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Preparation of Composite Membrane against H_2S Poisoning for Hydrogen Separation

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A new composite membrane is suggested taking into account membrane performance and resistance to undesirable impurities in gas mixtures. Thin Pd-Ag alloy films are deposited on various asymmetric porous ceramic supports using a dual sputtering technique. Zinc oxide is dispersed in the porous ceramic supports by sol-gel process. It is expected that this membrane has potentialities of high performance for hydrogen separation as well as high durability against H_2S poisoning.

Key words: metal/ceramic composite membrane, hydrogen separation, sol-gel process, thin film sputtering

1. INTRODUCTION

In recent years, the increased demand for hydrogen has led to a revival of interest in separation and purification method for new energy-related applications. Even though the most commonly used membrane of palladium metal exhibits high performance for commercial pure hydrogen production, many attempts have been carried out to develop lower-cost metal-metal or metal-ceramic composite membranes [1-4]. Moreover Pd membrane alloyed with other metals has been studied since pure Pd membranes suffer from embrittlement due to the phase transition and poisoning due to hydrogen sulfide and sulfur contaminants [5,6].

In order to overcome the above disadvantages, we suggest a new composite membrane of Pd-based thin film on porous ceramic support impregnated with zinc oxide as schematically shown in Fig. 1. It is expected that the damage on metal layer by H_2S poisoning can be potentially solved due to a pre-treatment of the feed gas by reversible chemisorption of H_2S on an active oxide such as ZnO dispersed in a porous ceramic support [7]. A mesoporous substrate would be in fact an efficient gas-solid contactor for chemisorption of H_2S. H_2-selective metallic layers are deposited on such composite substrates by sputtering.

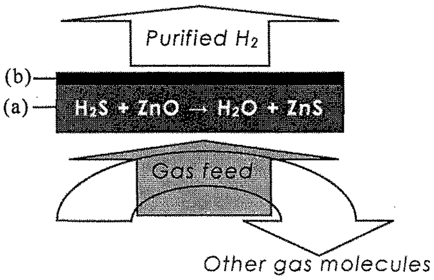


Fig. 1 Design of metal/ceramic composite membrane for hydrogen separation. (a) asymmetric ceramic support containing active zinc oxide; (b) metallic top layer.

2. EXPERIMENT

Three types of asymmetric porous ceramic substrates chosen according to their known properties [8,9] and some trial experiments are as follows: alumina substrate with 3 nm-mesoporous zirconia top layer (Inocermic GmbH.) and alumina substrates with 4 nm-mesoporous and 60 nm-porous alumina top layers (Noritake Co.).

2.1 Metal film deposition using sputtering method

Pd-Ag films on the chosen substrates were prepared in a DC sputtering system with two separate Pd and Ag targets (Purity of both, 99.99 %) in argon atmosphere. Voltage for each target can be controlled in the range of 0-600 V. The target-substrate distance and work pressure were set at 60 mm and 1.6 Pa, respectively. The voltage of Pd and Ag targets were fixed at 400 and 280 V, respectively, to get Pd-23Ag composition. The top layer side of the asymmetric porous ceramic substrate was cleaned using fast atom bombardment (FAB) for 30 min in the FAB chamber and transferred directly into sputtering chamber in vacuum ($< 1 \times 10^{-5}$ Pa). Deposition times were 50 s and 250 s for 100 nm-thick films on 3 or 4 nm-mesoporous top layers and 500 nm-thick film on 60 nm-porous layer, respectively. After sputtering, the sample was transferred back into the FAB chamber. The sputtering system and the optimized conditions are detailed in the previous works [1,2].

2.2 ZnO dispersion using sol-gel process

ZnO precursor solution was simply prepared as follows. 2.19 g (0.01 mol) zinc acetate dehydrate, 50 ml absolute ethanol, 2 ml deionized water and 0.2 ml acetic acid were mixed together and vigorously stirred at 40 °C for 20 min. The obtained transparent solution was then aged in a water bath at 65 °C for 2 h [10]. Following another 15-h aging at room temperature, the obtained precursor solution was used for impregnation of porous ceramic substrates. The samples were dried at room temperature and in the oven at 100 °C, and then treated at 450 °C for 2 h in air. In same way, powder sample and dip-coated glass were also prepared. They were characterized by

SEM, XRD and EDX analyses.

3. RESULTS AND DISCUSSION

3.1 Pd-Ag thin film deposition

SEM images of Fig. 2 (a) and (b) show that 100 nm-thick Pd-23Ag films were homogeneously deposited on the mesoporous top layer of asymmetric ceramic substrates. For the substrate with 60 nm-top layer, film was prepared 500 nm thick as the surface is rougher to get homogeneity (Fig.2c).

