Hydrogen Absorption and Desorption by Niobium and Tantalum

V. A. Dekhtyarenko, D. G. Savvakin, O. O. Stasiuk,
and D. V. Oryshych

G. V. Kurdyumov Institute for Metal Physics, N.A.S. of Ukraine,
36 Academician Vernadsky Blvd.,
UA-03142 Kyiv, Ukraine

Studies are shown that tantalum and niobium have different kinetics of hydrogen uptake. Tantalum, in contrast to niobium, is able absorb actively hydrogen at room temperature, reaching a hydrogen capacity at the level of $TaN_{1.9}$. Active absorption of hydrogen by niobium is observed only at heating to temperatures of 400−500°C, reaching the hydrogen capacity of $NbH_{1.23}$. The kinetics of hydrogen evolution from both hydrogen-saturated metals is similar, the process takes place at room temperature, but in different pressure conditions.

Key words: niobium, tantalum, hydrogenation, dehydrogenation, powder.

Проведене дослідження показало, що тантал та ніобій мають різну кінетику поглинання Гідроґену. Тантал, на відміну від ніобію, здатен активно поглинати Гідроґен при кімнатній температурі, досягаючи водневої місткости на рівні $TaH_{1.9}$. Активне поглинання Гідроґену ніобієм спостерігається лише при температурах 400−500°C, досягаючи водневої місткости $NbH_{1.23}$. Кінетика виділення Гідроґену з обох насичених Гідроґеном металів має схожий характер, процес відбувається при кімнатній температурі, але в різних баричних умовах.

Ключові слова: ніобій, тантал, гідрування, дегідрування, порошок.

Corresponding author: Volodymyr Anatoliyovych Dekhtyarenko
E-mail: Devova@i.ua

1. INTRODUCTION

Influence on the phase composition and physical and mechanical characteristics of metallic materials through their interaction with hydrogen is the basis of many technologies. In particular, the temporary saturation of metals and alloys with hydrogen provides an effect on the defects of their crystal structure, phase composition and microstructure (so-called hydrogen treatment) [1, 2], which is used to achieve the desired mechanical properties. Metal hydrides are brittle and rather low-strength materials compared to the source materials [3, 4]. Such mechanical characteristics of hydrides facilitate their grinding to obtain powders of a desirable dispersion, so the technology of hydrogenation-grinding and dehydrogenation of metals is widely used in the production of powders [5, 6]. In addition, a number of powder technologies for the manufacture of alloys are based on the use of hydrogen-saturated powders [7−9] as starting materials, which provides significant advantages for achieving the desired sets of characteristics of the final alloys. In particular, atomic hydrogen released from the crystal lattice of metals is able to reduce surface oxide films, which are always present on the surface of particles and are barriers to mutual diffusion in the powder system [10−12]. These phenomena lead to a significant activation of diffusion processes that accelerate sintering and chemical homogenization of blended elemental powder systems.

Hydrogen-saturated powders of titanium and zirconium are used for the synthesis of alloys based on these metals, including alloys of Ti−Zr−Nb and Ti−Zr−Nb−Ta systems, which are promising biomedical materials [13−20]. The production of alloys of these systems from multicomponent powder blends requires the use of starting powders of a determined size. Since niobium and tantalum are plastic metals [21], the production of powders of a given fraction is a complicated process. However, [22] like most transition metals, niobium and tantalum are able to inversely interact with hydrogen, and accordingly, obtaining hydrides based on them will allow to obtain powders of a given fraction. In addition, dissolved hydrogen in them has an additional positive contribution to the consolidation of particles under vacuum heating of the compacted powder blend.

In addition to the above, modern developments in the field of hydrogen energy are important, which require detailed knowledge of the kinetics of the processes of inverse saturation of materials with hydrogen for the development of hydrogen batteries [2, 23−25]. That is why the conditions of interaction of various metals and alloys with hydrogen, including thermal, pressure and time parameters of hydrogen saturation and the reverse process of hydrogen evolution from metals, are extremely important data for basic knowledge and applied developments.

The purpose of this study is to establish the temperature-pressure conditions of sorption−desorption of hydrogen by tantalum and niobium, which will allow the use of these hydrogenated materials in various technologies, in particular, to obtain powders of a given fraction.

