In-situ Measurement of Lattice Spacing of Ternary Ni-Ti-Nb Alloys during Hydrogen Absorption

Jun-ichi Shibano[1,a], Yasutaka Yamamoto[1], Michiaki Kobayashi[1,b], Kazuhiro Ishikawa[2,c] and Kiyoshi Aoki[2,d]

[1] Dept. of Mechanical Engineering, Kitami Institute of Technology, Kitami 090-8507, Japan

[2] Dep. of Materials Science, Kitami Institute of Technology, Kitami 090-8507, Japan

[a] jshibano@mail.kitami-it.ac.jp, [b] kobayasi@mail.kitami-it.ac.jp,

[c] ishikawa@ mail.kitami-it.ac.jp, [d] aoki@ mail.kitami-it.ac.jp

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Abstract. Microscopic deformation of each crystal of duplex phases of Ni-Ti-Nb alloy due to hydrogen absorption was investigated by X-ray diffraction technique. $Ni_{30}Ti_{30}Nb_{40}$ which is hydrogen permeation alloy and consists of the primary phase, NbTi, and the eutectic phases, NiTi + NbTi, was used as a specimen. The change of lattice spacing of the specimen during hydrogen absorption was measured by Cu-Kα characteristic X-ray. As a result, the lattice spacing of crystal of NbTi phase increased extremely, while that of NiTi phase increased slightly. It was pointed out that the NbTi phase is responsible for hydrogen absorption in the Ni-Ti-Nb alloy. When hydrogen gas was released from the specimen at high temperature, both lattice spacing returned nearly to those of them before hydrogen absorption, and the specimen kept its original shape. Therefore, it was confirmed that the volume expansion of crystal of the Ni-Ti-Nb alloy due to hydrogen absorption was elastic deformation.

Introduction

In recent years, non-palladium based hydrogen permeation alloys, which consist of duplex phases, NiTi and NbTi, in the Ni-Ti-Nb system, for hydrogen purification have been developed by K. Hashi et al. [1]. Those alloys resist superiorly the hydrogen brittleness, however its mechanism has not become clear yet. Therefore, if the mechanism becomes apparent, it is expected to develop more advanced alloys for hydrogen permeation. In this study, an in-situ measurement of crystal deformation of ternary Ni-Ti-Nb alloy due to hydrogen absorption is carried out by using X-ray diffraction technique. Disk of $Ni_{30}Ti_{30}Nb_{40}$ alloy, which consists of the primary phase, NbTi, and the eutectic phases, NiTi + NbTi, is used as a specimen. At first, the specimen in a vacuum furnace is heated from room temperature to 673K. After the hydrogen gas of 0.5MPa is introduced into the furnace, the change of lattice spacing of the specimen during hydrogen absorption is measured by Cu-Kα radiation.

Experiment Procedure

Ingot of $Ni_{30}Ti_{30}Nb_{40}$ alloy was made using an arc melting furnace with an argon atmosphere. Disk of 12mm in diameter and 0.7mm in thickness was cut out from the ingot by using electric discharge machine. Oxide layer of the disk surface was polished with an emery paper, a buff and α-alumina powder of 0.5μm particle diameter. After the disk was cleaned by ultrasonic washer, it was coated with palladium of 190nm in thickness using a magnetron sputtering machine. A scanning electron microscope (SEM) image of the as-cast $Ni_{30}Ti_{30}Nb_{40}$ alloy is shown in Fig.1. It is obvious that the alloy consists of the primary phase, NbTi, and the eutectic phases, NiTi + NbTi, which have a lamellar

