論　文

水素の吸蔵・放出サイクルに対する
ZrCo 及び ZrNi の耐久性

原　　正憲[*]・金坂　　績[*]・渡辺　国昭[**]・兜森　俊樹[***]

[*]富山大学理学部
[**]富山大学水素同位体機能研究センター
〒930 富山市五福3190
[****]日本製鋼所㈱室蘭研究所
〒051 室蘭市茶津町4

Durability of ZrCo and ZrNi against Absorption-Desorption Cycles in Hydrogen

Masanori HARA[*], Isao KANESAKA[*],
Kuniaki WATANABE[**], Toshiki KABUTOMORI[***]

[*]Faculty of Science, Toyama University
[**]Hydrogen Isotope Research Center, Toyama University
Gofuku 3190, Toyama 930, Japan
[***]The Japan Steel Works, Ltd.
4 Chatsu-cho, Muroran-shi, Hokaido 051, Japan.
(Received September 7, 1994; accepted November 28, 1994)

Abstract

Zirconium-alloys such as ZrNi and ZrCo have been developed so far as promising materials for storage, supply and recovery of tritium. They, however, easily lose their ability of reversible absorption-desorption of tritium in the presence of impurity gases such as O_2, H_2O, CO_2, CO and others. Although we have developed a method to lower this contamination effect, there is another possibility for the degradation of their properties by repeated heat cycles in an hydrogen atmosphere.

To examine this possibility, we studied the changes in the characteristics of those alloys for hydrogen absorption and desorption owing to the heat cycles in the presence of hydrogen in a system. The samples were used as grains. They were first exposed to a hydrogen gas to prepare respective hydrides of a form of $ZrMH_3$, where M is Ni or Co. Subsequently, the changes in the absorption-desorption characteristics were measured in a closed system during heat cycles between room temperature and 600°C.

No significant change in the equilibrium pressure of hydrogen was observed up to

50 heat cycles for ZrNi. X-ray diffraction analysis revealed that the sample kept ZrNi structure before and after the heat cycles. The hydride formed was always $ZrNiH_3$. Contrarily, ZrCo showed drastic changes in the absorption-desorption characteristics in 50 heat cycles. X-ray diffraction analysis showed that the $ZrCoH_3$ initially formed was decomposed to $ZrH_x + ZrCo_2$. Namely, the disproportionation of ZrCo took place. It is noteworthy that the disproportionation reaction did not occur in the absence of hydrogen isotopes in the system. On account of these observations, it was concluded that the degradation of absorption-desorption characteristics of ZrCo is due to the ease in disproportionation. ZrNi is much more durable to disproportionarion, and hence its ability is kept for a large number of heat cycles, namely storage, supply and recovery operations.

1. Introduction

Zirconium alloys such as ZrCo and ZrNi are attractive for tritium handling as storage, supply and recovery in thermonuclear fusion devices[1,2]. This is because of the ease in activation, sufficiently low equilibrium pressure of tritium at room temperature and moderate temperatures to release tritium gas at one atmospheric pressure. In addition, the rates of tritium absorption and desorption are quite high. On the other hand, They are expected to lose their activities in absorption-desorption by repeated heat cycles[3].

This is an important problem on this kind of materials not only for hydrogen storage and other applications but also for tritium handling in thermonuclear fusion devices. Concerning ZrCo, the degradation of the absorption-desorption characteristics has been observed in a pure hydrogen atmosphere and explained due to the disproportionation of ZrCo during hydrogen absorption[4]. Contrarily, no significant change has been observed in equilibrium pressure as well as rate of tritium absorption and desorption for ZrNi for a long time of usage, indicating that ZrNi is more stable to heat or absorption-desorption cycles. To understand reasons of such difference between the two alloys, the present authors have studied in detail the durability of them against heat cycles through changes in equilibrium pressure, rate of absorption/desorption of hydrogen isotopes, isotope effect and crystallographic structure. The present paper describes the experimental details and principal results.

2. Experimental

2. 1. Apparatus

The experimental apparatus used for absorption-desorption cycles in the present study is schematically shown in Fig. 1. It consisted of a reaction chamber, a hydrogen isotope supplier, vacuum and pressure gauges, and a quadrupole mass spectrometer. The system could be evacuated to below 1×10^{-6} Pa with a sputter ion pump and a turbomolecular pump backed with an oil-sealed rotary pump. The pressure gauges were MKS Baratron of type 122AA-0100BB and 122AA-1000BB. They were used for low and high pressure measurements, respectively. They will be denoted below as Baratron A and B, respectively. The size of the reaction chamber, which was made of a quartz glass tube, was 1.5 cm inner diameter and 34 cm height.

