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Development of tantalum–zirconium alloy for hydrogen purification

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HIGHLIGHTS

- Terminal solid solubility of Ta increases with Zr addition.
- Increase in lattice parameters of Ta due to Zr addition may be the possible reason.
- Enhance H solubility could also be explained on the change in e-DOS of Ta–Zr alloys.
- Ta–Zr alloys could be possible combination for hydrogen purification membrane.

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ABSTRACT

Terminal solid solubility of hydrogen in Ta–Zr alloys has been studied in connection with the development of tantalum based metallic membrane for hydrogen/tritium purification. The alloys were prepared by vacuum arc melting technique and subsequently cold rolled to 0.2 mm thickness. The terminal solid solubility of hydrogen in these cold rolled samples was investigated in a modified Sieverts apparatus. The terminal solid solubility of hydrogen was marginally increased with zirconium content. The change in the lattices parameter of tantalum upon zirconium addition and the higher affinity of zirconium for hydrogen as compared to tantalum could be the possible reasons.

1. Introduction

The development of hydrogen and its isotopes ($^3H_1$ & $^2H_1$) based energy utilizations such as in fuel cell and fusion reactor, are attractive in view of attendant benefits to reduce the CO_2 emission which is a burning issues of global warming [1,2]. Hydrogen based energy system could also be beneficial to chase the pace of industrialization of fast growing countries such as India and China. Furthermore, fast depleting reservoir of crude oil is creating a persistent interest worldwide in the search of energy carriers to condense and connect the renewable energy re-sources to the end users. In this connection, hydrogen and its isotopes are considered as the most suitable eco-friendly energy sources as well as energy carriers which can be used in many ways such as tritium/deuterium in fusion reactor and hydrogen in fuel cell/IC engines. International Thermonuclear Experimental Test Reactor (ITER) is one of the examples where $^3H_1$ will be generated in-situ from ^6Li containing ceramic breeder such as Li_2TiO_3 and flushed out by the carrier gas helium [3]. The $^3H_1$ thus produced needs to be separated from helium and other gaseous impurities, to be stored in a suitable forms and re-fuel it back into the ITER-plasma. Therefore, intensified research are going on worldwide on the development of economically feasible method for the hydrogen and its isotopes production, separation, purification and their safe storage. Out of the many methods available, the hydrogen purification system using metallic membrane attracts more attention in recent years. In this regards, Pd–Ag alloy has been developed and supposed to be used in ITER-France [4,5]. However; high cost associated with Pd is a big concern for its commercial viable application in the future fusion based power reactors and fuel cells. Therefore, research is going on worldwide to develop cost-effective materials to replace high cost of Pd based alloys. To understand the mechanism of hydrogen purification using metallic membrane, a schematic diagram has been illustrated in Fig. 1 [6]. The essential properties of the membrane are its chemical inertness with respect to gaseous impurities such as oxygen, carbon

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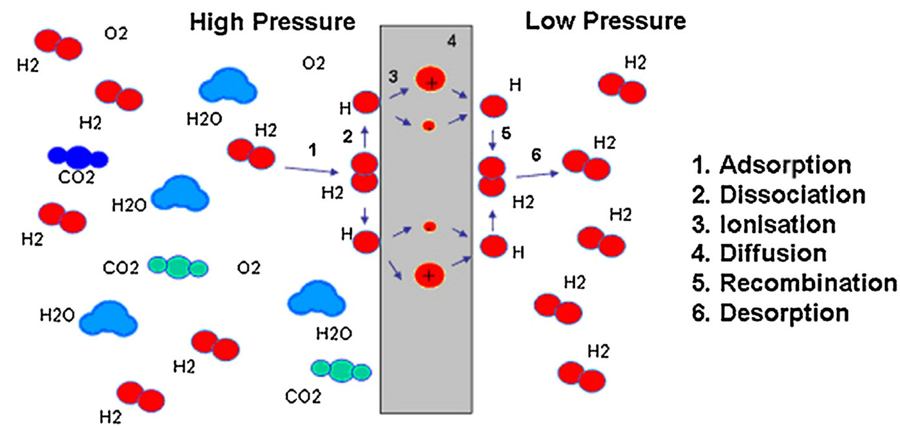

Fig. 1. Schematic illustration of the hydrogen permeation through metallic membrane [6].

