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Mechanochemical reaction of niobium with decalin and tetralin Hydrogenation of niobium with decalin and tetralin

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Abstract

Niobium hydride powders could be formed by a mechanochemical reaction at room temperature and at 1 atm. Niobium metal powder was ball-milled with liquid decalin and liquid tetralin. With decalin, niobium metal continuously changed to niobium hydride. Otherwise with tetralin, niobium hydride separately precipitated from niobium metal. It is considered that this hydrogenation was caused by a fresh surface effect which was made by ball-milling.

Keywords: Niobium; Decalin; Tetralin; Hydrogenation of niobium

1. Introduction

A number of production methods of metal hydrides have been proposed i.e., (1) direct reaction of metals with hydrogen gas, (2) electrolysis of metallic salt solutions and (3) decomposition of organo–metallic compounds [1]. In practice, they have been produced by the H_2 gas charging method. Hydrogen atoms can be also supplied by other processes, for example, the dehydrogenation of hydrocarbons. However, these reactions do not occur at usual conditions. The ball-milling method was used for mixing and crushing in the past. In recent years, it is reported that the fresh surface made by ball-milling is active to some chemical reactions like the room temperature reduction of metal oxide [2] and the synthesis of metastable metal carbide [3]. In a previous paper, the author indicated that some metal hydrides were produced by the ball milling method with liquid cyclohexane [4]. In this paper, the hydrogenation of niobium metal is reported, where niobium metal powder is ball-milled with liquid decalin and liquid tetralin.

2. Experimental

2.1. Sample preparation

Milling of niobium powder was carried out by using a vibrating ball-milling apparatus (SPEX8000). The vial and the balls (5ϕ) were made of zirconia. The purity of niobium metal is 99.9 atom-%. The particle size of the powders is about 100 μm.

Niobium powder was put into the vial with liquid decalin and liquid tetralin (20 ml) and balls (160 pieces). Milling was carried out at room temperature. All the samples were recovered after a constant milling time.

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2.2. Measurements

The crystal structures of milled powders were studied by X-ray diffraction analysis (Cu Kα, 45 kV, 35 mA). The morphology changes of the powders were studied by a scanning electron microscopy (SEM). The hydrogen content in the powders was evaluated by thermal conductivity detector (TCD) method, the hydrogen analyzer HORIBA EMGA-621.

3. Results and discussion

3.1. Function of ball-milling

Table 1 exemplifies the actions of ball-milling. The first action is the most fundamental and is the use of an automatic mortar. The second one is the refinement of the powders themselves and also their crystal grains. The third one is the introduction of strains, vacancies, dislocations and interfaces. This action promotes the diffusion of atoms and changes the internal energy. The fourth one is the creation of fresh surfaces by crushing. In the case of metal, the elastic deformation is expected. These actions are not independent from each other and plural actions play at the same time in the operation of the ball-milling.

In these actions, the fresh surface is the most important to the induction of various chemical reactions. The clean surfaces of metals can also be produced by an ultra high vacuum technique but the fresh surfaces made by ball-milling are more active than the clean surfaces. The ball-milling is the only method which can continuously create fresh surfaces. Table 2 shows the effects caused by ball-milling. Various reactions and various materials can be developed from these fresh surface effects.

Table 1
Actions of ball milling

1	Mixing and dispersion
2	Grinding and refinement
3	Introduction of strain and defects
4	Creation of fresh surface
5	Elastic deformation

Table 2
Effects of ball milling

1	Composite and nanostucture
2	Promotion of diffusion
3	Alloying
4	Amorphization
5	Induction of chemical reaction
6	Multi-layered structure

3.2. Niobium–hydrogen system

Fig. 1 shows the equilibrium phase diagram of the niobium–hydrogen system [5]. The crystal structure of pure niobium metal is body centered cubic (bcc). Hydrogen atoms solid-solute in the interstitial sites of its bcc lattice and isotopically expand the crystal lattice. The solid solubility of hydrogen in bcc niobium is about 5.4 atom-%. There are two stable hydrides, monohydride (β) and dihydride (δ) at room temperature. β-phase is formed at the usual condition and separately precipitates from niobium metal. The XRD peaks of these hydrides are at low angles with every XRD peaks of pure niobium.