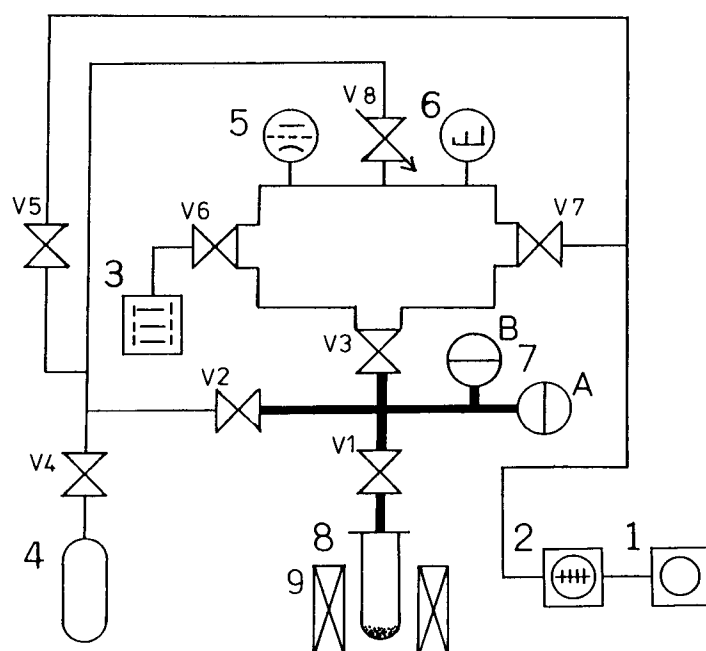Crystallographic changes due to the absorption-desorption cycles were analyzed by

Fig. 1. Schematic diagram of the vacuum equipment used for absorp-
tion desorption cycles.
1: Rotary pump, 2: Turbomolecular pump, 3: Sputter ion
pump, 4: Hydrogen isotope supplier, 5: Ionization vacuum
gauge, 6: Quadrupole mass spectrometer, 7: Diaphragm
gauge (Baratron A, B), 8: Reaction chamber, 9: Electric
furnace, V1-V8: Metal valves

using a X-ray diffractometer of Philips-PW1820 with Cu-Kα.

2. 2. Materials and sample preparation

Blocks of ZrCo and ZrNi of 100 g were prepared by argon arc-melting method. The purities of Zr, Co and Ni were above 99.8, 99.5 and 99.9%, respectively. Hydrogen and deuterium gases were purchased from Nihon Sanso Co. The purities of them were guaranteed as 99.9999 and 99.6%, respectively. They were used without further purification.

The block of ZrNi was crushed and powdered mechanically at room temperature and sifted to a size about 100-mesh. ZrCo was not so brittle as ZrNi and hence it was powdered with hydride formation. A block of ZrCo was cut to plates about 1.0×3.0 cm with 3 mm thickness. Several plates were mechanically polished and washed with acetone, and set at a time in the reaction chamber in Fig. 1. It was evacuated down to 10^{-5} Pa at room temperature and the plates were heated at 600°C for 2 hours in vacuum. Subsequently, hydrogen gas of about 10 mmol was introduced into the reaction chamber after evacuation of the system down to 10^{-5} Pa. The plates gradually absorbed hydrogen at room temperature and the hydrogen pressure decreased to 133 Pa in 10 hours. Subsequently, hydrogen was added into the system up to 10 mmol to cause further absorption. Several repetitions of this procedure gave stoichiometric hydride of the form as $ZrCoH_3$. At this moment, the block had been powdered to sizes around 100-mesh.

2. 3. Procedures

The powdered sample of ZrNi of about 1 g was set in the reaction chamber. After out-gassing of the sample at 600°C for 2 hours in vacuum, nearly stoichiometric hydride of the form as $ZrNiH_3$ (M=Co, Ni) was prepared with hydrogen absorption at room temperature by repeating the hydrogen charge of 10 mmol at a time. Both the as-prepared ZrNi and the hydride powder were examined with X-ray diffraction before the absorption-desorption measurements. As for ZrCo, a given amount of hydride powder was set in the reaction chamber and degassed at 600°C for 2 hours to prepare ZrCo powder. Both the ZrCo and the hydride powders were examined with X-ray diffraction.

