Fusion Engineering and Design xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Fusion Engineering and Design

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

High stability of palladium/kieselguhr composites during absorption/desorption cycling for hydrogen isotope separation

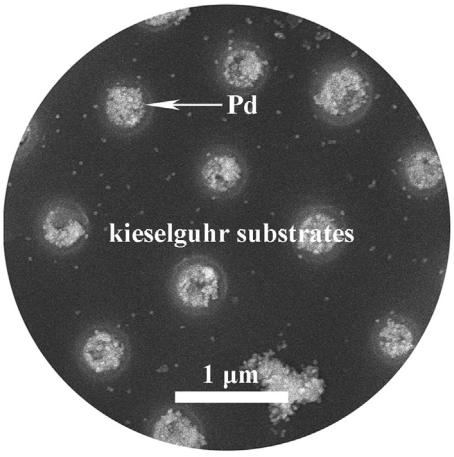
Yang Lei*, Xiaopeng Liu, Shuo Li, Lijun Jiang, Chao Zhang, Shuai Li, Di He, Shumao Wang

Department of Energy Materials & Technology, General Research Institute for Non-Ferrous Metals, Beijing 100088, China

HIGHLIGHTS

- Pd/K composites with as high as 57 wt.% of Pd have been successfully prepared.
- Palladium particles can be effectively packed into the pores of kieselguhr substrates.
- Variation of heat-treatment temperatures hardly affect hydrogen absorption capacity and hydrogen saturation time of the Pd/K.
- Anti-pulverization property of Pd/K can be improved by packing palladium into the kieselguhr internal pores and heating at 1300 °C.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 29 November 2015
Received in revised form 26 May 2016
Accepted 8 July 2016
Available online xxx

Keywords:
Palladium
Kieselguhr
Hydrogen isotope separation
Heat treatment
Cycle

ABSTRACT

Palladium/kieselguhr (Pd/K) composites with 57 wt.% of Pd were prepared by an improved dipping and thermal decomposition method and heated at elevated temperature to reduce breakdown during hydrogenation-dehydrogenation cycles. The hydrogen absorption kinetic properties of the samples heated at different temperatures were tested under the condition of 20 °C with 100 kPa hydrogen pressure. The 1300 °C heated Pd/K composites were repeated up to 4010 absorption and desorption cycles at temperature ranges between −40 °C and 200 °C. The results show that the phase structure, hydrogen absorption capacity and hydrogen saturation time of the Pd/K were not affected by the change of heat-treated temperatures. And after heat treatment at 1300 °C, the Pd/K particles were strengthened and fraction of larger than 80 mesh were as high as 93.4%.

1. Introduction

Since tritium-processing operations were established in 1955 [1], the separation of hydrogen isotopes (H, D, and T) has been an essential element for self-sustaining tritium cycles. The performance of separation materials is a key factor to produce high purity tritium gas from an isotopic mixture of H_2, D_2 and T_2. Palladium exhibits a large isotope effect and separation factors even

* Corresponding author at: Department of Energy Materials & Technology, General Research Institute for Non-Ferrous Metals, No.2 Xinjiekouwai Street, Xicheng District, Beijing 100088, China.
E-mail address: lei.y@outlook.com (Y. Lei).

http://dx.doi.org/10.1016/j.fusengdes.2016.07.024
0920-3796/

near room temperature [2], thus being widely used in tritium processing as the separation material. However, it tends to breakdown between the cycles of absorption and desorption of hydrogen isotopes, causing clogging problems in the process equipment and impeding the continuous operation. Therefore, palladium is usually loaded on a porous substrate such as ceramic or glass fiber [3,4]. Among the various palladium-based materials for use in hydrogen-absorbing processes, palladium/kieselguhr (Pd/K) composites have unique advantages, such as a large surface to volume ratio and high palladium content, which may provide adequate void space to prevent excessive pressure drops, promote Pd-H reactions, and mitigate aging effects in palladium tritide. Since 1980s, Pd/K has been used as the packing material to separate hydrogen isotopes in thermal cycling absorption process (TCAP) system at the Savannah River Site [5].

Pd/K composites are commonly synthesized through a dipping-thermo decomposition process using solutions of palladium chloride ($PdCl_2$) or ammonium nitrate palladium ($Pd(NH_3)_4(NO_3)_2$) [6,7]. Although the anti-pulverization performance of the composite material is largely improved comparing with pure palladium, it is still challenging that the loaded palladium of Pd/K composites with high weight fraction (>55 wt.%) can be maintained after several thousands of hydrogenation-dehydrogenation cycles. The conventional practices of rendering Pd/K more resistant to breakdown are heat treatment [8] or surface modification [9]. I.A. Fisher from Savannah River Site heated 40 mesh Pd/K at 1100 °C [8]. After 4500 cycles, particles larger than 50 mesh can reach 92%. However, the content of palladium in the Pd/K Fisher used should be no more than 55 wt.% [10,11], which may not be high enough for the high-efficiency operation of TCAP systems. Chen et al. prepared Pd/K materials without heat treatment, and particles smaller than 100 mesh accounted for 3.6 wt.% after 2000 cycles [12].

