Int. Journal of Refractory Metals and Hard Materials 29 (2011) 134–137

Contents lists available at ScienceDirect

Int. Journal of Refractory Metals and Hard Materials

journal homepage: www.elsevier.com/locate/IJRMHM

# Niobium hydrogenation process: Effect of temperature and cooling rate from the hydrogenation temperature

S.B. Gabriel [a,*], G. Silva [b], K.C.G. Candioto [c], I.D. Santos [d], P.A. Suzuki [c], C.A. Nunes [c]

[a] *Centro Acadêmico de Volta Redonda, Volta Redonda, (RJ), Brazil*
[b] *Universidade do Vale do Paraíba, São José dos Campos, (SP), 12244-000, Brazil*
[c] *Universidade de São Paulo, Escola de Engenharia de Lorena, Lorena, São Paulo, Brazil*
[d] *Pontifícia Universidade Católica do Rio de Janeiro, Rio de Janeiro, Brazil*

ARTICLE INFO

*Article history:*
Received 29 May 2010
Accepted 16 September 2010

*Keywords:*
Niobium powder
Hydride
Hydrogenation

ABSTRACT

High-purity niobium powder can be produced via the hydrogenation and dehydrogenation processes. The present work aimed at the effect of temperature and cooling rate conditions on the niobium hydrogenation process using hydrogen gas. The hydrogen contents of the materials were evaluated by weight change and chemical analysis. X-ray diffraction (XRD) was performed to identify and determine the lattice parameters of the formed hydride phases. No hydrogenation took place under isothermal conditions, only during cooling of the materials. Significant hydrogenation occurred in the 500 °C and 700 °C experiments, leading to the formation of a β-$NbH_x$ single-phase material.

## 1. Introduction

The metal niobium has been used in different applications due to its outstanding properties such as high melting point (2468 °C), relative low density, suitable nuclear properties, good corrosion strength and biocompatibility [1,2]. Powder Metallurgy Technique (PM) is a process route for the production of niobium-base parts from niobium powder and involves several application areas such as aerospace, chemistry, electronics and nuclear [1].

Niobium powder can be obtained by the hydrogenation–dehydrogenation (HDH) process [3–5]. The introduction of hydrogen atoms (hydrogenation) in the interstitial sites of the bcc niobium metal promotes the metal embrittlement. Through a mechanical grinding process, the hydrogenated material is reduced to fine powder, and then hydrogen is removed (dehydrogenation) from the powder, producing the niobium powder. The HDH technique has been used to obtain powders of niobium, tantalum, titanium and their alloys. The advantage of the HDH technique, compared with others is its relatively low cost [6]. Fundamental information concerning the thermodynamics and kinetics aspects associated to this technique has been extensively reported [3–5,7–13]. The Nb–H phase diagram [14] shows the following stable phases: i) α and α′ phases: disordered solutions where the hydrogen atoms are randomly distributed in the tetrahedric interstitial sites of the bcc niobium structure with low and high concentrations of hydrogen, respectively. They belong to the *Im3m* space group [15] and the lattice parameter *a* of α and α′ varies linearly with the concentration of hydrogen [16]; ii) β phase—an ordered solid solution where the hydrogen atoms occupy defined tetrahedric positions in an orthorhombic structure, space group *Ama2* [15], presenting the designation $NbH_x$ ($0.7<x<1.1$) [16]. This is the phase of interest because of its high brittleness and is usually designated as niobium hydride. The lattice parameters *a*, *b* and *c* of the β-$NbH_x$ phase vary according to its hydrogen content [17]. The lattice parameters for the $NbH_{0.89}$ composition registered in the JCPDS data base (7–263) are: $a = 4.84$ Å, $b = 4.90$ Å and $c = 3.45$ Å [18].

In spite of the significant amount of data concerning the fundamental aspects of niobium hydrogenation and dehydrogenation, there is a lack of data on technological aspects of niobium powder production by the HDH process. Thus, in this work results concerning the niobium hydrogenation process focusing on the effects of temperature and cooling rate from the hydrogenation temperature are presented.