2. EXPERIMENTAL/THEORETICAL DETAILS

Niobium of industrial production ГОСТ 26252-84 and tantalum ГОСТ 492-73 were used as starting materials. Industrially produced niobium powder (less than 100 μm in size) was also used in some experiments.

The study of the processes of interaction of the studied materials with hydrogen, in different conditions, was carried out using the IVGM-2M equipment [26], which allows to conduct research at temperatures from −160 to 750°C and hydrogen pressures from 0.01 to 10 MPa. The amount of hydrogen absorbed by the material was calculated from the pressure difference before and after heating in the closed volume in which the study was performed (volumetric method), and also controlled by the difference in sample weight before and after hydrogen saturation (gravimetric method).

Desorption of hydrogen from hydrogenation products was investigations on an automated dilatometric complex (ADC) with a mass spectrometric [27].

Investigations of the phase composition of the obtained hydrogenation and dehydrogenation products were performed on a Rigaku x-ray diffractometer using CuK_α ($\lambda = 1.5406$) radiation.

The grinding process was performed in a Retsch PM100 planetary mill in a steel drum with steel balls for 30 seconds. The capacity of the drum is 250 ml, the speed of rotation is 650 rpm, and the diameter of the balls is 14 mm.

The size of the powder particles is determined by a laser analyser Malvern Mastersizer 2000.

3. RESULTS AND DISCUSSION

3.1. Investigations of Sorption−Desorption Processes

The study of the process of interaction of both starting materials (niobium and tantalum) with hydrogen, in the monolithic state, was carried out under the same conditions (hydrogen pressure 0.6 MPa and different temperatures), for the possibility of correct comparison. In the first stage, the test materials were kept at room temperature and the specified pressure for 24 hours. It was found that these hydrogenation conditions led to the active absorption of hydrogen by tantalum, while the absorption of hydrogen by niobium was not recorded.

The interaction of tantalum with hydrogen began from the first seconds of contact of the sample with hydrogen (Fig. 1) and lasted for 60 minutes. The amount of absorbed hydrogen was reached 1.04% wt., which corresponds to the formula composition $TaH_{1.9}$. Increasing the holding time by another 120 minutes at the same hydrogen pressure did not lead to the continuation of the absorption process (Fig. 1). The reverse process of hydrogen evolution with the obtained tantalum hydride was investigated at an initial pressure of 0.0002 MPa. The study was performed in the same chamber without contact of the sample with the atmosphere (air) between experiments. As can be seen from the dependence (Fig. 1), the process of hydrogen evolution from tantalum is occurring at room temperature without the use of thermal or mechanical activations. Thus, in 180 minutes it is possible to remove all the absorbed hydrogen from the material, this result was also confirmed by gravimetric method. In addition, another indirect confirmation of the release of all hydrogen is that after the sorption−desorption cycle the metal sample remained ductile.

However, it should be noted that for the alloys manufacturing by powder technology from hydrogen-saturated powders, the evolution of all hydrogen at room temperature is undesirable. First, non-hydrogenated tantalum is a plastic material, so its grinding to obtain powders of a given fraction is a difficult and time-consuming process. Secondly, when sintering non-hydrogenated particles, there is no positive effect of hydrogen on the activation of diffusion processes [28].
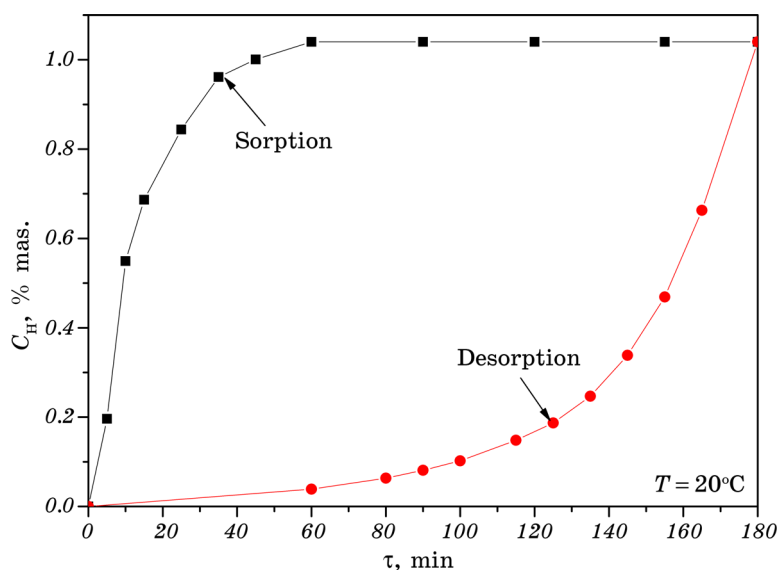

