

15th International Conference on Mechanics, Resources and Diagnostics of Materials and Structures Influence of Alloying Ti, Mo, Zr on Strength and Workability of Membrane Alloys (Nb-Ni, V-Ni)

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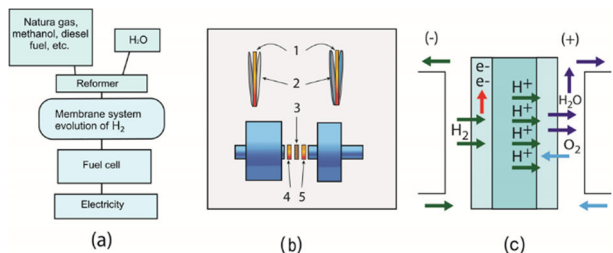


Fig. 1. Reforming of natural gases and other sources of hydrocarbon fuels (a); membrane cleaning module (b): 1-membranes, 2-protective coatings (Pd, Ni), 3- membrane, 4 and 5 sealing flanges (Cu); (c) -principle of operation of a hydrogen electric generator: hydrogen supply and oxidation reaction $2H_2 \rightarrow 4H^+ + 4e^- + O_2 = H_2O + 2H^+ + 2e^+$; poles of charges: (-) and (+).

Amorphous alloys Nb₈₅Ni₁₀Ti₅ and V₈₅Ni₁₀Ti₁₅, obtained by rapid quenching of melts in a chill mold or casting onto a rapidly rotating disk, followed by isothermal treatment at 698 K for 30 minutes in an inert atmosphere. With this heat treatment, the initial amorphous alloys (in the form of rolling disks and strips) are transformed into nanocrystalline alloys. In the same way, amorphous alloys with alloying additions – Mo, W are obtained. The obtained membrane alloys in the form of discs are tested for strength characteristics - for a fracture, under compression (compressive fracture strength). For the amorphous V₈₅Ni₁₀Ti₁₅ sample with additional doping with zirconium V₈₅Ni₁₀Ti₁₀Zr₅ Young's modulus was ~ 2770 MPa, which is significantly higher than for bulk amorphous alloys based on Pd – Cu – Zr (within 1700–1900 MPa) and for Pd – Zr – Cu – Hf (2000 –2500 MPa). The kinetic characteristics are monitored at a control injection of hydrogen and its flow through the tested membranes, Fig. 1. The applied gas pressure at the inlet is ~ 0.7-1.0 MPa and at a temperature from ~ 673K to 923K.

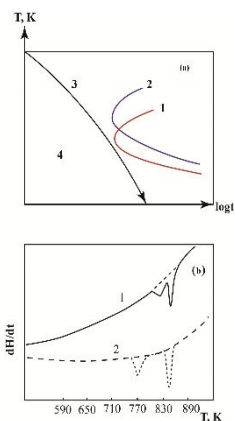


Fig. 2. Kinetic diagram of temperature and time regimes ("T-t") during rapid quenching of melts on a rapidly rotating cooler disk (a). Isothermal treatment of amorphous alloys at 698 K for 30 minutes in an inert atmosphere converts initially amorphous alloys into nanocrystalline alloys (the effect of two-stage crystallization).

The effect of substitution of Nb for Mo in crystalline alloys Nb_{80-x}Ti_xNi₁₅Mo₅ (x:5-10) [7] was also investigated with respect to microstructural features and dissolution, diffusion and penetration of hydrogen. Hydrogen diffuses through the crystalline alloy NbTi₃₀Ni₃₀, which was consisted of a primary phase BCC-Nb and a binary eutectic (BCC-Nb + B2-TiNi). Replacing Nb with Mo reduces the solubility of hydrogen in this Nb-Ti-Ni alloy. However, as the concentration of Mo increases, the diffusion and permeability of hydrogen increases. The disadvantage of amorphous membranes, Fig. 2, is their tendency to crystallization and hydride embrittlement when the operating temperatures of the 673K-723K range are exceeded. This elevated temperature promotes hydride formation and the formation of unwanted intermetallics (BCC-α and BCC-β).

