ARTICLE IN PRESS

Fusion Engineering and Design xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Fusion Engineering and Design

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

Effect of moisture in sweep gas on chemical compatibility between ceramic breeder and EUROFER97

Keisuke Mukai[a,*,1], Maria Gonzalez[b], Regina Knitter[a]

[a] *Institute for Applied Materials (IAM), Karlsruhe Institute of Technology, 76021 Karlsruhe, Germany*
[b] *National Fusion Laboratory, Division of Fusion Technology, CIEMAT, 28040 Madrid, Spain*

ARTICLE INFO

Keywords:
HCPB DEMO
Breeding blanket
Compatibility
EUROFER
Ceramic breeder

ABSTRACT

Effect of moisture in sweep gas on chemical compatibility between ceramic breeder (Li_4SiO_4 with 20 mol% of Li_2TiO_3) and EUROFER97 was examined in this study. These materials were contacted and heated at 623, 823, and 1073 K for up to 12 weeks where the H_2O concentrations of the outlet gas were 0.13-0.24 vol.%. In the two-phase breeder specimen, Li_4SiO_4 was preferably decomposed into Li_2SiO_3 with a possible formation of Li_2O or LiOH depending on environmental condition. Formation of corrosion layers on the EUROFER specimen was enhanced in the wet condition, especially at the elevated temperatures of 823 and 1073 K. Though these results showed parabolic growth rates, an extrapolation from data of the elevated temperatures to 623 K was not feasible in the wet atmosphere, which could derive from the difference of the chemical form in the breeder specimen. Effective diffusion coefficient of oxygen into EUROFER at 623 K was given to be 4.5×10^{-14} cm^2/s and a possible thickness of the corrosion layer after a 2-year use was predicted.

1. Introduction

The helium cooled pebble bed (HCPB) blanket concept is being developed toward a future implementation in a DEMO fusion reactor, in which ceramic breeder pebbles are packed to produce tritium by nuclear transmutation of Li [1]. During years of an operation period, the pebbles are contacted with structural steel of the blanket at an elevated temperature of 623 K, while the temperature of the pebble bed is elevated up to 1173 K [2]. EUROFER97, a reference structural material for the European DEMO blanket, is a high purity steel composed of Fe, 8.9% Cr, 1.1% W, 0.4% Mn, 0.2% V, 0.1% C, 0.1% Ta, 0.04% Si, and 0.009% Ti to owe high irradiation resistance and low activation capability [3]. Among ceramic breeder materials, the ternary oxides of Li_4SiO_4 and Li_2TiO_3 are the most promising candidates. The two-phase composition, Li_4SiO_4 with addition of 10–30 mol% of Li_2TiO_3, has been developed as an advanced breeder material to improve mechanical properties of the pebbles [4], while maintaining a reasonable capability for multiple reprocessing [5,6].

In the HCPB concept, inert sweep gas is employed for tritium recovery and transport from the surface of the breeder pebbles. The reference sweep gas is helium with 0.1% addition of H_2 for facilitating tritium release from the ceramic breeder pebbles by taking advantage of hydrogen isotope exchange. Yet, alternative sweep gas composition might improve tritium release. The Addition of water vapor to the sweep gas, namely He + H_2O, can be another option to facilitate tritium release substantially by promoting surface isotope exchange reaction between the gas and tritium on surface of the breeder pebble [7,8]. Furthermore, with a favored release of HTO a reduced permeation of T into the coolant may be obtained. Despite the benefits, it must be taken into account that the addition of water vapor could alter the chemical form of solid/gas in the blanket. Kiat et al. reported the evolution of LiOH(s,l) at high temperatures, including the temperature shift of the phase transformation between LiOH(s) and Li_2O(s) depending on the H_2O concentration [9]. This implies that, in a wet condition, tritium may form LiOT(s) and increase tritium inventory in the blanket. It was reported, by using Knudsen effusion mass spectrometry ($T >$ 1223 K), that the addition of water enhanced the volatility of LiOH(g) from Li_4SiO_4 and Li_2TiO_3, while Li(g) was a dominant Li-containing gas in dry D_2 gas condition [10,11]. In fact, mass loss due to evaporation was reported to increase by addition of H_2O during heating at 1173 K [12]. Such changes in phase equilibria of solid/gas might affect the corrosion behavior, however, chemical compatibility study between ceramic breeder and EUROFER steel has been limited to dry sweep gas atmosphere [13,14]. While the compatibility was studied under the dry sweep gas condition in our previous work [15], this study aims at examining the effect of water vapor on the chemical

