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# Hydrogen-induced amorphization of $YNi_2$ enhanced by mechanical grinding

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**Abstract**

The C15 Laves phase $YNi_2$, which transforms into amorphous phase by hydrogenation, was mechanically ground under various hydrogen partial pressures up to 1.0 MPa, to investigate the effect of mechanical grinding on hydrogen-induced amorphization (HIA) processes. The thermal stability of the amorphous phase and hydrogen contents dissolved in the compound were also examined. Under an initial hydrogen pressure of 1.0 MPa, the HIA processes are remarkably enhanced by grinding. Under an initial partial hydrogen pressure of 0.2 MPa, on the other hand, the $YNi_2$-H system decomposes into two phases, the α- and α'-phase by grinding, because the amount of hydrogen in the grinding vial is limited. Further grinding leads not only to an amorphization of the α'-phase but also to a transfer of hydrogen from the α'-phase to an amorphous phase and to a phase transformation of $YNi_2$ into $YNi_5$. Excess Y left in the phase transformation is dissolved into the amorphous phase. The difference between the above two processes depends on the initial hydrogen pressure and is understood by considering the free energy variation of the $YNi_2$-H system during mechanical grinding.

*Keywords:* Laves phase; Yttrium-nickel; Hydrogen; Amorphization; Reactive mechanical grinding

## 1. Introduction

Generally, mechanical grinding excites an equilibrium phase into a non-equilibrium state, in which additional mechanical grinding energy is mainly stored at the grain boundaries in the form of high density defects or dislocations. By longer grinding, the non-equilibrium state can be transformed into a metastable amorphous phase. It is well known that an intermetallic compound ZrNi amorphizes by mechanical grinding under an argon atmosphere [1,2]. Thus the mechanical grinding tends to reduce the thermal stability of ZrNi once, and to gain entropy.

In contrast to ZrNi, an intermetallic compound $YNi_2$ spontaneously transforms into amorphous $YNi_2H_x$ by hydrogenation [3,4]. This phenomenon is called hydrogen-induced amorphization (HIA) [5,6]. Since the coordination number of Y–Y pairs in the amorphous $YNi_2D_{3.6}$ is about twice as high as that in $YNi_2$ [7], deuterium atoms can occupy the tetrahedral sites surrounded by 4Y and 3Y1Ni. Consequently, the thermal stability of the $YNi_2$-D system gains by the amorphization.

We expect that the mechanical grinding under a hydrogen atmosphere, which is called reactive mechanical grinding (RMG), will cause a structural modification of the $YNi_2$-H system and a decomposition to more stable phases will occur. This has prompted us to investigate the effect of the mechanical grinding on the HIA process or hydrogen induced disproportionality in the $YNi_2$-H system under various partial hydrogen pressures.

## 2. Experimental

A mixture of 1 g $YNi_2$ as prepared by arc melting and 20 steel balls of 7 mm in diameter (weight ratio 1:30) were placed in a steel vial. The vial was directly degassed, and a high purity mixture of hydrogen and argon gas of 1.0 MPa (partial pressure of hydrogen was 0, 0.2 and 1.0 MPa) was introduced. Mechanical grinding was achieved by using a planetary ball mill apparatus (Fritsch P7) with 400 rpm for periods from 5 min to 1080 min at ambient temperature.

The samples were characterized by X-ray diffraction (Cu-Kα radiation) and thermal analyses; thermogravimetry (TG) and differential thermal analysis (DTA). The thermal

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analyses were carried out on a high purity argon flow of 50 $cm^3$ $min^{-1}$ with heating of 5 K $min^{-1}$ to 973 K

## 3. Results and discussion

Under an initial hydrogen pressure of 1.0 MPa, the system first forms hydrogen dissolved α'-$YNi_2H_y$ after 5 min (See Fig. 1c), and then the α'-$YNi_2H_y$ completely amorphizes after grinding at room temperature during 180 min (Fig. 1f). On the other hand, the hydrogenation of $YNi_2$ during 10 080 min without grinding does not induce any amorphous phase (Fig. 1b). Thus, mechanical grinding markedly enhances the amorphization of α'-$YNi_2H_y$, indicating that the activation energy of α'-$YNi_2H_y$ for amorphization decreases and the short range atomic diffusion is promoted by mechanical grinding.

