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Kinetics of thermal decomposition of niobium hydride

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A B S T R A C T
High-purity niobium powders can be obtained from the well-known hydride–dehydride (HDH) process. The aim of this work was the investigation of the structural phase transition of the niobium hydride to niobium metal as a function of temperature, heating rate and time. The niobium powder used in this work was obtained by high-temperature hydriding of niobium machining chips followed by conventional ball milling and sieving. X-ray diffraction measurements were carried out in vacuum using a high-temperature chamber coupled to an X-ray diffractometer. During the dehydriding process, it is possible to follow the phase transition from niobium hydride to niobium metal starting at about 380 °C for a heating rate of 20 °C/min. The heating rate was found to be an important parameter, since complete dehydriding was obtained at 490 °C for a heating rate of 20 °C/min. The higher dehydriding rate was found at 500 °C. Results contribute to a better understanding of the kinetics of thermal decomposition of niobium hydride to niobium metal.

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1. Introduction

Refractory metal powders like niobium, tantalum and their alloys can be obtained through the hydride–dehydride (HDH) process. In this process, the embrittlement of the metal is promoted through hydrogen dissolution in interstitial sites of the bcc structure forming brittle hydrides [1–7]. Through mechanical milling, the material is reduced to the powdered form. Following, the material undergoes dehydriding by heating under vacuum to obtain the corresponding metal powder. The great advantage of this technique is its low cost compared to other techniques such as atomization or electrolysis in molten salts [8].

During the dehydriding process the following crystalline phases are involved: i) β phase — an ordered interstitial solid solution with an orthorhombic structure, space group Amm2 [9]. The hydrogen atoms occupy the tetrahedral positions leading to a stoichiometry close to NbH4, where 0.7<x<1.1 [7,10]. This phase is normally designated as niobium hydride and it is extremely brittle. The lattice parameters a, b and c of the β-phase NbH4 present measurable variations as a function of the composition [6,11]. The lattice parameters of the β-phase NbH4, with a composition NbH4.95 registered in JCPDS data file (7–263 card) are a = 0.484 nm, b = 0.490 nm and c = 0.345 nm [12] and ii) α phase — disordered hydrogen solution in the tetrahedral interstitial sites of the niobium structure, that crystallizes in body-centered cubic structure, with low hydrogen content. It belongs to the space group Im3m [9]. The lattice parameter of the α phase varies linearly with the hydrogen concentration [10].

Understanding the underlying mechanisms associated to absorption and desorption of hydrogen in metal powders is necessary, for instance, to select suitable materials for solid hydrogen storage devices [13]. Literature brings a few examples where these investigations are carried out using specific experimental conditions and samples with simple geometries far from the actual conditions found in the manufacture of metal powders. Pick reported the calculation of the activation energy of hydrogen absorption and desorption in niobium foils using other techniques than X-ray diffraction [14]. Zheng and Zhang [15] reported results on the experimental determination of the activation energies for absorption and desorption of hydrogen electrochemical permeation in pure iron for distinct surface treatments.

For a better understanding of the dehydriding process in powdered samples, the phase transition from niobium hydride (β phase) to niobium (α phase) as a function of variables such as temperature, heating rate and time was investigated in this work by performing controlled X-ray diffraction experiments at high temperatures.

2. Experimental procedure

The niobium hydride powder used in this study was obtained by means of hydriding of niobium chips (99.9%). The machining chips were washed in soap solution at 60 °C followed by rinsing in a series of organic solvents, pure water and drying. Afterwards the material was etched using a HNO3:H2O solution (1:1:2.5–volume), rinsed with pure water and then dried at 120 °C for 1 h in air. The hydriding batch
experiments were carried out in a stainless steel reactor using approximately 200 g of Nb chips. 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 800 °C. After reaching the desired temperature, hydrogen gas (99.995% purity) was injected into the reactor up to a pressure of 1.5 bar, keeping both pressure and temperature constant for 1 h. The hydriding process takes place during cooling of the material under constant hydrogen pressure. After hydriding, the material was ball milled resulting in a hydride powder with mean particle size smaller than 20 μm.

In order to identify the phases present in the hydride powder, X-ray diffraction experiments were carried out using a SEIFERT diffractometer, model ISO-1001 DEBYEFLEX under the following conditions: Cu-Kα radiation (λ = 0.15418 nm); Ni filter; 40 kV; 30 mA, 2θ = 20°–90°, step 0.05° and counting time of 3 s. The diffractograms were compared with those from simulated patterns, using the Powdercell software and crystallographic data of niobium hydride[9] and pure niobium[12].

The diffraction experiments at high temperatures were performed under high vacuum using a Büehler HDK2.4/SO chamber attached to the SEIFERT diffractometer. The following conditions were adopted: Cu-Kα radiation (λ = 0.15418 nm); Ni filter; 40 kV; 30 mA, 2θ = 20°–90°, step 0.05° and counting time of 2 s. The measurements were made in a narrow angular range (35.0° ≤ 2θ ≤ 40.0°), where the most intense reflections of the niobium hydride (111) and pure niobium (110) are found.

Measurements were conducted by using different conditions, according to Tables 1 and 2. Table 1 presents experiments performed at temperatures from 380 °C to 520 °C. For each experiment, the sample was initially heated to 380 °C and a measurement was done. The sample was then heated in steps of 20 °C using different heating rates in order to perform isothermal measurements.

