

## Membrane Hydrogen Separation from Ionized Hydrocarbon Gases

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New hydrogen separation technologies using nanocrystalline membranes immersed in the ionized hydrocarbon gases are discussed. Grain boundary engineering forms basics for membrane fabrication technologies with nanochannels for hydrogen separation. The maintenance of the atomically clean membrane surfaces by physical and chemical sputtering processes is considered.

**Keywords:** hydrogen separation, membranes, ionized gases, sputtering.

### 1. INTRODUCTION

The following steps may be distinguished in the mechanism of C chemical sputtering in hydrogen containing plasmas [1]: (i) energetic ions extracted from plasma break C-C bonds, (ii) H atoms arriving from plasma or/and after dissociative adsorption of H<sub>2</sub> molecules passivate broken bonds, (iii) repetition of (i) and (ii) until volatile hydrocarbon, CH<sub>4</sub>, are formed, and (iv) desorption of volatile hydrocarbons and removal of C atoms from the surface. It is well established, that chemical sputtering of carbonaceous materials takes place during simultaneous C adsorption of reactive neutral species and H ion irradiation. The characteristic features of chemical sputtering are: (i) very low ion threshold energy, (ii) high erosion yield, (iii) dependence of erosion yield on ion-to-neutral ratio, and (iv) dependence of erosion yield on temperature.

The erosion of hydrocarbon films Ar and Ar+H<sub>2</sub> plasmas has been studied in [2, 3]. The coupled effects of physical and chemical sputtering have been investigated in recent publication [4]. The main conclusions of the previous research for the erosion due to simultaneous interaction of H and Ar<sup>+</sup> may be summarized as following: (i) chemical sputtering demonstrates high erosion yield below threshold for physical sputtering (threshold energy for physical sputtering ≈60 eV), (ii) chemical sputtering at 20 eV Ar<sup>+</sup> irradiation many times (20–30) exceeds pure chemical erosion, and (iii) chemical sputtering rate at 100 eV Ar<sup>+</sup> irradiation exceeds 10 times physical sputtering rate for neutral/ion ratio equal to about 400 K and 340 K. In [4] it is shown that C erosion in Ar+H<sub>2</sub> plasma rate depends on the quantity of impurities contained in C.

The production of H<sub>2</sub> is based on the fact that hydrogen is produced from fossil fuels using, for example, CH<sub>4</sub> as a working gas. In plasma, CH<sub>4</sub> molecules dissociate forming CH, CH<sub>2</sub> and CH<sub>3</sub> hydrocarbons, C and H. About 1 % of neutrals are ionized in plasmas. Ionized particles are extracted and accelerated through the plasma boundary layer and interact with the substrate material covered by carbon. Usually, the membrane for hydrogen separation

consists of 200 μm thick porous membrane support, Al<sub>2</sub>O<sub>3</sub>, covered by 5 μm–10 μm thick of metallic membrane, Pd, which contacts the ionized gas. The energy of incidents ions depends on the bias voltage of membrane in plasma which may be verified and equals to about 100 eV–300 eV. The carbon atoms and compounds (neutral and ionized) arriving from plasma are adsorbed on the surface of the membrane and modify the hydrogen permeation properties through the membrane. At the same time, the working gas contacting membrane includes contaminants as sulfur, which poisons the membrane [5]. For the effective operation of the membrane, the C and contaminants have to be removed continuously from the surface. In the present work, a suggestion is made to clean membrane surfaces during hydrogen separation process employing processes of physical and chemical sputtering.

For simulations, the following assumptions have been made: (i) the membrane, which is covered by C layer, is bombarded by ions extracted from plasma (mainly CH<sub>3</sub><sup>+</sup>) during simultaneous adsorption of C atoms and contaminants arriving from the ionized gases, (ii) incident ions break C-C bonds and generate activated C atoms with free bonds on the surface, (iii) the hydrogen atoms saturate free C bonds and form volatile CH<sub>4</sub> molecules which are thermally desorbed.

### 2. HYDROGEN SEPARATION IN NANOMATERIALS

If an inorganic membrane is homogeneous, its permeance is inversely proportional to the membrane thickness. Permeance is defined as volumetric flow rate per unit area per unit pressure drop across the membrane. If the membrane is to be commercially useful, it must be very thin, no more than one-to-two micrometers thick, and preferably less. For this case, the size of pores has to be less than 10 nm. The membrane must be layered on a strong porous support material, either metal or ceramic. Metal is preferred because modules can be more easily and less expensively constructed.

