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Preparation of fine Nb_3Al powder by hydriding and dehydriding of bulk material

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Abstract

Structural changes of the intermetallic compound Nb_3Al before and after hydriding and dehydriding have been investigated by X-ray diffraction, electron microscopy and thermal analysis. A fine powder of this compound with an average particle size less than 14 μm can be easily prepared by hydriding at 773 K for 86.4×10^3 s and dehydriding at 1073 K for 10.8×10^3 s.

Keywords: Hydriding; Dehydriding; Intermetallic compounds; X-ray diffraction; Electron microscopy; Thermal analysis

1. Introduction

The intermetallic compound Nb_3Al has received much attention as a superconductor material [1–3] and also as a high-temperature structure material [4,5]. However, because Nb_3Al exhibits the A15 structure, the poor mechanical properties associated with this structure, particularly the lack of deformability, cause many problems in applications [6–8]. The powder-metallurgical method has been considered as the most suitable way to solve these problems, since a brittle to ductile transition may occur as the particle size is decreased [1,9]. For this reason, it is very important to be able to produce fine Nb_3Al powder. Although many attempts to prepare Nb_3Al powder have been made, to the best of our knowledge, no effective method has yet been developed. The main problems for industrial production are as follows: (1) it is difficult to restrict the particle size to less than 50 μm, (2) Nb_2Al and other impurity components infiltrate easily, (3) the oxygen content is high, and (4) the equipment is complicated and the production costs are high [10,11]. These problems are intimately connected with the strong oxidizability of both Nb and Al and the large differences in both melting point and specific gravity of Nb and Al. Another difficulty arises from the high melting point of Nb_3Al.

Recently, we have investigated the hydriding–dehydriding processes of Nb-based alloys and found that the hydriding–dehydriding process can be applied successfully to the production of fine Nb_3Al powder with particle sizes averaging less than 14 μm, without using expensive equipment and without high production costs.

In this paper, we will describe the changes in structure, shape and particle size distribution of the Nb_3Al alloys during the hydriding–dehydriding process and discuss the formation mechanism of fine Nb_3Al powder.

2. Experimental

The raw materials used in this investigation were niobium, purity 99.9%, and aluminium, purity 99.99%. According to the phase diagram, button ingots for the Nb-based alloys were prepared by arc melting the raw materials four times in an argon atmosphere at a pressure of about 700 Torr. The ingots were homogenized at 1223 K for 605×10^3 s in a vacuum of 1.33×10^{-4} Pa and were then cut into small blocks for hydrogen absorption. After an activation treatment at 773 K for 3.6×10^3 s in a vacuum, the samples were brought into contact with high-purity hydrogen (7N) at 5 MPa between 300 K and 773 K for 86.4×10^3 s. The amount of hydrogen absorbed was determined by

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measuring the change of the H_2 pressure in a constant volume reactor and also by chemical analysis. The stability of Nb_3Al hydride was studied in a flow of pure argon gas at a heating rate of $0.333\ K\ s^{-1}$ using a differential scanning calorimeter (DSC). The dehydriding process was performed at 1073 K for 10.8×10^3 s. The structures of the samples before and after hydriding–dehydriding were identified by X-ray diffraction (XRD) using the monochromated CuKα radiation. The 2θ angle was calibrated with silicon powder. The microstructure of the same sample was observed by scanning electron microscopy (SEM) and the particle size distribution of powder was measured by a laser diffraction method.

3. Results and discussion

Fig. 1 shows XRD patterns of Nb–Al alloys in various states. The XRD pattern of the original sample, which is in the bulk state and has been heat-treated at 1223 K for 605×10^3 s, represented by (A), was indexed on the basis of Nb_3Al with a lattice parameter of $a = 0.5185$ nm along with small amounts of Nb_2Al and other compounds. Our experiments show that it is difficult to obtain single-phase Nb_3Al even if the composition of the sample is varied around Nb_3Al, or if a heat treatment is carried out at higher temperatures and for longer times [12]. This can be understood from the Nb–Al phase diagram [13], which shows that Nb_3Al is formed through a peritectic reaction. Consequently Nb_2Al and other components are usually formed simultaneously with Nb_3Al. Because the quantities of the impurity phases are much less than that of Nb_3Al, we will call this alloy Nb_3Al for convenience.

After hydrogenation, the original sample became a powder. The XRD pattern of the powder is represented by (B) in Fig. 1. The diffraction peaks have shifted to lower angles in comparison with pattern (A), but the pattern (B) has remained similar to pattern (A). The peaks can be indexed on the basis of Nb_3Al hydride, which has the same structure as Nb_3Al but has a different lattice parameter, $a = 0.5363$ nm. The volume expansion of Nb_3Al hydride, caused by the hydrogenation, is about 10.5%. Although this is much smaller than the values of rare earth alloy hydrides [14,15], it is of the same order as the transition metal hydrides and is large enough to lead to strong stress in the sample [16]. The peaks corresponding to Nb_2Al in this sample become much weaker than in pattern (A).