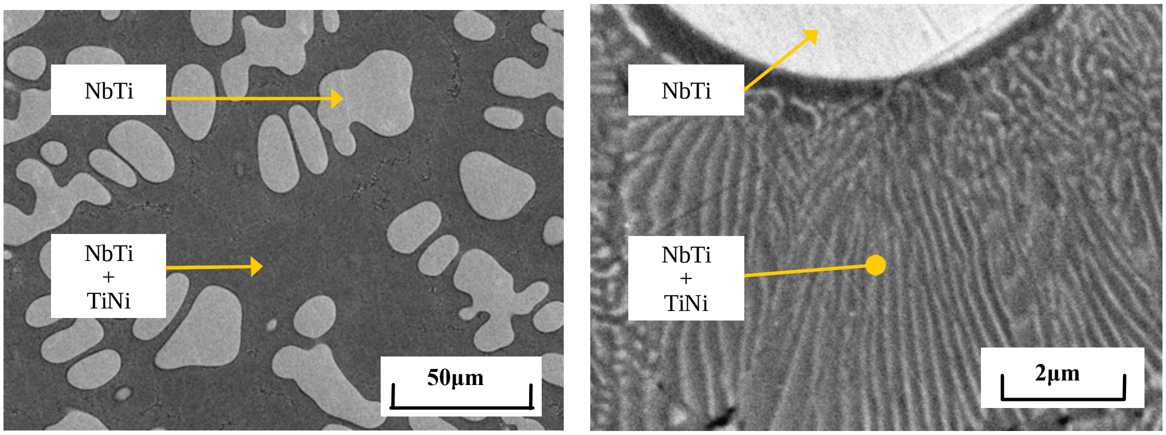

Fig. 1 SEM images of the as-cast $Ni_{30}Ti_{30}Nb_{40}$ alloy which consists of the primary phase, NbTi, and eutectic phase, TiNi + NbTi.

structure.

The in-situ measurement of a lattice spacing of crystal of $Ni_{30}Ti_{30}Nb_{40}$ alloy in an atmosphere of hydrogen at a high temperature is carried out by using X-ray diffraction method. The lattice spacing of crystal can be obtained by Bragg low as shown in Eq.1.

$$\lambda = 2d \sin\theta, \tag{1}$$

where λ is an wavelength of X-ray, d is a lattice spacing and θ is Bragg angle.
The strain ε of crystal is calculated by Eq.2.

$$\varepsilon = \frac{d - d_0}{d_0} = \frac{\sin\theta_0 - \sin\theta}{\sin\theta}, \tag{2}$$

where d_0 and θ_0 are the lattice spacing and the Bragg angle for non-strained specimen, respectively. Cu-kα characteristic X-ray (wave length λ = 0.15405nm) was used for the measurement. The vacuum heating furnace with a thin beryllium window, which allows X-ray to path through easily, was used to provide the in-situ measurement in the atmosphere of hydrogen at the high temperature. X-ray diffraction profile of $Ni_{30}Ti_{30}Nb_{40}$ alloy in a normal-atmosphere environment at room temperature is shown in Fig.2. There are many diffraction peaks from duplex phases of the alloy and coating film of palladium.

At first, a deformation behavior of crystal in the alloy with a temperature under the presence or absence of hydrogen gas is investigated. The lattice spacing of both NbTi(310) and TiNi(211) are measured at the temperature decreasing from 673K to room temperature in steps of 100K in a vacuum. In addition, the deformation behavior of crystal in the alloy before and after the absorption of hydrogen gas is examined. Because the X-ray diffraction intensity of TiNi(211) decreased extremely in the atmosphere of hydrogen at the high temperature, TiNi(110) is used for the in-situ measurement. The lattice spacing of both NbTi(310) and TiNi(110) are measured at the temperature of 673K under the partial pressure of hydrogen gas of 0.5MPa, following they are measured at holding temperature of 673K under the partial pressure of hydrogen gas of 0MPa in the vacuum.

Results and Discussion

Figures 3 and 4 show the change of the lattice spacing of both NbTi(310) and TiNi(211), respectively, when the temperature decreased from 673K to 373K in the vacuum. By converting a variation in lattice spacing to a strain using Eq.2, the strain of NbTi(310) was -1800×10^{-6} and that of TiNi(211) was