The prepared sample of ZrCo or ZrNi of about 0.9 g was set in the reaction chamber to examine the changes in hydrogen absorption-desorption characteristics and of crystallographic structure due to heat cycles. After out-gassing of the sample at 6 0 0 °C

for 16 hours in vacuum, the reaction chamber was separated from the main system by closing the valves of V2 and V3. Then hydrogen gas of 8 mmol was introduced into the reaction chamber through the valve, V2. The amount of introduced hydrogen corresponds to the atomic ratio of $[H]/[Zr] = 3.1$, where $[Zr]$ indicates the number of Zr atoms in 0.9 g of the sample. After closing the valve, V2, the chamber was heated at 600°C for 30 min, during which the equilibrium pressure at 600°C was measured. Subsequently. the chamber was cooled and kept at room temperature for 60 min to measure the equilibrium pressure. The pressures at 600°C and at room temperature were measured with Baratron B and A, respectively. A set of those procedures comprised one heat cycle in the present study.

3. Results and discussion

3. 1. Changes in equilibrium pressures

Figure 2 shows an example of pressure changes with the heat cycles. At the first heat cycle, the hydrogen pressure increased with heating due to decomposition of ZrCo hydride and attained to an equilibrium pressure of 44.7 kPa in 30 min. On cooling, the pressure decreased due to absorption and attained to an equilibrium pressure of 3.84 kPa at room temperature in 60 min. The pressures at 600°C and at room temper-
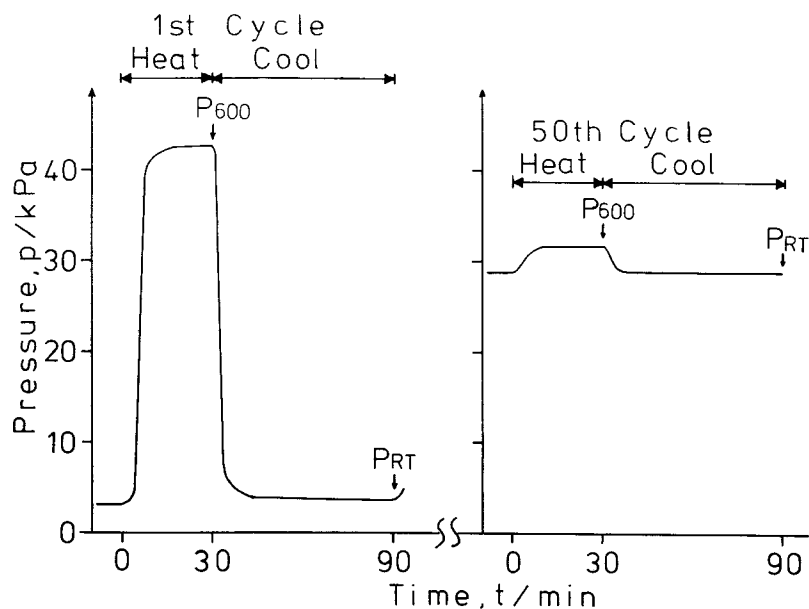

Fig. 2. Pressure changes with a heat cycle for ZrCo at the first and 50th heat cycles.

ature will be denoted as P_{600} and P_{RT}, below. Repeated heated cycles caused gradual decrease in P_{600} and increses in P_{RT}. Eventually, the pressure change with a heat cycle became considerably small as shown in the right of Fig. 2.

Figure 3 summarizes those measurements for ZrCo. At the initial stage of the heat cycles, the pressures, P_{600} and P_{RT}, did not change much with the heat cycle. At the middle stage, P_{600} decreased gradually and P_{RT} increased with increasing number of the heat cycles. At the final stage, the pressure difference between P_{600} and P_{RT} became quite small. Namely, only a small amount of hydrogen could be absorbed or released by the sample at this stage, indicating that the sample undergoes some intrinsic changes due to the heat cycles.

