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ARTICLE

Mechanical Properties of Nb-Ti-Ni Alloy Membranes for Hydrogen Permeation

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Abstract: The microstructure and the mechanical property of Nb-Ti-Ni alloy membranes for hydrogen permeation were investigated. XRD and SEM were employed to characterize the structures of Nb-Ti-Ni alloys, and the bending property of the alloy membranes was measured by three-point bending tests. The results indicate that the as-prepared alloy is mainly composed of two phases, i.e. the primary bcc-Nb(Ni,Ti) solid solution phase, and [bcc-Nb(Ni, Ti)+β2-NiTi] eutectic phase. The former acts as functional cell for hydrogen permeation and the later is structural cell to keep the stability of alloy membrane. Mechanical properties of Nb-Ti-Ni alloy membranes have been improved to a certain degree by magnetic heat-treatment (MHT) along the three directions (0°, 45° and 90°). An obvious improvement has been made in the case of N7 sample by MHT at both of 0° and 45°, and in the case of N5 sample by MHT at 90° angle. MHT can lead to the change of grain sizes and grain orientations. In the case of MHT at 0° angle, a tiny bar-like region (consisting of eutectic phase) is formed and spreads along the direction of membrane surface, while some oral-like (or spot-like) region is regularly arranged on the surface, and the region extends vertically to the surface in the case of MHT at 90° angle. It is suggested that suitable MHT is beneficial to the improvement of the bending property of Nb-Ti-Ni alloy membranes.

Key words: Nb-Ti-Ni alloy membrane; hydrogen permeation; magnetic heat treatment (MHT); three-point bending test

With the increasing demand for high-purity hydrogen in fuel cells, semiconductors and other fields, considerable attention has been focused on the development of hydrogen separation and purification technology. Owing to its high hydrogen permeability, Nb-based hydrogen permeable alloy is one of the most promising candidates to replace Pd and its alloys[1,2]. However, poor mechanical properties of Nb-based alloy membranes, caused by hydrogen embrittlement, restrict its direct application. Alloying is an effective way to improve its mechanical properties. Takano et al.[3] reported that Nb39Ti31Ni30 and Nb10Zr45Ni45 had good performance of hydrogen permeation. Body-centered cubic-(Nb,Ti) phase was responsible for hydrogen permeation, and (NiTi + NbTi) eutectic phase resisted to hydrogen embrittlement; then they proposed a "Dual-phase composition, function sharing" alloy-design philosophy. Luo et al.[4] confirmed that the hydrogen permeability of Nb68Ti17Ni15 alloy with 74% (volume fraction) of the primary phase (Nb, Ti) and 26% (volume fraction) of eutectic phase ((Nb, Ti) +TiNi) reached 4.91×10^{-8} mol H^2 m^{-1} s^{-1} $Pa^{-1/2}$, which is 3.5 times as large as that of pure palladium. Tokui et al.[5] reported that the extension of (Nb, Ti) phase in Nb40Ti30Ni30 alloy was parallel to the direction of hydrogen flow, and its hydrogen permeability was 2.15 times as large as that of as-cast sample. Kishida et al.[6] also confirmed that rod-type eutectic microstructure of Nb41Ni40Ti alloy with Nb rods aligned parallel to the growth direction was obtained by directional solidification in an optical floating zone furnace. The values for the specimens with Nb rods aligned perpendicular to the membrane surface are about an order of magnitude larger than those for the specimens with Nb rods parallel to the surface. These reports supported that Nb-Ni-Ti alloy with

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reasonable properties for hydrogen permeation can be obtained by suitable composition adjustment and structural modulation.

