Journal of Membrane Science 362 (2010) 12–28

Contents lists available at ScienceDirect

Journal of Membrane Science

journal homepage: www.elsevier.com/locate/memsci

Review

Non-Pd BCC alloy membranes for industrial hydrogen separation

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ARTICLE INFO

Article history:
Received 23 April 2010
Received in revised form 29 June 2010
Accepted 30 June 2010
Available online 7 July 2010

Keywords:
Hydrogen
Membrane
Alloy
Vanadium
Niobium
Body centred cubic

ABSTRACT

With low cost raw materials and high hydrogen permeabilities, body-centred-cubic (BCC) alloys comprising Group IV and V metals are of considerable interest for high-temperature hydrogen separation applications. Until recently, their tendency to embrittle severely has tempered the enthusiasm for these materials in the membrane research community, but efforts to develop BCC alloy membranes suitable for industrial H_2 separation processes have increased recently and significant gains have been made in overcoming the inherent instability of these materials in hydrogen.

Compared to competing face-centred-cubic alloys, BCC alloys have much higher solubilities that provide them with a high driving force for hydrogen permeation. This high solubility, however, exacerbates the problem of hydrogen embrittlement. Given their low cost components and high permeabilities, the development of membranes with sufficient durability and embrittlement resistance remains the greatest barrier to the widespread uptake of BCC membrane technology. This review discusses the key scientific issues pertaining to the development of BCC alloy membranes in high-temperature industrial processes, including hydrogen solubility and diffusivity, embrittlement and manufacturing. Compositional modification to tailor the hydrogen solubility, maximize the rate of hydrogen diffusion and inhibit the onset of embrittlement is discussed.

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doi:10.1016/j.memsci.2010.06.068

1. Introduction

The demand for H_2 is expected to grow rapidly in coming years with the uptake of low-emission transport and power generation technologies. As H_2 does not occur naturally in abundance, the conversion of H_2O via chemical or electrolytic means represents the most likely route for large-scale production. In countries without an abundance of renewable electricity sources (e.g., hydro, wind, solar PV), the conversion of fossil fuels such as coal, natural gas and biomass to H_2 through reaction with steam is the most likely path via which future H_2 demand can be met. Given the energy input required, H_2 is an energy carrier only, but it enables emission-free power generation from distributed or large point sources.

As the method and volume of H_2 production changes, technologies capable of separating and purifying H_2 will be forced to adapt accordingly. The benefits of membrane-based H_2 separation have been reported previously [1], and of the several main classes of H_2-selective membranes, alloy membranes are the most mature technology. Pd-alloy membranes already form the basis of current bench-scale purifiers and methanol reforming units, but a step-change in membrane scale, performance, operation and cost will be required to accommodate future gigawatt-scale H_2 production plants.

1.1. Hydrogen from fossil fuels

Presently, steam methane reforming to produce synthesis gas (a mixture of CO and H_2, also referred to as syngas) represents around 90% of global H_2 production, but this syngas is utilized almost exclusively (with a few fuel cell public transport trials being the exception) within refineries for fuel and chemical manufacture. The growing interest in coal and biomass gasification also introduces a potentially large H_2 source, but as with methane reforming, most of the product syngas is used in the manufacture of chemicals and fuels.

Increasing restrictions on CO_2 emissions, driven primarily through public and governmental attitudes towards CO_2-induced climate change, is likely to accelerate the uptake of H_2 technologies. The conversion of the CO component of syngas to CO_2 via the water-gas-shift (WGS) reaction, and separation of the CO_2 and H_2, remains a significant economic barrier.

In calculating the cost of a conceptual 300 tonne-per-day H_2 – from coal plant, based on presently – available technology, several economic modelling exercises [2,3] incorporated a cold clean-up (via water quenching), high- and low-temperature water-gas-shift conversion reactors, amine-based CO_2 removal and pressure swing absorption (PSA)-based H_2 purification downstream of the gasifier. This sequence incurs major efficiency and cost penalties due to the thermal losses, the large number of unit processes and the non-continuous nature of the consecutive gas separation stages.

Reducing the number of unit steps, and increasing overall efficiency, is the subject of a major global research effort. H_2-selective membranes are a step-change technology, either as stand-alone separators, or as part of a catalytic membrane reactor, the latter of which can replace multiple WGS conversion and gas separation stages. The uptake of membrane-based separation will be driven by efficiency and economics, and only when membrane separators can achieve the necessary H_2 flux, operating temperature, cost, durability and tolerance to impurities will this technology become attractive. Benchmarks for these performance characteristics have been established by the US DOE [4], and membrane developers around the world strive to meet all these criteria. Most important of these are temperature (250–500 °C), flux (150 cm^3/cm^2/min with $dP(H_2)$ of 100 psia), cost (~\$US 1000/m^2) and durability (5 years).

1.2. Alloy membranes

Operating via a solution-diffusion mechanism that intrinsically produces pure H_2 (suitable for direct use in a PEM fuel cell, for example), alloy membranes are also stable in the temperature range corresponding to a range of fossil fuel conversion reactions, for example, water-gas-shift reaction, the reforming of methanol and methane, and catalytic coal gasification. Pd and its alloys have been studied extensively for almost a century [5], while a concerted research effort into inexpensive alternatives has been underway only for the last 2 decades. Recent years, however, have seen a dramatic increase in publications concerning these non-Pd membrane materials.

1.2.1. Pd-alloy membranes

To give context to the discussion of BCC-type alloy membranes, an introduction of the benchmark alloy membrane material, that is Pd-based alloys, should be made. Pd-alloys are suitable for high-temperature separation at temperatures relevant to methane reforming and WGS, produce pure H_2 via a solution-diffusion mechanism, are tolerant to H_2O, CO, CO_2 and H_2S (in some cases). The main drawback of palladium is the cost, which has been as high as \$US 589 per oz [6] within the last 5 years. This equates to a cost per m^2 per μm thickness of over \$US 200. Given the 2015 DOE cost target of \$1000 m^{-2}, a 5-μm-thick Pd membrane will exceed the cost target, even before the manufacturing and modulization costs are accounted for.

Increased demand through the increased uptake of Pd-alloy based H_2 separation membranes can only drive the Pd price higher. Research is therefore being driven in two directions: firstly, to the development of Pd-alloy membranes of ever-decreasing thickness [7–9], and secondly, to the development of alloy membranes containing little or no palladium. Several thorough reviews of Pd-alloy membranes [5,10] have been published, as well as numerous articles detailing performance, fabrication and durability.