Figure 4 shows an example of the pressure changes due to the heat cycles over the ZrNi sample. The pressure changes due to
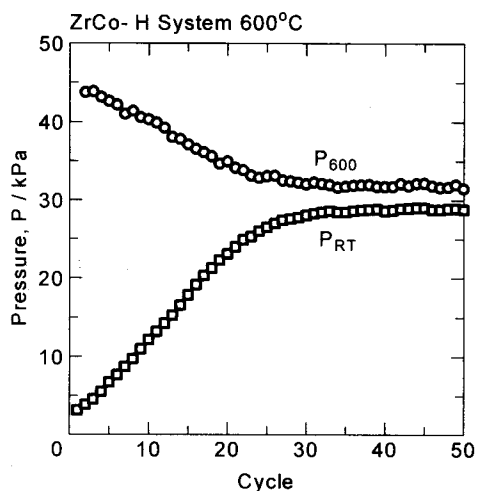
Fig. 3. Changes in P_{600} and P_{RT} with heat cycles for ZrCo-H system.
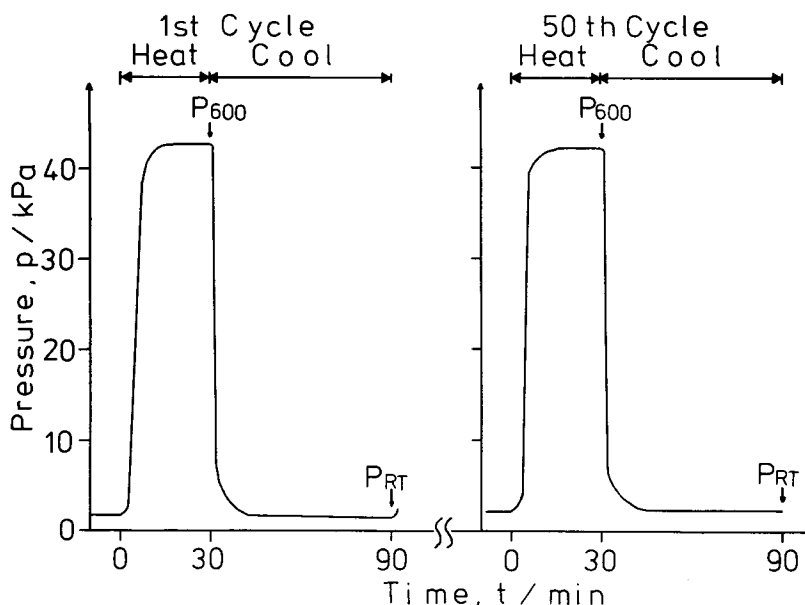
Fig. 4. Pressure changes with a heat cycle for ZrNi at the first and 50 the heat cycles.

heating and cooling were also considerably fast as the ZrCo sample. In this case, however, it was found that characteristic features of the pressure changes at the first heat cycle were almost unchanged with repetition of up to 50 heat cycles as seen in this figure, although there were small changes in the equilibriu pressures at $600°C$ and at room temperature.

Figure 5 is the summary of those measurements. In comparison with ZrCo, it is evident that the ZrNi sample did not show any significant changes in P_{600} and P_{RT}. The small changes mentioned above are not

Fig. 5. Changes in P_{600} and P_{RT} with heat cycles for ZrNi-H system.

apparent in those plots. The results indicate that ZrNi is more stable than ZrCo against repeated operations for hydrogen storage-supply. This is consistent with our experience for tritium handling as storage, supply and recovery with ZrNi alloy.
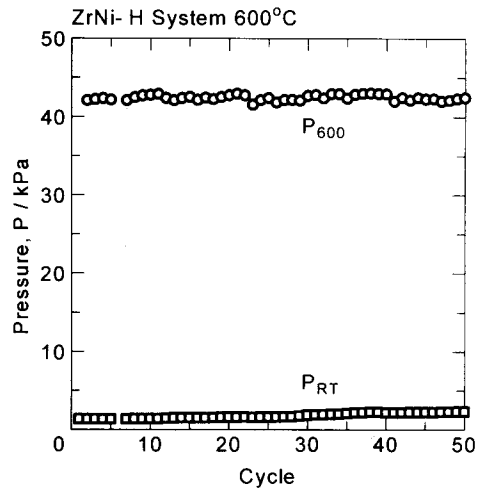
3. 2. Crystallographic analysis

