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Xenon diffusion behaviour in pyrolytic SiC

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The fractional release of ^{133}Xe, produced in pyrolytic SiC by fission recoil, has been measured below 1753° C both in isochronal and isothermal annealings. The release behaviour is interpreted for three temperature ranges; below 1200° C, from 1200 to 1400° C and above 1400° C. The release in the highest temperature region (>1400° C) would be due to vacancy mechanism, and the apparent diffusion coefficient is expressed as

$$D = 3.7 \times 10^6 \exp(-157 \times 10^3/RT)\ \text{cm}^2\ \text{sec}^{-1}.$$

The release in the medium temperature region (1200 to 1400° C) is probably due to the grain-boundary diffusion coupled with the migration of C or Si atoms in the boundary, and the apparent diffusion coefficient is expressed as

$$D = 8.6 \times 10^{-6} \exp(-78 \times 10^3/RT)\ \text{cm}^2\ \text{sec}^{-1}.$$

The release in the lowest temperature region (<1200° C) is explained by assuming the interstitial diffusion of Xe ejected from the trapping sites.

1. Introduction

Pyrolytic silicon carbide (SiC) is used for the coating material of HTGR and GCFR fuel particles, because it is not only stable [1, 2], but also excellent as the barrier to fission product diffusion under fast neutron irradiation at high temperatues. Release of the fission products from coated fuel particles during high temperature irradiation is largely inhibited by use of SiC as the coating layer sandwiched between pyrolytic carbon layers [3, 4]. Studies on the diffusion behaviour of the fission products in SiC are, however, few despite its excellent properties. It is reported that Cs migration in SiC is affected by the presence of micro-pore and micro-cracks [5], and Cs diffusion is strongly dependent on the deposition temperature [6]. Concerning the diffusion coefficients in SiC, although there are some reported values [7-10], the information is still small. Several studies on ion-bombardment of SiC [11-18] have been reported, and defect models have been proposed. The diffusion mechanism of induced ions is not, however, presented.

Thus, knowledge of diffusion of impurity atoms in SiC is scanty despite its extensive usage, so the present work is aimed to study the Xe diffusion behaviour in SiC at high temperatures by measuring the release of ^{133}Xe produced by fission recoil.

2. Samples and experimental method

Dense β-SiC, deposited from $SiCl_4$ and hydrocarbon gas under H_2 gas flow at 1200° C, was used as the sample. From the X-ray diffraction analysis, the sample was found to contain a slight amount of hexagonal type SiC, but not free Si. The crystallite size calculated from the above analysis was 180 Å. Although chemical analysis of the C/Si ratio in the sample indicated a value 1.11, the carbon phase was not observed in the X-ray analysis. The density of the sample measured by the sink-float method was 3.206 g cm^{-3}. The etched surface of as-deposited SiC perpendicular to the deposition direction showed the typical

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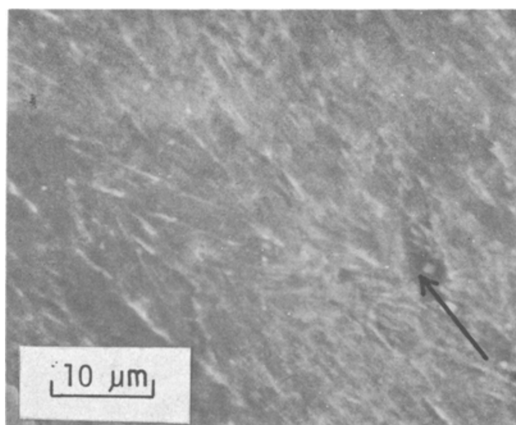

Figure 1 Microstructure of SiC etched by fused alkali; arrow indicates deposition direction.

dendrite structure as shown in Fig. 1.

The sample was crushed to powder and sieved into three parts whose effective radii measured by the B.E.T. surface method were 10.2, 16 and 26 μm.

The powdered samples, dipped in aqueous uranyl nitrate solution and then dried, were irradiated in JRR-2 at ambient temperature ($\sim 80^\circ$ C) to a thermal neutron dose of 8.4×10^{16} nvt and a fast neutron dose of 1.5×10^{15} nvt, in order to produce ^{133}Xe-recoiled SiC. From the surface area of samples obtained by the B.E.T. method, the fission density on the powder was 4×10^{10} fissions/cm^2, and as the fission recoil range of ^{133}Xe in SiC is 9.6 μm [19], the mean ^{133}Xe concentration in the fission recoil range after a week's decay was calculated to be 2×10^{-6} ppm. Following the irradiation, the sample was stored for 7 days or more in order to allow ^{133}I, the mother nuclide of ^{133}Xe (half life, 20.8 h), to decay, and then the surfaces were washed in nitric acid solution to remove the uranyl nitrate.

Annealing of the sample was carried out in a long graphite crucible under a He gas flow. The equipment is schematically shown in Fig. 2. In isochronal annealing, the crucible containing the sample was placed in the highest temperature section of the furnace from the beginning of the annealing, while isothermal annealing was made by lowering the crucible from the upper section to the highest temperature section at a desired temperature. For precise temperature measurement of the sample, a W–W/Re thermocouple was used, taking care that the couple was positioned at the same point as the sample.