Heat treatment is a low cost and adaptable process to further enhance the mechanical strength of the Pd/K compared to surface modification for TCAP system, but it is generally accepted that exceedingly high temperature of heat treatment may influence the hydrogen absorption of Pd/K composites, particularly those with high-palladium content. The objective of this work is to show the results of the performance of 1300 °C heated Pd/K with 57 wt.% palladium we prepared after over 4000 absorption/desorption cycles.

2. Experimental details

2.1. Materials

The kieselguhr we used was purchased from Tianjin chemical reagent Co., LTD. (Tianjin, China) and their particle sizes were 20–60 mesh (about 250–850 μm). Palladium acetylacetonate ($Pd(acac)_2$) and trichloromethane ($CHCl_3$), as the impregnating solution, were obtained from National Center of Analysis and Testing for Nonferrous Metals and Electronic Materials(NCATN) and Beijing chemical reagent company, respectively. All the reagents were used without further purification.

2.2. Instrumentation

The morphology, composition and structure of the prepared Pd/K were characterized using scanning electron microscope (SEM, Hitachi S4800), energy dispersive X-ray spectra (EDS) and X-ray powder diffraction (XRD, Rigaku Dmax-RB). The particle sizes before and after cycles of the heated and non-heated samples were both measured by laser particle size analyzer (Malvern 2000). Hydrogen absorption experiment was carried out by a volumetric method with a specially designed Sieverts type apparatus at 20 °C, which was introduced in our previous work [13,14].

2.3. Preparation of Pd/K composites

Both of the non-heated and the heat treated Pd/K samples were prepared by a dipping and thermal decomposition process with some technical improvements. $Pd(acac)_2$ was dissolved in $CHCl_3$ to serve as the impregnating solution. The porous substrate, kieselguhr, was immersed in the solution of $Pd(acac)_2/CHCl_3$. $Pd(acac)_2$ infiltrated into the pores and was coated onto the surface of the kieselguhr. The impregnating solution was then evaporated and $Pd(acac)_2$/K particles were obtained. After being calcined in H_2 atmosphere, the $Pd(acac)_2$/K changed into Pd/K. This process was repeated until the palladium content reaches 57 wt.% of the composition. For the heated sample, the heating process was in atmosphere of air for 2 h.

2.4. Absorption/desorption cycling tests

The Pd/K composites were loaded into a 100 ml stainless steel vessel filled with H_2 at 100 kPa. The system, which can record the temperature and pressure and control the heating and cooling to the vessel, was designed in our lab. A series of hydrogenation-dehydrogenation processes of the 1300 °C heated Pd/K composites were repeated up to 4010 cycles between −40 °C and 200 °C. The absorption/desorption cycling was tested in auto mode. The heating and cooling periods are both 10 min, respectively. The hydrogen absorption kinetic properties of the samples heated by 800, 1000, 1100, 1200, 1300 °C, respectively, were tested under the condition of 20 °C with 100 kPa hydrogen pressure.

3. Results and discussion

3.1. Characterization of Pd/K composites

The kieselguhr with main composition of SiO_2 is disk-shaped and has a highly developed porous structure. Typical SEM images of the Pd/K composites are exhibited in Fig. 1a and b. The ordered and homogeneous macropores with a diameter range from 200 to 300 nm are completely filled with uniform palladium particles of about 50 nm. We can control Pd grew larger without destroying the porous structure of the substrate. The Pd grains coating of the substrate surface is rare. The corresponding EDS spectra in Fig. 1c indicate that the Pd/K composites mainly consist of Si, O, and Pd. The elements Al and C with low content are derived from the kieselguhr and $Pd(acac)_2$. All the results above confirm that the existence of palladium loaded in the substrate and the pure and high quality Pd/K we obtained. The crystalline structures of the Pd/K after heat treatment at 800, 1000, 1100, 1200 and 1300 °C, respectively, are revealed by XRD patterns, shown in Fig. 1d. It is noticed that all the samples of the heated Pd/K are well-crystallized quartz silica and the characteristic peaks of palladium appear in the patterns. Compared to the standard XRD data file (JCPDS 65-2867), the peaks at $2\theta = 40.1°$, 46.6° and 68.1° corresponding to the lattice planes of Pd (111), Pd (200) and Pd (220) can be observed for all Pd/K samples. No other crystalline forms of silica and palladium were found, which demonstrates that the peak position of the Pd/K has no shift and the phase structure of Pd/K is not affected with the temperature variation of the heat treatment.

3.2. Hydrogen absorption kinetic properties

The hydrogen absorption curves of the uncycled Pd/K heated at different temperatures, with the hydrogen pressure of 100 kPa and the temperature kept constant at 20 °C, are plotted in Fig. 2. The results show that all curves present a typical kinetic of hydrogen absorption properties of palladium. The hydrogen saturations are

Please cite this article in press as: Y. Lei, et al., High stability of palladium/kieselguhr composites during absorption/desorption cycling for hydrogen isotope separation, Fusion Eng. Des. (2016), http://dx.doi.org/10.1016/j.fusengdes.2016.07.024