaOH solution at 25°C, respectively. These images clearly revealed that the surface oxide-films formed on the as-prepared sputter-deposited W-Ti alloys are very smooth and highly reflective as shown in Fig. 3(a) and the passive films formed on the alloys in 1 M NaOH solution are different than those of the oxide-films of the alloys as shown in Fig. 3(b). The dissolution is obvious and surface is roughened considerably in 1 M NaOH solution. In particular, the pitting corrosion is clearly observed for W-30Ti and W-53Ti alloys in 1 M NaOH solution. Number of pits per area on the surface of passive film for the tungsten-rich W-30Ti alloy is more than that on the surface of the passive film for the W-53Ti alloy. In particular, the localized breakdown of the passive film formed on the W-30Ti alloy is more clearly observed than that of the W-53Ti alloy. However, the pitting corrosion is not observed on the surface of the passive film formed on the titanium-rich W-90Ti alloy. These results clearly revealed that the high corrosion rate of the W-30Ti alloy than those of W-53Ti and W-90Ti alloys is most probably due to the pitting corrosion of the W-30Ti alloy in 1 M NaOH solution.

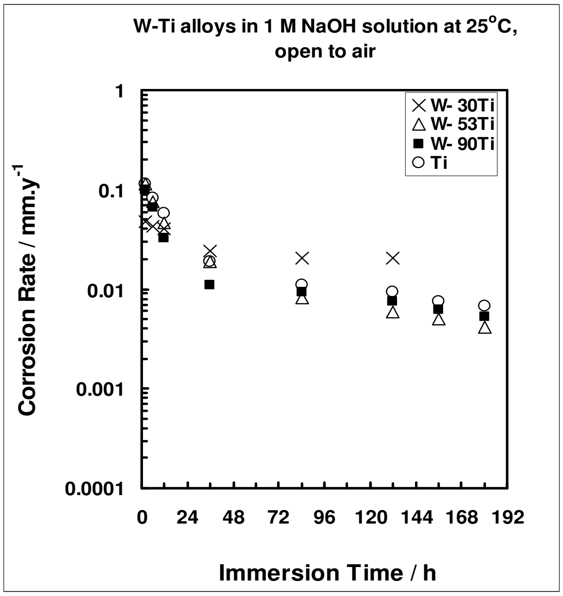

Figure 2: Changes in corrosion rates of the sputter-deposited W-Ti alloys including the sputter-deposited titanium metal in 1 M NaOH solution at 25°C, open to air as a function of immersion time.

Electrochemical measurements were carried out for a better understanding of the passivation behavior of the. Figure 4 shows the changes in open circuit potentials for the W-Ti alloys including tungsten and titanium metals after immersion for 2 h in 1 M NaOH solution at 25°C, open to air as a function of immersion time. The open circuit potentials of the alloys are generally shifted towards more positive direction with immersion time. The steady state of the open circuit potentials of the W-Ti alloys is observed after immersion for about 30 minutes and they are located between those of the open circuit potentials of tungsten and titanium metals. Furthermore, the open circuit potentials of the alloys are shifted to more noble direction with increasing the titanium content. These facts coincide with the changes in the corrosion rates of the W-Ti alloys in 1M NaOH solution as shown in Figs 1 and 2.

Conclusion

The passivation behavior of the sputter-deposited amorphous or nanocrystalline W-Ti alloys is studied in 1 M NaOH solution at 25°C, open to air by corrosion tests, elctro-