The separating membrane layer can be applied directly to the support material or on top of an intermediate layer. Early works focused on developing a hydrogen separation membrane that could operate at temperatures of 600 °C–800 °C. Few conventional metals are stable in

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long term use at these temperatures, especially in a sulfidizing environment typical of coal gasification systems. For operation under these conditions, a porous aluminum oxide (alumina) tubes have been developed to be used as a support for application of the ceramic separative layers. However, an extremely thin separative layer requires an intermediate layer having a pore size much smaller than the support tube.

Recently [5], coal gasification research has shown that high efficiency can still be achieved with gas cleaning at lower temperatures than previously considered necessary and now the target temperature is in the range of 250 °C–500 °C. At these temperatures, an alumina support tube can still operate without degradation.

There are several transport mechanisms that can govern the flow of gas molecules through membranes. Viscous flow occurs when the gases flow through a membrane as a fluid without any differentiation between gases and results in no separation. Molecular sieving occurs when a membrane's pores are sized such that the smaller gas molecules can pass through the membrane while the larger ones do not fit through the pores and are thus rejected. Knudsen separation occurs by taking advantage of differences in molecular velocities. Lighter molecules transport faster through pores than heavier molecules resulting in an enhancement of the lighter molecules product stream. Lastly, surface diffusion occurs when one of the gas molecules is adsorbed on the surface of the pores and travels along the surface rather than in the gas phase. The adsorbed molecules can block the pores so that the flow of other gas molecules are impeded resulting in an enhancement of the concentration of adsorbable molecules in the permeate stream.

For gas separations by molecular sieving, the effective mean pore diameter must be on the order of the diameter of the gas molecules, normally 2 nm or less.

Up to now little is known about emerging new membrane fabrication technologies based on recent understanding about the gas transport properties through nanocrystalline materials.

The nanocrystalline solids comprise of small crystals separated by grain boundaries. New techniques to create nanophase materials have resulted in the development of new class of materials, which have an appreciable fraction of their atoms residing in defect environment. For instance, a nanophase material with an average grain size of 5 nm has about 50 % of the atoms within the first two nearest neighbour planes of a grain boundary in which significant displacements from normal lattice positions are exhibited. The basic idea being to produce new nanomaterials which contain highly developed interfaces with controllable properties.

The internal interfaces separate neighbouring disoriented single crystals in a polycrystalline solid. These interfaces, which are frequently planar, have a two-dimensionally periodic atomic structure. The main feature is a very high density of grain boundary core in nanocrystalline solids (60 %–70 %) in metals and 80 % in ceramics, compared to conventional materials. The atomic structure of grain boundary core averages about  $10^{19}$  boundary cores per ccm as suggested by studies on Fe

(6 nm) and Cu (10 nm). A polycrystalline cube 1 cm on edge, with grains 10 nm in diameter, would contain  $10^{18}$  crystals with a grain boundary area of  $6 \cdot 10^6$  square kilometres. Thus, grain boundaries play an important role in controlling the properties and kinetics of processes in nanomaterials. The properties are influenced by the detailed atomic structure of the grain boundaries, as well as by the defects that are present [6].

The atomic arrangement formed in the core of an interface is known to be an arrangement of minimum energy in the potential field of two adjacent crystal lattices with different crystallographic orientation on either side of boundary core. Owing to the different orientation, the two adjacent crystal lattice match poorly. The poor matching results in an atomic density lower than that in the perfect crystal. The boundary core density is found to be reduced by 15 %–40 % relative to density of perfect lattice. Such boundary conditions are not found in glasses or perfect crystals.

Grain boundaries generally have very different atomic configurations and local atomic densities act as sinks for doping atoms, which tend to segregate to interface. These doping atoms at grain boundaries have highly pronounced effects on the properties of the material. Examples are phosphorous and sulfur in steel or gallium and mercury in aluminum.

Despite a remarkable progress and availability of state of art tools such as nanoscope, AFM, STEM and EMS of sub nanometer resolution we are just at the beginning to understanding the essential features of structures of nanophase materials.

