CHAPTER 1 INTRODUCTION

In a High Temperature Gas-cooled Nuclear Reactor (HTGR) safety is one of the most significant considerations. In the Pebble Bed Modular Reactor (PBMR), such as the South African Pebble Bed Modular Reactor (SA PBMR) which had been proposed – one of the HTGR safety factors is achieved by retaining the radioactive fission products (FPs) from the nuclear chain reactions in the fuel so as to avoid contamination of the primary cooling circuit components, which complicates the reactor's maintenance, thus increasing the maintenance cost and putting the personnel involved in danger.

A nuclear chain reaction is a continuous process where a slow neutron reacts with a fissile isotope which then fissions into many different FPs and fast neutrons while energy is liberated in the process. Some of the FPs are radioactive. In the HTGR the fast neutrons are cooled down by means of materials with a low neutron cross section (e.g. carbon) so that they will further react with fissile isotopes (e.g.^{235}U), to produce more heat. By passing the coolant between particles, heat is transferred to the coolant (viz. helium), which, in the direct cycle PBMR, drives the turbine motor for the purposes of electricity generation. The radioactive FPs are retained by coating layers for safety purposes.

In the modern PBMR high-temperature nuclear reactor, the fuel particles are encapsulated by chemical vapour deposited (CVD) layers which serve as a barrier in preventing the FPs' release. In recent designs the fuel kernels are surrounded by four successive layers of low-density pyrolytic carbon buffer, inner high-density pyrolytic carbon (IPyC), silicon carbide (SiC) and outer high-density pyrolytic carbon (OPyC) - see figure 1. This kind of particle is termed TRISO (TRistructural ISOtropic). The fuel kernel (UO_2) is 0.5 mm in diameter, the buffer layer is 95 μm thick, the IPyC and the thickness of the OPyC are of the order of 40 μm thick while the SiC is of the order of 35 μm. The functions of these coating layers in a TRISO particle are strongly determined by their physical and chemical properties. Carbon usage is based on the following properties: stability up to a very high temperature, a low neutron capture cross section, reasonable moderator (low *Z*), and its being non toxic and cheap. Silicon carbide usage is based on the following physical and

chemical properties: high thermal conductivity, extreme hardness, high temperature stability, small neutron capture cross-section and good dimensional stability under neutron radiation [Hua97] [Sen03]. The main functions of the low-density PyC layer, which is also known as the buffer layer, are to attenuate the fission recoils and to provide voids for the gaseous FPs and carbon monoxides that are produced. The IPyC retains gaseous fission products. The SiC layer retains solid FPs or acts as a barrier to solid FPs and provides adequate structural stability during fuel compact fabrication. The outer high-density PyC protects silicon carbide mechanically. In the pebble bed reactor, 11,000-15,000 fuel particles are mixed with a graphite (5 mm) material to form a 60 mm diameter fuel spheres known as pebbles. These pebbles are inserted from the top of the core in the reactor and circulate from the top to the bottom until they have reached minimal burn up.

At the high end of the envisaged operating temperatures of the PBMR, the TRISO particles quite effectively retain most of the important FPs such as cesium, iodine, xenon and krypton, but the release of silver seems to present a major problem. The failure of these particles to retain silver has raised concerns about the effectiveness of the SiC layer as a layer that is impenetrable to fission fragments, despite the low fission yield of the stable ^{109}Ag (0.03% for ^{235}U) and its low conversion rate of 0.1% ^{110m}Ag by neutron capture. ^{110m}Ag is considered to be one of the dangerous FPs because of its longer half- life ($t_{1/2}$ = 253 days) and the high gamma-rays dose rate.

Due to this problem with respect to silver, a number of studies have been undertaken in order to understand its migration mechanism, but to date the results are contradictory. For example, the studies by [Nab77] and [Min00] have indicated that a significant amount of ^{110m}Ag was released from the coated particles at high temperatures ranging from 1500 ^{o}C to 1700 ^{o}C, which was strongly believed to be associated with its migration through grain boundaries of the coated polycrystalline SiC enhanced by traces of free silicon [Nab77]. However, in a follow-up study it was revealed that particle-particle variations in the release behaviour of silver could not be explained only by the presence and/or absence of cracks in the SiC coating layer [Min00]. In addition, the work by MacLean et al [Mac02], [Mac03] and [Mac04] indicated that silver did not move by diffusion, neither in the matrix nor along grain boundaries; hence a flow mechanism through nano-pores was suggested as the

