

INVESTIGATION OF TRITIUM RELEASE FROM LITHIUM TITANATE

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OBJECTIVE

The objective of this work is to obtain tritium release information for lithium titanate, a low activation material being considered for tritium breeding in fusion reactors.

SUMMARY

Tritium release from lithium titanate has been investigated using isothermal anneal experiments. These experiments suggest that the rate-controlling step for tritium desorption is desorption of HTO from a titanium site on the Li_2TiO_3 surface. The experiments also indicate that the presence of hydrogen in the purge gas helps the tritium release by increasing the fraction of tritium released at a given temperature.

PROGRESS AND STATUS

Introduction

Lithium titanate is a low activation ceramic with potential as a tritium breeding material for fusion technology. To date, very little work has been done to characterize tritium release from lithium titanate and develop the requisite properties data base. Initial studies indicate that lithium titanate has excellent tritium release characteristics, comparable to those for lithium oxide or lithium zirconate. To fill in the data base for lithium titanate, we have performed several isothermal anneal tests of tritium release.

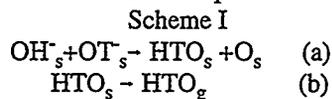
Experimental

Lithium titanate was obtained from AECL Research. The material was formed from an extrusion/tumbled mixture of Li_2TiO_3 , water, and a binder. The resulting pebbles were sintered at 1673 K to provide Li_2TiO_3 . [1] Several of these pebbles were sealed in aluminum capsules and irradiated in the TRIGA reactor at the University of Illinois, Urbana-Champaign, for approximately 1 h. The pebbles were removed from the aluminum capsules under an inert atmosphere and transferred to the annealing apparatus in a specially designed, sealed sample holder. The annealing apparatus has been described previously. [2] The isothermal anneals were performed by preheating the furnace to the desired temperature, while the pebbles were positioned in the cool, sealed sample holder. After the furnace had reached the desired temperature, the pebbles were introduced into the heated zone. Tritium release was monitored on-line using a proportional counter. Integrated values for the amount of tritium released over the duration of an anneal were obtained by oxidizing the tritium over a copper oxide bed and collecting the tritiated water in a set of ethylene glycol traps. The anneals were performed for 24 h at the initial temperature (300-500°C) at which point the ethylene glycol traps were replaced. The pebbles were then heated to 900°C for an additional 24 h to remove residual tritium.

Results and Discussion

Tritium anneals were performed with two purge gases, pure He and He+0.1% H_2 . The tritium release data were fit to first-order desorption equations to obtain a desorption rate constant. These rate constants are plotted in Figure 1 as a function of inverse temperature. Within the scatter of the data, the rate constant for desorption into pure He is the same as that for desorption into He+0.1% H_2 .

One of the reaction schemes proposed for tritium desorption is



If the rate-controlling step is recombination of surface hydroxyls with OT [step (a)], the rate constant would be dependent on the surface concentration of OH, and this concentration should change with changing hydrogen pressure. However, if the rate-controlling step is desorption of the surface bound water molecule [step (b)], the desorption rate constant would be independent of the hydrogen pressure. Our finding that the rate constant for desorption into pure He is essentially the same as that for desorption into He+0.1%H₂ suggests that step (b) is the rate-controlling step for tritium desorption. The activation energy for desorption determined in this work is 37 kJ/mol. This value is in agreement with the value of 35 kJ/mol determined from temperature programmed desorption (TPD)

measurements on Li₂TiO₃. [1,3] This activation energy is quite low and suggests that the rate-controlling step does not involve breaking covalent M-OH and O-H bonds. In comparison, the desorption of tritium from Li₂O, which is believed to follow step (a) as the rate-controlling step, has an activation energy between 102 and 132 kJ/mol. [4] This step involves breaking Li-OH and Li-O-H bonds.

Some insight into the desorption of tritium from Li₂TiO₃ may be gained by studying the adsorption and desorption of water from TiO₂. Egashira et al. [5] and Lo et al. [6] report that water is adsorbed and desorbed mainly as an intact molecule from a stoichiometric TiO₂ surface; however, dissociative adsorption can occur when Ti³⁺ defects are present. The TPD experiments of Egashira et al. indicate two types of surface bound water molecules which desorb from the TiO₂ surface with desorption activation energies ranging from 36 to 69 kJ/mol. [5] In contrast, desorption of water from recombination of hydroxyl groups appears to have a desorption activation energy of 104 kJ/mol. [5,6] Electron spectroscopy and ultraviolet photoemission spectroscopy have been used to identify the species responsible for these desorption peaks as intact water molecules on the TiO₂ surface, or as hydroxyl groups. [6] Assuming that the crystallographic differences between the surfaces of TiO₂ and Li₂TiO₃ have a minimal impact on the binding of water to a Ti⁴⁺ or O²⁻ ion in the structures, the similarity of the observed tritium desorption activation energy of 37 kJ/mol to the activation energy for desorption of water from TiO₂ suggests that the rate-controlling step for tritium desorption from Li₂TiO₃ in these isothermal anneals is desorption of HTO from the Li₂TiO₃ surface.

