Hydrogen Separation Using $LaNi_5$ Films Deposited on Polymer Membranes

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Hydrogen separation has been investigated using $LaNi_5$ films deposited by means of a sputtering method on a nickel-coated Teflon or on a nickel-coated polyimide membrane. Separation factors were estimated for an H_2(50 mol%)-Ar(50 mol%) gas mixture. The permeation rate of the Ni/$LaNi_5$ multilayered film was found to be larger than that of the Ni film. Hydrogen was concentrated to as high as 97.6 mol% under the best conditions.

Hydrogen separation has been studied using films of polymers, porous glasses, and metals.[1] A palladium film is known to exhibit excellent properties for hydrogen separation.[2] The film is, however, very expensive and must be operated at an elevated temperature. The use of a cheaper metal or an alloy instead of palladium would be advantageous for the hydrogen industries. $LaNi_5$ is considered to be a good candidate as a hydrogen separation material[3] because it is less expensive than Pd and has an admirable ability to absorb hydrogen at moderate temperatures and pressures. Some $LaNi_5$ films have been prepared by means of a flash evaporation[4-6] and of a sputtering method and have been investigated with respect to the hydrogen content in the films[7] and mechanical properties.[8] One of its most remarkable characteristics is that these films do not pulverize after more than 100 cycles of the hydrogen absorption-desorption process.

This finding led us to explore the possibility of hydrogen separation using the films.[9] We have previously reported the hydrogen-separation characteristics of the films deposited on a porous metal filter.[10]

In the present study, polymer membranes were used as a substrate on which the $LaNi_5$ layer was formed, and the hydrogen-separation capability for the $LaNi_5$-deposited polymer separator was investigated.

Experimental

Preparation of Films. The $LaNi_5$ ingot was supplied by the Santoku Metal Industry Co., Ltd., Kobe. The substrates were two kinds of polymer membranes, Teflon (Toyofuron, 25 μm thick, Toray Co., Ltd.) and polyimide (Kapton, 40 μm thick, Toray-Du Pont Co., Ltd.). These substrates were cleaned in an ultrasonic washing machine filled with acetone.

The metal layers were deposited with an r.f. magnetron sputtering apparatus made by the Daia Vacuum Engineering Co., Ltd., from an Ni or an $LaNi_5$ target. The r.f. generating power applied was 400 W, and the substrate temperature was in the range of 300—373 K. The atmosphere used for the discharge was 99.99%-pure argon at a pressure of 0.395 Pa. The $LaCo_5$ films were prepared by means of a flash evaporating method which has been described in previous papers.[4-6]

Measurement of Properties. A disk membrane 10 mm in diameter was inserted in a separation apparatus as is shown in Fig. 1. The stainless steel filter (Tokyo Seikoh Co., Ltd.) was used as a support for the film against the pressure.

An H_2 (50 mol%)-Ar (50 mol%) gas mixture with a pressure of 1.5×10^5 Pa at 368 K was applied to the $LaNi_5$-deposited side of the membrane. The gas passed through the film was collected in gas samplers at the outlet. The permeation rate was measured from the pressure variation, and the composition of the resulting gas was analyzed using a Hitachi RMU-6E mass spectrometer.

Results and Discussion

Structures of the Films. Figure 2 illustrates the structures of the films used for the experiments. Since the mechanical strength and the durability of the sputtered films were greater than those of the evaporated ones, the metal films were mainly prepared using a sputtering method.

Film b is an $LaNi_5$ film directly deposited on a

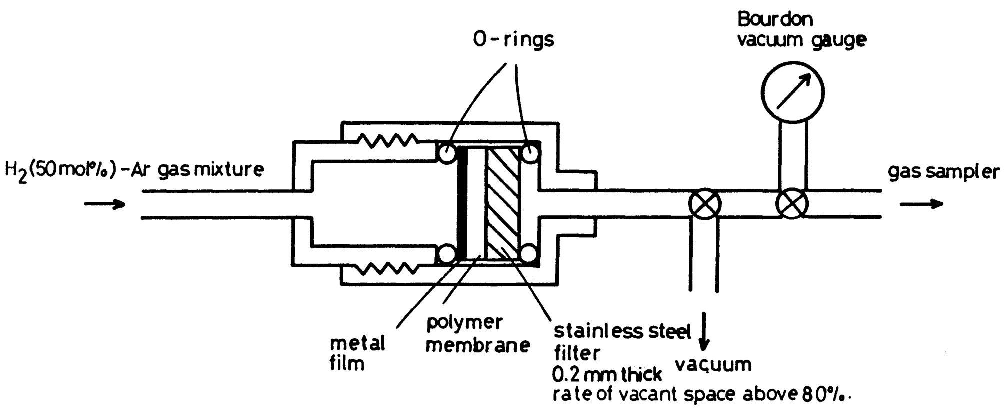

Fig. 1. Apparatus for gas separation.

