Effect of Surface Modification by Ion Implantation on Hydrogenation Property of TiFe Alloy

Takanori Suda¹, Masaki Ohkawa^{1, *1}, Shougo Sawada^{1, *2}, Seiichi Watanabe¹, Somei Ohnuki¹ and Shinji Nagata²

¹Department of Materials Science, Faculty of Engineering, Hokkaido University, Sapporo 060-8628, Japan ²Institutes for Materials Research, Tohoku University, Sendai 980-8577, Japan

In order to improve initial activation properties of TiFe alloy, simple ion implantation and ion mixing with the deposition of $LaNi_5$ were carried out at room temperature. The results show that argon-ion mixing caused extensive improvement of initial activation, wherein hydrogenation was easily effected at 373 K and 1 MPa. Those results are related to several irradiation effects; the re-crystallization of amorphous film of LaNi₅ and the local segregation of composed elements. Both of these irradiation effects greatly improve the initial hydrogenation process of TiFe alloy.

(Received May 20, 2002; Accepted October 10, 2002)

Keywords: hydrogen storage alloy, ion implantation, ion mixing, surface modification, TiFe alloy, activation

1. Introduction

TiFe,^{1,2)} an AB-type alloy, has excellent hydrogen-storage properties; high hydrogen capacity (1.8 mass%), low dissociation pressure (0.5 MPa at room temperature), and low cost. An important material issue in relation to this alloy is improving initial activation properties. The reason for difficulty in initial activation is that a thick oxidation film forms on the surface of TiFe. According to Reilly *et al.*, the temperature range for activation of particulate TiFe alloy is 673–723 K, and minimum hydrogen pressure is 7 MPa.

Several investigations have been carried out in an effort to improve the initial activation properties of TiFe. One method for improving such properties is addition of certain elements to TiFe alloy, such that a second phase precipitates on the alloy surface. Presumably, the second phase acts as the starting point of hydrogenation, thereby promoting initial activation. Therefore, in various studies elements have been added for reducing initial hydrogenation temperature; $oxygen^{3-6}$ (precipitation of Fe₇Ti₁₀O₃), carbon⁷) (precipitation of TiC), Mm^{8,9}) (Mm(misch metal) oxidation), and excess Ti¹⁰) (precipitation of β -Ti).

Other methods for improving activation properties include ion implantation and ion mixing, even if these can modify only the subsurface region; *i.e.*, the region within less than 1 μ m from the surface. Ion implantation is expected to remove surface films by sputtering, to produce lattice defects by ion irradiation, and to introduce excess solute atoms with non-equilibrium concentration; therefore, this method has the potential for enhancing surface activation of alloys. In this paper, we show that ion- implantation and ion mixing are useful for improving initial activation properties of TiFe alloys.

2. Experiments

A button-shaped sample of TiFe alloy was prepared by an argon arc-melting. After homogenization for 24 h at 1423 K under an argon atmosphere, the sample was cut into sheets and subjected to mechanical polishing. A Siverts'-type apparatus was used for surveying hydrogenation properties. The chamber was evacuated by a rotary pump, after which hydrogen gas was introduced at a pressure of 0.1 MPa, and this process was repeated three times. In order to determine activation temperature and gas pressure of the hydrogenation, a stepped process was carried out; *i.e.*, if after 30 minutes activation was not detected under some temperature and pressure, the temperature and pressure were increased for the next step. This process was repeated in order to confirm the reduction in hydrogen pressure up to 373–673 K and 1–10 MPa.