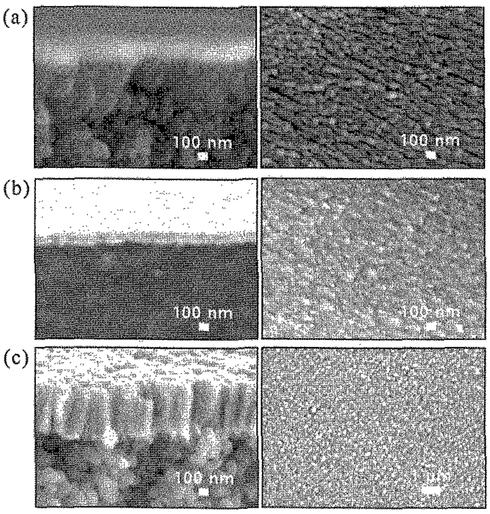


Fig. 2 SEM images of metallic layers deposited by sputtering on asymmetric ceramic supports with top layer of (a) 3 nm-porous ZrO_2, (b) 4 nm-porous Al_2O_3 and (c) 60 nm-porous Al_2O_3 (left: cross-section; right: surface).

3.2 ZnO nanoparticle dispersion

The prepared ZnO particle was characterized by XRD. While the pattern shows only precursor peaks after drying at 100 °C (Fig 3.a1), 450 °C-treated sample shown in Fig. 4 has polycrystalline ZnO phase (Fig 3.a2).

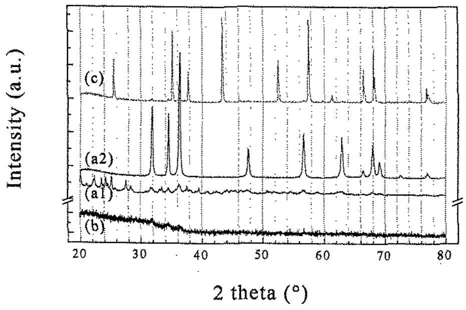


Fig. 3 XRD patterns of (a1) 100 °C-dried precursor powder, (a2) 450 °C-sintered ZnO powder, (b) ZnO film on a glass substrate, and (c) ground powder of ZnO-impregnated alumina.

XRD patterns in Fig.3(b) and (c) prove that ZnO coated on a glass substrate (Fig. 5) as well as ZnO dispersed in a porous substrate (Fig. 6) were also successfully prepared by sol-gel process, as showing the main peaks of ZnO with substrate peaks.

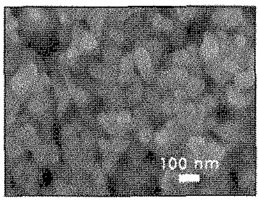


Fig. 4 SEM image of ZnO powder synthesized by sol-gel process.

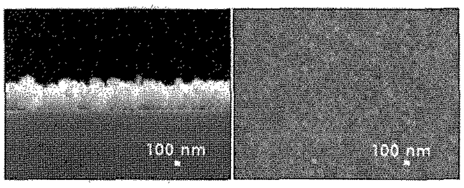
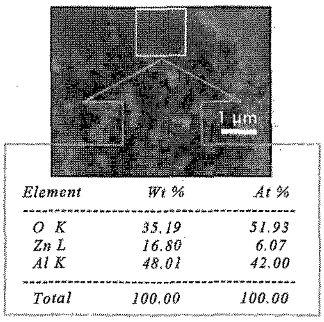


Fig. 5 SEM images of ZnO film prepared on a slide glass (left: cross-section; right: surface).

Even though the synthesized ZnO particles without any substrate have a few tens nm size, larger than the top layer-mesoporosity of asymmetric ceramic substrate as shown in Fig. 4, ZnO dispersion in the mesopores could be easily obtained due to sol-gel process. It was proved by EDX analysis in Fig. 6.

ZnO dispersion can be done either before thin film sputtering or after.



Element	Wt %	At %
O K	35.19	51.93
Zn L	16.80	6.07
Al K	48.01	42.00
Total	100.00	100.00

Fig. 6 EDX analysis of a ZnO-dispersed porous alumina substrate (square area: 4 nm-porous).

The potential advantages of this membrane are as follows: high permeability of hydrogen and reduction of embrittlement due to Pd-Ag alloy [11], cost reduction due to thin film, and high resistance to hydrogen sulfide and sulfurous constituents in gas mixture due to the porous ceramic substrate with zinc oxide dispersion. The poisoning of the metal by H_2S, known as a severe problem of dense metallic membranes for hydrogen separation, can potentially be solved by a pre-treatment of the feed gas by reversible chemisorption of H_2S on an active oxide dispersed in a porous ceramic support. If only the poisoning problem is considered, Pd-Cu alloy may be better as the deposited thin film [12]. For our new composite membrane, however, it is expected that Pd-Ag alloy brings other advantages and ZnO dispersion gives the resistance to poisoning. This is also helpful to evaluate correctly the potentiality of active oxide dispersion itself.

Such metal/ceramic composite membrane for hydrogen purification should have much better quality in terms of permeability and durability than dense metal films deposited on ceramic supports in the other publications [13,14].

4. CONCLUSION

Pd-Ag thin films were homogeneously prepared by sputtering on different asymmetric ceramic substrates. For the composite membrane against H_2S-poisoning, an active oxide ZnO was dispersed in the pores of substrates. In order to evaluate the potentiality of these membranes, they will be tested for hydrogen permeability performance by using H_2 gas mixed with a very small amount of H_2S.

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