Study of hydrogen redistribution in Ti$_{49.1}$Ni$_{50.9}$ alloy (at %) with nanocrystalline structure by resistometric and durometer methods

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Abstract. The electrolytical hydrogenation of TiNi-based alloys with shape memory and superelasticity results in a significant (by 1.5 times) increase in the microhardness of the surface layer. It is shown that the change of microhardness at long-term aging at room temperature in wire samples of Ti$_{50.1}$Ni$_{50.9}$ (at %) alloy with nanocrystalline structure can be used for estimation of diffusion mobility of hydrogen. On wire samples with different diameters it is shown that the increase in the relative electrical resistance at 83K at long-term aging at room temperature for this alloy is also associated with the diffusion mobility of hydrogen. Estimates of the hydrogen diffusion coefficient $D_H$ show that in nanocrystalline samples Ti$_{50.1}$Ni$_{50.9}$ (at %) the diffusion mobility of hydrogen is higher than in coarse-grained samples. This is connected with the increased contribution of grain boundary hydrogen diffusion in samples with nanocrystalline structure.

1. Introduction
Titanium alloys are widely used as implants in medicine due to their high corrosion resistance, biocompatibility, good strength and specific weight [1,2]. Nickel-Titanium based alloys are distinguished in this class of alloys due to the presence of shape memory effects and superelasticity [3]. However, hydrogen penetrates into the surface layer of implants manufactured from titanium alloys as a result of preparatory operations (acid etching, sterilization, etc.), as well as during interaction with the physiological medium. The local concentration of hydrogen in the surface layer can be so high that leads to the formation of hydrides, leading to cracks in the surface layer and early destruction of implants under load [4]. In TiNi-based alloys, hydrogen atoms from the near-surface layer can be diffused from the near-surface layer into the material volume. This leads to the suppression of martensitic transformations, which determine the temperature range of functional properties [5,6]. As a result of aging at room temperature, the mechanism of embrittlement of TiNi-based alloys also changes [7]. The redistribution of hydrogen atoms is determined by their diffusion mobility, so to predict the change in properties of TiNi-based alloy products over time, it is necessary to know the hydrogen diffusion coefficient. In wire samples, which are often used in medical practice, the methods usually used to analyze the distribution of hydrogen atoms [8,9] cannot be applied.

It is known that the introduction of hydrogen into the near-surface layer of metal, for example, by chemical etching or electrolytic method leads to an increase in microhardness by quite noticeable value (one and a half times and more). The paper [10] substantiates the use of the durometry method for the study of the diffusion mobility of hydrogen atoms both in pure metals and in alloys and intermetallic
compounds, including wire samples. In this method, it is assumed that the change in microhardness during hydrogenation of samples is directly proportional to the hydrogen concentration. In case of prolonged hydrogenation, the microhardness distribution profile takes several tens or even hundreds of micrometers. It can be measured accurately and compared with the predictions that follow from the Fick equations, and thus determine the hydrogen diffusion coefficient $D_H$. The values of $D_H$ determined by this method are quite well correlated with the results obtained by direct methods.

Another method that can be used to investigate hydrogen distribution is the resistometric method. In [11,12] it is shown that increase of electrical resistivity in metals and intermetallics at hydrogenation of samples is connected with concentration of hydrogen by linear dependence. In this paper, the study of diffusion redistribution of hydrogen after electrolytic hydrogenation and subsequent aging of TiNi based alloy at room temperature by the methods of resistometry and durometry is carried out. Hydrogen diffusion coefficients were determined.

2. Materials and methods

The study was carried out on samples made of 1.1 mm and 0.55 mm wire of Ti$_{49.1}$Ni$_{50.9}$ (at %) alloy manufactured by «Matek-Sma Ltd.». The wire in the as received state had nanocrystalline structure with average grain size/subgrain of 85 nm, figure 1.

Electrolytic hydrogenation of the samples was carried out at room temperature in physiological solution (0.9% NaCl) at current density 20 A/m$^2$. Hydrogenation time was 3 hours. Under these conditions, the samples were in the high-temperature B2 phase. Measurement of concentration of hydrogen atoms was made on the gas analyzer RHEN 602 by LECO. The content of hydrogen atoms in the initial samples was 6-8 wppm. The initial hydrogen content in the samples immediately after hydrogenation was 500 wppm.