possible migration path. The study by Jiang et al [Jia04] indicated that there is no significant diffusion of implanted silver in single crystalline SiC during annealing at a temperature up to 1300 ^{o}C, but that the silver tends to diffuse towards the surface in amorphous SiC at 1300 ^{o}C. The contradiction in the above results might be due to the structural differences between the samples investigated since they were manufactured by different manufacturers. In order to better understand the migration path of silver through a CVD-SiC layer of a TRISO particle, one needs first to understand the diffusion in single crystalline SiC and then that in polycrystalline SiC. From the various measurements that have been carried out on such systems [Nab76] [Mac04] [Jia04] no consistent diffusion coefficients of silver have been determined. The published results differ by more than several orders of magnitude. In order to understand the transport of silver through SiC coatings, the importance of volume and grain boundary diffusion and the effects of radiation damage on these two have to be clarified.

In this thesis the diffusion of silver in single crystalline SiC (6H-SiC) was investigated. This should to yield in the same results as in single crystalline SiC (3C-SiC) because they only differ in stacking order as explained in chapter 3. Two methods were used in our investigations. For analyses of in-diffusion, a silver layer was deposited onto clean single crystalline 6H-SiC samples. The samples were then annealed under a vacuum at temperatures below the melting point of silver. The post annealing Rutherford backscattering spectroscopy (RBS) and scanning electron microscopy (SEM) results indicated no in-diffusion of silver, but rather the disappearing of silver at these temperatures. This is due to a wetting problem between silver and SiC. Further in-diffusion of silver was performed by encapsulation. Samples were encapsulated in a quartz ampoule together with a silver source to maintain the silver layer on the samples' surface during annealing. The encapsulated samples were annealed at temperatures below the quartz's softening temperature (1200 ^{o}C). The post annealing RBS and SEM analyses results also indicated no in-diffusion of silver into 6H-SiC and the disappearing of silver on 6H-SiC surfaces.

Due to the negative results of in-diffusion of silver into 6H-SiC, further research was undertaken on silver diffusion in 6H-SiC. Silver was implanted in 6H-SiC at different temperatures (i.e. room temperature (23 ^{o}C), 350 ^{o}C and 600 ^{o}C for 6H-SiC) at a

fluence of 2×10^{16} cm^{-2}. The samples were then annealed from the temperatures below the melting point of silver to 1600 ^{o}C for different annealing times. Using RBS, the silver depth profiles after implantation and after annealing were compared to calculate diffusion coefficients. RBS, combined with channelling (RBS-C), was employed to investigate the production and annealing of radiation, while scanning electron microscopy (SEM) was used to investigate the changes that occurred in the samples' surfaces during annealing.

The rest of this thesis is organized as follows: Chapter 2 discusses diffusion, Chapter 3 ion implantation, Chapter 4 analytical techniques used in this thesis, Chapter 5 experimental procedures, Chapter 6 the previously published results, while Chapter 7 presents and discusses the results of this study. Chapter 8 summarises the results of this study and furnishes a number of insights into the work that still needs to be done; Chapter 9 is the appendix.

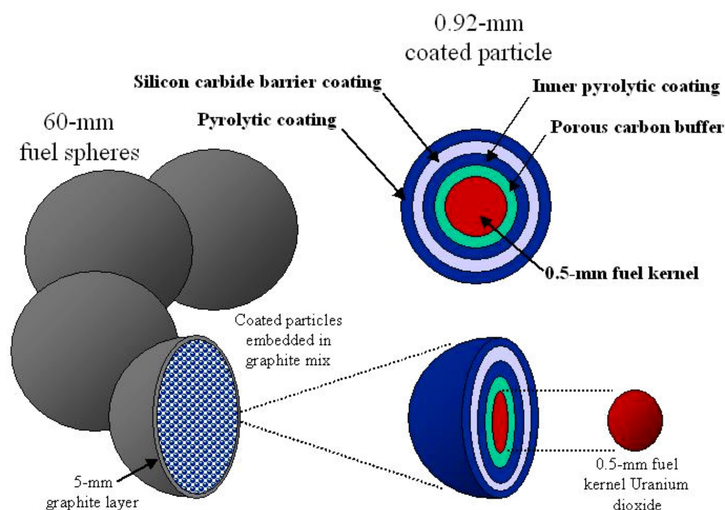

Figure 1. The fuel for a pebble-bed reactor consists of a 0.5 mm sphere of UO_2 surrounded by a porous carbon buffer, an inner layer of isotropic pyrolytic carbon, a barrier layer of SiC, and an outer layer of isotropic pyrolytic carbon which completes a TRISO particle of PBMR [www1].