Fig. 1. Kinetics of sorption−desorption of hydrogen by tantalum at room temperature.

That is why it was important to find conditions that would allow to keep at least part of the absorbed hydrogen in the crystal lattice of tantalum at room temperature. Dissolved hydrogen in the crystal lattice increases the brittleness of the metal and, upon further heating, improves the sintering kinetics of the particles.

In the experiment described above, tantalum was saturated with hydrogen at room temperature and a hydrogen pressure of 0.6 MPa. After that, activation heating was carried out to a temperature of 600°C at the same hydrogen pressure (Fig. 2). This heating temperature was chosen by analogy with the temperature range (400−600°C) of the active interaction of titanium with hydrogen [29]. After carrying out the specified activation heating, cooling to room temperature and removing of hydrogen environment, 0.16% wt. Hydrogen in tantalum was preserved in open air, which corresponds to the composition $TaH_{0.29}$. It is important that the amount of hydrogen stored in the metal led to a significant embrittlement of tantalum, *i.e.*, to the possibility of obtaining powders of the required size fraction.

It was established by x-ray phase analysis (Figure 3) that the obtained hydrogenated product consists of tantalum, which has a cubic lattice and the unit cell parameter $a = 0.3333 \pm 0.0009$ nm, as well as tantalum hydride with orthorhombic lattice and unit cell parameters $a = 0.4810 \pm 0.0009$ nm, $b = 0.3450 \pm 0.0009$ nm, $c = 0.4801 \pm 0.0009$ nm. This result confirms that the activation heating allows to remain the
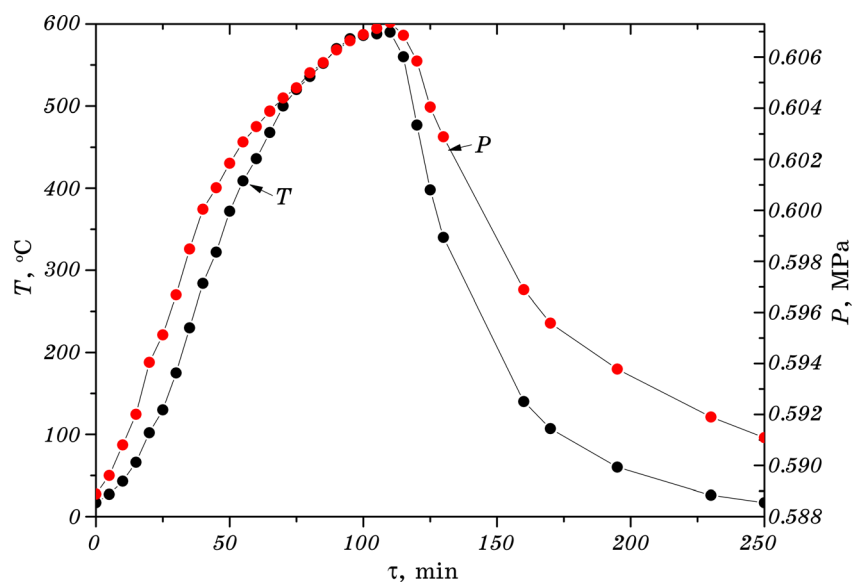

