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Suitability of Amorphous Thin – Film Alloys for Hydrogen Purification

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Introduction

Hydrogen separation membranes combined with Steam Methane Reforming (SMR) or Coal Gasification (CG) could provide a high volume of ultra-high purity hydrogen provided that the cost of separation membranes is reduced in line with US DoE targets [1]. Dense metallic membranes used for hydrogen purification are dominantly based on Pd and Pd alloys [2,3]. However, the application of Pd and Pd alloy membranes for large-scale hydrogen purification is too expensive [1]. In addition to the high cost of Pd, the susceptibility to hydrogen embrittlement [4] and surface poisoning by impurity gases such as CO_2, CO and H_2S [5], encourage searching for alternative hydrogen separation materials.

Amorphous alloys have been investigated as potential hydrogen purification membranes because of their good mechanical properties, corrosion resistance, higher resistance to hydrogen embrittlement, and significantly lower cost [6]. Some of the amorphous zirconium and nickel-based alloys have been shown by computational [7,8] and experimental studies [7,9] to have hydrogen permeability values close to that of Pd. For example, $(Ni_{0.6}Nb_{0.4})_{70}Zr_{30}$ alloy showed comparable hydrogen permeability to Pd (1.3×10^{-8} mol m^{-1} s^{-1} $Pa^{-0.5}$ at 400°C) while offering acceptable surface catalytic activity for hydrogen dissociation/recombination. The hydrogen permeability in this alloy showed to increase by increasing the Zr content, but forming a less thermally stable alloy [9,10]. $Zr_{54}Cu_{46}$ and $Zr_{30}Cu_{60}X_{10}$ (T=Sc, Ta, Y, and Ti) alloys were also computationally predicted to offer higher hydrogen permeability than Pd [11,12]. However, the surface oxidation could significantly lower the hydrogen permeability in these alloys [13].

In general, higher hydrogen solubility is seen in amorphous alloys due to an increased in the population of defective sites suitable for hydrogen occupation [14]. Unlike the crystalline materials, hydrogen diffusivity in amorphous materials depends on the hydrogen concentration. This attributes to the existence of hydrogen occupation sites with different binding energies. Initially, hydrogen mobility is low due to the occupation of high–energy sites with higher hydrogen affinity. As hydrogen concentration increases and high–energy sites are filled, hydrogen atoms will occupy low–energy sites, which results in a higher mobility as hydrogen is not strongly bound to this sites [15].

Fabrication of thinner membrane can significantly improve the hydrogen diffusion in membranes and therefore achieving a higher permeability. Amorphous membranes with thicknesses of 30 to 50 μm [16] were successfully fabricated by melt spinning. We also recently demonstrated [17] the possibility to fabricate dense binary and ternary Zr–based amorphous thin–films (less than 10 micron) by the Closed Field Unbalanced Magnetron Sputtering Ion Plating (CFUMSIP) (Figure 1). Using this method, we could produce amorphous thin–films in a wider compositional range with a better control over the size, shape and thickness of the films.