Magnetic field is a non-contact, orientation physical fields, which can be used in crystal grow process and crystal orientation constraint by suppressing thermal convection in a conductive fluid such as heat and mass transfer in solidification process. Therefore, magnetic field is generally employed in metal solidification process in order to modify its microstructure, and obtain some special properties[7,8]. Savitsky et al[9] reported that MnBi grain was oriented along the magnetic field direction when Bi-Mn alloy was solidified in a strong magnetic field (2.5 T). Asai et al.[10] confirmed that the orientation of precipitated phase particle of Al-11%Si-2%Fe alloy was perpendicular to the magnetic field direction, and arrangement of transverse orientation of Al-Ni alloy was obtained by Ren et al. [11-13]. As we know, Ni element is a ferromagnetic material and Ti element is a paramagnetic element. So it is feasible to modify the microstructure of Nb-Ti-Ni alloys in magnetic field. In the present paper, the effects of magnetic heat-treatment on the structure and mechanical properties of Nb-Ti-Ni alloy for hydrogen permeation were investigated, and the influences of composition and phase proportion were discussed.

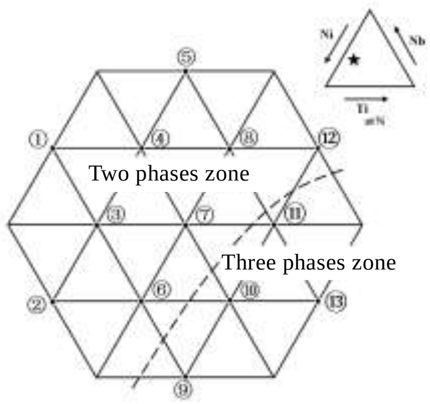
1 Experiment

The composition (at%) of Ni30Ti31Nb39 was the original one, which was adjusted by a percentage of 5at%, so a series of Nb-Ti-Ni alloys were designed and prepared. The sample diagram is shown in Fig.1. Alloy samples were produced by melting elemental Nb (purity: 99.9%), Ni (purity: 99.97%) and Ti (purity: 99.9%) in a KW-II non-consumable electrode induction melting furnace (Beijing Opto-electronic Technology limited company). The ingots were turned 2~3 times to homogenize the alloy composition. The X-ray diffraction (XRD) analysis was carried out using a Bruker D8 diffractometer (Cu Kα radiation). The surface morphologies of the alloys were examined by an JSM-5600LV scanning electron microscope (SEM, Japan Electronics Co, Ltd.), the surfaces of the samples were treated with 4% alcohol solution of nitric acid. Before the test of hydrogen permeability, the alloy membranes (Φ=12 mm, d=0.6 mm) were fabricated by the wire-cutting method, then grinding, polishing and other processes. A catalytic Pd layer for H_2 dissociation was deposited in the gas-inlet surface of the membrane by a magnetron sputtering technique.

Alloy samples with the same composition were divided into 3 groups. The angles between the membrane surface and the direction of magnetic field were 0^{o} (parallel), 45^{o} and 90^{o} (perpendicular), respectively. Magnetic heat-treatment started from room temperature to 673 K and these samples stayed for 30 min at 673 K, and then heated from 673 K to 873 K in magnetic field (B=1 T) for 40 min. At last a magnetization was stopped and the samples were cooled to room temperature for using. The heating rate of 0.5 K/s was adopted in the heating process. Fig.2 shows the equipment for magnetic heat treatment.

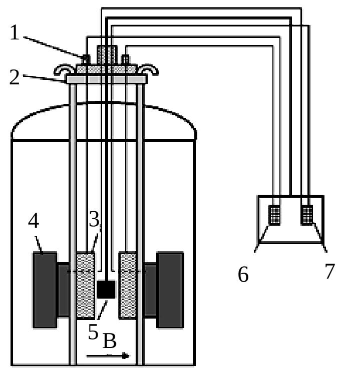
Hydrogen permeability of the membranes was measured in a double electrolytic cell by Devanathan-Stachurski (DS) methods. Before testing, a catalytic Pd layer for H_2 dissociation was deposited in the reaction side of the membrane by electrochemical plating.