Yoshioka et al. showed that single amorphous phase was obtained by hydrogenation of $YNi_2$ for 108 h (6480 min) under an initial hydrogen gas pressure of 1.0 MPa at 273 K [4], whereas HIA does not occur by hydrogenation under a similar atmosphere in this experiment. This difference can be explained by the difference of hydrogen gas pressure at the final state. HIA easily occurs under higher hydrogen pressure as revealed in the $GdFe_2$-H system by Aoki et al. [5]. In this experiment, the amount of hydrogen in the vial is limited, so that the hydrogen gas pressure fell from initial 1.0 MPa to about 0.3 MPa at the final state. In contrast, the hydrogen gas pressure did not change so much in the pressure cell used by Yoshioka et al. [4].

X-ray diffraction profiles of the samples ground under the partial hydrogen pressure of 0.2 MPa are shown in Fig. 2. We can see in Fig. 2b that hydrogenation of $YNi_2$ without grinding leads to decomposition into two phases with different hydrogen contents, such as $YNi_2H_\delta$ (α-phase) and $YNi_2H_y$ (α'-phase), because the amount of hydrogen gas in a vial is limited. Next, by mechanical grinding under a partial hydrogen gas pressure of 0.2 MPa, the structural transformation is enhanced. The processes can be divided into three stages, as follows.

(1) In the initial stage of milling (5 – 15 min), the $YNi_2$-H system decomposes into two phases of the α- and α'-phases. The diffraction peaks of the α-phase shift to lower angles compared to those of the hydrogenated sample without grinding, indicating that the hydrogen solubility in the α-phase increases with grinding. This result implies that a modification to the free energy curve of the α-phase is caused by mechanical grinding. The details will be discussed later. After grinding for 15 min, the diffraction peaks of the α'-phase disappear (Fig. 2d), showing an amorphization of the α'-phase.

(2) In the middle stage (15 – 180 min), the hydrogen solubility of the α-phase decreases with increasing the grinding period. The α-phase returns to the initial compound $YNi_2$ without dissolved hydrogen atoms after grinding for 60 min. The total hydrogen content in the

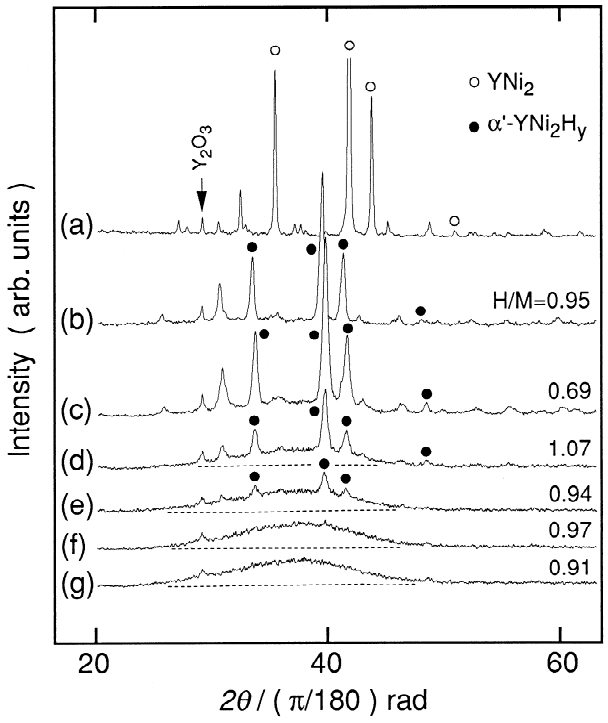


Fig. 1. X-ray diffraction profiles (Cu-Kα) of $YNi_2$ (a) prepared by arc melting, (b) hydrogenated for 10 080 min under a hydrogen pressure of 1.0 MPa without grinding and ground for (c) 5, (d) 15, (e) 60, (f) 180 and (g) 1080 min under a hydrogen atmosphere.

