

Powder Fabrication of Nb-Ti Alloys Using Hydrogenation Process

Satoshi Semboshi^{1a}, Naoya Masahashi^{2b}, Toyohiko J. Konno^{1c}, Shuji Hanada^{2d}

¹: Department of Materials Science, Osaka Prefecture University
Gakuen-cho 1-1, Sakai, Osaka, 599-8531, Japan

²: Institute for Materials Research, Tohoku University
Katahira 2-1-1, Aoba-ku, Sendai, Miyagi, 920-8577, Japan
^asemboshi@mtr.osakafu-u.ac.jp, ^bmasahasi@imr.tohoku.ac.jp
^ctjkonno@mtr.osakafu-u.ac.jp, ^dhanada@imr.tohoku.ac.jp

Abstract

Nb-Ti alloys were hydrogenated to prepare fine and contamination-free powders. Cracks were introduced in the alloys when they were annealed at 1473 K and cooled in a hydrogen atmosphere. The fragments produced by hydrogen-induced cracking are brittle and the friability enhanced with the Ti content of the alloy, which is beneficial for further refinement of particle size. We also demonstrate that Nb-Ti powders with the average particle size less than 1 μm can be produced by ball milling at a temperature lower than 203 K. Furthermore, hydrogen-free powders can then be obtained by annealing above the temperature corresponding to hydrogen desorption from Nb solid solution.

Keywords : powder fabrication, Nb-Ti alloys, hydrogenation, milling, powder size distribution

1. Introduction

In the field of electric industry, porous compact structures of pure Nb and Nb alloys such as Nb-Ti and Nb-N are widely used as a metal substrate for electrolytic capacitors, which realize a large electrical capacity in a surface layer of Nb pentoxide [1]. Here, the porous compacts are generally produced from the material powders, and one of the ways to improve the performance is to employ powders having finer particle size under 1 μm and higher purity so as to increase the relative surface area of porous compacts with sound pentoxide layers. Therefore, it is strongly important to develop a powder fabrication process for Nb alloys.

It is well recognized that some bulk alloys are easily broken into small debris or powders only by exposing to a hydrogen atmosphere. In recent studies, it has been proposed that hydrogenation-mill-dehydrogenation procedures can be employed as a powder fabrication process for Ti, Nb and Ta based alloys when chemical composition, microstructure and procedure conditions are well controlled [2-4]. Thus, in this study, we applied the hydrogen-induced cracking and pulverization to Nb-Ti alloys, which is one of the most possible materials for electrolytic capacitors. Furthermore, we demonstrated the fabrication of high quality alloy powders by a hydrogenation - milling - dehydrogenation procedures.

2. Experimental Procedures

We prepared button ingots of Nb-Ti binary alloys with

the nominal compositions of 0 to 18 at. % Ti by argon arc melting, followed by annealing at 1673 K for 24 hours in an argon atmosphere for homogenization. These alloys were subsequently hydrogenated by a gas-solid thermal reaction system: they were put in the furnace, in which a high-purity hydrogen gas (99.99999 pct) was kept flowing and annealed at 1473 K for 3 hours, followed by furnace cooling to room temperature. To evaluate the friability of hydrogenated Nb-Ti alloys and to prepare fine powders, a portion of the hydrogenated alloys were mechanically ground using a planetary ball-milling system with tungsten-carbide balls and a container in air for 60 minutes at room temperature or below 203 K. Particle-size distributions of the powders prepared by the milling procedure were measured by using a laser diffraction method. In order to remove hydrogen in ball-milled alloy powders, they were annealed at 773 K for 60 minutes in vacuum. We found that the temperature corresponding to the hydrogen desorption from Nb solid solution was about 724 K by a DSC measurement. Hydrogen contents of Nb-Ti alloys were analyzed by an argon gas fusion thermal conductivity method. The hydrogenated alloys were observed by an optical microscopy and a scanning electron microscopy (SEM).

3. Results and Discussion

Concentric and micro cracks about several 100 μm intervals were induced after the hydrogenation, resulting in partial pulverization to flaky debris and powders. For all the prepared Nb-Ti alloys with Ti content between 0 and 18

at. %, their hydrogen-induced cracking was observed to occur, and powders with sizes ranging from several to 1000 μm were directory obtained. The hydrogen content of the hydrogenated Nb was about 49 at. %, and that of Nb-Ti alloys increase as Ti content increases. This is probably because that the affinity of Ti for hydrogen is higher than that of Nb.