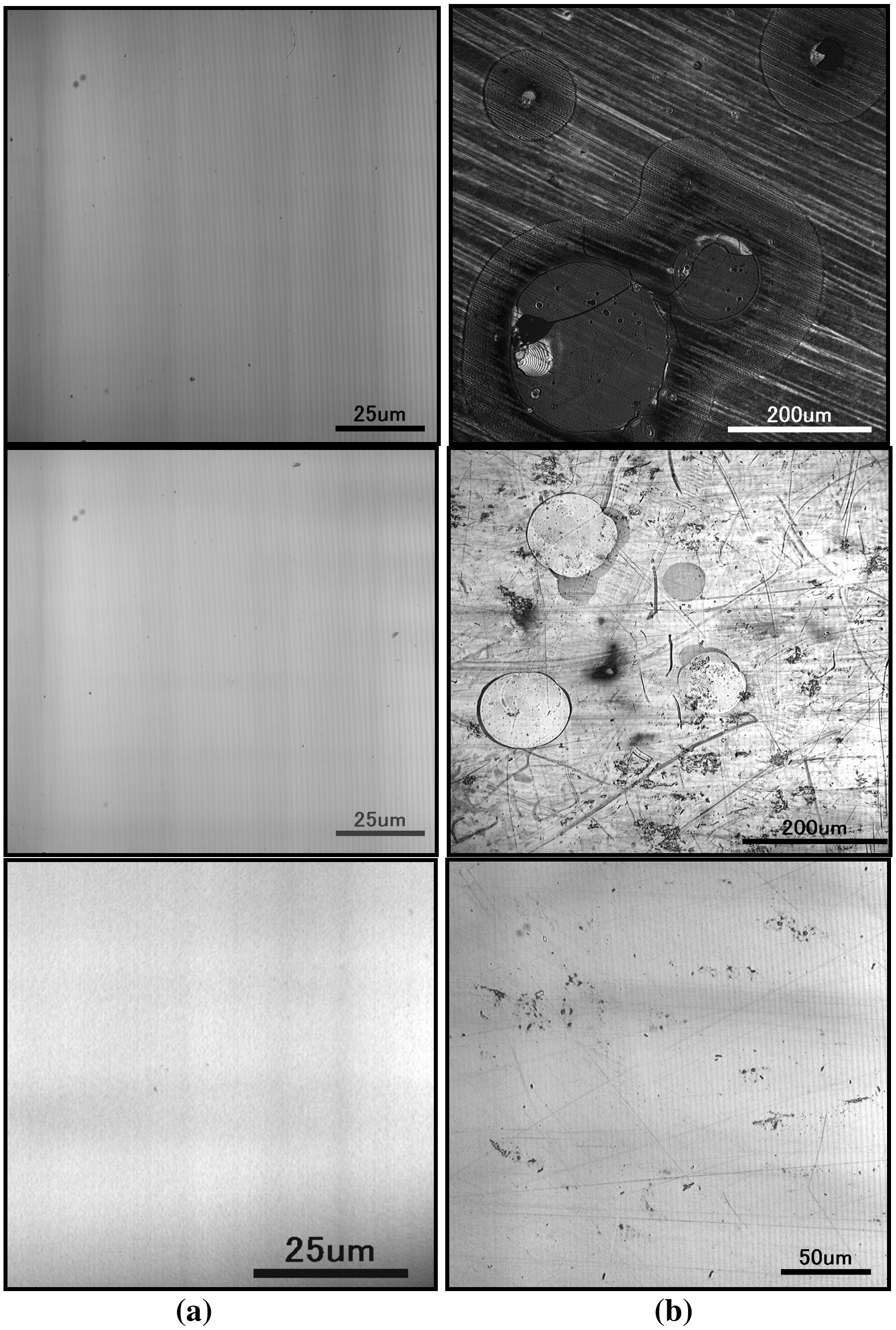

Figure 3: The confocal scanning laser microscopic images of the sputter-deposited W-Ti alloys (a) as-prepared sputter-deposited and (b) after immersion for 24 hours in 1 M NaOH solution at 25 °C, open to air.