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CHAPTER 2 DIFFUSION

Atoms in a crystal are oscillating around their equilibrium position or their lattice positions. If these oscillations are large enough the atom can change lattice sites. This can only occur if it overcomes the potential energy barrier between itself and its neighbours. The atoms in motion collide with other atoms in the same material, which causes them to move. Since collisions influence the movement of atoms, their paths form zigzags and the overall movement of the atoms exhibits an observable drift from a region of high concentration to one of low concentration in the inhomogeneous material. The movement of atoms from a region of higher concentration is called diffusion. This implies that diffusion is a transport phenomenon, which strongly depends on concentration gradients and alters the physical and chemical properties of materials.

In order to understand the diffusion process, one needs to know how fast the atoms move from the region of high concentration to the region of lower concentration. This information is provided by the diffusion coefficient. The latter is a quantity that provides information regarding how many atoms are passing through an area per unit time, as can be seen in Fick's first law [Fic55], which macroscopically connects the diffusion coefficient D and the gradient of the concentration (C) gradient to the flux J (see equation 2.1). In equation 2.1 D is calculated for the scenario where the concentration gradient does not alter over time for one-dimensional diffusion in the x direction.

$$J = -D\frac{dC}{dx} \qquad \ldots 2.1$$

However, in most systems where diffusion takes place, the concentration gradient changes over a period, and this modifies equation 2.1 for calculating the diffusion coefficient. This scenario is explained by Fick's second law which is derived from Fick's first law, i.e. equation 2.1, by assuming diffusion in the positive x-direction of a cylinder of a unit cross section and from the continuity equation:

$$\frac{\partial C}{\partial t} = -\frac{dJ}{dx} \qquad \ldots 2.2$$

If D does not depend on position, one can substitute $J=-D\frac{dC}{dx}$ into equation 2.2 to yield [She89]:

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} \qquad ...2.3$$

This can be written for diffusion in three dimensions as:

$$\frac{\partial C}{\partial t} = D\nabla^2 C \qquad …2.4$$

Equations 2.3 and 2.4 are solved by taking into consideration the boundary conditions. There are many examples where this has been done for different conditions of this type [Bar51]. At the temperature range where diffusion takes place, the diffusion coefficient (D) is often found to obey an Arrhenius type temperature relationship:

$$D = D_0 \exp(\frac{-E_a}{RT}) \qquad …2.5$$

where R is the gas constant, E_a is the activation energy, D_0 is the pre-exponential factor and T is the absolute temperature.

In crystalline materials diffusion occurs mainly via defects. The types of defects found in such materials are point, extended and complex defects; all play a role in the diffusion rate. Some of these defects are introduced either during creation of the crystalline materials or during the treatment of the sample, such as the ion implantation that is used in this study. During implantation (explained in chapter 3) the defects that are retained in the implanted material depend on the implantation temperature, the implantation rate and the kind of material they are implanted into. For example, in SiC which is investigated in this study, more defects are retained for implantation at low temperatures compared to high temperatures [Wen98]. This is owing to the fact that at low temperature atoms have less kinetic energy to move around, compared to high temperature implantations where atoms possess enough kinetic energy to move around and recombine with their original lattice sites.

In crystals the defects sometimes act as locations of minimum energies for displaced impurity atoms. This requires the said atoms to have more activation energy so as to move from the sites of minimum energies to other sites. In some cases movement of atoms in a crystal seems to be the movement of vacancies. Therefore, the vacancies also possess activation energy. For example, if there are N atoms, the equilibrium number n of vacancies is given by [Kit76]:

$$\frac{n}{N-n} = \exp(-E_V / k_B T) \qquad \ldots 2.6$$

where E_V is the energy required to displace one atom from one lattice site to a lattice on the surface and k_B is the Boltzmann constant. If $n<<N$ equation 2.6 can be written as:

$$n = N \exp(-E_V / k_B T) \qquad \ldots 2.7$$

If diffusing atoms/impurities are trapped in lattice defects they can precipitate or undergo chemical reactions with the matrix elements. In such a scenario, equation 2.4 has to be adjusted in order to describe a Fickean diffusion process in the presence of a trapping mechanism. If this is done, it leads to [Soa04] [Tam95] [Kas94]:

$$\frac{\partial C_f}{\partial t} = D\frac{\partial^2 C_f}{\partial x^2} - AC_f + BC_t, \; C_f = C_f(x,t) \qquad \ldots 2.8$$

$$\frac{\partial C_t}{\partial t} = AC_f - BC_t, \quad C_t = C_t(x,t) \qquad \ldots 2.9$$

where C_t and C_f represent the concentrations of trapped and free atoms respectively. $C=C_f+C_t$ is the total concentration of ions, while B and A are the probability rates for atoms trapping and detrapping respectively and are respectively given by:

$$B = v\exp(-Et/kT) \quad \text{and} \quad A = 4\pi r_s D c_s$$

Where v is the jump frequency, E_t the activation energy for the trapping process, r_s the effective trapping radius, D the diffusion coefficient and c_s the concentration of the effective trapping centres. Equations 2.8 and 2.9 have been solved numerically using the finite difference method [Smi78] [Kas94].

2.1 DIFFUSION MECHANISMS

Since crystals display different defects such as point, planar (dislocation or stacking faults) and complex defects (defects resulting from clustering of point or planar defects) which play a role in diffusion, it is vital to understand the various mechanisms by which diffusion takes place. Therefore, in this section only the three main diffusion mechanisms are discussed. A discussion of the other mechanisms is furnished in the book by Heitjans et al. [Hei05].

2.1.1 VACANCY MECHANISM

All crystals have vacancies, i.e. lattice sites that are not occupied, and that play a role in the diffusion of impurities. If one of the neighbour atoms jumps into the vacancy, the atom is said to have been diffused by the vacancy mechanism. This is due to the fact that when atoms jump or move into the vacancies, they leave vacancies behind as a result. Therefore, during this process the vacancies seemed to have also moved or jumped in the opposite directions of the atoms, as depicted in figure 2-1. In this figure, the dotted circle and solid circle represent the vacancy and atom respectively while (a) and (b) illustrate the position before and after diffusion.

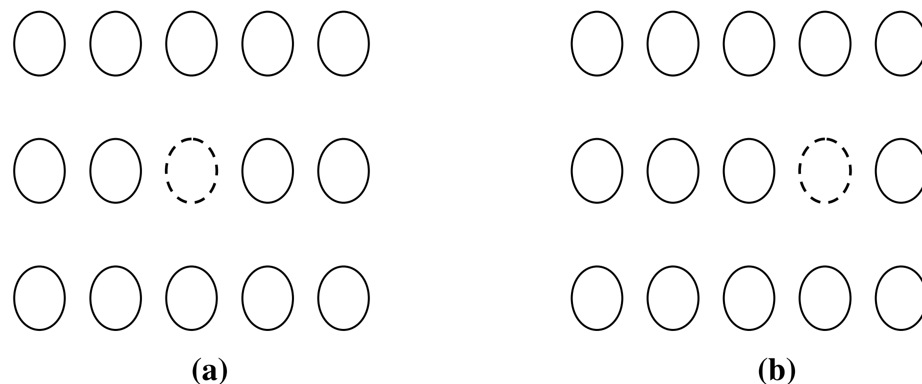

Figure 2-1: Vacancy diffusion mechanism: the dotted circle represents a vacancy, the open circles represent atoms, (a) and (b) represent positions before and after diffusion respectively.

2.1.2 INTERSTITIAL AND INTERSTITIALCY MECHANISMS

In (crystalline) materials there are atoms situated not on their regular site, but between other atoms, i.e. on the interstitial sites: they are called interstitials. Interstitial atoms can be smaller or bigger than the host atoms. Interstitial diffusion occurs when an

interstitial atom jumps from one interstitial site to the other as shown in figure 2-2, where the interstitial is depicted as an atom of smaller size. In some cases interstitial diffusion occurs faster than vacancy diffusion because there are more interstitial sites than vacancies and interstitial atoms are smaller [Sha70]. In the case where interstitial atoms are of the same size as the lattice sites, the interstitial atom can move into another normal lattice site by pushing a neighbouring normal lattice atom into an adjacent lattice site, as shown in figure 2-3. This process is known as interstitialcy diffusion [Sha70] [She89].