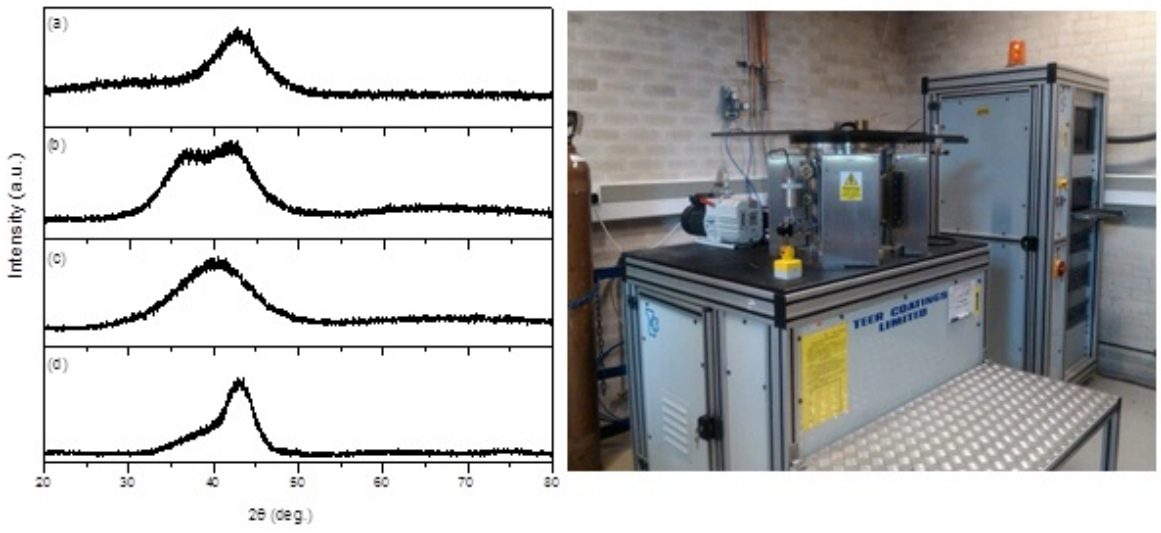

Figure 1: XRD patterns of (a) $Zr_{40.5}Ni_{59.5}$, (b) $Zr_{56.2}Cu_{43.8}$, (c) $Zr_{30}Cu_{57.7}Y_{12.3}$, and (d) $Zr_{32}Cu_{57.3}Ti_{10.7}$ thin–films fabricated by CFUMSIP system (right picture).

The metastable thermodynamic state of amorphous membranes imposes temperature limitation during the amorphous membranes operation. Crystallisation can occur in amorphous membranes at high temperatures during the operation and even below the theoretical crystallisation temperature if kept for a long time [18]. Upon crystallisation, alloys will lose their resistant to hydrogen embrittlement followed by a substantial decrease in the alloy's hydrogen permeability. We noticed [19] that thermal stability of the fabricated thin–films is mainly dominated by the alloys composition rather than the fabrication route. However, the crystallisation process in these films seemed to be different compared to bulk materials. Alloys were particularly sensitive to the oxidation and amorphous phase decomposition during structural analysis under inert and hydrogen atmospheres. As a result, phase separation was substantial in the case of Cu and Ni in the $Zr_{56.2}Cu_{43.8}$ and $Zr_{40.5}Ni_{59.5}$ sputtered thin–film alloys. Cu and Ni phase separation could effectively alter the local atomic structure, hence affecting the crystallisation thermodynamic. An effective method to reduce the level of Cu phase separation was [19] to fabricate $Zr_{30}Cu_{57.7}Y_{12.3}$, and $Zr_{32}Cu_{57.3}Ti_{10.7}$ ternary amorphous thin–films. However, the kinetic studies revealed that the atomic size mismatch of Y and Ti in these ternary alloys may change the local atomic microstructure and reduce the atomic packing density. Thermal behaviour of amorphous alloys strongly depends on the existence of the Short Range Order (SRO) metastable icosahedra-like clusters with highest atomic packing density. The formation of crystal like structure was encouraged in the $Zr_{30}Cu_{57.7}Y_{12.3}$, and $Zr_{32}Cu_{57.3}Ti_{10.7}$ ternary amorphous thin–films, which could act as nucleation sites and therefore reducing the thermal stability of the alloys.

Although, some amorphous binary and ternary Zr–based alloys proposed to offer a comparable hydrogen permeability to Pd, oxidation, phase separation and the lack of thermal stability, especially under hydrogen, can hinder the application of amorphous thin–film membranes. The suitability of amorphous thin–films (and even bulk alloys) as potential hydrogen purification membranes can be better judged after more careful studies on the crystallisation mechanism and thermal stability controlling factors under hydrogen.

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