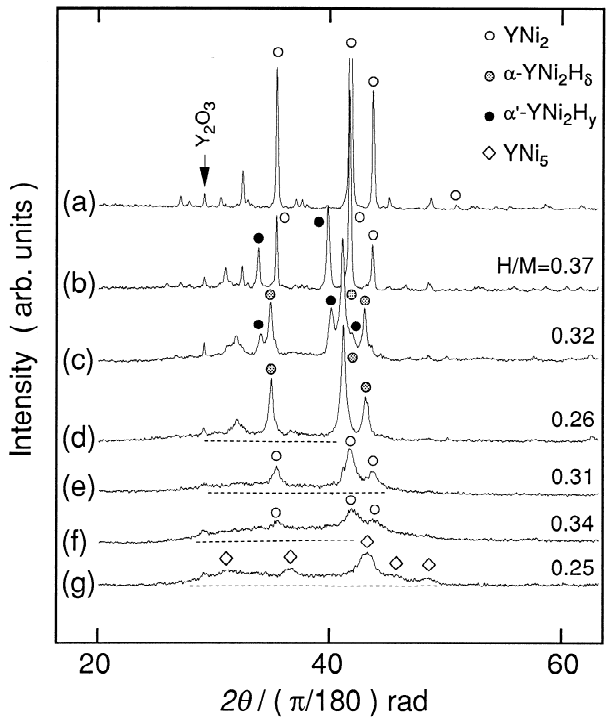


Fig. 2. X-ray diffraction profiles (Cu-Kα) of $YNi_2$ (a) prepared by arc melting, (b) hydrogenated for 10 080 min under a partial hydrogen pressure of 0.2 MPa without grinding and ground for (c) 5, (d) 15, (e) 60, (f) 180 and (g) 1080 min under the partial hydrogen pressure of 0.2 MPa.

product, however, changes little in this stage. Furthermore, the intensity of the halo corresponding to the amorphous phase increases as the grinding process continues. Therefore, it seems likely that the hydrogen atoms dissolved into the α-phase move near the amorphous phase which starts to grow in this stage.

(3) In the final stage (180 – 1080 min), the $YNi_2$ phase transforms into $YNi_5$. Excess Y left by this phase transformation will be dissolved into the amorphous phase, because yttrium has a strong affinity to hydrogen atom.

These structural changes induced by mechanical grinding under low hydrogen pressure are likely to cause a change of thermal stability of hydrogen in the $YNi_2$-H system. In order to clarify this point, derivative thermogravimetry (DTG) experiments were carried out, whose results are in Fig. 3. In the first stage, the large peak corresponding to the dehydriding reaction from the solid solution (α- and α'-) phases appears around 450 K. In the middle stage, hydrogen is released at higher temperature, corresponding to the decomposition temperature of the amorphous phase (about 620 K). In the final stage, the stability of hydrogen considerably increases and a new peak of dehydriding reaction appears around 735 K.

In order to clarify the new dehydriding reaction in the final stage, we performed X-ray diffraction analyses of heat treated samples below and above the temperature at which the new peak occurred in the DTG profile (indicated by arrows in Fig. 3e). In the sample quenched from 673 K shown in Fig. 4b, $YH_2$ newly appears but the diffraction profile of $YNi_5$ does not change except for the intensity of their peaks. In the sample quenched from 773 K, on the other hand, $YNi_5$ transforms into $YNi_3$ but no change occurs for $YH_2$ (Fig. 4c). Thus, the new dehydriding reaction corresponds to a partial dehydriding from $YH_2$.