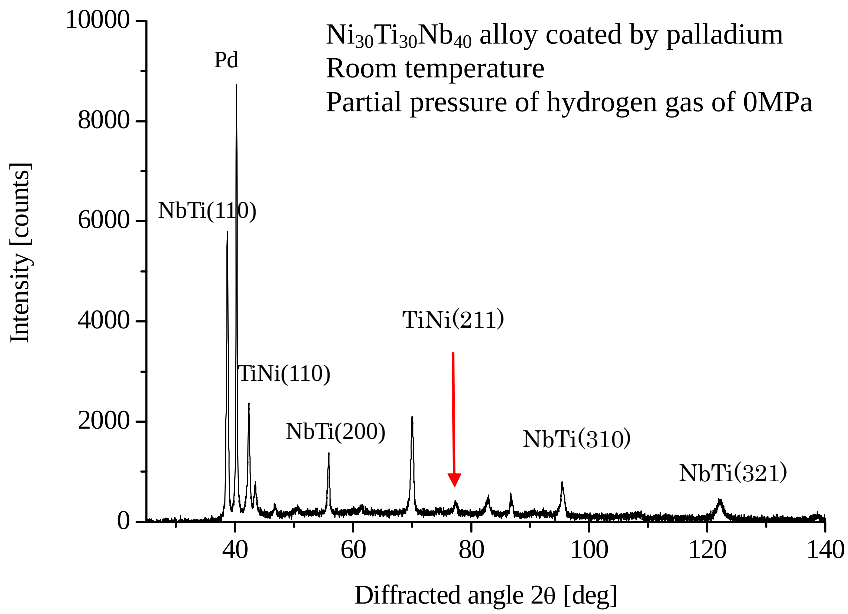

Fig. 2 Diffraction X-ray profile of the as-cast $Ni_{30}Ti_{30}Nb_{40}$ alloy.

-2600×10^{-6}. Figures 5 and 6 show the change of the lattice spacing of both NbTi(310) and TiNi(110) due to hydrogen absorption, respectively. The strain of NbTi(310) was 6100×10^{-6}, while that of TiNi(110) was 22700×10^{-6}. From Figs. 5 and 6, it was confirmed that very large strain was produced in TiNi(110) due to decrease the temperature with holding the hydrogen absorption. After the experiment, there were many microcracks in the specimen, and it became significantly brittle. It supposes that the hydrogen embrittlement occurs in the $Ni_{30}Ti_{30}Nb_{40}$ alloy.

The change of the lattice spacing of both NbTi(310) and TiNi(110) before and after the hydrogen absorption is shown in Figs.7 and 8, respectively. When the alloy was under the partial pressure of hydrogen gas of 0.5MPa at the temperature of 673K, the strain of NbTi(310) was 36600×10^{-6} and that of TiNi(110) was 2400×10^{-6}. It is therefore supposed that the hydrogen atom was absorbed in mainly NbTi phase. The strain of NbTi(310) equates to the stress with the magnitude of several gigapascals. After the hydrogen gas released from the alloy, the strains of both NbTi(310) and TiNi(110) at the room temperature in the vacuum were -1900×10^{-6} and -1100×10^{-6}, respectively. The lattice spacing of them returned to the almost same condition before hydrogen absorption. It indicates that both of NbTi phase and TiNi phase deformed keeping in the elasticity during hydrogen absorption and release. The mechanism to accept such large elastic deformation in the $Ni_{30}Ti_{30}Nb_{40}$ alloy is not clear yet, and it is a significant challenge of our next study. After the experiment, there were many microcracks in the surface of specimen, but it didn't become brittle. In this case, the hydrogen embrittlement didn't occur in the $Ni_{30}Ti_{30}Nb_{40}$ alloy.

Conclusion

The in-situ measurement of crystal deformation of $Ni_{30}Ti_{30}Nb_{40}$ alloy due to hydrogen absorption was carried out by using X-ray diffraction technique. The results are as follows.

(1) The strain of the primary phase NbTi(310) of the alloy was 36600×10^{-6} under the partial pressure of hydrogen gas of 0.5MPa at the temperature of 673K, and the stress calculated from the strain equates with the magnitude of several gigapascals.

(2) The volume expansion of each crystal of $Ni_{30}Ti_{30}Nb_{40}$ alloy during hydrogen absorption is elastic deformation.

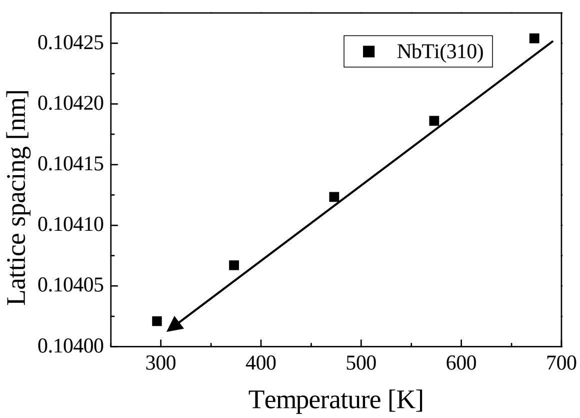

Fig. 3 Change of lattice spacing of NbTi(310) plane with temperature.

