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Synergistic effect of hydrogen and impurity segregations on the grain boundary embrittlement in Nb

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Abstract

Niobium and its alloys are the candidate materials for fusion reactors and can be used at high-temperatures. This paper was intended to study embrittlement of niobium by high-concentrations of hydrogen and impurity segregation at grain boundaries. Specimens of commercial Nb were subjected to heat treatment at 1100°C and 500°C and subsequently charged with deuterium in an electrolytic cell. The charged specimens were placed into the high-vacuum chamber of a special self-made Auger electron spectrometer. They were then fractured under high-vacuum conditions and the chemistry of grain boundaries was analysed. Carbon and oxygen were found as the main impurities on the grain boundaries and effective energies for hydrogen–impurity-grain boundary interaction have been estimated. It was found that there is a noticeable reduction of fracture strength corresponding to the grain boundary oxygen and carbon segregation levels.

1. Introduction

Niobium is a very promising structural material for fusion reactors, in particular, for high-temperature applications and for tritium permeation membrane devices. Its usefulness is limited in many cases because of its susceptibility to hydrogen embrittlement. It was established that low- and medium-temperature mechanical properties of Nb are very sensitive to the presence of such impurities as carbon and oxygen. However, in many cases the heterogeneous distribution of trace impurities is more important than the average bulk concentration. This might be especially significant when a large amount of hydrogen is introduced into Nb under service conditions if there is an interaction between impurity segregation and hydrogen embrittlement. This potential synergism has not been well studied at present. This paper is intended to observe the effect of the grain boundary impurities on hydrogen embrittlement in Nb under conditions of low-speed tensile testing at room temperature.

2. Experimental procedure

The niobium samples used in this experiment contained the following impurities (wt%): O 0.036; C 0.024; S 0.007. The shape of the specimens was the same as that of Ilyin and Golovanov [1]. Specimens were heat treated at 1100°C, 1 h and then at 500°C for 1 and 2 h under a vacuum of $P = 2 \times 10^{-4}$ Pa. Grain size was about 90 μm. Specimens were charged with deuterium in an electrolytic cell with D_2O at a current density of 300 mA/cm^2. Clear grain boundary fracture was observed after 10 h of charging followed by tensile testing at a low-strain rate (2×10^{-4}). Specimens were fractured at room temperature in a high-vacuum chamber of a special Auger electron spectrometer and fracture surfaces were analysed under UHV-conditions of about 10^{-7} Pa.

3. Results

Results of Auger spectroscopy of the fracture surfaces and relative data fracture strength are presented in Fig. 1. In Fig. 2, the values of relative fracture strength are plotted against deuterium charging time for the B1-specimens.

Since sulfur has an Auger-peak near 152 eV, which can overlap with Auger-peaks of niobium (166 and

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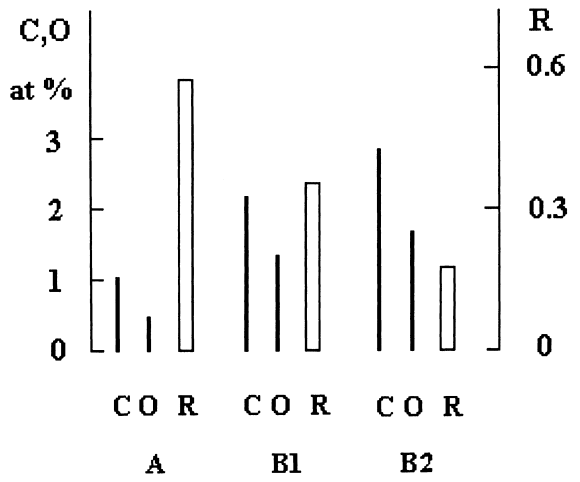

Fig. 1. Histograms – carbon and oxygen grain boundary concentrations and relative value of the fracture strength R for the embrittled specimens after heat treatment at 1100°C, 1 h (A) and after annealing at 500°C during 1 h (B1) and 2 h (B2). $R = \sigma/\sigma_0$, where σ_0 is the value for specimens without hydrogen. Statistical errors for impurity concentrations – 15%.