It is plausible that oxidation and/or other kinds of surface contamination during the heat cycles are responsible for the significant changes in P_{600} and P_{RT} for ZrCo and small changes for ZrNi. Another possibility is the disproportionation of the alloys. This has been pointed out for ZrCo by Penzhorn et al[4]. To identify the mechanisms,
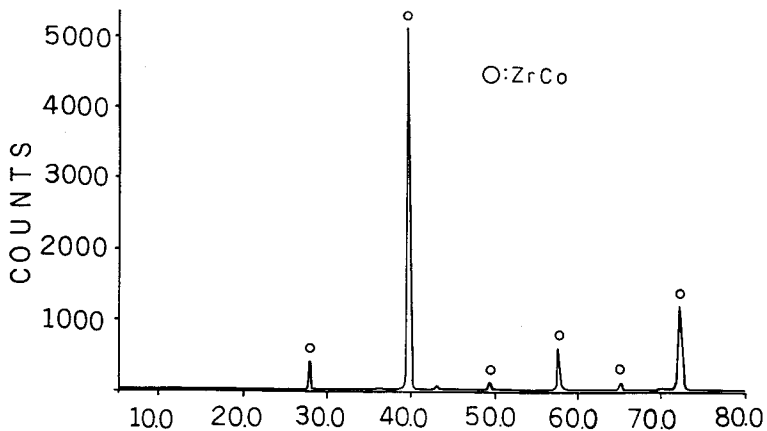

Fig. 6. X-ray diffraction pattern of ZrCo sample.

the samples were analyzed with X-ray diffraction before and after the heat cycles.

Figure 6 shows the X-ray diffraction pattern observed for ZrCo powder. It agreed very well with the diffraction pattern appears in literature[5]. Figure 7 is the pattern observed after the hydrogen absorption at room temperature, where the extent of absorption was evaluted to be as $ZrCoH_3$. The diffraction patterns shown above indicate that the crystallites changed from cubic structure of ZrCo to orthorhombic one by hydride formation. The diffraction pattern shown in Fig. 7 is consistent with that of $ZrCoH_3$ appeared in literature[6]. On the other hand, the pattern observed after 50 heat cycles was quite different from that of $ZrCoH_3$, as shown in Fig. 8. This pattern was found to be a superposition of $ZrCo_2$[7] and ZrH_x[8], where x was not determined explicitly from the X-ray analysis. There was no diffraction peak of ZrCo and
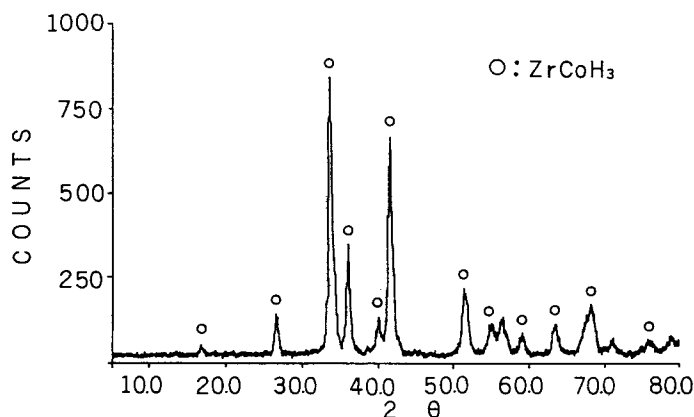

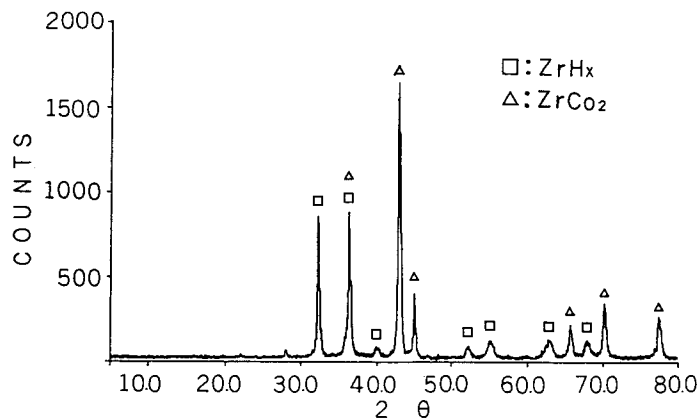Fig. 7. X-ray diffraction pattern of hydrogen-charged ZrCo sample before the heat cycles.

Fig. 8. X-ray diffraction pattern after the 50th heat cycle for ZrCo-H system.

ZrCoH₃. In addition, no noticeable sign of oxide formation was detected.