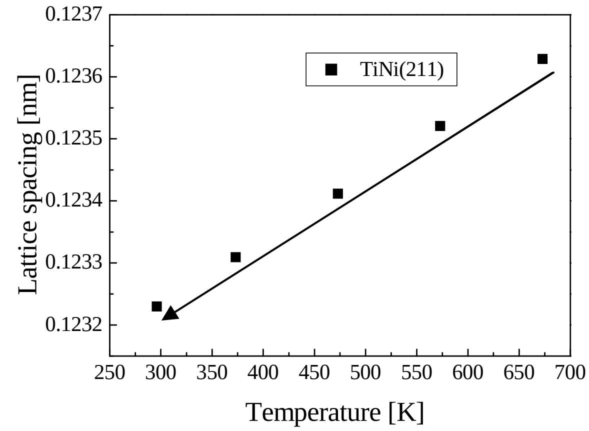

Fig. 4 Change of lattice spacing of TiNi(211) plane with temperature.

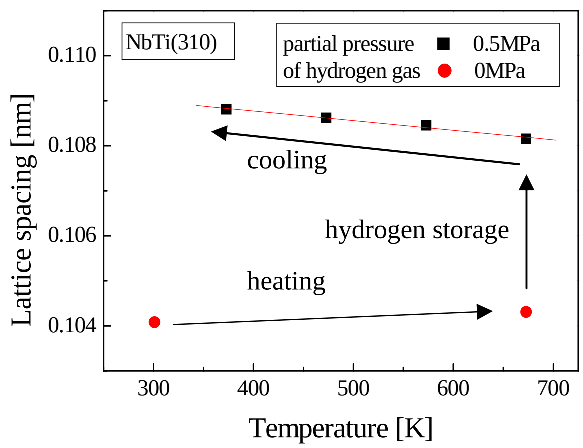

Fig. 5 Change of lattice spacing of NbTi(310) plane with temperature.

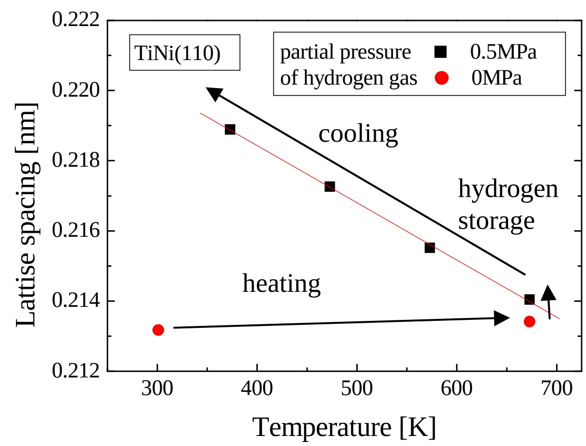

Fig. 6 Change of lattice spacing of TiNi(110) plane with temperature.

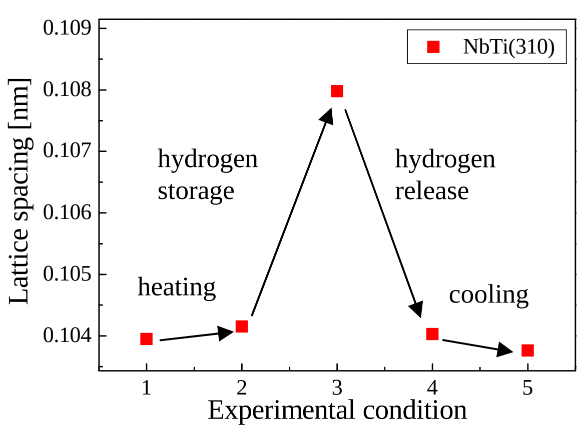

Fig. 7 Change of lattice spacing of NbTi(310) plane due to hydrogen absorption.

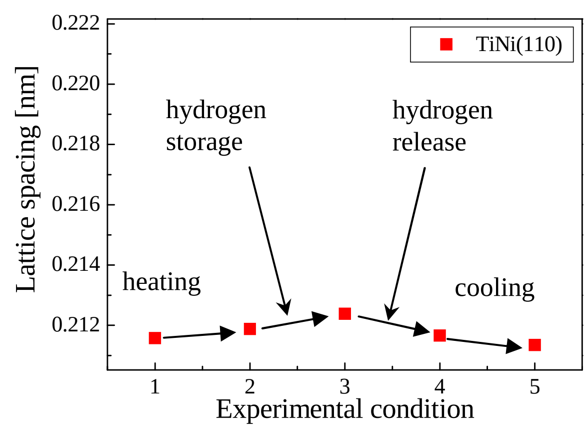

Fig. 8 Change of lattice spacing of TiNi(110) plane due to hydrogen absorption.

Reference

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