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Xenon migration behaviour in titanium nitride

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Abstract

Titanium nitride is one of the inert matrixes proposed to surround the fuel in gas cooled fast reactor (GFR) systems. These reactors operate at high temperature and necessitate refractory materials presenting a high chemical stability and good mechanical properties. A total retention of the most volatile fission products, such as Xe, I or Cs, by the inert matrix is needed during the in pile process. The thermal migration of xenon in TiN was studied by implanting 800 keV Xe^{++} ions in sintered samples at an ion fluence of 5×10^{15} cm^{-2}. Annealing was performed at temperatures ranging from 1673 to 1923 K for 1 and 3 h. Xenon concentration profiles were studied by Rutherford backscattering spectrometry (RBS) using 2.5 MeV α-particles. The migration behaviour of xenon corresponds to a gas migration model. It is dominated by a surface directed transport with a slight diffusion component. The mean activation energy corresponding to the diffusion component was found to be 2.2 ± 0.3 eV and corresponds to the Brownian motion of xenon bubbles. The directed Xe migration can be interpreted in term of bubble transport using Evans model. This last process is mostly responsible for xenon release from TiN.

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1. Introduction

Within the frame of the Generation IV project, two concepts of gas cooled reactors have been selected: the very high temperature reactor (VHTR) and the gas cooled fast reactor (GFR) [1–4]. In both cases, the fuel may operate at about 1273–1473 K in normal conditions and may reach 1873–1973 K in case of accident. Concerning the GFR concept, the fuel cycle has to be optimised to recycle actinides and to minimise the waste production. (Pu, U)C carbides and (Pu, U)N nitrides are candidates for the fuel kernel because of their high actinide density, and their elevated decomposition temperature and thermal conductivity [5,6]. Several geometries for the fuel assembly have been proposed for GFR, prismatic block or pebble bed for example, in which the fuel is surrounded by several coating layers and an inert matrix [7,8]. The principal criteria for the

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choice of the inert matrix are: chemical compatibility with the fuel, mechanical and irradiation resistance, thermal properties allowing high gas temperatures and total retention of fission products during the in pile process. The following ceramics, SiC, TiC, ZrC, TiN, ZrN [5–13], have been proposed for core structures in GFR reactor.

Titanium nitride is known as a material of choice for the coating of cutting and grinding tools as protection against wear, erosion and chemical attack [14–17]. It is also widely used in microelectronic instrumentation as diffusion barrier and adhesion promoter between metallic layers such as Al, Si, Cu, Ag or Pt [18–21]. The ability of titanium nitride to act as a diffusion barrier combined to its mechanical and thermal properties make it relevant for the previously described nuclear applications.

Few studies have been carried out on the retention properties of TiN for fission products and no diffusion coefficients have been reported in literature to our knowledge. Xenon is one of the most volatile fission products and is known to segregate in many materials because of its very low solubility [22–24]. In the case of UO_2, for example, Nicoll et al. [25] showed that the maximum solubility of xenon was about 10^{-5} at.%. Weber et al. [26] also observed a precipitation of gas bubbles at the TiN/Ti interface after irradiation with 250 keV Xe^+ ions at ion fluences of 10^{15}–10^{17} cm^{-2}. These last authors estimated the critical concentration for precipitation of xenon in titanium nitride to be less than 0.5 at.%. Different views still exist concerning the particular behaviour of precipitated gas bubbles in solids during annealing. For example, some authors consider gas bubble coarsening in UO_2 as a consequence of bubble migration and coalescence [27] whereas others invoke Ostwald ripening (thermal resolution) [28,29]. Concerning metals, Evans [30] explained the directed He-bubble diffusion observed by Marochov et al. [31] in nickel with a model based on thermal vacancy flow from free surfaces to bubble population. According to Evans, the directed motion of the gas bubbles toward the surface is also responsible for the dramatic acceleration of xenon release from UO_2 [30,32,33]. The aim of the present work is to study the thermally activated migration of xenon implanted into sintered titanium nitride. The evolution of the xenon concentration profile was characterized by RBS as a function of the temperature and the results are discussed in term of gas bubble behaviour.

2. Experimental

2.1. Sample preparation and annealing

Samples are sintered pellets of TiN $15 \times 15 \times 2\ mm^3$ in size. They are polished to micron using diamond powders. Sample density was found to be 5.18 (theoretical density = 5.39) g cm^{-3} and major impurities are oxygen, about 2 at.%, and metals such as Fe and Ni, lower than 1 at.%.

In a first stage, pre- and post-implantation annealing of the samples was achieved, in a resistance tubular furnace, at 1273 K – 10 h and 1173 K – 10 h respectively, to relax the constraints and damages induced by polishing and ion implantation near the surface [34].

The second stage consists in annealing at higher temperatures, ranged from 1473 to 1923 K for 1 h (series 1: $T = 1673$ and 1773 K) and 3 h (series 2: $T = 1823$, 1873 and 1923 K), using a 12 kW EFD® induction heating system. In this system, the sample is supported by a tungsten susceptor disposed in a silica tube under a vacuum of about 10^{-7} mbar. The tube is then placed within the induction coil as represented in Fig. 1. The temperature is monitored using an Impac® bichromatic pyrometer. The infrared wavelengths used to determine the temperature are 0.9 and 1.1 μm. The emissivity ratio between both wavelengths was chosen to be 1.0 in the considered temperature range. The time needed to reach the annealing temperature was about 20 min in each case. During the heating ramp, the pressure never exceeded 5×10^{-6} mbar. At the end of the annealing, the power of the induction system was switched-off and the temperature of the sample decreased to the ambient in a few minutes.

2.2. Xenon implantation and RBS analysis

The xenon implantation was performed using the 400 kV accelerator of the Nuclear Physics Institute

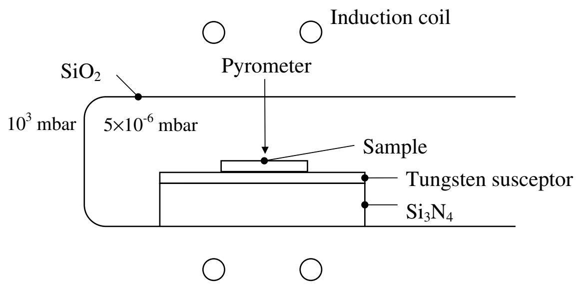

Fig. 1. Cross sectional scheme of the induction heating system.