The influence of aging time and annealing temperature on the sequence and temperature of martensitic transformations (MT) was studied from the analysis of temperature dependences of electrical resistance $\rho(T)$ obtained by the four-point potential method in the temperature range (83-333) K.

Microhardness measurement of Ti$_{49.1}$Ni$_{50.9}$ (at %) alloy samples was carried out before and after hydrogenation at room temperature on the automatic complex for microhardness measurement on the basis of microhardness tester Duramin-5, Stuers A/S, Denmark (Shared use center “Nanotech” of ISPM SB RAS). The exposure time of the samples under the load of 100 grams was 10 seconds.

3. Results and discussion

Influence of aging at room temperature on temperature dependence of electrical resistance of Ti$_{49.1}$Ni$_{50.9}$ (at %) alloy samples.
One of the important characteristics, which are influenced by hydrogen atoms, is the martensite transformations temperature. In [5], the authors noted that the aging time of the samples after hydrogenation affects the development of martensitic transformations into them. In this work, the study was carried out on wire samples of Ti$_{49.1}$Ni$_{50.9}$ (at %) alloy with a diameter of 1.1 mm, with a coarse-grained structure (grain size 10 µm) and with a nanocrystalline structure (grain size 85 nm). The samples were charged with hydrogen at room temperature by electrolytic method. The results of the study showed that after hydrogenation and subsequent aging, the maximums on the heat release and absorption curves of differential scanning calorimetry and the maximums on $\rho(T)$ associated with MT R$\leftrightarrow$B19', disappear. The influence of hydrogen atoms on MT B2$\leftrightarrow$R was not detected.

In this paper, similar studies of changes $\rho(T)$ in hydrogenation under the same conditions were carried out for samples of the same composition and structural-phase state with a sample diameter half as small as in [5]. Measurements have shown that the same qualitatively similar evolution of dependences $\rho(T)$ is observed during aging, which, however, occurs much faster than in samples with a larger diameter. When the aging time increases, the value of hysteresis associated with MT R$\leftrightarrow$B19' decreases on the $\rho(T)$ dependences during cooling and heating of the samples up to its almost complete disappearance, figure 2a. It is connected with the suppression of MT R$\leftrightarrow$B19' by hydrogen atoms at cooling of samples. Figure 2b shows the change in the relative electrical resistance during aging of the samples with a diameter of 1.1 mm and 0.55 mm studied in this paper. The figure 2b shows that the rate of change in relative resistance depends on the aging time of the samples. Dependence $\Delta \rho/\rho_0$ on the aging time of the samples, shown in figure 2b, can be used to estimate the diffusion mobility of hydrogen atoms in the samples studied.

![Figure 2](image-url)

**Figure 2.** Temperature dependences of electrical resistance for nanocrystalline hydrogenated and aged samples of Ti$_{49.1}$Ni$_{50.9}$ (at %) alloy with a diameter of 0.55 mm (a) and relative change of electrical resistance at 83K for samples with a diameter of 1.1 mm investigated in [5] and 0.55 mm depending on the aging time at room temperature.

**Model for estimating the diffusion mobility of hydrogen atoms in B2 phase from resistometric data for Ti$_{50.1}$Ni$_{50.9}$ (at %) alloy samples.**

As follows from the results of the studies described above, the evolution of dependences $\rho(T)$ during the aging of samples is most likely due to the diffusional redistribution of hydrogen atoms. As the diffusion saturation of the sample by hydrogen atoms is increased, MT is suppressed in a larger volume. At the same time, the range of microstructural changes in B2 phase before the start of direct MT into B19' phase expands, that is expressed in the increase of electrical resistance on the $\rho(T)$ dependence,
and the increase of electrical resistance at 83K. At diffusion of hydrogen atoms in TiNi we have a case, which is called a case with a reflecting boundary. The fact is that there is a barrier layer TiO\textsubscript{2} on the surface of samples, the diffusion coefficient of hydrogen atoms in which is two or three orders of magnitude lower than in TiNi [13]. This leads to the fact that the diffusion of hydrogen atoms is carried out only in one direction - from the surface to the inside of the samples.