## 2. Experimental procedure

The Nb material used in this work was initially in the form of chips which had been machined from an Nb ingot produced via electron beam melting. Before hydrogenation, the chips were submitted to the following cleaning steps, in this order: washing in a soap solution at 60 °C; washing in pure water; sinking in isomethilbutilcetone solution; washing in pure water; sinking in acetone; and drying. After these cleaning steps the material was etched using a $HNO_3$:HF:$H_2O$ solution (1:1:2.5-volume), washed with pure water and then dried at 120 °C for 1 h in air.

The hydrogenation experiments were carried out in a stainless steel reactor using approximately 200 g of Nb chips in each experiment.

---

* Corresponding author. Tel.: +55 2433213848.
*E-mail address:* sinarab@msn.com (S.B. Gabriel).

0263-4368/$ – see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.ijrmhm.2010.09.006

**Table 1**
Hydrogen content (wt-1) of the hydrogenated materials produced by cooling using forced air (VC) from different temperatures.

| Hydrogenation temperature (°C) | Hydrogen weight contents (wt.%)—wt-1 |
|---|---|
| 400 | 0.0 |
| 450 | 0.1 |
| 500 | 0.9 |
| 700 | 0.9 |

Initially, the chips were placed inside the reactor, which was then closed and evacuated at room temperature (RT) up to $10^{-2}$ mbar. The reactor was then heated under vacuum in a furnace up to the initial temperature of each experiment (400, 450, 500 and 700 °C). After reaching the desired temperature, hydrogen gas (99.995% purity) was injected into the reactor up to a pressure of 1.5 atm, keeping the pressure and temperature constant for 1 h. The reactor was then allowed to cool down to RT under constant pressure of hydrogen (1.5 atm). Three different cooling conditions were carried out: (1) reactor removed from the furnace then cooled using forced air (VC — ~15 °C/min), (2) reactor removed from the furnace then cooled under static air (~AC — 10 °C/min), and (3) furnace cooled (RC ~0.7 °C/min). All the hydrogenated materials were mechanically milled under the same conditions in an epicycloidal mill with pitcher and balls of pure Nb, the milled material being referred here as hydride powder.

In this work, the hydrogen content of the materials is based on the mass variation (before and after hydrogenation), referred as wt-1. The hydrogen contents determined via chemical analysis are referred as wt-2.

Additional experiments were carried out in order to produce the β-$NbH_x$ phase of different H/Nb (atomic) ratios in order to evaluate the effect of this ratio on its lattice parameters.

The phases present in the hydride powder were determined via X-ray diffraction (Cu-Kα radiation), with its lattice parameters refined using Rietveld method. The hydride powder morphology was also evaluated via scanning electron microscopy (SEM).

## 3. Results and discussion

The first important experimental finding was that the Nb chips could not be hydrogenated isothermically in any temperature from 400 °C to 700 °C. The hydrogenation only occurred during cooling of the reactor from high temperature. Several experiments were carried out in order to destabilize the very thin oxide layer present on the surface of the Nb chips in order to isothermically hydrogenate the material, however, no success was achieved.

Table 1 shows the hydrogen content (wt-1) of the hydrogenated materials produced by cooling using forced air (VC) from different temperatures. No hydrogenation and partial hydrogenation occurred in the 400 °C and 450 °C experiments, respectively. However, in the 500 and 700 °C experiments, extensive hydrogenation was observed, the hydrogen contents being near 0.9 wt.% for both materials.

Table 2 shows the hydrogen contents (wt-1) of the materials from the 450, 500 and 700 °C experiments, for the different cooling rates imposed. Partial hydrogenation took place in the 450 °C experiments for all cooling conditions. On the other hand, similar hydrogenation occurred in the 500 and 700 °C experiments, all leading to near 0.9 wt.% H in the materials. The hydrogen contents of the 500 and 700 °C experiments were all statistically equivalent from ANOVA statistical analysis (α = 0.05).