Fig. 2. Changes in pressure and temperature versus time on tantalum heating under hydrogen atmosphere.
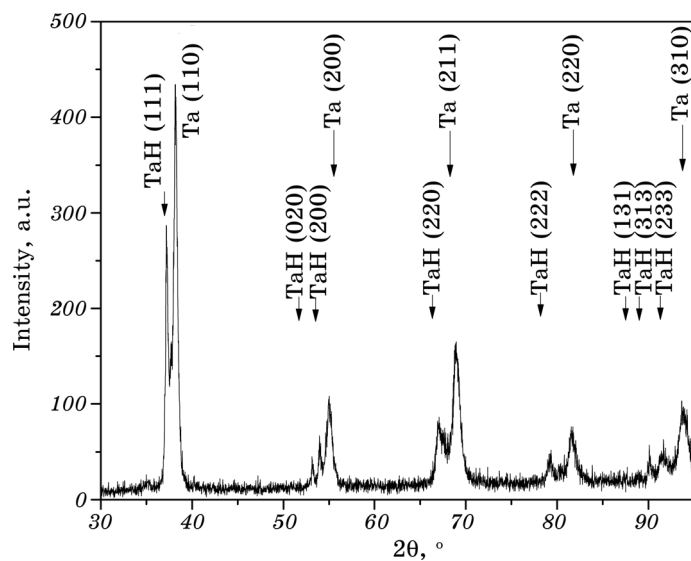
Fig. 3. X-ray diffraction patterns of hydrogenated tantalum.

part of the absorbed hydrogen in the tantalum at room temperature in open air.

As for niobium, the process of hydrogen uptake at 0.6 MPa and room temperature did not begin within 24 hours. It was suggested that the inactivated niobium surface is a barrier for hydrogen sorption, thus, this process requires a longer incubation period. To test this assumption, niobium was additionally aged at the specified hydrogenation pa-
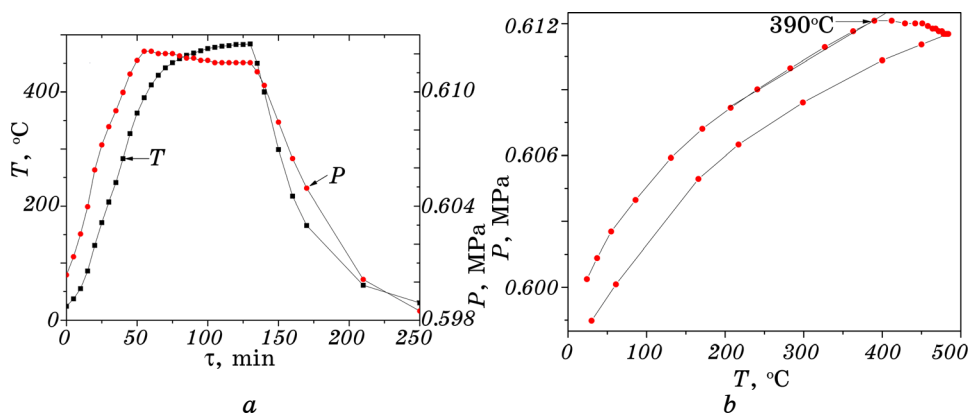

Fig. 4. Dependences at the hydrogenation of niobium: temperature and pressure of hydrogen in the chamber versus time (*a*), pressure versus temperature (*b*).

rameters for 48 hours, but the increase in holding time did not lead to appreciable hydrogen uptake. Active hydrogen uptake by niobium was recorded only during heating (Fig. 4) and during isobaric-isothermal exposure at temperatures of 400−500°C and the pressure of 0.6 MPa. This temperature range of hydrogenation was chosen by analogy with titanium [29] and tantalum for the possibility of correct comparison of the obtained data. In addition, the ability to saturate all elements necessary for the synthesis of alloys of Ti−Zr−Nb and Ti−Zr−Nb−Ta in one chamber (simultaneously) will greatly simplify the process of powder manufacturing