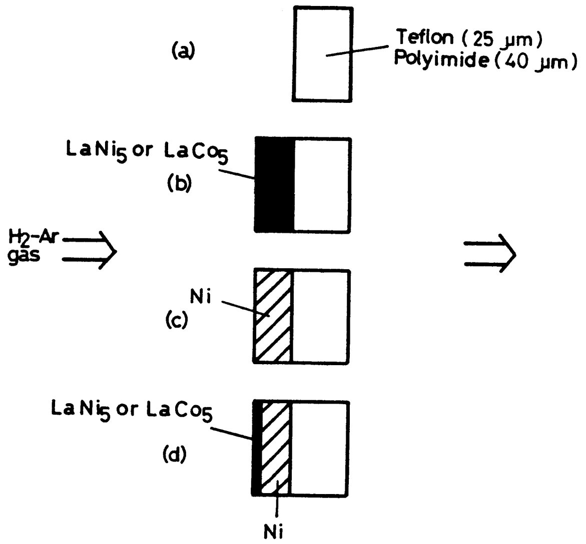

Fig. 2. Structure of films.

Teflon or on a polyimide membrane. The thickness of the metal layer was 0.75 μm. For film d, nickel was first deposited on the substrates (0.73, 1.23, or 1.48 μm thick). The nickel layer was to reinforce the durability of the films. Subsequently, $LaNi_5$ was deposited on the nickel layer. Films a and c were for blank tests.

Performance Characteristics of the Films. Nickel films with various thicknesses deposited on the Teflon membranes were prepared, and the effects of the thickness of the metal layer on the hydrogen separation were studied. As is shown in Fig. 3, for a 0.5 μm-thick film the hydrogen concentration in the permeated gas was slightly larger than that for the Teflon-only membrane. It seems probable that most of the gas mixture passed through pinholes in the nickel film. However, for a 0.75 μm-thick film the hydrogen concentration increased remarkably. It can be considered that, above thickness of 0.75 μm, the Teflon membrane was almost

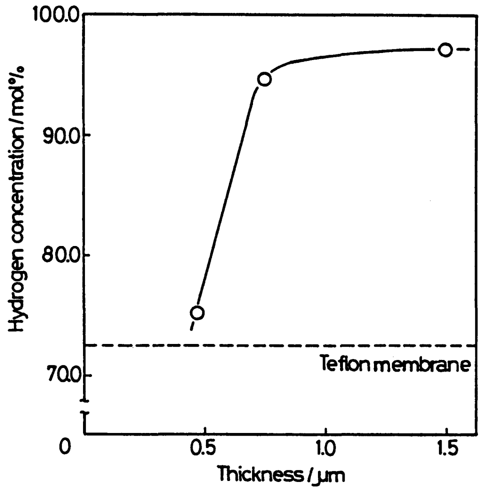

Fig. 3. Effects of thickness of nickel layer on hydrogen concentration in permeated gas.

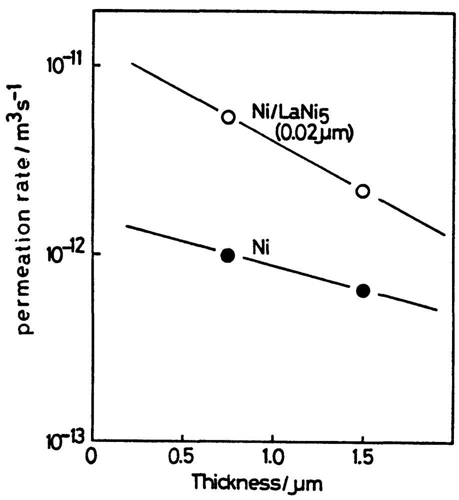

Fig. 4. Relationship between permeation rate and thickness of metal layer.

Table 1. Performance Characteristics of $LaNi_5$ and $LaCo_5$ Films Deposited on the Teflon Membrane

Gas composition mol%	Film composition	Permeation rate $m^3s^{-1} \times 10^{-12}$	Permeability coefficient $m^2s^{-1}Pa^{-1/2} \times 10^{-16}$ a)	Hydrogen content after treatment mol%	Separation factor
Ar(50)-H_2(50)	Teflon (T) (25 μm)	43	2400	74.8	2.97
	0.75 μm				
	T/$LaNi_5$	5.3	5.7	89.5	8.52
	T/Ni	0.99	1.1	94.7	17.9
	T/Ni/$LaNi_5$ (0.02 μm)	5.4	6.3	91.9	11.3
	T/$LaCo_5$	<0.5	<0.5	75.2	3.03
	1.50 μm				
	T/Ni	0.55	1.2	97.2	34.7
	T/Ni/$LaNi_5$ (0.02 μm)	2.2	5.1	91.0	10.1
	1.31 μm				
	T/Ni/$LaCo_5$ (0.08 μm)	<0.5	<1.0	83.1	4.92