X-ray analyses for ZrNi are shown in Figs. 9-11. The ZrNi sample showed the diffraction pattern of orthorhombic structure of ZrNi appeared in literature[9] as seen in Fig. 9. The pattern of Fig. 10 was observed after the hydrogen absorption amounting to ZrNiH₃. This pattern coincided very well to the orthorhombic structure of ZrNiH₃[9]. Namely, the crystallographic structure did not change with hydrogen absorption, but lattice expanded approximately 20% by hydride formation. In contrast to ZrCo, the crystal structure did not change from ZrNiH₃ after 50 heat cycles as seen Fig. 11. In addition, there was no noticeable change of pattern indicating oxidation of the sample.
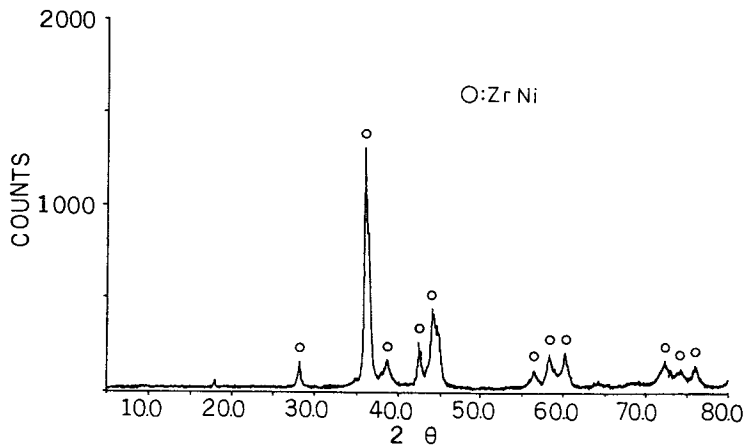
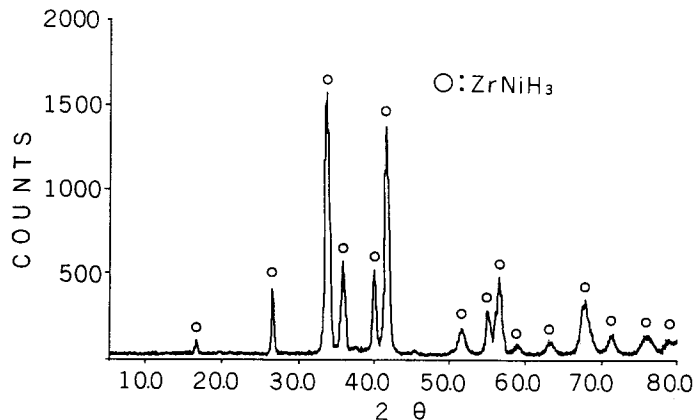Fig. 9. X-ray diffraction pattern of ZrNi sample.

Fig. 10. X-ray diffraction pattern of hydrogen-charged ZrNi
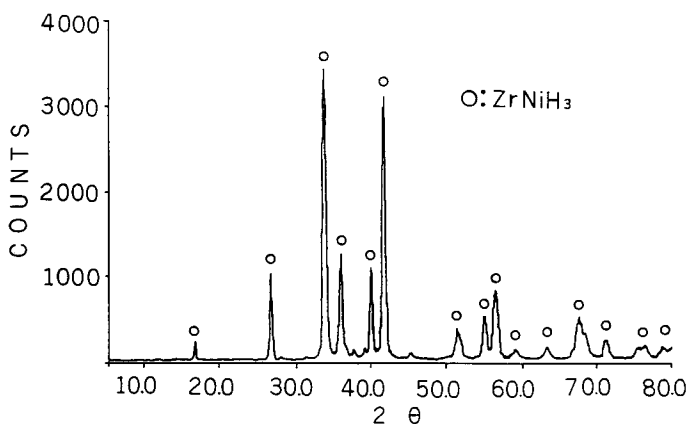sample before the heat cycles.

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Fig. 11. X-ray diffraction pattern after the 50th heat cycle for ZrNi-H system.

3. 3. Mechanisms of reactions

As described above, both the volumetric absorption-desorption measurements and X-ray analysis indicate the formation of the hydride of $ZrCoH_3$ for ZrCo at room temperature at the initial stage of the heat cycle. Namely, the reaction

$$ZrCo + (3/2)H_2 \rightleftarrows ZrCoH_3 \qquad (1)$$

took place at room temperature with the hydrogen over-pressure of 3.12 kPa in the present study. With heating, the reverse reaction took place to attain to the equilibrium pressure of 43.8 kPa. The pressure difference betwee P_{600} and P_{RT} is a consequence of the reversibility of Eq. (1).