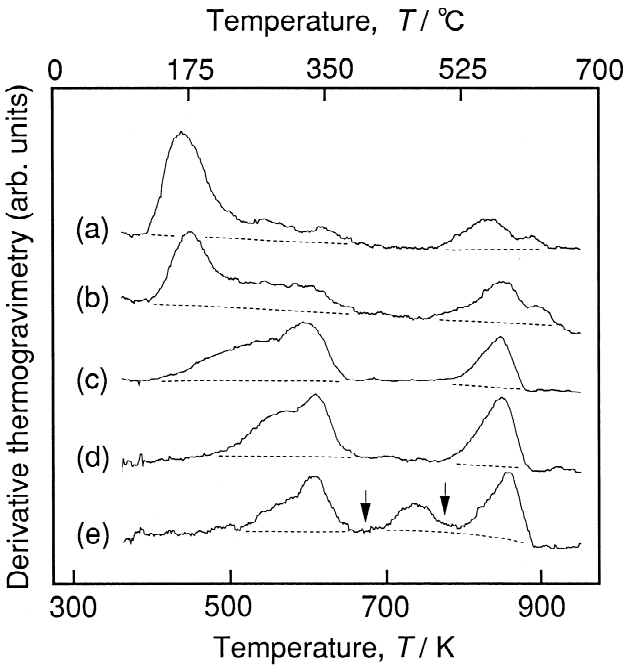


Fig. 3. Derivative thermogravimetric (DTG) curves of $YNi_2$ mechanically ground for (a) 5, (b) 15, (c) 60, (d) 180 and (e) 1080 min under a partial hydrogen pressure of 0.2 MPa.

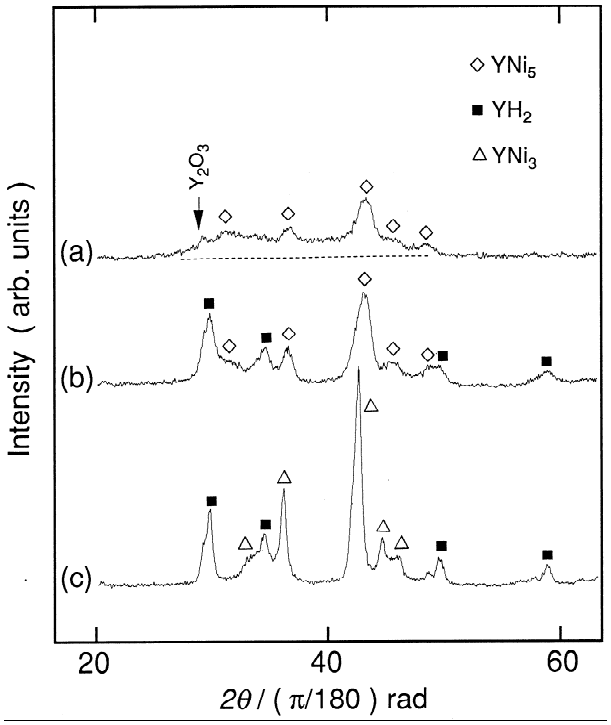


Fig. 4. X-ray diffraction profiles (Cu-Kα) of $YNi_2$ ground for 1080 min under the partial hydrogen pressure of 0.2 MPa, (a) before the heat treatment, and after heat treatment at (b) 673 K and (c) 773 K.

Finally, we will discuss the effect of mechanical grinding on the HIA in the $YNi_2$-H system from the viewpoint of the free energy. Fig. 5 schematically shows the free energy variation in the system during the reactive mechanical grinding. In the $YNi_2$-H system, there are two equilibrium α- and α'-phases with different hydrogen contents. Therefore, the system separates into two equilibrium phases if the hydrogen content is not sufficient to form a single α'-phase. A metastable amorphous phase might also exist, which is more stable than the α'-phase and has the same hydrogen content.