3.3. Hydrogenation of niobium with liquid decalin

Fig. 2 shows the changes in the X-ray diffraction patterns with milling time for niobium

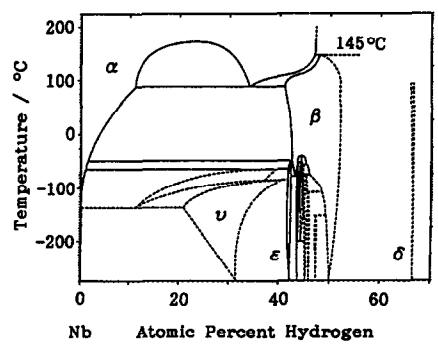

Fig. 1. Equilibrium phase diagram of niobium-hydrogen system [5].

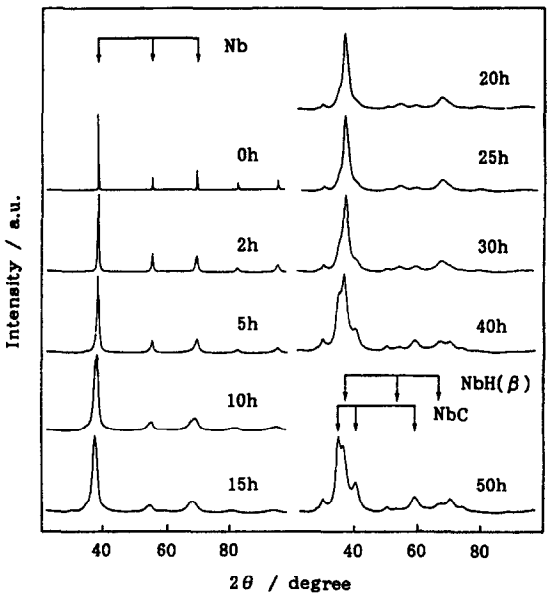

Fig. 2. Changes in the X-ray diffraction patterns with milling time for pure niobium powders milled with liquid decaline at room temperature (Nb = 7.137 g, decalin = 20 ml).

powders milled with liquid decalin. 7.137 g niobium and 20 ml decalin were used. The structure of niobium is bcc: the (110), (100) and (211) peaks are mainly observed in the starting powders. These diffraction angles are 38.6°, 55.7° and 69.7°, respectively. With the milling time, all the peaks continuously changed to the β-phase, contrary to the phase diagram. The main peaks of the β-phase are 37.3°, 53.2° and 66.2°, respectively. It is possible that the phase obtained is a super-saturated solid solution. In the latter stage niobium carbide was formed with β-phase. When the metal hydrides are strongly distorted, they decompose and release hydrogen atoms. After the formation of metal hydride, the high energy milling-process is not necessarily appropriate for the single hydride phase without carbonization.

Fig. 3 shows the changes in the X-ray diffraction patterns with milling time for pure niobium powders milled with liquid decalin. 14.274 g niobium was used. Similar to the result for niobium = 7.137 g, the diffraction peaks changed to β-hydride. A single phase of β-hydride was nearly obtained after 50 h milling. The diffraction $2\theta = 30.4°$ is from zirconia of the vial and the balls. The carbonization is less than the result for niobium = 7.137 g. This is due to the decrease of the distortion introduced into the particles. It is considered that operation under low-energy conditions and for a long time is appropriate to obtain the single phase of metal hydride.

Fig. 4 shows the morphological changes of niobium powders with milling time. In the early stage of milling, 2 or 5 h, the particles were micro-rolled and changed to the lamellar structure with the texture. Since then, the particles were crushed and reduced to less than 2 μm at 50 h milling.

Fig. 5 shows the changes in the hydrogen contents with milling time, including the experiment with niobium = 21.410 g. ○, □ and ● are the results with niobium = 7.137 g, niobium = 14.274 g and niobium = 21.410 g, respectively. Hydrogen contents monotonically increased in all the results, but did not saturate even at 50 h milling. The content in the powders (niobium = 7.137 g) was about 4300 ppm