We assume that hydrogen atoms diffuse at room temperature at a distance of $\Delta r = (D_H t)^{1/2}$, where $\Delta r$ is the width of diffusion zone the wire sample, and $t$ - aging time at room temperature. In the process of diffusion hydrogen atoms fill octahedral interstitials in a crystal lattice of B2 phase in a corresponding diffusion layer of the sample that causes suppression of MT into a phase B19\textsuperscript{'} in this layer. According to [7], 100 wppm of hydrogen atoms is enough to suppress MT in TiNi-based alloys, and the average concentration of hydrogen atoms in our samples is 500 wppm. Suppression of MT in the diffusion layer causes a corresponding increase in the specific electrical resistivity at 83K by the mechanism described above on the value of $\Delta \rho$. We assume that the value of $\Delta \rho$ is proportional to the volume fraction of the material in which MT has been suppressed. In fact, this is a case of increasing the thickness of the diffusion layer in the process of so-called reactive diffusion [15]. Then, according to [15], in our case, the dependence of the change in the value of the relative resistivity on the aging time $t$ ($\Delta \rho_t(83K)/\rho_o(83K)$) can be linearized depending on $t^{1/2}$, if the process of changing the value of the relative resistivity is determined by diffusion. It is a fact that on the dependences ($\Delta \rho_t(83K)/\rho_o(83K)$ on $t^{1/2}$, which are shown in figure 3, there are linear regions.

![Figure 3](image_url)

**Figure 3.** Dependence from the aging time of the relative change in electrical resistance at 83 K for Ti\textsubscript{49.1}Ni\textsubscript{50.9} (at %) alloy with nanocrystalline structure with a samples diameter of 1,1 mm (a) and 0.55 mm (b).

In samples of alloy Ti\textsubscript{49.1}Ni\textsubscript{50.9} (at %) with diameter of 1.1 mm up to time of ageing ~ 400 hours the linear dependence is observed, and at the further ageing of samples electric resistivity does not change any more. It is logical to assume that the saturation yield is connected with the fact that the reactive diffusion has been completed, i.e. the hydrogen atoms have reached the center of the sample, and they are approximately uniformly distributed over the volume of the sample. Then the characteristic time $t_s$ of yielding the dependence ($\Delta \rho_t(83K)/\rho_o(83K)$ on $t^{1/2}$ on saturation can be used to estimate the hydrogen diffusion coefficient $D_H$. This can be done according the equation $D = r^2/2t_s$, where $r=0.55$ mm is the radius of the wire sample, and $t_s = (460\pm10)$ hours. With these parameters of the diffusion process of hydrogen atoms we obtain that $D_H \approx (9\pm0.5) \times 10^{-14}$ m\textsuperscript{2}/s.

Figure 3 also shows the data on the evolution of the relative electrical resistance dependence for wire samples of Ti\textsubscript{49.1}Ni\textsubscript{50.9} (at %) with a diameter in two times smaller than in the previous case. It should be expected that if the process of hydrogen atoms motion is controlled by diffusion, the achievement of hydrogen atoms close to uniform distribution will be achieved in four times less time for this sample. As can be seen from figure 3, the saturation yield for this series of samples is achieved at the time...
\[ t_s = (120 \pm 10) \text{ hours}, \] which is approximately four times less than for samples with a diameter of 1.1 mm. Calculations show that in this case \( D_H \approx (8.7 \pm 0.5) \times 10^{-14} \text{ m}^2/\text{s}, \) it is well coincides with the previous \( D_H \) estimate. This value of \( D_H \) is significantly higher compared to the value of \( D_H = 3.6 \times 10^{-15} \text{ m}^2/\text{s} \) obtained by extrapolation to room temperature of the \( D_H \) temperature dependence measured in TiNi samples with coarse-grained B2 structure [16].

*Estimation of the diffusion mobility of hydrogen atoms from the durometric data in Ti_{49,1}Ni_{50,9} (at %) alloy samples.*

The results of the simple diffusion model described in the previous section can be verified by another independent method. As we noted in the introduction, the hydrogen diffusion coefficient can be estimated by the change in microhardness depending on the depth of the hydrogen diffusion zone.

Figure 4 shows the microhardness distribution profiles for the depth of hydrogenated wire samples of Ti_{49,1}Ni_{50,9} (at %) with a diameter of 1,1 mm with different aging times at room temperature.

**Figure 4.** Distribution of microhardness according to the depth of hydrogenated samples Ti_{49,1}Ni_{50,9} (at %) for different aging times at room temperature. ■ - freshly hydrogenated sample, ▲ - aging time 24 hours, △ - aging time 48 hours, * - aging time 120 hours.