Primary pressure: 1.5×10^5 Pa; temperature of film, 368 K, a) Units $m^2s^{-1}Pa^{-1/2}$ is derived from (volume of permeated gas (STP))$\times$(thickness of the sample)$\times$(surface area of the sample)$^{-1}$ $\times$(the time required for permeation)$^{-1}\times$(difference in pressure)$^{-1}$.

Table 2. Performance Characteristics of $LaNi_5$ and $LaCo_5$ Films Deposited on the Polyimide Membrane

Gas composition (mol%)	Film composition	Permeation rate ($m^3s^{-1}\times10^{-12}$)	Permeability coefficient ($m^2s^{-1}Pa^{-1/2}\times10^{-16}$)	Hydrogen content after treatment (mol%)	Separation factor
Ar(50)-H_2(50)	Polyimide (I) (40 μm)	3.1	188	95.2	19.8
	1.25 μm				
	I/Ni	2.1	3.8	96.6	28.4
	I/Ni/$LaNi_5$ (0.02 μm)	2.7	5.0	97.6	40.7
	1.31 μm				
	I/Ni/$LaCo_5$ (0.08 μm)	<0.5	<1.0	95.1	19.4

Primary pressure: 1.5×10^5 Pa; temperature of film, 368 K.

Table 3. Estimation of $LaNi_5$ Films Deposited on the Polymer Membrane for Hydrogen Separation

	Thickness of the metal layer (μm)	Permeation rate	Hydrogen-separation factor
Pd	100—200	1	Above 66
Metal filter substrate	50	$1/10^2$	2.25—20.6
Polymer substrate	1	$1/10^3$	10—40

completely covered with the nickel film and that the hydrogen applied permeated through the nickel layer.

Table 1 shows the hydrogen-separation ability of the $LaNi_5$ films deposited on the Teflon membrane. A gas of 50 mol% H_2 was found to be concentrated to 74.8 mol% by the use of the Teflon membrane alone. When the metal films were deposited on the Teflon, the hydrogen concentration increased greatly. It was found that the permeation rate of the $LaNi_5$ film was several times as large as that of the Ni film, though the hydrogen concentration for the $LaNi_5$ film was slightly lower than that for the Ni film. There were no differences in characteristics for the permeation rate and the separation factor between the $LaNi_5$ film and the Ni/$LaNi_5$ multilayered film. The nickel film is able to permeate hydrogen easily because the thin $LaNi_5$ film coated on the nickel surface dissociates the hydrogen molecule easily and absorbs much hydrogen. Figure 4 shows the relationship between the permeation rate and the thickness of the metal layer and also the effects of the $LaNi_5$ layer on the hydrogen permeation of the Ni film. The permeation rate decreased with the increase in the thickness of the metal layer. Also, for the 1.5 μm-thick film, the permeation rate for the Ni/$LaNi_5$ multilayered film was larger than that for the Ni film.

Table 2 shows the hydrogen separation characteristics of the $LaNi_5$ film deposited on the polyimide membrane. The polyimide membrane itself exhibited a high hydrogen-separation factor. The highest separation factor was obtained for the Ni/$LaNi_5$ multilayered film. The reason why the separation capability of the Ni/$LaNi_5$ film is excellent seems to be that the adhesion between the polyimide membrane and the metal film was superior to that between the Teflon membrane and the metal film.

An $LaCo_5$ film is not suited for the hydrogen separator because the mass of the permeated gas obtained from the films deposited on both the Teflon and polyimide membranes was extremely small and these separation factors were not so good (Tables 1 and 2). This seems to be caused by the small hydrogen concentration in the $LaCo_5$ film.[1]

In Table 3, the characteristics of the $LaNi_5$ film using the polymer as a substrate for the hydrogen separation are compared with those of the $LaNi_5$ film deposited on a porous stainless steel filter as well as those of a Pd film.[2,12] As for the thickness of the metal layer, high-purity hydrogen gas was obtained with a $LaNi_5$ film only 1 μm thick for the polymer-substrate sample. The permeation rate for the $LaNi_5$ film coated on the polymer is very low, but this is not a serious problem, because for the polymer membrane it is easy to increase the area of the gas contact surface. For instance, if a hollow fiber on which the metal layer is formed is bundled, a large surface area can be obtained.

The $LaNi_5$ films deposited on the nickel-coated polymer substrate are relatively cheap and easy to prepare.

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