---

[*] Corresponding author.
E-mail address: k-mukai@iae.kyoto-u.ac.jp (K. Mukai).
[1] Present address: Institute of Advanced Energy, Kyoto University Gokasho, Uji, Kyoto 611-0011, Japan.

http://dx.doi.org/10.1016/j.fusengdes.2017.10.001
Received 19 May 2017; Received in revised form 9 August 2017; Accepted 3 October 2017
0920-3796/

Please cite this article as: Mukai, K., Fusion Engineering and Design (2017), http://dx.doi.org/10.1016/j.fusengdes.2017.10.001

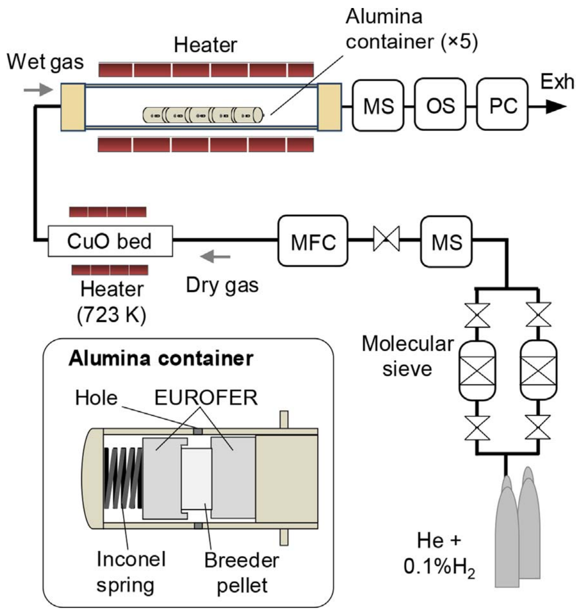

Fig. 1. Schematic image of the alumina container and the tube furnace that is connected with moisture sensor (MS), mass flow controller (MFC), oxygen sensor (OS), and pressure controller (PC) [15]..

compatibility between ceramic breeder and EUROFER plate. These materials were kept contacted and heated for up to 3 month at 623, 823, and 1073 K under humid atmosphere. Then, these specimens were characterized by x-ray diffraction (XRD), scanning electron microcopy (SEM) combined with energy dispersive x-ray microanalysis (EDX), and secondary ion mass spectrometry (SIMS). The results were quantitatively analyzed based on diffusion kinetics for obtaining effective diffusion coefficient and then compared with the previous results in the dry sweep gas condition. The possible thickness of a corrosion layer on EUROFER plate after the use for 2 years was predicted by using the coefficient at 623 K.

2. Method

The atmosphere controllable tube furnace was used for heating specimens [15]. As shown in Fig. 1, water vapor was supplied into the alumina tube by heating the CuO bed at 723 K as a result of the reduction of CuO particles to cupper metal. In the alumina container, a breeder pellet was sandwiched between two EUROFER 97 plates (11 mm ϕ × 5 mm h) in the container by using an Inconel spring. Five of the alumina containers were heated at 623, 823, or 1073 K in the tube furnace where the heating temperature was uniform. These five containers were extracted after 3, 7, 14, 21, and 28 days in the heating experiments at 823 and 1073 K, while those were taken after 7, 14, 28, 56, and 84 days in case of 623 K. During a sample extraction, temperature of the furnace was cooled down to 573 K. Flow gas rate and pressure were controlled to be 1200 ml/min and 1.2 bar, respectively. The breeder pebbles with the two-phase composition (Li_4SiO_4 with 20 mol% of Li_2TiO_3), fabricated by the melt process [16], were crushed and then shaped into a pellet with a diameter of 8 mm. The breeder pellets were heated at 1123 K in Ar gas flow condition for 5 h. The height and the sintering density of the pellets were 3 mm and 90–92%, respectively.