For the purpose of understanding the thermal stability of Nb_3Al hydride, a DSC experiment on this alloy was carried out. The result is shown in Fig. 2. One small endothermic peak around 373 K and one large endothermic peak around 823 K are observed as a result of hydrogen desorption from this sample. Therefore, in order to obtain Nb_3Al powder without hydrogen, dehydriding must be performed at a temperature higher than 823 K. This is why the temperature of 1073 K for the dehydriding process was chosen for this experiment.

For comparison, the XRD pattern of the sample

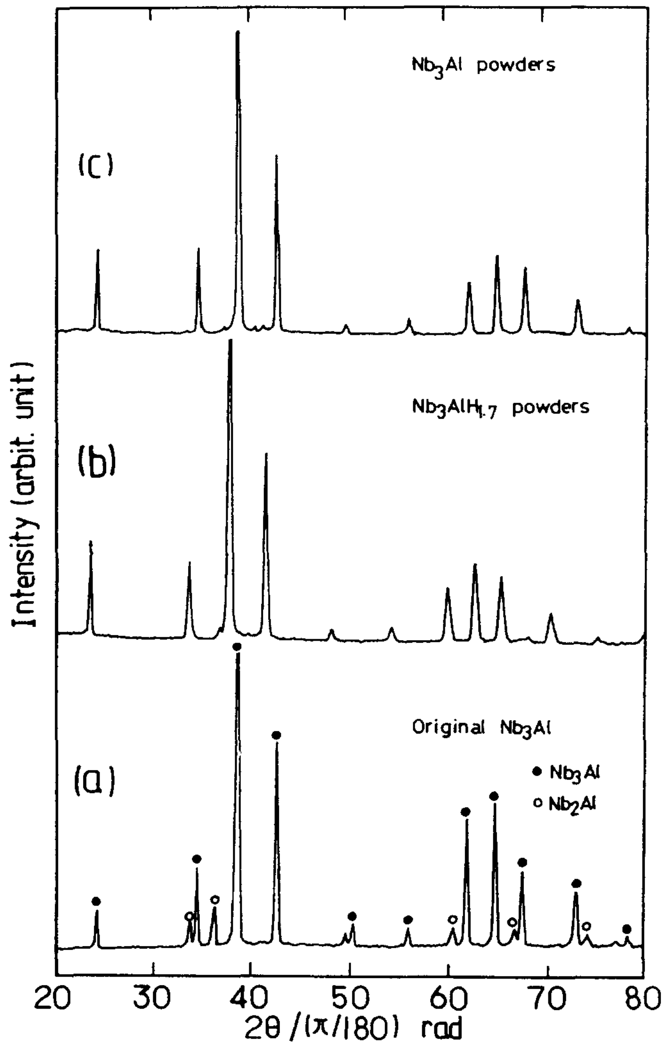

Fig. 1. The XRD patterns of the Nb_3Al compound in several states.

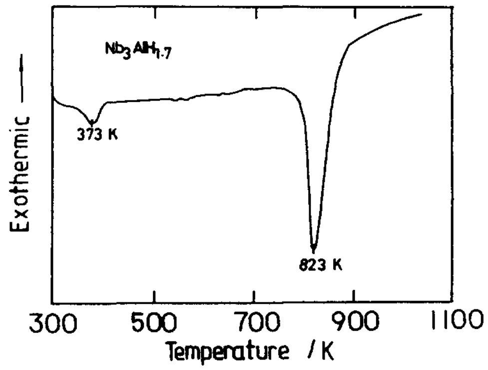

Fig. 2. The DSC curve of Nb_3Al hydride.

after dehydriding is also shown in Fig. 1 (see pattern (C)). The peaks can be indexed as Nb_3Al with A15 structure and a lattice parameter of $a = 0.5185$ nm. The peaks in pattern (C) are similar to those in pattern (A), although the two samples are in the powder and bulk states, respectively. The difference between them is that the diffraction peaks corresponding to the impurity phase are difficult to discover in pattern (C). This fact suggests that a fine powder of single-phase Nb_3Al can be prepared by the hydriding–dehydriding process. Preparing single-phase Nb_3Al powder is quite important for applications, because its properties decline quickly as impurity phases increase.

Our attention will be focused on the last two samples in the following discussion. Table 1 gives the amounts of oxygen, nitrogen and hydrogen contained in the two samples. The amount of hydrogen absorbed in Nb_3Al hydride is 0.43 (H/M) (hydrogen atoms per one metal) or, in other words it is 0.57 H/Nb, which is much closer to the value in niobium hydride [16]. Thus, this alloy can be written in the form $Nb_3AlH_{1.7}$. After dehydriding at 1073 K, the amount of hydrogen in the sample, i.e. in the Nb_3Al powder, has decreased to 1.82×10^{-3} H/M, which illustrates that the dehydriding process has been performed effectively. From this table it can also be seen that the amount of oxygen in Nb_3Al is only half of that in $Nb_3AlH_{1.7}$, which suggests that there is an effect of deoxidation during dehydriding. The amount of oxygen in Nb_3Al powder prepared by the present method is much lower than that reported by Watanabe et al. [7–11].