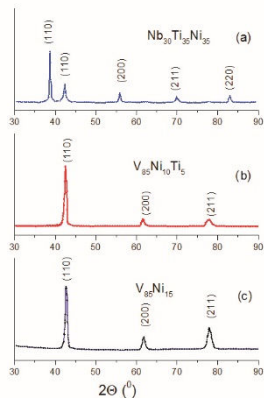


Fig. 3. Diffraction patterns of samples of membrane alloys based on niobium: Nb₄₀Ti₃₀Ni₃₀ (a) and vanadium: V₈₅Ni₁₀Ti₅ (b) and V₈₅Ni₁₅, (c).

Thus prepared ready-made samples of membrane alloys were tested for permeability and diffusion intensity and with an assessment of the released hydrogen, followed by observations (X-ray - XDR), Fig. 3, of changes in microstructures under the influence of hydrogen. According to the diagram, ternary alloys Nb – Ti – Ni are solid solutions with B2-TiNi and BCC (Nb, Ti) phases. In hydrogenated Nb-enriched solid solutions of composition Nb₃₉Ti₃₁Ni₃₀, the eutectic phase {(Nb, Ti) + TiNi} and the primary phase (Nb, Ti), respectively, with concentrations of Nb_{20.5}Ti_{38.5}Ni₄₁, but not at all concentrations of the Nb – Ti – Ni alloy hydrides are formed. Based on in-situ X-ray (XRD) data, Figure 2, the structural changes during hydrogenation (0.5 MPa H₂) in the niobium-enriched alloy Nb₆₈Ti₁₇Ni₁₅ were recorded 26 vol% of the eutectic phase Nb_{20.5}Ti_{38.5}Ni₄₁, and 74 vol.% of the primary phases Nb₄₀Ti₃₀Ni₃₀ and Nb₈₃Ti₁₃Ni₄, respectively {BCC- (Nb, Ti) + TiNi} + (Nb, Ti)} without the presence of hydride formation only due to the presence of the eutectic phase Nb₃₉Ti₃₁Ni₃₀ and also the preselected element concentrations.

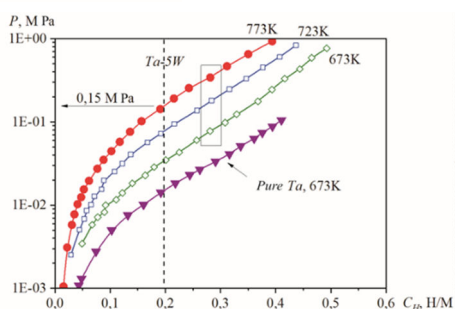


Fig. 4. Curves for the Ta_{94.9}W_{5.1} alloy obtained for the temperature range 673-773 K and hydrogen concentrations up to 0.6 H/M. For comparison, the curve for pure Ta at 673 K is also shown.

It is well established that the interaction of hydrogen with metals leads to a deterioration in their mechanical properties due to the formation of hydrides and the subsequent development of hydrogen brittleness of membrane alloys. However, elements of group 5 in their pure form lose their plasticity due to embrittlement at increased hydrogen concentrations near H / M = 0.25 not only at low temperatures, but also at functional temperatures in the range 573-773 K. However, with all advantages of these metals, the problem of hydrogen embrittlement is solved by creating not only binary alloys, but also ternary ones with alloying with elements Ti, Zr, and W. This is achieved by appropriate selection of their concentrations ensuring resistance to hydrogen embrittlement. Fig. 4 shows for comparison the curves for the membrane alloy Ta_{94.9}W_{5.1} and for pure Ta, which characterize the processes of hydrogenation and permeability. The contrast in the efficiency of the alloyed W alloy is obvious precisely due to the inhibiting properties of W and the effect of blocking hydride formation.