The temperature of the beginning of intensive hydrogen absorption by niobium was determined from hydrogen pressure-temperature dependence (Fig. 4, *b*), while the amount of absorbed hydrogen and the time required to achieve this concentration were determined from the temperature vs. time and hydrogen pressure vs. time dependences (Fig. 4, *a*). The active absorption of hydrogen for niobium begins at a temperature of 390°C, and the absorption process itself takes about 65 minutes, after which it ends. As a result, it is possible to achieve the amount of absorbed hydrogen at 1.31% wt., which corresponds to the formula composition of $NbH_{1.23}$. The movement of hydrogen-saturated niobium from the hydrogen environment to open air at room temperature leads to the beginning of the reverse process of hydrogen evolution. Under these conditions, the concentration of absorbed hydrogen
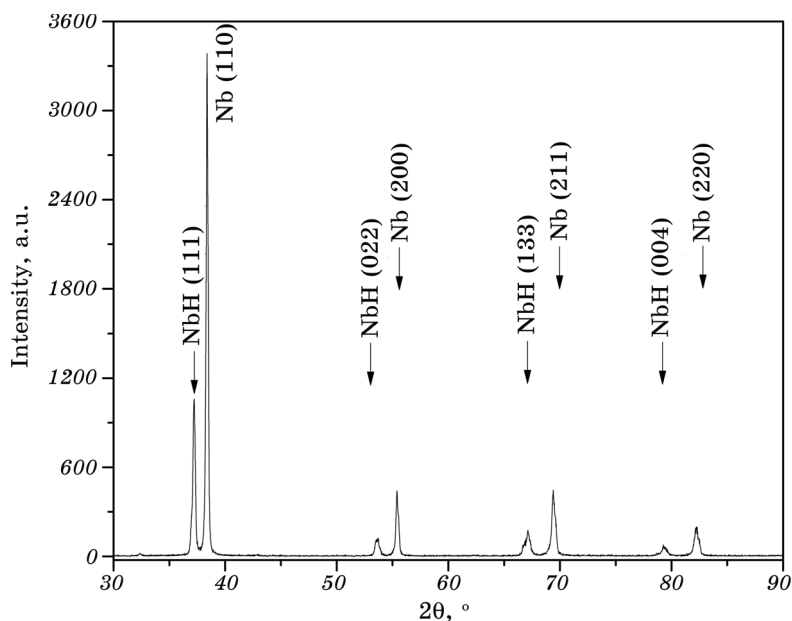

Fig. 5. X-ray diffraction patterns of hydrogenated niobium.

in niobium is reduced to 0.52% wt., which corresponds to the formula composition $NbH_{0.48}$.

It was determined by x-ray phase analysis (Figure 5) that the obtained hydrogenated product consists of metal niobium, which has a cubic lattice and the unit cell parameter $a = 0.3314 \pm 0.0009$ nm, as well as niobium hydride phase with orthorhombic lattice and unit cell parameters $a = 0.3401 \pm 0.0009$ nm, $b = 0.4836 \pm 0.0009$ nm, $c = 0.4839 \pm 0.0009$ nm.

The process of hydrogen evolution from niobium resumes when material was placed under vacuum at room temperature. A sample of hydrogen-saturated niobium was placed in a vacuum ($4 \cdot 10^{-3}$ Pa) chamber and kept for about a day at room temperature, after which the sample was removed from the chamber and x-ray phase studies were performed again. It was found that only metal niobium is present in the structure (Fig. 6.) with the crystal lattice parameter $a = 0.3310 \pm 0.0009$ nm.

3.2. Investigations of Powders

It was important to show that the involved modes of saturation of these metals with hydrogen provide their embrittlement, which facilitates
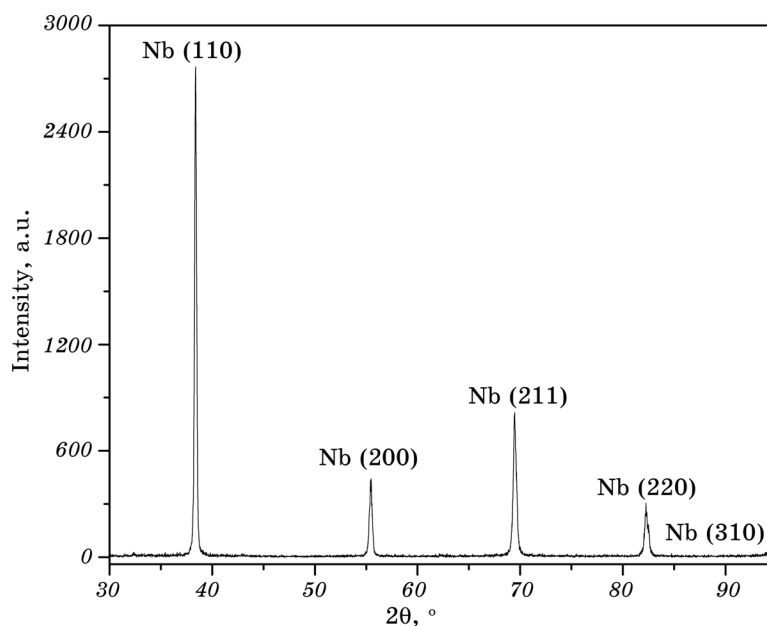