Fig. 3 shows the bright field image (a) of $Nb_3AlH_{1.7}$ and (b) of Nb_3Al. As can be seen from Fig. 3(a), there are bright and flat steps on the surface of each particle and intracrystalline cracks in some of the particles. This indicates that brittle fracture took place during the powder formation process. The quick cracking of the block sample in the form of brittle fracture, which is induced by the huge stress during hydrogenation, can be considered as the mechanism of formation of $Nb_3AlH_{1.7}$ powder. It can be seen from Fig. 3(b) that Nb_3Al remains in a fine powder state with a polygonal appearance, even though the dehydriding process has been carried out. There is little difference between the two samples in shape and particle size.

Fig. 4 shows the particle size distributions of $Nb_3AlH_{1.7}$ and Nb_3Al powders. The particle sizes of each have almost the same distribution and the majority are concentrated in the range 4–32 μm. The average particle sizes are about 13.6 μm and 13.3 μm, respectively. Instead of particle growth during the dehydriding process, there is a slight size reduction. One reason for this is that the dehydriding temperature is much lower than its melting point. Another one is attributed to the hydrogen desorption.

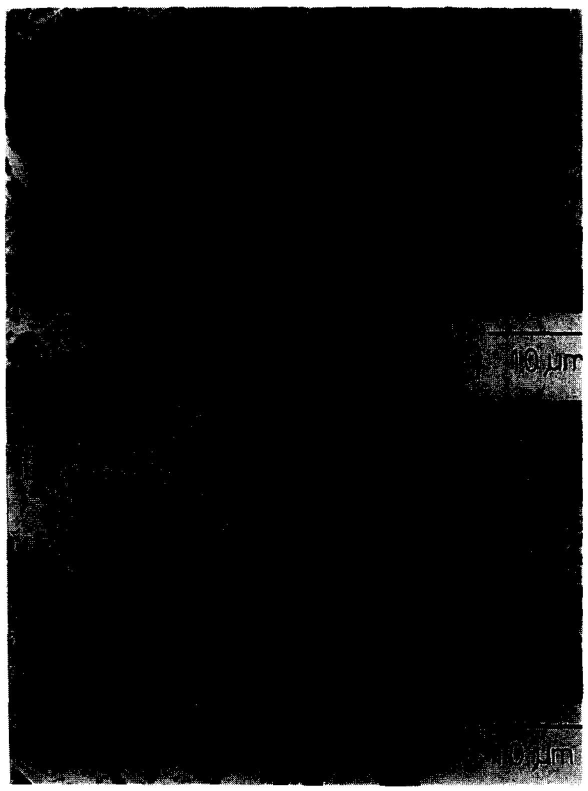

Fig. 3. The bright field image (a) of $Nb_3AlH_{1.7}$ powder and (b) of Nb_3Al powder.

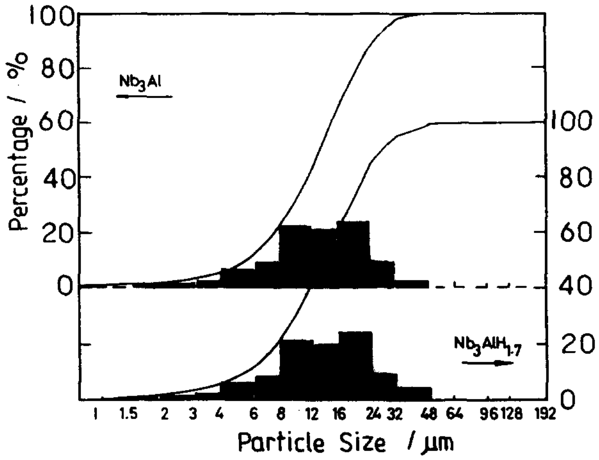

Fig. 4. The particle size distributions of $Nb_3AlH_{1.7}$ and Nb_3Al powders.

Table 1
The amounts of hydrogen, oxygen and nitrogen in the samples

Sample	Hydrogen (H/M)	Oxygen (wt.%)	Nitrogen (wt.%)
$Nb_3AlH_{1.7}$	0.5800	0.12	0.030
Nb_3Al	0.0024	0.06	0.053

4. Summary and conclusions

By hydriding bulk Nb_3Al at 773 K for 86.4×10^3 s and dehydriding at 1073 K for 10.8×10^3 s, fine powder of the A15 type compound Nb_3Al can be easily prepared, having an average particle size less than 14 μm. The Nb_3Al particles obtained by this method have a polygonal appearance and contain less oxygen and few impurity phases.

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