For the experiments in Table 2, the samples were directly heated to the desired temperature and isothermal measurements performed as a function of time. The relative amounts of α and β phases during dehydriding were estimated from the integrated intensity of the (111) reflection of β-phase, using the following equations:

\[
\%\beta\ phase = \frac{I_β}{I_β(T_r) + 100}
\]

\[
\%\alpha\ phase = 100 - \%\beta\ phase
\]

where, 

\[I_β(T_r)\] intensity of the (111) reflection of the β-phase

\[I_β\] intensity of the (111) reflection of the β-phase at room temperature

3. Results and discussion

In the diffractogram of the hydride powder, only reflections from the β hydride phase were observed. The diffraction patterns from the experiments according to Table 1 (heating rate of 20 °C/min — experiment #3) are shown in Fig. 1. It is possible to notice that the onset of dehydriding occurs at a temperature near 400 °C. The absence of a peak position shift for the (111) β-phase reflection indicates that there is no significant variation of the lattice parameter of this phase during dehydriding, indicating that a possible decrease of lattice parameter due to hydrogen removal could be compensated by thermal expansion effects. The α and β phases amounts as a function of temperature for experiment # 3 is shown in Fig. 2, noting that at 500 °C most of the β → α transformation has already occurred.

The amount of α-phase as a function of time and temperature for different heating rates (Table 1) is shown in Fig. 3. It is possible to notice that the onset of dehydriding occurs near 380 °C for all the conditions. It is observed that at the highest heating rate (20 °C/min), total dehydriding takes place. On the other hand, partial dehydriding occurred for heating rates of 5 °C/min and 10 °C/min, despite a longer duration of these experiments. No reasonable explanation could be found for these findings and further investigations are necessary to address this point.

Fig. 4 shows the amount of α-phase as a function of time for isothermal experiments at 500 °C (Table 2, experiments # 7 and # 8). The zero in the time scale corresponds to the moment when the temperature of 500 °C temperature is reached in each experiment. The time required for complete dehydriding at a heating rate of 20 °C/min is considerably shorter than that when applying a heating rate of 5 °C/min. In addition, complete dehydriding was not achieved for the smaller heating rate. This result is an agreement with those previously discussed, showing a more efficient dehydriding for higher heating rate.

Fig. 5 shows the α-phase proportion as a function of time for isothermal measurements at 420, 480, 490 and 500 °C for a heating rate of 20 °C/min (Table 2). In the time of the experiments, complete dehydriding was observed only for runs performed at 490 and

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<td><strong>Table 2</strong></td>
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<td>Dehydriding experiments under isothermal conditions. The samples were heated to the test temperature and isothermal measurements were performed as a function of time.</td>
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<td><strong>N° of the experiment</strong></td>
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**Fig. 1.** Diffractograms from the dehydriding experiment #3 (Table 1).
500 °C. The behavior exhibited by the curves can be fitted by a sigmoid function [16].

The data on the kinetics of thermal decomposition of the niobium hydride can be obtained from the curves of α-phase proportion versus time for isothermal conditions. In general, the rate of hydride decomposition as a function of temperature can be described by an Arrhenius-type equation:

\[
A = A_0 \exp\left(-\frac{E_o}{kT}\right) \tag{3}
\]

where,

- \(A\) decomposition rate;
- \(A_0\) constant;
- \(E_o\) activation energy;
- \(k\) Boltzmann constant
- \(T\) absolute temperature.

The natural logarithm of the decomposition rate can be linearly correlated with the reciprocal temperature \((1/T)\) and the activation energy determined by the slope.

The time required for decomposition of half of the hydride \((t_{1/2})\) was obtained from data displayed in Fig. 5. Fig. 6 shows \(\ln\left(\frac{(t_{1/2})}{t_{1/2}}\right)\) as a function of the inverse of temperature. The linear fitting of these data resulted in the following equation:

\[
y = 8(5) - 9(5)10^3 x \tag{4}
\]

The apparent activation energy calculated from the slope of the curve gives 74 kJ mole\(^{-1}\). This value is close to the value reported in the literature for \(\beta\)-NbH \((77\) kJ mole\(^{-1}\)) and slightly higher than the values reported for the thermal decomposition of \(\beta\)-MgH\(_2\) \((62\) kJ mole\(^{-1}\)) [17] and TiH\(_2\) \((63\) kJ mole\(^{-1}\)) [5]. It is worth mentioning that the apparent activation energy of the dehydriding process may be related to other mechanisms and only its magnitude is reliable for purpose of comparison.

4. Conclusions

The onset of the structural transition of niobium hydride to niobium starts at about 380 °C. It was found that the heating rate during dehydriding is an important variable, since complete dehydriding was obtained at 490 °C for a heating rate of 20 °C/min.

The kinetics of dehydriding is higher at the beginning of the process. The concentration curve of \(\alpha\) phase versus time can be described by a sigmoid function. The apparent activation energy of the
decomposition of the niobium hydride was found to be 74 kJ mole\(^{-1}\). This apparent activation energy is in agreement with the value of decomposition heat of niobium hydride reported in the literature.

The proportion of \(\beta\) phase can be calculated from an equation that correlates the integrated intensity of \(\alpha\) and \(\beta\) phases provided by high-temperature X-ray diffraction measurements.

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### References