- (1) Ion implantation: Argon or hydrogen ions were implanted, in view that the former is a heavy element which may produce much energy transfer, and the latter is a light element which may produce less energy transfer, but enhance hydride formation to a much greater depth. Samples were implanted at room temperature with 100 keV ions to a concentration of 5×10^{15} – 3.6×10^{17} cm⁻². In order to analyze the distribution of defects and solutes, Rutherford Backscattering Spectroscopy (RBS)¹¹ was carried out by use of 2.8 MeV helium ions, which integrated the dose of $5 \,\mu$ C. In addition, in order to estimate the distribution of damage and implanted atoms, Transport of Ions in Matter (TRIM)¹² calculation was carried out.
- (2) Ion mixing: Prior to ion mixing, LaNi₅ was deposited on the sample surface to a thickness of 5 nm, because bulk LaNi₅ shows excellent properties for initial hydrogenation. The ion mixing was carried out by use of 100 keV hydrogen ions or argon ions to 5×10^{13} – 5.0×10^{16} cm⁻² at room temperature. Changes in microstructure were observed by 200 kV Transmission Electron Microscopy (TEM).

^{*1} Graduate Student, Hokkaido University.

^{*&}lt;sup>2</sup>Graduate Student, Formerly with the Hokkaido University.

3. Results and Discussion

Figure 1 compares argon-ion mixing and hydrogen-ion mixing in terms of the effect of improving initial hydrogenation. Figure 1(a) shows minimum hydrogen pressure for initiating activation as a function of hydrogen ion dose. Black dots and the shaded area show the minimum range for starting hydrogen absorption after ion mixing with LaNi₅ deposition. The triangular mark represents data for hydrogen-ion implantation without deposition. As compared with the case of the ion-mixing specimen after deposition, activation of the specimen without deposition required higher temperature and pressure (673 K and 7 MPa). In this case, activation did not occur below 673 K, even when pressure was raised to 10 MPa. In contrast, in the case of the specimen that was ion-mixed to $5 \times 10^{14} \,\mathrm{cm}^{-2}$ with deposition, activation occurred when hydrogen pressure was as low as 3 MPa, even when the reaction temperature was 473 K.

Figure 1(b) shows minimum hydrogen pressure as a function of argon ion dose. In the case of argon-ion implantation without deposition, the minimum hydrogen pressure was 5 MPa at 673 K, and activation did not occur below 673 K, even when pressure was raised to 10 MPa. After ion mixing to 1×10^{15} cm⁻² with deposition, the minimum hydrogen pressure was greatly improved to 1 MPa, while the reaction temperature was reduced to 373 K.

According to results of ion implantation, both hydrogenand argon-ion implantation lowered the hydrogen pressure slightly, and argon-ion implantation had a stronger effect on hydrogenation than did hydrogen-ion implantation, but the effect of argon-ion implantation was not sufficient to account for the improvement. The results suggest that argon ions can greatly enhance the effects of removing surface film and producing lattice defects, which enhance hydrogen diffusion from the surface to bulk. In the case of ion mixing after deposition, activation was improved considerably, especially in argon-ion mixing, which shows that the deposited LaNi₅ film has an extensive effect on the activation properties that can be enhanced by ion mixing.

Figure 2 shows a sequence of the microstructure changing after 100 keV argon-ion mixing at room temperature. Figure 2(a) shows microstructure and diffraction from untreated TiFe (un-deposited and un-implanted), which has a crystalline structure without obvious defects. Figure 2(b), which shows an as-deposited specimen, includes diffraction spots and a halo-ring, which indicate that deposited LaNi₅ film has a amorphous structure. Figures 2(c) and (d) are from specimens after ion mixing at room temperature. In the case of high dose, shown in Fig. 2(d), the halo-ring disappears and a Debye-ring develops. This suggests that the amorphous structure is re-crystallized during the course of ion mixing, where black dots are presumed to be micro-crystals. The re-



Fig. 1 Improvements in initial hydrogenation pressure in TiFe alloy by LaNi₅ deposition and ion mixing; (a) hydrogen ion mixing at 473 K, (b) argon ion mixing at 373 K.



Fig. 2 Changes in microstructure and diffraction of TiFe alloy on which LaNi₅ is deposited, followed by argon ion implantation; (a) no implantation, (b) 5×10^{14} , (c) 1×10^{15} , (d) 5×10^{15} Ar⁺/cm².