dioxide, water vapor and inert gasses at the operating temperature and pressure conditions. Besides, it should also have desired mechanical integrity in hydrogen atmosphere. The hydrogen permeation behavior of various potential candidate metals have been presented in Fig. 2. It is clear from the figure that the refractory metals such as Nb, Ta and V, have very high hydrogen permeation property because of their bcc crystal structure [7]. Particularly, tantalum attracts more attention as it forms thermodynamically unstable hydride at low working temperature and comparatively less oxidizing in nature. However, the mechanical integrity of the tantalum membrane in hydrogen atmosphere is poor because of embrittlement cause by high stresses developed due to dissolved hydrogen. This could be avoided by developing a tantalum alloy resistant to oxidation and hydrogen embrittlement. Substantial investigation have been carried out on various binary alloys of tantalum and found that many of the alloying components decrease the hydrogen solubility in tantalum [8–12]. Reduction of hydrogen solubility resulted in un-desirable decrease in hydrogen permeation. It was reported earlier [13,14], that the alloying component having high affinity for hydrogen as compared to main metal matrix may increase the hydrogen solubility. The zirconium is an obvious choice as it has high affinity for hydrogen and oxidation resistant property due to formation of submicron level adherent oxidation protective layer of ZrO_2 film. Thin film of ZrO_2 formed at the

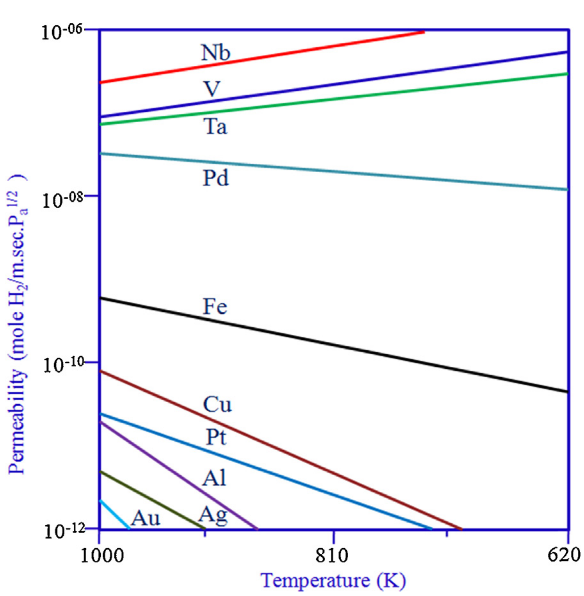

Fig. 2. Comparative illustration of hydrogen permeability in various bcc and fcc metals.

surface could also enhanced the molecular hydrogen dissociation [13] at the initial stage of hydrogen adsorption which may favors the hydrogen permeability. In present study, the hydrogen solubility in two Ta–Zr alloys has been investigated at various pressure and at a desired working temperature. The result thus obtained indicates that Ta–Zr alloy could be a potential candidate to be developed as hydrogen permeation membrane.

2. Experimental

2.1. Sample preparation

Tantalum one and two atom% zirconium alloys were prepared using arc melting in an argon atmosphere. High purity (>99.8%) Aldrich make tantalum foil and 99.99% purity, in-house make Zr crystal bar were used as starting materials. The melting was repeated 5 to 6 times to make the alloys homogeneous. The alloys were obtained in a button form which was subsequently cold rolled to 0.2 mm thickness. After cold rolling, the sheets were sliced into small pieces of dimension 1 mm × 1 mm × 0.2 mm (length × width × thickness) using an electronic discharge cutting machine (EDM). Before hydrogen charging, all the samples were cleaned manually, polished on emery paper followed by chemical cleaning with non-oxidizing acid and acetone. The homogeneity of the alloys was confirmed by X-Ray florescence (XRF) and electron dispersive spectroscopy (EDS) analysis. Detailed chemical composition of all samples analyzed by inductively coupled atomic emission spectroscopic (ICP-AES) techniques are presented in Table 1. The phase analysis of the alloys was performed using X-ray diffraction (XRD) and presented in Fig. 3

2.2. Hydrogen charging

A modified Sievert's apparatus was used to investigate the terminal solid solubility of hydrogen [15]. The samples were placed into a quartz sample holder and kept inside the reaction chamber. The reaction chamber was placed in a movable resistance heating furnace. High dynamic vacuum of the order of 10^{-5} mbar was created in the reaction chamber using rotary followed by diffusion

Table 1
Concentration of the impurities in atom percent analyzed by X-ray florescence and IC-PAES.

Samples	Zr	O	N	Ta
Ta	–	0.01	0.01	Balance
Ta1Zr	1.07	0.02	0.02	Balance
Ta2Zr	2.09	0.01	0.01	Balance