In general, hydrogen-induced brittle crack is easy to be produced due to heavy stress concentration, which is induced by hydrogen absorption and desorption within the alloy membrane. A three point bending test was conducted to measure the bending stress of the membranes. When in



① Nb44Ni35Ti21， ② Nb34Ni40Ti26, ③ Nb39Ni35Ti26, ④ Nb44Ni30Ti26, ⑤ Nb49Ni25Ti26, ⑥ Nb34Ni35Ti31, ⑦ Nb39Ni30Ti31, ⑧ Nb44Ni25Ti31, ⑨ Nb29Ni35Ti36, ⑩ Nb34Ni30Ti36, ⑪ Nb39Ni26Ti35, ⑫ Nb44Ni20Ti36, ⑬ Nb34Ni25Ti41

Fig.1 Sketch map of designed alloy composition of Nb-Ti-Ni system



1-line connecting device; 2-seal valve; 3-heating furnace; 4-superconducting magnet; 5-sample; 6-temperature controller; 7-superconducting magnet controller

Fig.2 Sketch map of equipment for magnetic heat treatment the elastic range, the maximum bending stress of the sample is σ ($\sigma=M/W$). Here $M=FL_s/4$, $W=(bh^2)/6$[14], F is the bending force, L_s is span length, b and h are the width and thickness of the membrane sample, respectively. The testing device is shown in Fig.3.

2 Results and Discussion

2.1 Structure and mechanical properties of Nb-Ti-Ni alloy membranes

Some Nb-Ti-Ni alloy membranes with good hydrogen permeability were used to measure their mechanical properties by three point bending test. The results are shown in Table 1. It can be seen that after electrochemical hydrogen permeation testing (EHPT), mechanical properties of those samples inordinately decrease. Without EHPT, the maximum force is 1444.49 N for N5, and the maximum displacement is 3.15853 mm for N10 sample. While after EHPT, poor mechanical property is observed in N5 sample, and the maximum force decreases from initial 1444.49 N to 368.9 N. While, N9 sample presents better mechanical property than samples, whose maximum force is 1485.42 N, and maximum displacement is 1.195 mm, indicating that N9 has good bending strength against hydrogen embrittlement.

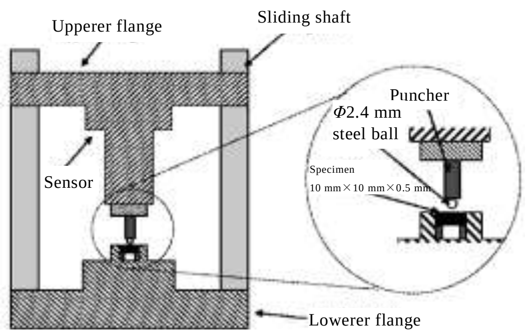


Fig.3 Schematic drawing of the experimental apparatus for three-point bending test

Material property is greatly dependent on its composition and microstructure. We can confirm that N1, N2, N3, N5, N7 and N8 are all two-phase alloys, consisting of the primary bcc-Nb (Ni, Ti) solid solution phase and [bcc-Nb(Ni, Ti)+β2-NiTi] eutectic phase[15,16]. However, a small amount of NiTi2 is also found in N9, N10 and N11 samples, which plays a "pinning" effect. In general, the primary bcc-Nb(Ni,Ti) solid solution phase acts as functional cell for hydrogen permeability. The eutectic phase is a structural cell to keep the stability of alloy membrane. Hydrogen diffusion coefficient (D) increases with increasing of proportion of precipitation of solid solution phase. The increase of Ni and Ti content will lead to higher eutectic phase volume fraction. It can be seen that N5 sample has the maximum Nb content and N10 sample has the maximum contents of Ni and Ti as shown in Table 1. SEM images of N3, N5, N7 and N9 are shown in Fig.4. It can be clearly seen that N5 sample with high Nb content has a big volume fraction of solid solution phase (Fig.4b), while N9 sample with low Nb content has a small volume fraction of solid solution phase (Fig.4d). It is suggested that net-like texture consisting with eutectic phase is easily formed in the sample with low Nb content. Such structure can effectively restrict structure expansion of solid solution phase in the process of hydrogen permeability. So N5 sample has good hydrogen permeability and poor mechanical property. And N9 sample has the opposite property according to these results in Table 1.