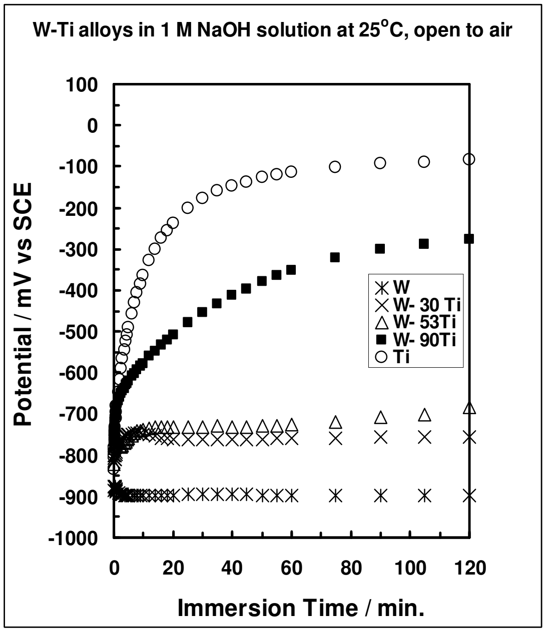

Figure 4: Changes in open circuit potentials of the sputter-deposited W-Ti alloys including tungsten and titanium metals in 1 M NaOH solution at 25 °C, open to air as a function of immersion time.

chemical measurements and confocal scanning laser microscopic techniques. The following conclusions are drawn:

1. The corrosion-resistant of the W-Ti alloys containing 53 at% or more titanium are nearly two orders of magnitude higher than that of the sputter-deposited tungsten and cannot exceed than that of titanium metal.

2. The pitting corrosion is observed on the surface of W-Ti alloys containing 30-53 at% titanium in 1 M NaOH solution from CSLM studies.

3. The open circuit potentials of the alloys are located between those of the alloy-constituting elements (that is, tungsten and titanium) and are shifted to more noble direction with titanium content in 1 M NaOH solution.

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References

1. K. Hashimoto, in *Rapidly Solidified Alloys; Processes, Structures, Properties and Applications* (ed. H. H. Liebermann), Marcel Dekker Inc., NewYork, 1993, p.591.
2. K. E. Heusler and D. Huerta, in *Proc. Sym. Corrosion, Electrochemistry and Catalysis of Metallic Glasses* (eds. R. B. Diegle and K. Hashimoto). The Electrochem. Soc., Pennington, USA, 1988, p.1.
3. K. Asami, S. C. Chen, H. Habazaki, A. Kawashima and K. Hashimoto, *Corros. Sci.,* 1990, **31,** 727.
4. K. Asami, S. C. Chen, H. Habazaki and K. Hashimoto, *Corros. Sci.,* 1990*,* **35,** 43-49.
5. J. H. Kim, E. Akiyama, H. Yoshioka, H. Habazaki, A. Kawashima, K. Asami and K. Hashimoto, *Corros. Sci.,* 1993, **34,** 975.
6. E. Akiyama, H. Habazaki, A. Kawashima, K. Asami and K. Hashimoto, *Mater. Sci. Eng.*, 1994, **A 181 / A 182**, 1128-1132.
7. H. Habazaki, K. Takahiro, S. Yamaguchi, K. Shimizu, P. Skeldon, E. G. Thompson and C. G. Wood, *Philos. Mag .A,* 1998, **78**, 171-187.
8. Y. Z. Liu, X. T. Zu, C. Li, S. Y. Qiu, X. Q. Huang and L. M. Wang, *Corros. Sci*., 2007, **49**, 1069-1080.
9. J. H. Kim, H. Yoshioka, H. Habazaki, A. Kawashima, K. Asami and K. Hashimoto, *Corros. Sci.,* 1992*,* **33,** 1507.
10. J. H. Kim, E. Akiyama, H. Habazaki, A. Kawashima, K. Asami and K. Hashimoto, *Corros. Sci.,* 1993, **34,** 1817.
11. J. H. Kim, H. Yoshioka, H. Habazaki, A. Kawashima, K. Asami and K. Hashimoto, *Corros. Sci.,* 1993, **34,** 1947.
12. J. H. Kim, E. Akiyama, H. Habazaki, A. Kawashima, K. Asami and K. Hashimoto, *Corros. Sci.,* 1994, **36,** 511.
13. P. Y. Park, E. Akiyama, H. Habazaki, A. Kawashima, K. Asami and K. Hashimoto, *Corros. Sci.,* 1994, **36,** 1395.
14. P. Y. Park, E. Akiyama, H. Habazaki, A. Kawashima, K. Asami and K. Hashimoto, *Corros. Sci.,* 1995, **37,** 307.
15. P. Y. Park, E. Akiyama, A. Kawashima K. Asami and K. Hashimoto, *Corros. Sci.,* 1995, **37,** 1843.
16. P. Y. Park, E. Akiyama, A. Kawashima, K. Asami and K. Hashimoto, *Corros. Sci.,* 1995, **38,** 397.
17. P. Y. Park, E. Akiyama, H. Habazaki, A. Kawashima, K. Asami and K. Hashimoto, *Corros. Sci.,* 1996, **38,** 1731.
18. J. Bhattarai, E. Akiyama, A. Kawashima, K. Asami and K. Hashimoto, *Corros. Sci.,* 1995, **37,** 2071.
19. J. Bhattarai, E. Akiyama, H. Habazaki, A. Kawashima, K. Asami and K. Hashimoto, *Corros, Sci.,* 1997, **39,** 355.
20. J. Bhattarai, E. Akiyama, H. Habazaki, A. Kawashima, K. Asami and K. Hashimoto, *Corros. Sci.,* 1998, **40,** 19.

