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Niobium has a high corrosion resistance in many environments and is capable of replacing expensive and scarce tantalum. However, it absorbs hydrogen intensively even at a low rate of cathodic evolution of hydrogen [1].

We investigated the hydrogen embrittlement of niobium during cathodic polarization in hydrochloric acid.

Ingots of niobium obtained by electron beam melting* were rolled to a thickness of 25 mm, annealed, and rolled to a thickness of 0.2 mm. Samples 50 × 5 mm were cut along the rolling direction and annealed. As in the previous case, annealing was conducted at 1200°C for 2 h in vacuum (10^{-6} mm Hg). Hydrogen absorption tests were made by the method described earlier [2] in 0.1 N HCl + 10 mg/liter SeO_2 at a cathode current density of 0.1 A/cm² at 25°.

After hydrogen absorption, the samples were tested for hydrogen embrittlement by multiple bending (90°) in a specially designed apparatus [3]. The ductility of the metal was taken as the relative number of bends to failure:

$$F = \frac{n_H}{n_0} \cdot 100\%,$$

where n_0 is the number of bends to failure of the original material; n_H is the number of bends to failure of the samples with absorbed hydrogen.

*The niobium contained (%): C < 0.01, O ≈ 0.0078; W, Mo, Fe, Ti ~ 0.005; Ni 0.001; Ta and Si < 0.005; H < 0.001.

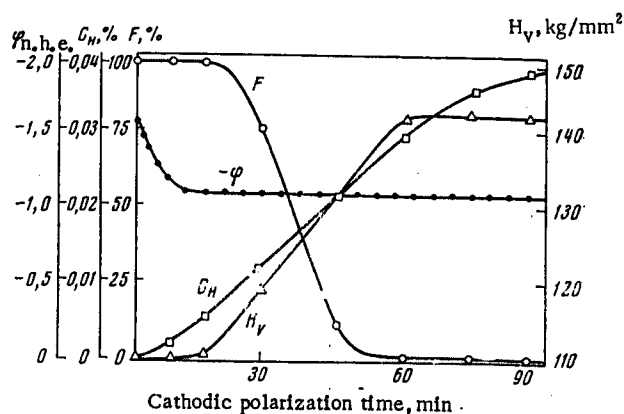


Fig. 1. Relative number of bends to failure F , microhardness H_V , hydrogen concentration C_H , and electrode potential as a function of cathodic polarization time for niobium in 0.1 N HCl + 10 mg/liter SeO_2 at a current density of 100 mA/cm² and 25°C.

The same samples were used for measurements of the microhardness, analysis for hydrogen by vacuum fusion at 950°, and metallographic and x-ray analysis (diffraction patterns in K_{α} Fe radiation with a Mn filter).

The variation of the mechanical properties with the cathodic polarization time (Fig. 1) shows three stages of hydrogen absorption. In the first stage (polarization time 15 min) the ductility and microhardness (curves F and H_V) remain unchanged. In the second stage (from 15 to 60 min) the ductility decreases and the microhardness increases. In the third stage (after 60 min of polarization) the samples become brittle and the microhardness remains constant. With continued polarization for 120 min the samples are covered with a network of cracks that are transcrystalline in the rolling direction, and then fracture spontaneously.

The hydrogen concentration of the samples increases linearly during polarization. After 60 min the hydrogen absorption slows down somewhat. The ductility begins to decline at a hydrogen concentration of 0.005%, and embrittlement occurs with 0.030% H.

The electrode potential of niobium in a solution of 0.1 N HCl + 10 mg/liter SeO_2 after the polarization current has been shut off for 10 min shifts to the positive side and then remains constant.

X-ray analysis showed a linear increase in the lattice constant of niobium from 3.300 to 3.308 Å with increasing hydrogen concentrations up to 0.033 mass %. With further increase of the hydrogen concentration the lattice constant remains unchanged, which indicates the occurrence of second phase in the Nb-H system. This phase, determined at a concentration of 0.040 mass % H, is niobium hydride with a lattice constant of 3.420 Å. Metallographic analysis of niobium containing this amount of hydrogen showed the presence of hydride phase in the grain boundaries and slip planes.

The data obtained indicate that hydrogen begins to reduce the ductility of niobium at a concentration considerably smaller than that at which the hydride phase appears. This same opinion was expressed in [4, 5] on the basis of comparing data from mechanical tests with the Nb-H phase diagram [6, 7], but was not verified experimentally. Evidently the drop of the ductility before the appearance of hydride phase is due to hydrogen in solid solution that creates stress in the lattice (second stage of hydrogen absorption). The close values of the hydrogen concentration corresponding to the change to the brittle condition and the appearance of hydride phase lead to the assumption that embrittlement of niobium occurs when hydride phase is precipitated in the metal (third stage of hydrogen absorption). Having a volume larger than that of the matrix, the hydride creates high stresses that with increasing concentrations of hydrogen are capable of inducing spontaneous fracture of the samples.

The data obtained do not exclude the fact that hydrides may be formed in niobium in the process of deformation at hydrogen concentrations below the solubility limit and affect the ductility of the metal in the second stage of hydrogen absorption. The formation of hydrides in this case may be due to local accumulations of hydrogen at obstacles during dislocation movements, which carry hydrogen atoms with them in the form of Cottrell atmospheres [9].

The shift in the potential of niobium to the positive range during cathodic polarization in a solution of 0.1 N HCl + 10 mg/liter SeO_2 may be due to the formation of a hydride film on the surface of the sample that does not prevent diffusion of hydrogen into the metal and, unlike the hydride phase in the structure, has no effect on the mechanical properties of niobium.

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