After the hydrogenation without grinding under an initial hydrogen pressure of 0.2 MPa for 10 080 min, the amount of hydrogen in the system does not exceed 0.3 in H/M, because of the limited amount of hydrogen gas in the vial. Then a phase separation occurs and the free energy curves have a common tangent (Fig. 5a). The slope gives the chemical potential of each phase. The free energy at $YNi_2$ without hydrogen will increase by mechanical grinding because of the formation of nano-structure involving an accumulation of energy in grain boundaries, while that of the α'-phase will decrease toward the amorphization. As a result of grinding this system, the slope of the free energy with a common tangent will change to a large

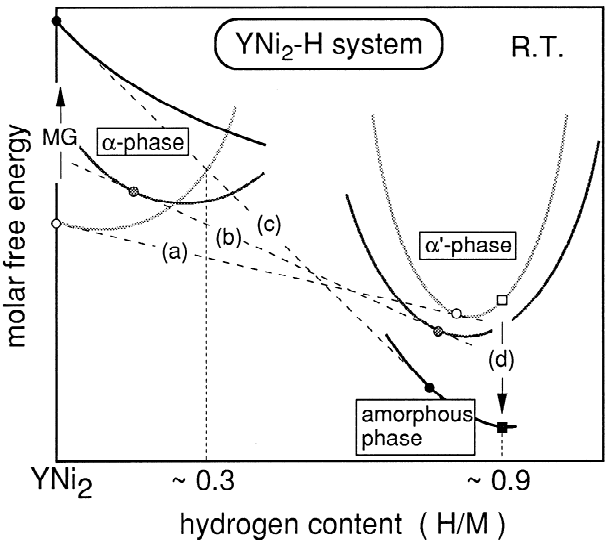


Fig. 5. Free energy variation of the $YNi_2$-H system as a function of mechanical grinding (schematic figure); (a) hydrogenation for 10 080 min under a partial hydrogen pressure of 0.2 MPa, after grinding for (b) 5 min, (c) 60 min under the atmosphere, (d) during the grinding process under a hydrogen pressure of 1.0 MPa.

negative value. Thus after grinding for 5 min, the α-phase can dissolve a larger amount of hydrogen compared to only hydrogenation (Fig. 5b). Furthermore, after grinding for 60 min, the α-phase returns into $YNi_2$ with no hydrogen (Fig. 5c). Since the decrease of the free energy of the α'-phase accompanied by amorphization can not compensate for the increase of that of the α-phase by mechanical grinding, the system becomes thermodynamically unstable. We believe that this instability causes the transformation of $YNi_2$ into $YNi_5$ after grinding for 1080 min.

Under an initial hydrogen pressure of 1.0 MPa, on the other hand, the hydrogen content reaches a value of up to $H/M=0.9$, so that the α'-phase only exists as an equilibrium phase and is transformed into the amorphous phase by the mechanical grinding. Therefore, the free energy of the system decreases during the amorphization of the α'-phase (Fig. 5d).

In conclusion, we found that the mechanical grinding remarkably enhances the HIA. Furthermore, we found that the stability of the $YNi_2$-H system changes so as to minimize the total free energies, dependent on the hydrogen content. Under an initial hydrogen pressure of 1.0 MPa, $YNi_2H_x$ transforms into a single amorphous phase during a short period of mechanical grinding, before the system becomes more stable. Under a initial partial hydrogen pressure of 0.2 MPa in contrast, the thermodynamic stability of the system reduces with the mechanical grinding in spite of the partial amorphization because of the phase separation of $YNi_2$-H system into the α- and α'-phase, which is caused by the limited hydrogen content in the grinding vial. Consequently, the non-equilibrium state of $YNi_2$ is transformed into more stable state of $YNi_5$. These results can be understood by considering the free energy variation of the α- and α'-phase by mechanical grinding.

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