After the heating experiments, surface XRD analysis was carried out with a Bruker D8 using Cu-Kα radiation by collecting diffraction data in the 2θ range from 15 to 70°. The polished surface of the EUROFER plate before the heating test exhibited a diffraction pattern of ferritic steel (α-Fe) body-centered-cubic (bcc) structure. It is noted that the heating temperature of 1073 K is lower than the ferrite-austenite (α-γ) transformation temperature of EUROFER97, which is reported to be 1099 K for an infinitely slow heating rate [17]. XRD patterns were analyzed by Rietveld analysis by using TOPAS-academic software, by refining lattice parameter while fixing atomic position, occupancy, and isotropic displacement parameter because of weak intensity and high orientation. Cross-sections were studied by scanning electron microscopy (SEM SUPRA 55 by Zeiss) with an angle selective backscatter (AsB) detector to visualize a compositional contrast. Element distributions were investigated by energy dispersive X-ray microanalysis (EDX, Genesis XM2, Apollo 40 detector). For a SIMS measurement, the EUROFER plate heated at 1073 K for 3 days was chosen as a thick corrosion layer is unsuitable for the time-consuming sputtering process. The specimen was sputtered by oxygen primary ion using the ion source (IG-20 by Hiden) and then analyzed by the quadrupole mass analyser (MAXIM by Hiden). Though SIMS measurement originally gave information of element profile as a function of time, the time was converted into distance from surface x by measuring the depth of the ion eroded crater using the Bruker's DektakXT profilemeter. Based on a constant sputtering rate during the measurement and by assuming it to be independent of any compositional changes, even in case of a corrosion layer, the rate of the EUROFER was estimated to be 0.20 ± 0.03 nm/s.

The effective diffusion coefficient of Li into EUROFER was estimated from the result of SIMS measurement by considering a simple case of diffusion to the bulk. In this case, concentration C can be fitted by using the complementary error function as follows:

$$C = C_0 erfc\left(\frac{x}{2\sqrt{Dt}}\right) \tag{1}$$

where C_0, D, and t are concentration on the surface, diffusion coefficient (cm^2/s), and heating period (s), respectively.

In addition to the above approach, effective diffusivity of oxygen was estimated by measuring the thickness of the oxygen layer detected by SEM/EDX. The effective diffusion coefficient of oxygen D (cm^2/s) is given as follows:

$$D = d^2/t \tag{2}$$

where d is the thickness of the oxidized layer on the EUROFER plate and t is the heating period. The oxygen diffusion coefficient at each temperature was derived by fitting with a parabolic curve from the origin.

3. Result and discussion

3.1. Heating test

Fig. 2 shows averaged moisture concentrations of the outlet gas in each heating period where "period 1" is the initial period until the first sample extraction and "period n" (n > 1) represents the period between n-1th and nth extraction. The initial moisture concentrations of outlet gas were 0.23-0.24 vol.%, while those in the dry sweep gas condition were in the range of 0.01-0.03 vol.% [15]. It means that approximately 0.2 vol.% of H_2O was added by CuO bed in the initial

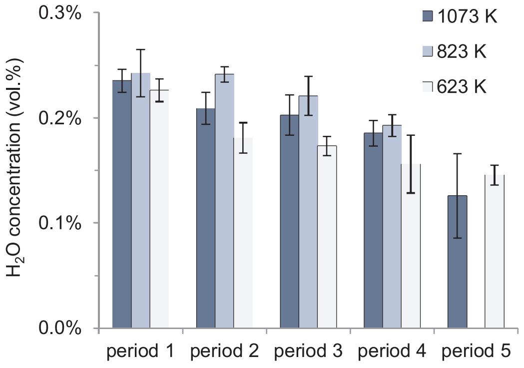

Fig. 2. Moisture concentrations of the outlet gas in each heating period.