However, for the time of hydrogenation used in this paper (3 hours), the microhardness distribution profile of the sample depth is rather narrow, figure 4, and it is difficult to use it for correct \( D_H \) estimations. Therefore, another original scheme was used to estimate \( D_H \). At aging of hydrogenated sample, the diffusion redistribution of hydrogen atoms from the surface to the inside of the sample takes place. In this case, the value of microhardness, which is proportional to the hydrogen concentration, should decrease in the near-surface layer and increase in the deeper layers. Figure 5 shows the change in microhardness at a distance of 15 microns and 40 microns from the sample surface in the process of its aging.

**Figure 5.** Change in a microhardness at a distance of 15 microns and 40 microns from the surface as a function of aging time for hydrogenated nanocrystalline samples Ti_{49,1}Ni_{50,9} (at %).
Thus, the process of diffusion of hydrogen atoms should follow the case of diffusion from a surface source [17]. The diffusion coefficient of hydrogen atoms for this case can be calculated by the formula:

\[
D = \frac{4}{x_2^2 - x_1^2} \left( \frac{\ln H_2}{\ln H_1} \right)^{1} (4\tau)^{-1}
\]  

(1),

where \(H_1\) and \(H_2\) value of microhardness at the depth of \(x_1 = 15\) microns and \(x_2 = 40\) microns, respectively, and \(\tau\) - aging time of samples at room temperature.

Calculations have given value for effective hydrogen diffusion coefficient at room temperature \(D_H = 4 \times 10^{-14} \text{m}^2/\text{s}\). This value is close to the value of \(D_H\) obtained in the previous section for nanocrystalline samples. In [18], the durometer method obtained the value of \(D_H = 8 \times 10^{-15} \text{m}^2/\text{s}\) for coarse-grained samples in the B2 phase of TiNi, which is significantly less than in our nanostructured samples.

Thus, the estimates of the hydrogen diffusion coefficient \(D_H\) by two independent methods show that in nanocrystalline samples of Ti\(_{49.1}\)Ni\(_{50.9}\) (at %) alloy in B2 phase the diffusion mobility of hydrogen atoms is higher than in coarse-grained samples. According to the literature, the effective value of \(D_H\) in metal samples is determined by two contributions: \(D_H = (1-f) \times D_l + f \times s \times D_{GB}\), where \(D_l\) is the lattice coefficient of diffusion of hydrogen atoms, \(D_{GB}\) is the grain boundary coefficient of diffusion of hydrogen, \(f\) - relative fraction of grain boundaries, and \(s\) is the segregation factor [19]. In the case when the diffusion of hydrogen atoms along grain boundaries with high-angle misorientations of grain boundaries prevails, where the increased free volume, the effective value of \(D_H\) will increase as \(D_{GB} >> D_l\) [20]. The microstructure shown in figure 1 is characterized by the predominance of equiaxial nanograins, which is typical for grains with high-angle boundaries. Probably, it determines the increase of value of \(D_H\) in comparison with coarse-grained samples for our nanocrystalline samples.

4. Conclusion

1. It is shown by the method of temperature resistometry that electrolytic hydrogenation of nanocrystalline wire samples of Ti\(_{49.1}\)Ni\(_{50.9}\) (at %) alloy in B2 phase with the subsequent aging at room temperature leads to suppression of MT \(R \leftrightarrow B19'\) that is accompanied by a considerable increase of relative electrical resistance at 83K. Suppression of MT is connected with diffusion redistribution of hydrogen atoms in the volume of wire samples.

2. Electrolytic hydrogenation of samples leads to significant increase of microhardness of their surface layer. It is established that with the increase of aging time the value of microhardness near the surface of samples decreases, and in deeper layers it increases that is connected with redistribution of hydrogen atoms.

3. It is shown that from the kinetic dependences of the change in the relative electrical resistance and microhardness as a function of aging time it is possible to estimate the diffusion coefficient of hydrogen atoms \(D_H\) in the samples under study. The higher value of \(D_H\) in nanocrystalline samples in comparison with coarse-grained ones is associated with the increased contribution of accelerated grain boundary diffusion in samples with nanocrystalline structure to the effective hydrogen diffusion coefficient.

Acknowledgments

The work was supported by Fundamental Research Program of the State Academies of Sciences for 2013–2020 (III.23.2.2), Russian Foundation for Basic Research (grant No. 18-48-700040)

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