Fig. 3 RBS spectrum of TiFe alloy before and after ion implantation (2.8 MeV He⁺).

sults of hydrogenation and this microstructural change suggest that the micro crystals act as starting points of hydrogenation.

In order to estimate the distribution of damage and implanted atoms, TRIM calculation was carried out. In the case of argon, lattice damage and argon atoms should locate at the depth of about 50 nm, where the local concentration of argon is estimated to be 8 at%. In the case of hydrogen, the positions are much deeper, 500–600 nm, where the local concentration of hydrogen is estimated to be less than 2 at%. From the calculations, we can deduce that hydrides may not be formed just after hydrogen-ion implantation and ion mixing, whereby large amount of lattice defects and atomic mixing may have a very important effect on the improvement of activation properties due to ion mixing.

Figure 3 shows RBS spectrum from random direction after ion implantation. The flatness of the profile shows the uniformity of the element distribution in the depth direction. In the case of hydrogen-ion implantation up to 5×10^{16} cm⁻², no obvious difference is observed. In the case of argon-ion implantation, especially at the dose of 5×10^{16} cm⁻², the backscattered yield increased at 350–400 channel, and the yield of titanium and iron greatly decreased in the vicinity of the surface. Those results indicate that the implantation resulted in the segregation of composed atoms at sub-surface as well as the increase in implanted atoms. The microstructural change is also an important factor for improving hydrogen properties. Such local compositional change and microstructural change influenced hydrogen dissolution on the surface and the diffusion in the sub-surface area.

4. Conclusion

For the improvement of initial activation properties in TiFe alloy, simple ion implantation and ion mixing with LaNi₅ deposition was carried out at room temperature. The results show that argon-ion mixing achieved more extensive improvement of initial activation than did hydrogen-ion mixing and other simple ion implantation. Hydrogenation took place easily at 373 K and 1 MPa. Those results are related to several irradiation effects; the re-crystallization of amorphous film of LaNi₅, the local segregation of composed elements, and change in microstructure. All of those factors affected the hydrogen dissolution on the surface and the diffusion in sub-surface area.

Acknowledgments

This work has been partially supported by a Grant-in-Aid for Scientific Research on Priority Area A of "New Protium Function" from the Ministry of Education, Science, Sports and Culture.

REFERENCES

- 1) J. J. Reilly and R. H. Wiswall, Jr.: Inorg. Chem. 13 (1974) 218–222.
- M. Amano, Y. Sasaki and T. Matsumoto: J. Japan Inst. Metals 43 (1979) 809–814.
- M. Amano, Y. Sasaki and T. Yoshioka: J. Japan Inst. Metals 45 (1981) 957–964.
- M. Amano, Y. Sasaki, R. Watanabe and M. Shibata: J. Less-Common Met. 89 (1983) 513–518.
- M. Amano, M. Shibata and Y. Sasaki: J. Japan Inst. Metals 51 (1987) 871–878.
- 6) T. Schober: J. Less-Common Metals 89 (1983) 63-70.
- D. Khatamian, N. S. Kazama and F. D. Manchester: J. Less-Common Met. 91 (1983) 267–273.
- V. Bronca, P. Bergman, V. Ghaemmaghami, D. Khataminan and F. D. Manchester: J. Less-Common Met. 108 (1985) 313–325.
- B. K. Singh, A. K. Singh and O. N. Srivastava: Int. J. Hydrogen Energy. 21 (1996) 111–117.
- 10) M. Amano, T. Hirata, T. Kimura and Y. Sasaki: Trans., JIM 25 (1984) 657–661.
- L. C. Feldman and J. W. Mayer: Fundamentals of Surface and thin film analysis, (Nort-holland, Amsterdam, 1986).
- 12) J. F. Zieglar, J. P. Biersack and U. Littmark: *The stopping and range of ions in solids*, (Pergamon press Inc., New York, 1985).