During the isothermal anneal experiments, it was found that not all of the tritium was released during the first 24 h anneal. The fraction of tritium released in the first anneal (total determined by the amount of tritium released during the first anneal plus the amount released during the subsequent anneal at 900°C) is plotted versus anneal temperature in Figure 2. There is a striking difference in the fraction of tritium released into a purge of pure Ar and one of Ar+0.1% H₂. For example, at 300°C, 60% of the tritium in the sample is released in 24 h when the purge is Ar+0.1% H₂ while only about 18 % is released in 24 h at 302°C in pure Ar.

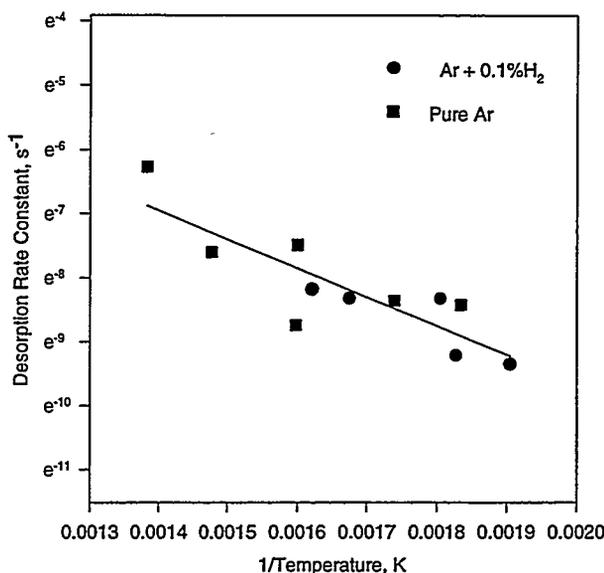


Figure 1. Effect of hydrogen pressure on the tritium desorption rate constant

It is clear that hydrogen addition to the purge gas is beneficial for tritium release from these lithium titanate pebbles. The benefit occurs as a result of increasing the fraction of tritium released at low temperatures. The fraction released is not determined by kinetics, since the calculated fraction of tritium released in 24 h is consistently greater than 99% if it is determined from the desorption rate constant obtained from the fits to the desorption data. The observation that the fraction released is less than this percentage suggests that not all of the tritium is available for immediate release. This may be due to more than one chemical form of tritium in the solid (or on the surface), at least one of which is being released very slowly or not at all at the temperatures of the anneals. This hypothesis is supported by TPD experiments which indicate several desorption peaks.^{1,3}

However, more work needs to be done to determine whether different chemical forms of tritium actually exist on the surface or in the solid and to identify these species. The role of hydrogen in changing the fraction of tritium released during the low temperature anneals is not understood at this time. It may be influencing electronic defects, reacting with impurities in the solid which control tritium release, or affecting the equilibria between reduced and oxidized tritium species.

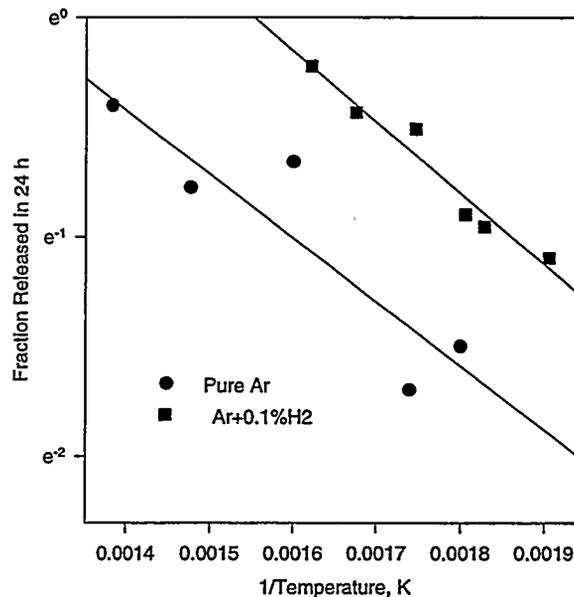


Figure 2. Effect of hydrogen pressure on the fraction of tritium released in 24 h.

FUTURE WORK

Additional experiments are planned to determine the role of hydrogen in assisting tritium release from ceramic breeder materials. These include diffuse reflectance infrared spectroscopic studies to determine if different hydrogenic species occur on the surface (TiOH , LiOH , LiH , TiH , etc), as well as isothermal anneals in purge gases with varying hydrogen concentrations.

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