In terms of alloy composition and phase, the increase of Nb content will benefit the improvement of hydrogen permeability of Nb-Ti-Ni alloys. The addition of Ni and Ti will reduce hydrogen permeability to some extent, but an obvious increase of mechanical property is obtained for the formation of net-like texture. And the formation of dispersive distribution of NiTi2 phase can effectively mitigate stress concentration due to hydrogen embrittlement.

Table 1 Data of three point bending test of Nb-Ti-Ni alloy before/after hydrogen permeation test by DS method

Alloy	Alloy composition	Before hydrogen permeation test		After hydrogen permeation test	
		Max force, F/N	Max displacement, L/mm	Max force, F/N	Max displacement, L/mm
N1	Nb44Ni35Ti21	334.32	0.2306	49.27	0.1325
N2	Nb34Ni40Ti26	1079.86	1.3215	130.96	0.1490
N3	Nb39Ni35Ti26	1266.93	2.7310	217.66	0.2085
N5	Nb49Ni25Ti26	1444.49	2.6620	368.90	0.2895
N7	Nb39Ni30Ti31	1154.75	2.6985	612.97	0.5365
N8	Nb44Ni25Ti31	724.26	0.5141	602.12	0.5015
N9	Nb44Ni20Ti36	968.00	1.3790	1485.42	1.1950
N10	Nb29Ni35Ti36	904.60	3.1585	474.33	0.9945
N11	Nb34Ni30Ti36	547.87	1.9525	503.93	0.7030

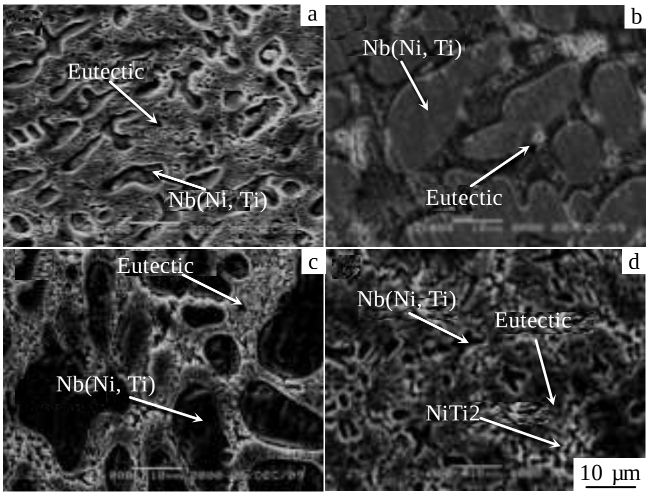


Fig.4 SEM images of N3 (a), N5 (b), N7 (c), and N9 (d) samples

2.2 Effect of magnetic heat-treatment on structure and mechanical properties of Nb-Ti-Ni alloy membranes

The data of three-point bending test of Nb-Ti-Ni samples with/without magnetic heat treatment (MHT) are shown in Table 2. It can be clearly seen that the maximum force and displacement obviously increase to different degrees after MHT at 0°, 45° and 90°, indicating that MHT is an effective method to improve mechanical property of Nb-Ti-Ni membranes. However, an exception is in the case of the three samples (N7, N9, N11, MHT at 90°). Based on Table 2, the maximum force is 1244.09 N (N7, MHT at 0°) and 1380.62 N (N7, MHT at 45°), and the maximum displacement is 3.379 mm (N9, MHT at 45°) and 3.030 mm (N5, MHT at 45°). Considering that N5 and N7 samples present the better hydrogen permeability, they have been selected to investigate the relationship between structure and mechanical property.