On the other hand, the X-ray analysis clearly showed the formation of $ZrCo_2$ and ZrH_x after 50 heat cycles. This indicates that a part of ZrCo hydride underwent the disproportionation as

$$2ZrCoH_3 \rightarrow ZrCo_2 + ZrH_x + (6-x)/2H_2 \qquad (2)$$
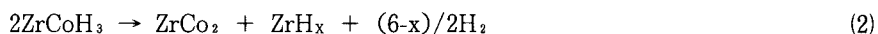
Namely, the ZrCo hydride decomposes to form $ZrCo_2$, ZrH_x and hydrogen. Zirconium hydride is much more stable than $ZrCoH_3$ and the equilibrium pressures of hydrogen at 600°C and at room temperature are 53 and below 1×10^{-8} Pa^2, respectively. It means that the zirconium hydride does not decompose appreciably to zirconium and hydrogen gas at 600°C. Namely, hydrogen free Zr-phase is hardly formed by the heating in the present experimental conditions. Consequently, hydrogen absorption by Zr does not occur with the subsequent cooling in a heat cycle. With respect to $ZrCo_2$, it is a stable Laves phase and does not absorb hydrogen much[10]. It has been reported that

this phase can absorb hydrogen only up to $ZrCo_2H_{0.2}$. Namely, once the above reactions occur, the reactions (1) and (2) do not proceeds to the reverse direction. Suppose that those reactions take place during the heat cycles step by step, the amount of ZrCo in the sample decreases and the stable ZrH_x increases. Eventually, P_{600} decreases with heat cycles. On the other hand, upon cooling of the sample to room temperature, only a smaller amount of hydrogen than that at the initial stage can be absorbed by the sample due to the existence of a smaller amount of ZrCo phase. Hence, the pressure at room temperature increases. By the progression of this disproportionation reaction, one can understand the gradual decrease in P_{600} and increase in P_{RT} for ZrCo with heat cycle as seen in Fig. 3. The reversible absorption-desorption at the last stage is understood due to the reaction

$$ZrCo_2 + 0.1H_2 \rightleftarrows ZrCo_2H_{0.2} \tag{3}$$

With respect to ZrNi, the absorption of hydrogen or hydride formation takes place by two steps[11] as

$$ZrNi + (1/2)H_2 \rightleftarrows ZrNiH \tag{4}$$

$$ZrNiH + H_2 \rightleftarrows ZrNiH_3 \tag{5}$$

Both the volumetric absorption measurements and X-ray analyses showed that the reactions attained to completion in the present experimental conditions. Upon heating, the reverse reactions took place. Hence, there was no noticeable changes in P_{600}, P_{RT} and crystallographic structure. This is a reason of the good stability of ZrNi for repeated heat cycles and/or absorption-desorption cycles.

4. Conclusions

Absorption-desorption characteristics of ZrCo and ZrNi were studied from a view point of durability against heat or absorption-desorption cycles. ZrCo showed considerable degradation of the characteristics in 50 heat cycles between 600°C and room temperature in hydrogen atmosphere. On the other hand, ZrNi was stable to the heat cycle under the similar conditions for ZrCo.

X-ray diffraction analyses revealed that ZrCo absorbed and released hydrogen reversibly following $ZrCo + 1.5H_2 \rightleftarrows ZrCoH_3$ at the initial stage of the heat cycles. However, it decomposed as $2ZrCoH_3 \rightarrow ZrH_2 + ZrCo_2 + 2H_2$ with repeating further the heat cycle. Namely, ZrCo underwent disproportionation due to the heat cycles in the presence of hydrogen. On the other hand, ZrNi showed no sign of the dispropor-

tionation under the similar conditions. In addition, there was no noticeable evidence of the formation of surface oxides which act as poison for the absorption-desorption. It is, therefore, concluded that the severe degradation of the characteristics of ZrCo is due to the decomposition of ZrCo to stable ZrH_x and $ZrCo_2$. The difference between the ZrCo and ZrNi in the stability against the disproportionation is considered due to differences in thermodynamic properties on the one hand, and in kinetic properties on the other. Factors affecting the different behaviors of the two alloys will be reported in detail in near future.

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