The specific features of diffusion processes in nanocrystalline materials have been widely experimentally measured and discussed. Theoretical models are suggested that describe the effects of transformations (climbing, splitting) of grain boundary dislocations and declinations on self-diffusion in nanocrystalline materials. It is shown that climbing of grain boundary dislocations strongly enhances diffusion processes in nanocrystalline materials, causing the self diffusion coefficient to be increased by several orders. A decrease in grain size from 10  $\mu$ m to 10 nm increases the creep rate by nine orders of magnitude. The grain boundary diffusivity is also higher, which allows ceramics and intermetallics to be plastically deformed. The atomic diffusion process in nanocrystalline solids is orders of magnitude higher than that observed in conventional crystals and glasses. With the decrease of size of nanocrystallites the properties of grain boundaries become dominant. By measuring the fraction of atoms redistributed at the grain boundary, and by knowing the grain size of the material, it is possible to deduce the average width of grain boundaries in metallic alloys. It is found [6] that these widths are approximately 0.5 nm for *fcc* alloys and slightly larger than 1.0 nm for *bcc* alloy. It is known that stress relaxation processes in composites form nanogaps with their size which depends on the doping material and its concentration, matrix material interface properties between substrate and nanocoating.

The main goal this work is to understand and get knowledge how apply interfaces of nanomaterials for hydrogen separation.

Prerequisites for the search of nanomaterials for fabrication of hydrogen separation membranes are following:

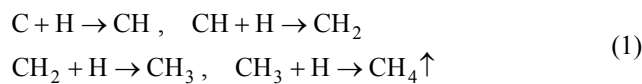
- grain boundary engineering technologies are emerging with new possibilities to modify properties of grain boundaries by insertion of atoms of different types at the interface boundaries,
- it is shown experimentally that surface layers of metals with the initial grain size equal to tens of microns become nanocrystalline as result of crystal fragmentation under high stresses generated by nitrogen atoms at the interface of grains during plasma nitriding [7, 8]. The twinning involves slip and initiates plastic deformation of grains; as result of it the grain size reduces effectively and nanostructuring takes place.
- it is well known that the microstructure of thin film coatings fabricated by physical vapor deposition technologies (PVD) may be modified if during deposition the growing film is affected by the external ion irradiation. Ion bombardment during the deposition densifies the microstructure of growing film.

These facts may be used for the fabrication of thin membranes for hydrogen separation with differing hydrogen permeation properties.

### 3. REMOVAL OF DEPOSITS IN PLASMAS CONTAINING HYDROGEN

For the removal of C layer from the membrane surface, the C etching rate has to be higher than the C layer growth rate. This may be realized if C surface atoms are constantly reacted with chemicals supplied from the plasma, reaction products are volatile and instantaneously removed.

Let us consider, the removal of C layer, which is grown during hydrogen separation process on the surface of membrane, in plasma containing H atoms. It is widely accepted that the formation of volatile  $\text{CH}_4$  is the result of the following heterogeneous reactions



The rate of each reaction step is proportional to the surface concentration of atomic hydrogen,  $[\text{H}]$ , and can be written as

$$R_j^{ch} = K_j [\text{H}], \quad (2)$$

where index  $j$  indicates the reaction step for Eq. (1).

The working gas used for the production of hydrogen contains impurities, which are adsorbed on the surface. It means that the model has to consider simultaneous action of the heterogeneous reactions of C with H and the deposition and sputtering of impurities arriving from plasma. It makes that at least 6 components have to be considered on the surface: C, CH,  $\text{CH}_2$ ,  $\text{CH}_3$ ,  $\text{CH}_4$ , and impurities (Im). Denoting the relative surface concentration as  $c_i$  ( $\sum_{i=1}^6 c_i = 1$ ), the system of the kinetic equations for each component on the surface may be written as

$$\begin{cases} \frac{dc_1}{dt} = \sum_{j=2}^6 w_j c_j - R_1^{ch} c_1 - \kappa c_1 \\ \frac{dc_i}{dt} = -w_i c_i + R_{i-1}^{ch} c_{i-1} - R_i^{ch} c_i, & i = 2, 3 \text{ and } 4 \\ \frac{dc_5}{dt} = -w_5 c_5 + R_4^{ch} c_4 \\ \frac{dc_6}{dt} = -w_6 c_6 + \kappa c_1 \end{cases} \quad (3)$$