**Table 2**
Hydrogen contents (wt-1) of the materials from the 450, 500 and 700 °C experiments, for the different cooling rates imposed.

| T (°C) | VC (15 °C/min) | AC (10 °C/min) | RC (0.7 °C/min) |
|---|---|---|---|
| 450 | 0.1 | 0.1 | 0.1 |
| 500 | 0.9 | 0.8 | 0.9 |
| 700 | 0.9 | 0.8 | 0.9 |

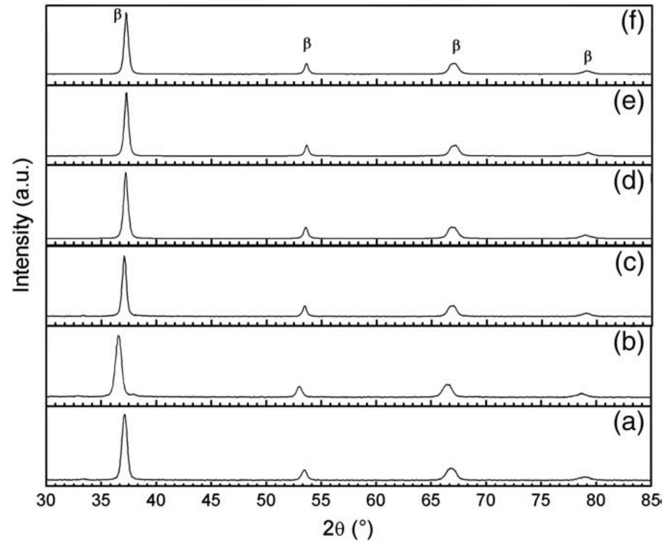

**Fig. 1.** XRD patterns of the hydride powder obtained in the experiments: (a) 500 °C-VC (b) 500 °C-AC, (c) 500 °C-RC, (d) 700 °C-VC, (e) 700 °C-AC and (f) 700 °C-RC.

The hydrogen contents of the materials from the 500 and 700 °C experiments, measured by chemical analysis (wt-2), were all close and near 1.2 wt.%, which is not significantly different from the 0.9 wt.% value of the wt-1 method.

Fig. 1 shows the X-ray diffraction (XRD) pattern of the niobium hydride powder from the 500 and 700 °C experiments. In all the patterns, the reflections were indexed with data from the β-$NbH_{0.89}$ phase [18]. No peaks associated to the chip material (Nb) could be observed, indicating a complete (or near complete) hydrogenation of the Nb chips in the 500 and 700 °C experiments.

Fig. 2 shows the variation of the lattice parameters *a*, *b* and *c* of the ß-$NbH_x$ phase as a function of the H/Nb ratio (atomic). A small variation was observed in the lattice parameters ($\Delta a = 0.018$ Å, $\Delta b = 0.032$ Å and $\Delta c = 0.032$ Å) with a change of the H/Nb ratio from 0.7 to 1.1 in the ß-NbHx phase. The increase of lattice parameters is attributed to the entry of H atoms in the tetrahedric sites of the bcc Nb structure [11]. The estimated standard deviation of the lattice

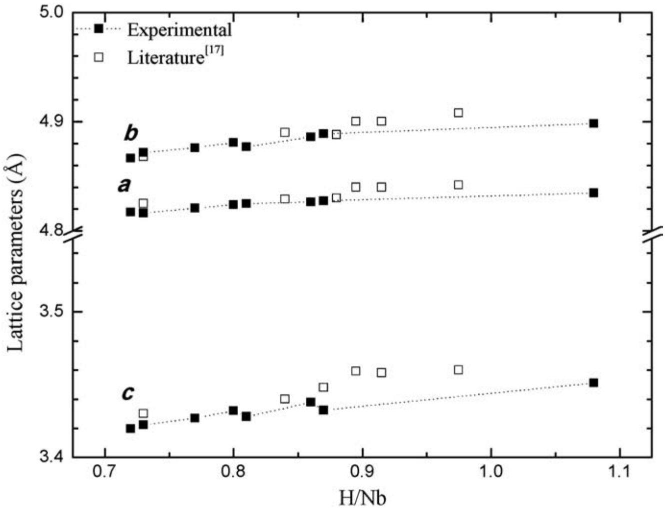

**Fig. 2.** Lattice parameters *a*, *b* and *c* of the β-$NbH_x$ phase as a function of the H/Nb ratio.