Table 2 Data of three point bending test of Nb-Ti-Ni alloy samples after hydrogen permeation test by DS method with/without magnetic heat-treatment (MHT)

Alloy	MHT at 0 °angle		MHT at 45 °angle		MHT at 90 °angle		Without MHT	
	Max force, *F*/N	Max displacement, *L*/mm	Max force, *F*/N	Max displacement, *L*/mm	Max force, *F* /N	Max displacement, *L*/mm	Max force, *F*/N	Max displacement, *L*/mm
N2	418.18	1.3530	178.14	1.9135	749.61	1.4740	130.96	0.1490
N5	992.16	2.3055	778.75	3.0300	1036.69	1.7925	368.90	0.2895
N7	1244.09	2.7310	1380.62	2.3095	584.72	0.6405	612.97	0.5365
N9	1005.83	1.3215	1221.06	3.3785	548.63	0.7015	968.00	1.1950
N11	1122.27	2.6620	765.33	2.1700	380.11	0.1475	503.93	0.7030

XRD patterns and SEM images of N5 sample (with/without MHT) are shown in Fig.5 and Fig.6, respectively. When MHT is at different angles, an obvious change occurs in the relative intensity of Nb(Ni,Ti) and sharp shape peaks are formed. Further SEM results confirm that as-adopted MHT can change grain sizes and grain orientations, while the sizes and the shape of phase region (eutectic phase) will change after MHT. In the case of MHT at 0°, a tiny bar-like region is formed, such bar-like region spreads along the direction of membrane surface (Fig.6b). In the case of MHT at 90°, some oral-like (or spot-like) region is regularly arranged on the surface (Fig.6d), which possibly suggests that this region extends along the direction of magnetic field (vertical to the membrane surface). In the case of MHT at 45°, the region shape and arrangement can be attributed to the combination of vertical and horizontal cases. XRD patterns and SEM images of N7 sample (with/without MHT at 45°) are shown in Fig.7 and Fig.8. Here the net-like region of eutectic phase changes to some small spot-like regions, which disperses in the matrix consisting of Nb (Ni, Ti) solid solution phase.

Based on the results obtained from the above mentioned structure analysis and mechanical property tests, the following points can be drawn. (1) Mechanical properties of Nb-Ti-Ni alloy membranes can be generally improved by MHT at the three angles, which may be attributed to the microstructural modification induced by magnetic field. (2) The direction of magnetic field plays an important role in structural changes of alloy samples. In the case of MHT at 0° (the membrane surface is parallel to the direction of magnetic field), the eutectic phase region changes to some tiny bar-like regions and spreads along the surface. In the case of MHT at 90°, some small oval-like regions of eutectic phase are formed and regularly arranged on the surface. (3) The effect of MHT on mechanical property is related to the alloy composition. MHT at the angle of 90° is a good way to improve mechanical property of N5 sample (the max force is 1036.69 N), the max force is 1380.62 N for N7 sample by MHT at 45°, and 1221.06 N for N9 sample by MHT at 45°. (4) Nb-Ti-Ni alloy membrane must meet both requirements of hydrogen permeability and mechanical property. And MHT will be able to satisfy the

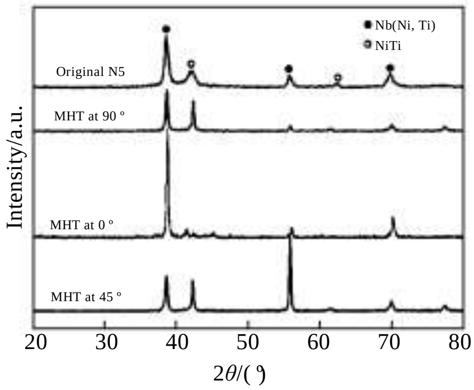


Fig.5 XRD patterns of N5 sample with/without MHT

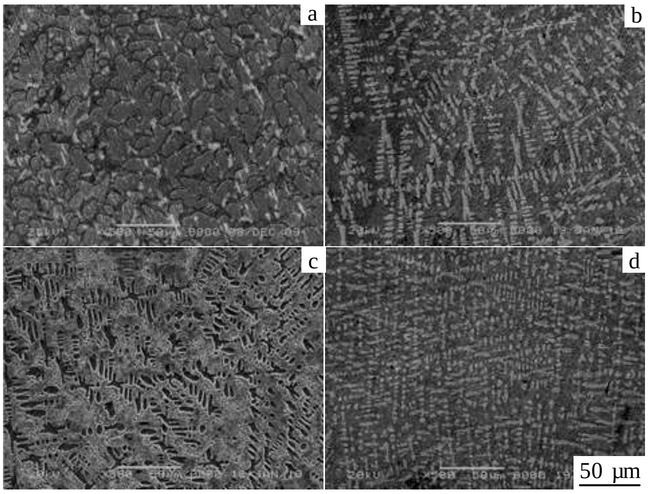


Fig.6 SEM images of N5 sample with/without MHT: (a) original, (b) MHT at 0°, (c) MHT at 45°, and (d) MHT at 90°