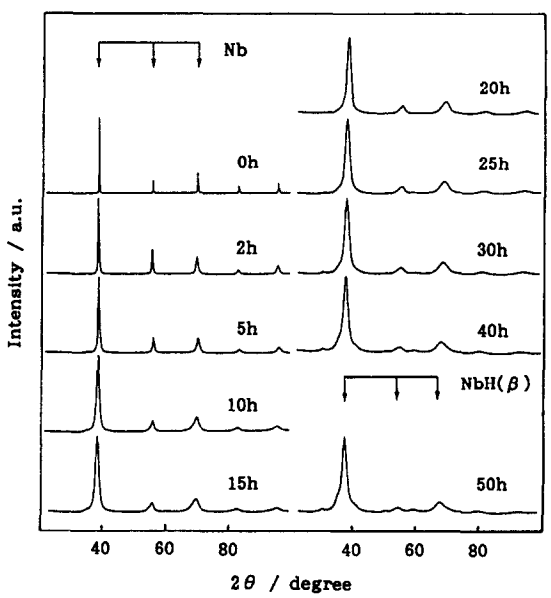

Fig. 3. Changes in the X-ray diffraction patterns with milling time for pure niobium powders milled with liquid decalin at room temperature (Nb = 14.274 g, decalin = 20 ml).

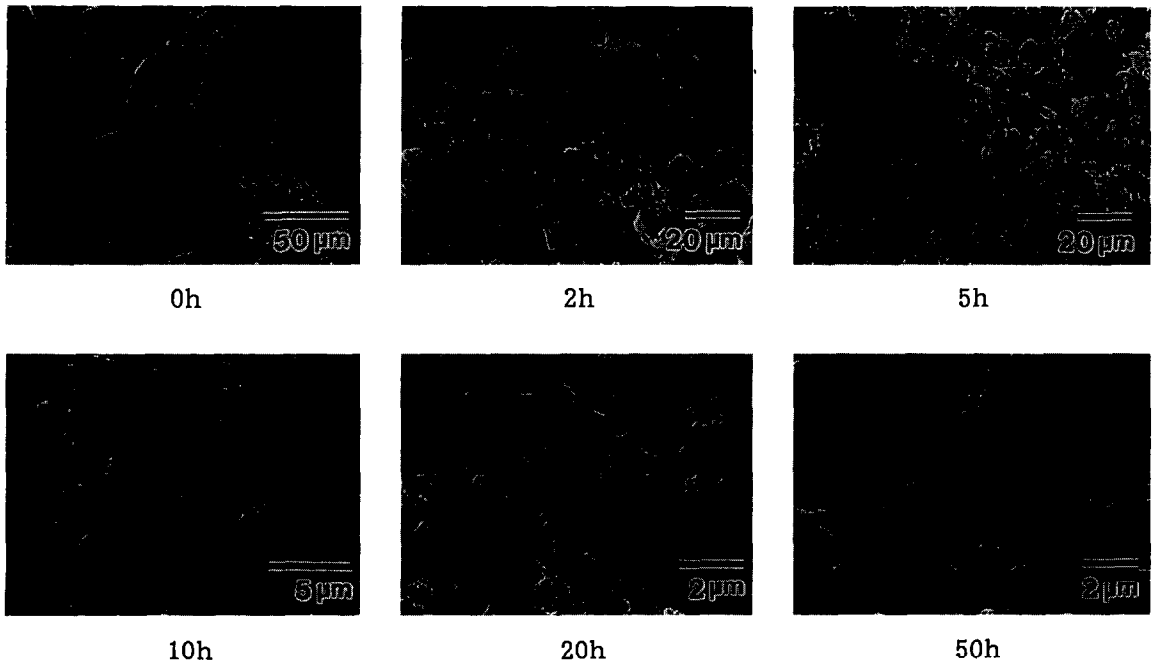

Fig. 4. Changes in the morphologies with milling time for niobium (7.137 g) milled with liquid decalin (20 ml) at room temperature.

after 50 h. With increasing the niobium weight, the hydrogen content diminishes.

3.4. Hydrogenation of niobium with liquid tetralin

Hydrogenations of niobium with liquid tetralin were carried out to compare the activity for hydrogenation. Fig. 6 shows the changes in the X-ray diffraction patterns with milling time. The weight of niobium was 7.137 g and 20 ml tetralin was used. Differently from the result

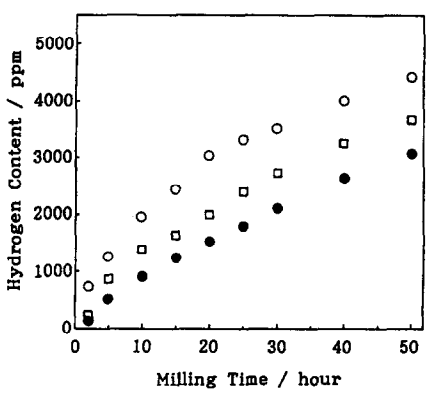

Fig. 5. Changes in the hydrogen contents in niobium powders milled with liquid decalin. ○, □ and ● are the results with niobium = 7.137, 14.274, and 21.410 g, respectively.