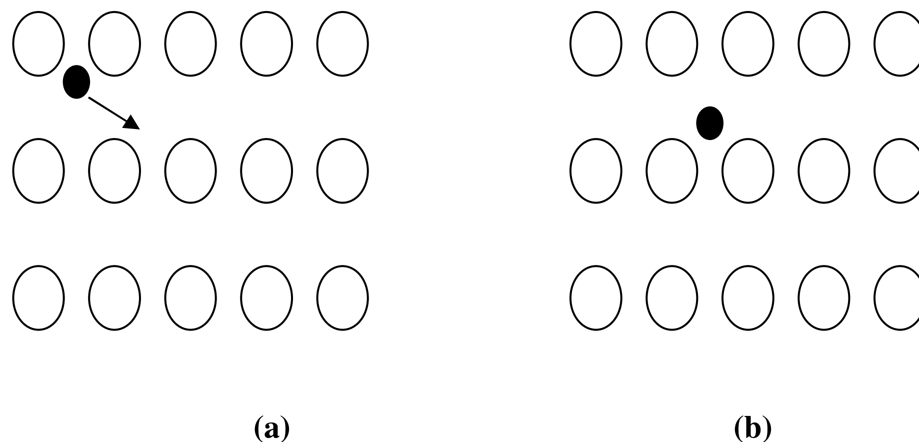

Figure 2-2: *Interstitial mechanism, (a) before and (b) after an interstitial diffusion.*

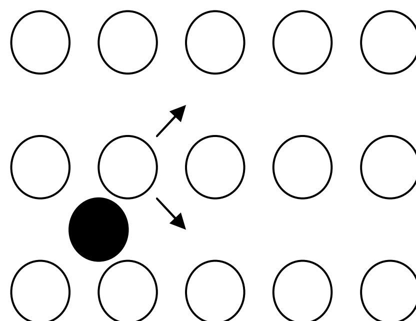

Figure 2-3: *The process of interstitialcy diffusion.*

2.1.3 HIGH DIFFUSIVITY PATHS

The diffusion mechanisms discussed above for volume diffusion are found to be temperature dependent, whereas diffusion along high diffusivity paths, i.e. via

dislocations loops, grain boundaries, surfaces, etc., is often found to be more or less temperature independent compared to the former. These kinds of diffusion mechanisms are those that take place when the regular lattice structure is broken down: for example in polycrystalline systems. Details of these mechanisms are found in [Poa78] and in references therein.

2.2 ANALYSING DIFFUSION COEFFICIENTS

There are several methods that are used in analyzing diffusion of impurities in different materials, some of which are discussed by Poate et al. and Heitjans et al. [Poa78] [Hei05]. RBS was used in this thesis. RBS is discussed in detail in chapter 4 but, briefly, it is based on the backscattering of charged particles of known incident energy (the alpha-particle was used in this study) from the specimen of interest. The backscattered alpha particles are then detected and the yield versus channel number is recorded, from which concentration and depth profiles are calculated.

2.2.1 DETERMINING DIFFUSION COEFFICIENTS

In this thesis the diffusion coefficients were determined by comparing the silver depth profiles before and after annealing steps. This was motivated by the fact that the depth profiles of our results were almost Gaussian. Fick's diffusion equation for the dilute limit leads to a particularly simple solution if the original profile at time t = 0 can be described by a Gaussian distribution [Mye74]. After annealing for a time t the concentration profile stays in a normal distribution given by [Mye74]:

$$C(x,t) = K[\pi Dt]^{-1/2} \exp(-x^2/4Dt) \qquad \text{...2.10}$$

where K is an adjustable constant, while the position of maximum concentration is unchanged at $x = 0$. If the profile width $W(t)$ is defined as the full width at half maximum *(FWHM)*, the following relationship between final and original width obeys equation 2.11.

$$[W(t)]^2 = 4Dt\ln(2) + [W(0)]^2 \qquad \text{...2.11}$$

From equation 2.11, it is clear that the slope of $[W(t)]^2$ versus annealing time at constant temperature gives the diffusion coefficient D. The pre-exponential factor (D_0) and activation energy E_a to completely describe diffusion are found by establishing the diffusion coefficients at three or more different temperatures and using them to solve for the unknowns (i.e. D_0 and E_a) in the Arrhenius equation, i.e. equation 2.5.

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