The fragment of hydrogenated Nb-Ti alloys were extremely brittle and friable in comparison to the original alloys, suggesting that finer powders can be produced by low energy mechanical grinding. For example, Fig. 1(a) shows particle size distribution of hydrogenated Nb-6at.%Ti powders milled for 60 minutes at room temperature. It shows that the average value of particle size is about 2.3 μm . On the other hand, Fig. 1(b), which is the size distribution of particles milled at a temperature lower than 203 K, shows that the average particle size is less than 1 μm with a better uniformity. Figs. 2(a) and (b) show the average particle sizes and deviations of hydrogenated Nb-Ti powders as a function of Ti content, which were prepared by ball-milling for 60 minutes at room temperature and below 203 K, respectively. These results show that finer powder can be produced from a Nb-Ti alloy with a higher Ti content, suggesting that a friability of a hydrogenated Nb-Ti alloy can be enhanced with a higher Ti content. It is probably because Nb-Ti alloys with a higher Ti content absorb higher hydrogen, leading to easier embrittlement. Additionally, it was also shown that finer powder can be obtained at a lower temperature rather than at room temperature. This finding can be explained by the formation of the ordered NbH and long-period structured λ -NbH at lower temperatures^[5], resulting in the enhancement of the intrinsic friability of hydrogenated Nb-Ti alloys.

Subsequent dehydrogenation procedure was conducted at 773 K in vacuum. After dehydrogenation, hydrogen content decreases to less than 0.01 wt. %, indicating that the dehydrogenation treatment is in fact effective to remove hydrogen from hydrogenated alloys. Thus, we have demonstrated that the use of hydrogen as a temporary alloying element in powder metallurgy allows production of high quality Nb-Ti alloy powders by hydrogenation, ball milling and dehydrogenation. This would be one of the most effective methods for not only Nb-Ti alloy but also other Ti, Nb and Ta alloys

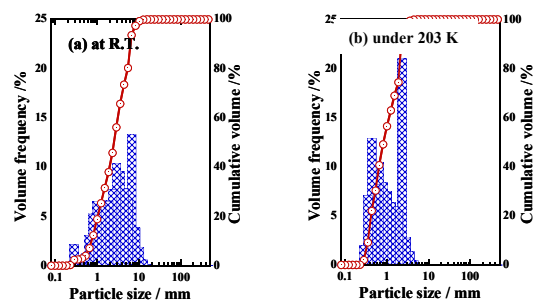


Fig. 1 Particle size distributions of hydrogenated Nb-6 at.% Ti powders produced by ball milling for 60 minutes at room temperature (a) and below 203 K (b). The average particle sizes of Nb-Ti powder are about 2.3 μm and 0.89 μm , respectively.

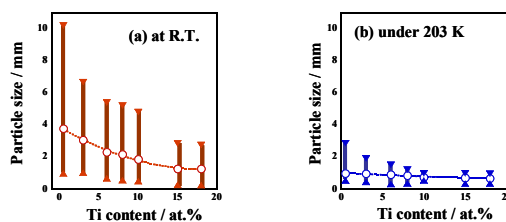


Fig. 2 The average particle sizes and deviations of the hydrogenated Nb-Ti alloy powders as a function of Ti content, which were ball-milled for 60 minutes at room temperature (a) and below 203 K (b).

4. Summary

Hydrogen induced pulverization was investigated for Nb-Ti alloys consisting of a single-phase Nb solid solution. Cracks were propagated in the alloys, resulting in pulverization to flakes like powder, when they were annealed at 1473 K and cooled in a hydrogen atmosphere. The brittle fragments produced by hydrogen induced cracking were beneficial for further refinement of particle size. Additionally, a friability of hydrogenated alloys was enhanced by increasing Ti content and lowering the milling temperature; and fine Nb-Ti alloy powders having good size uniformity can be produced using hydrogenation and mechanical milling procedures. Dehydrogenation at a temperature higher than 724 K permitted to obtain hydrogen-free Nb-Ti powders.

5. References

- [1] K. Kukli, M. Ritala and M Leskela, *J. Electrochem. Soc.*, **148** (2), F35.
- [2] N. Eliaz, D. Eliezer and O. L. Olson, *Mater. Sci. Eng. A.*, **A289**, 41(2000).
- [3] S. Semboshi, N. Masahashi, T.J. Konno and S. Hanada, *Metall. Mater. Trans. A.*, **37A**, 1301 (2006).
- [4] S. Semboshi, N. Masahashi and S. Hanada, *Metall. Mater. Trans. A*, **34A**, 685 (2003).
- [5] J.M. Welter and F. Schondube, *J. Phys. F: Met. Phys.*, **13**, 529 (1983).