If to introduce new denotations

$$d_i = \frac{R_i^{ch}}{R_{i+1}^{ch} + w_i}, \quad i = 1, 2 \text{ and } 3 \quad (4)$$

$$D = 1 + d_1 + d_1 d_2 + d_1 d_2 d_3$$

the steady state surface concentrations of components,  $c_i$ , may be expressed as

$$\begin{cases} c_1 = \frac{1}{D + \frac{R_4^{ch}}{w_5} d_1 d_2 d_3 + \frac{\kappa}{w_6}} \\ c_{i+1} = d_{i+1} c_i, & i = 1, 2 \text{ and } 3 \\ c_6 = \frac{\kappa}{w_3} c_1 \end{cases} \quad (5)$$

For the analysis of Eq. (5), let us assume that rates of all intermediate reactions,  $R_i^{ch}$ , and sputtering rates of reaction products,  $w_i$ , are equal ( $R_i^{ch} = R^{ch}$ ,  $w_i = w_1$ ,  $i = 1, 2, 3$  and 4). In this case, the stationary etching rate of C can be expressed as

$$v^{(T)} = \frac{w_1 D + R^{ch} d^3}{D + \frac{R^{ch}}{w_5} d^3 + \frac{\kappa}{w_6}} \quad (6)$$

Fig. 1 (dotted lines) illustrates calculated dependences of C etching rate in dependence on the concentration of H atoms in relative units for different values of the ratio  $\kappa/w_6$ , where  $\kappa$  is the adsorption rate of impurities and  $w_6$  is the physical sputtering rate of impurities.

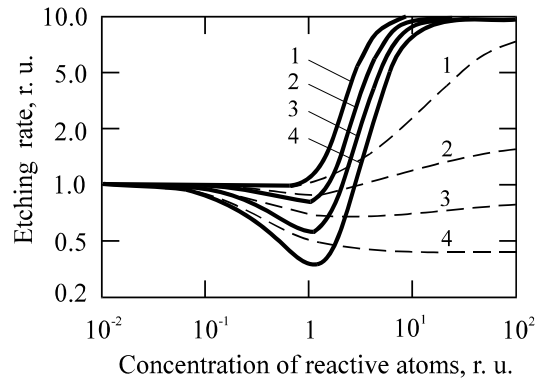


Fig. 1. The dependences of the erosion rate of carbon layer on the concentration of hydrogen atoms

The relative H surface concentration is expressed in units  $x = ([\text{H}] + [\text{Im}]) / N_0$ , where  $N_0$  is the H concentration in the absence of impurities. The values of parameters used for calculations are following:  $[\text{H}] = [\text{Im}]$ ;  $w_5/w_1 = 10$ ;

$w_6/w_1 = 0.1$ ;  $R^{ch}/w_1 = 0.1$  for  $\kappa/w_6 = 0$ ; 0.2; 0.5 and 1.0 (curves 1–4, respectively).

If the rates of intermediate reactions presented by Eq. (1) are very fast, they can be considered as the one reaction,  $C + 4H = CH_4\uparrow$ . For this case, the number of constants determining the etching rate of C decreases as surface consists of three components: C,  $CH_4$  and Im. The steady state etching rate may be expressed as

$$v^{(r)} = \frac{w_1 + R^{ch}}{1 + \frac{\kappa}{w_3} + \frac{R^{ch}}{w_2}} \quad (7)$$

The dependences of the steady state etching rate of carbon on the concentration of hydrogen atoms in plasma for different values  $\kappa/w_3$  are presented in Fig. 1 (solid lines). In the range of high substrate temperatures this assumption is justified because the rates of chemical reactions depend on the temperature and are high in the range of considered temperatures. It is important to note that the rate of physical sputtering does not depend on temperature in a wide temperature range [1].

#### 4. DISCUSSIONS AND CONCLUSIONS

The analysis of simulation results show that the etching rate of C increases as H concentration increases. The etching rate in dependence of the relative concentration  $x$  is shown in Fig. 1. In the range of small values of  $x$ , the erosion rate is limited by the kinetics of chemical reaction,  $C + 4H = CH_4\uparrow$ , and approaches the value  $w_1$ . As value  $x$  increases, the etching rate approaches the value  $w_2$ , which defines the removal rate of the reaction products.

The adsorption of impurities, which may be removed from the surface only by physical sputtering, decreases the erosion rate of C. The steady state surface concentration of impurities depends on the ratio of their adsorption and sputtering rates. The presence of impurities on the surface blocks the heterogeneous reaction between H and C and decreases the rate of C chemical sputtering. To minimize the effects of impurities on the surface the rate of physical sputtering of impurities has to be equal and higher than the flux of impurities arriving to the surface. It may be

achieved by verification of the flux and energy of incident ions extracted from plasma.

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