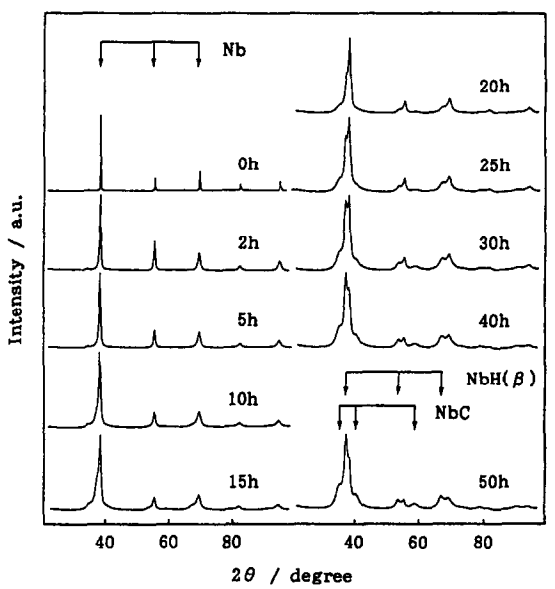

Fig. 6. Changes in the X-ray diffraction patterns with milling time for pure niobium powders milled with liquid decaline at room temperature (Nb = 7.137 g, tetralin = 20 ml).

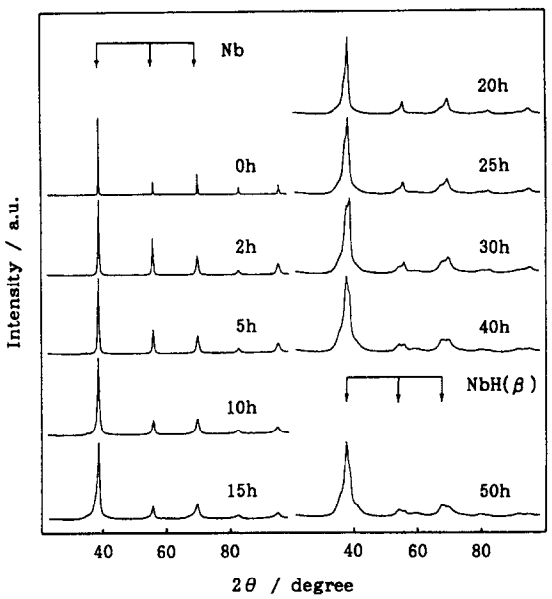

Fig. 7. Changes in the X-ray diffraction patterns with milling time for pure niobium powders milled with liquid decaline at room temperature (Nb = 14.274 g, tetralin = 20 ml).

with decalin, niobium hydride separately precipitated from metal niobium. Shoulders appeared at the low angle of every peak in the 10 h milled powder. These shoulders are peaks of niobium hydride. They grew with milling time and had almost the same intensity as niobium metal in 30 h milled powders. After 50 h milling, niobium hydride was formed with its carbide.

Fig. 7 shows the changes in the X-ray diffraction patterns with milling time. The weight of niobium powders was 14.274 g. Niobium hydride separately precipitated from metal niobium at this case too. Shoulders appeared in the 15 h milled powders and grew with milling time. After 50 h milling, niobium hydride was obtained following the remaining metal niobium and its carbide. The formation of carbide is decreased when the quantity of metal powders is increased. This may be caused by the cushioning effect of the powder used itself. The hydrogenation rate is a little decreased compared with the result of 7.137 g niobium used.

4. Conclusion

It was shown that niobium hydride was formed by mechanochemical reaction between metal niobium and liquid decalin and liquid tetralin. With decalin, metal niobium continuously changed to niobium hydride. With tetralin, niobium hydride separately precipitated from metal niobium. Niobium carbides were also formed, when metal powders were used in small quantities.

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