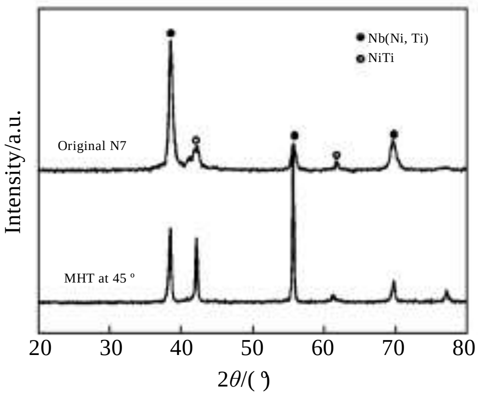


Fig.7 XRD patterns of N7 sample with/without MHT at 45°

maximum various comprehensive evaluation for the application of hydrogen permeability. The effect of MHT on hydrogen permeability will be discussed in other works.

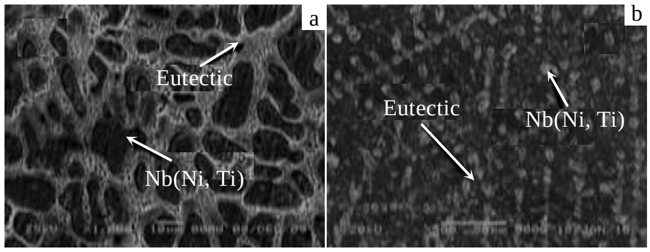


Fig.8 SEM images of N7 sample with/without MHT: (a) original and (b) MHT at 45°

3 Conclusions

1) The increase of Ni and Ti content will lead to the increase of volume fraction of (bcc-Nb(Ni, Ti)+β2-NiTi) eutectic phase, following by good mechanical property. The dispersive distribution of NiTi2 phase in eutectic area is beneficial to the improvement of the mechanical properties of alloy samples.

2) Mechanical properties of Nb-Ti-Ni alloy membranes are inordinately improved by magnetic heat-treatment along the three directions (0°, 45° and 90°). MHT can lead to the change grain size and orientation.

3) In the case of MHT at 0°, a tiny bar-like region (consisting of eutectic phase) is formed and spreads along the direction of membrane surface. In the case of MHT at 90°, some oral-like (or spot-like) region is regularly arranged on the surface and the region extends vertically for the surface.

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Nb-Ti-Ni 体系氢分离合金膜的抗弯性能研究

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摘　要：开展了Nb-Ti-Ni体系氢分离合金膜的结构和抗弯性能研究。采用XRD/SEM分析了合金膜的结构和组织特征，利用三点弯曲法测定了合金膜的抗弯强度。实验结果表明，制备的Nb-Ti-Ni合金主要由bcc-Nb（Ni, Ti）固溶体和 (bcc-Nb(Ni,Ti)+β2-NiTi) 共晶相构成，前者是渗氢功能相，后者是结构支撑相。经渗氢实验后，合金试样的抗弯性能均有下降，具有网状结构特征的合金有较好的抗弯性能。经磁场热处理后，合金微结构出现晶粒细化、晶粒沿磁场方向定向排列、固溶体相区分布改变等明显变化，合金膜的抗弯强度有不同程度的改善，其中 N7试样经0°和45°磁热处理，N5试样经90°磁热处理，其抗弯性能改善明显，说明通过磁热处理可对合金微结构进行调制，从而提高其抗弯强度。

关键词：Nb-Ti-Ni 合金膜；氢渗透；磁热处理；三点弯曲试验

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