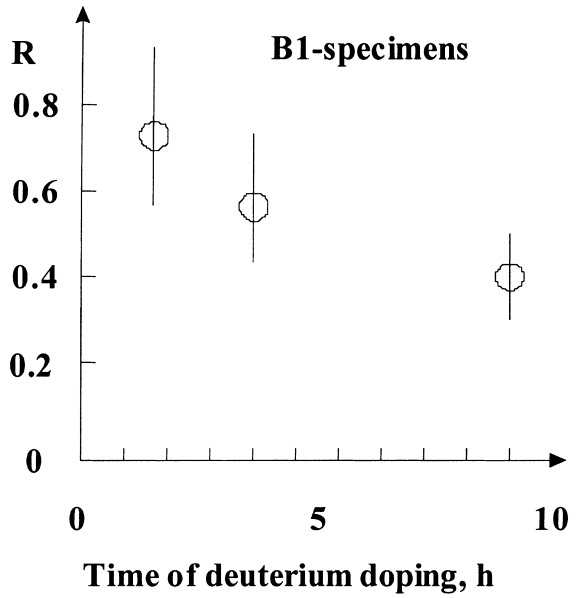

Fig. 2. Deuterium doping time dependence of the relative fracture strength, R (B1-specimens).

142 eV), we performed an accurate comparison of the spectra shapes with spectra of ductile fracture surfaces, free of sulfur segregation. Auger analysis showed that oxygen and carbon were the only impurity elements on the fracture surfaces. Some amount of carbide was observed by special treatment of the fine satellite structure of the carbon Auger-peak. It is shown in Fig. 1 that the relative fracture strength decreased when carbon and oxygen levels on the grain boundaries increased. Results presented in Fig. 2 demonstrate similar decreases in relative fracture strength with increases in deuterium charging time.

4. Discussion

The results obtained showed the significant role of grain boundary carbon/oxygen and hydrogen charged co-acting in the embrittlement of niobium at room temperature. For better understanding about possible physical mechanisms, we consider grain boundary segregation of hydrogen and some impurities. The equation of Prosen and Sachs, based on the free-electron model [2], can be used to obtain the energy of segregation as follows:

$$G = \frac{\alpha e^2}{8\pi^2}(3\pi^2\rho)^{2/3}\frac{(\ln 2r(3\pi^2\rho)^{1/3})}{r^2}K_{\mathrm{m}} + E(\mathrm{H},\mathrm{i})\,K_{\mathrm{i}},$$

where α is the polarizability of the adsorbate (here it was used the electron contribution into α), ρ the free electron density, r is the distance between the adsorbate atom and metal surface. K_{m} and K_{i} are the relative parts of a free metal surface and that covered with impurity, $E(\mathrm{H},\mathrm{i})$ is the hydrogen–impurity interaction energy on the grain boundary [3]. The bonding energy increases with ρ. It is well known that carbon and oxygen are electron donors, providing an increase in ρ. This suggests that when hydrogen segregates to a grain boundary containing C or O, the bonding energy tends to increase. Moreover, the same effect will take place for C or O atoms segregating to a grain boundary containing hydrogen. For the Nb–D-system r can be as small as 5 nm. In this case the bonding energy is equal about 0.2 eV/atom. Obviously, this value relates to theoretically pure Nb-grain boundary surface. When we consider, for example, the grain boundary covered with C the interaction energy for the D–C system is much higher than 0.2 eV/atom. The bonding energy of hydrogen atoms introduced into surface cluster, consisting of X hydrogen and Y carbon atoms can be approximated by the free energy of formation for H_XC_Y. For example, in the case where $X \approx 4$, $Y \approx 1$, value for CH_4 can be used (it is equal about 0.5 eV/atom). This value can be taken as the effective grain boundary bonding energy for hydrogen. These data are sufficiently larger than that known for atomic couples C–H or O–H in the Nb-lattice [4].

5. Conclusions

The effect of grain boundary chemistry on Nb, doped by deuterium in electrolytic cell after 1100°C and 500°C treatment, on the fracture strength at room temperature has been observed. Carbon and oxygen appeared to be

the only grain boundary impurities promoting intergranular fracture.

The effective energy of hydrogen–grain boundary impurity segregation interaction was estimated.

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