21. J. Bhattarai, E. Akiyama, H. Habazaki, A. Kawashima, K. Asami and K. Hashimoto, *Corros. Sci.*, 1998, **40**, 155.

22. J. Bhattarai, E. Akiyama, H. Habazaki, A. Kawashima, K. Asami and K. Hashimoto, *Corros. Sci.,* 1998, **40,** 757.
23. J. Bhattarai, E. Akiyama, H. Habazaki, A. Kawashima, K. Asami and K. Hashimoto, *Corros. Sci.,* 1998, **40,** 1897.
24. K. Hashimoto, J. Bhattarai, X. Y. Li, P. Y. Park, J. H. Kim, E. Akiyama, H. Habazaki, A. Kawashima, K. Asami and K. Shimamura, in *Proc. of the Special Symposium on Passivity and its Breakdown* (eds. P. M. Natishan, H. S. Isaacs, M. Janik-Czachor, V. A. Macagno, P. Marcus and M. Seo). The Electrochemical Society Inc., 10 South Main St., Pennington, NJ, USA, 1998, p.369-383.
25. J. Bhattarai, and K. Hashimoto, *Tribhuvan University J.,* 1998, **21-2,** 1.
26. J. Bhattarai, *J. Nepal Chem. Soc.,* 2000, **19,** 1.
27. J. Bhattarai, *J. Nepal Chem. Soc.,* 2000, **19,** 32.
28. H. Jha and J. Bhattarai, *J. Alloys and Compounds,* 2007 (in press).
29. A. A. El-Moneim, B. P. Zhang, E. Akiyama, H. Habazaki, A. Kawashima, K. Asami and K. Hashimoto, *Corros. Sci.,* 1997, **39,** 305.
30. J. Bhattarai, *J. Nepal Chem. Soc.*, 2001, **20,** 24.
31. J. Bhattarai, S. P. Sah and H. Jha, *J. Inst. Sci. Technol.*, 2007 (in press).
32. J. Bhattarai, S. P. Sah and H. Jha, in *Proc. Intl. Conf. on Emerging Issues on Research and Development*, 2007, Kathmandu, Nepal, 2007, **TS VI-6**, pp.1-10.
33. J. Bhattarai, *J. Nepal Chem. Soc.,* 2006, **21**, 19.
34. J. Bhattarai, *Nepal J. Sci. Technol.*, 2001, **4**, 37-43.
35. J. Bhattarai, A. Kawashima, K. Asami and K. Hashimoto, in *Proc. 3rd National Conf. Sci. Technol.* Nepal Academy of Sciences and Technology, Kathmandu, Neapl. 2000, **vol.1**, p.389.
36. M. Pourbaix, in *Atlas of Electrochemical Equilibrium in Aqueous Solution*, National Association of Corrosion Engineers, Huston, TX, 1974, pp. 213-280.
37. J. Bhattarai, *Tailoring of Corrosion-Resistant Tungsten Alloys by Sputtering,* Doctoral Thesis, Department of Materials Science, Faculty of Engineering, Tohoku University, Sendai, Japan, 1998, pp. 229.