Fig. 6. X-ray diffraction patterns of preliminary hydrogenated niobium after subsequent holding in vacuum chamber at room temperature.
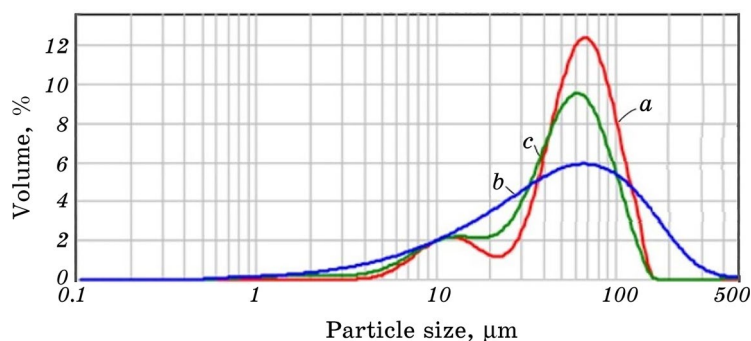
Fig. 7. Size distribution curves of niobium powder: *a*—the initial state, *b*—initial powder after grinding, saturated with hydrogen, *c*—followed by grinding.

the process of grinding and obtaining powders of a given fraction. Industrial niobium powder with an average particle size of 70 μm was selected for the study (Fig. 7, *a*). In the first stage of the study, this powder was ground in a planetary mill for 30 seconds (Fig. 7, *b*). As can be seen from the powder size distribution curve (Fig. 7, *b*), the average particle size has not changed, at the same time the number of small particles (30 μm or less) was increased and particles of significantly larger size (up to 400 μm, not observed in the original powder) appeared. The increased number of fine particles is the result of grinding the powder, however, the simultaneous appearance of large particles is associated with their deformation and adhesion to each other during grinding, which indicates their sufficient plasticity.

In the second stage, the starting powder was first saturated with hydrogen, as described above, and then subjected to grinding (Fig. 7, *c*). From the curve (Fig. 7, *c*) it is seen that the powder particles were crushed, the average particle size decreases from 70 (in the original) to 60 μm, with an increase in the relative number of smaller particles and a decrease in the number of particles larger than 60 μm. This also indicates that during grinding there is no significant deformation and adhesion of particles to each other. The obtained result suggests that the hydrogen-saturated powder is brittle enough to grind.

Summarizing all the above, it can be argued that to obtain partially hydrogenated niobium and tantalum with the formation of hydride phases, we can use the temperature range of hydrogenation of titanium (400–600°C) [29]. However, the involved hydrogen saturation modes do not allow the creation of tantalum and niobium hydrides, which would be quite stable at room temperature, retaining a significant amount of absorbed hydrogen on the air. Moreover, the release of all absorbed hydrogen by niobium that occurs in a vacuum at room

temperature is a negative trait, because of effect of hydrogen on the activation of diffusion processes during sintering is lost.

4. CONCLUSIONS

1. The process of absorption and release of hydrogen by tantalum occurs at room temperature without the use of thermal or mechanical activation treatments, solely due to changes in pressure conditions. Heating in a hydrogen atmosphere to a temperature of 600°C increases the amount of hydrogen absorbed by tantalum, and after cooling to room temperature and removing the hydrogen atmosphere allows to partially preserve hydrogen in the metal.

2. The process of active interaction of niobium with hydrogen is observed only when metal is heated to 400−500°C. The release of hydrogen from hydrogenated niobium occurs at room temperature due to changes in pressure conditions, in particular in a vacuum niobium loses all absorbed hydrogen.

3. Hydrogenated niobium and tantalum when kept at room temperature in open air partially retain the absorbed hydrogen in an amount that provides sufficient fragility of these metals and facilitates the production of powders of a desirable size fraction.

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