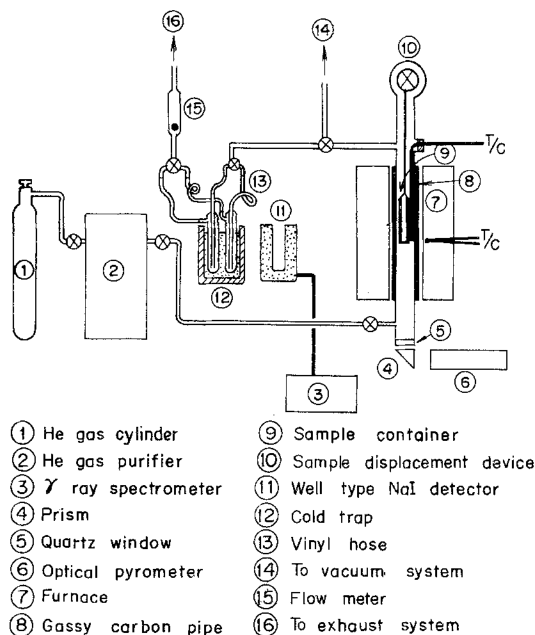

Figure 2 Equipment for measuring ^{133}Xe release.

The ^{133}Xe released during the annealing was collected in a charcoal trap cooled with dry ice and its activity was measured intermittently by γ-ray spectrometry. The escape of ^{133}Xe from the charcoal trap during activity measurement was negligibly small. After annealing, the ^{133}Xe remaining in the sample was measured also by γ-ray spectrometry in order to obtain the fractional release during annealing.

3. Results

The fractional release and the release rate of ^{133}Xe from the 10.2 μm radius powder sample during isochronal annealing are shown in Fig. 3. The sample was annealed twice: the first annealing was made by raising the temperature at a uniform heating rate of 2.65° C min^{-1} from room temperature to 1710° C, and the sample was then immediately removed to the cool section of the furnace to give rapid cooling. The cooling rate of the sample was inferred to be over 100° C min^{-1} from 1710° C to about 800° C, and over 50° C min^{-1} from 800 to 500° C. The fractional release of ^{133}Xe after the first annealing was 9.5×10^{-2}. The sample was then annealed again in the same manner after about 50 h. It is seen in the figure that the release rate below 1200° C has several peaks whereas there is a rapid rise above 1200° C

The release in the second annealing is similar to the first. It is, however, somewhat different from the results obtained in UO_2 powder [20] and in

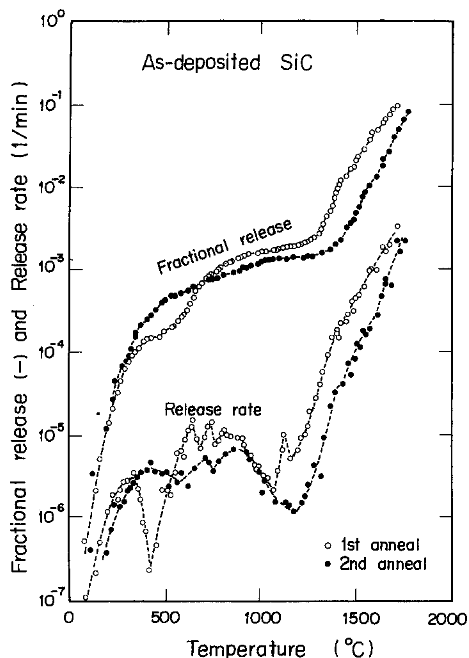

Figure 3 Fractional release and release rate of ^{133}Xe in isochronal annealing.

graphite similarly tested [21, 22]. In these latter cases, the release during the second annealing scarcely occurred below about 1000° C, and it was presumed that, once the defects trapping Xe atoms were annealed in the first annealing, no further release from the annealed sample occurred. In the present case, the peaks in the second annealing are hardly affected by the presence of ^{133}I, which is only about 1% of the ^{133}Xe after a week's decay. For example, if the ^{133}Xe and ^{133}I release are the same and if the fractional release is 10^{-1} for each after the first annealing, then the rate of ^{133}Xe generated from ^{133}I, (released during the first annealing and attached elsewhere on inner wall of the equipment) would be about $1 \times 10^{-7}\,\text{min}^{-1}$ after 50 h. This value is less than 10% of the release rate of ^{133}Xe during the second annealing.

Isothermal annealing of the sample was carried out in two different ways: in one way used previously by Auskern [23], a single sample was annealed for a given time at one temperature by increasing stepwise from 1073° C to 1657° C. The duration of the annealing at any temperature was from 130 to 200 min and it took about 15 min to raise the temperature from one annealing step to the next. The results are shown in Fig. 4, in which the zero point of time axis is that at which the annealing temperature is first reached. In the other way, one sample was annealed isothermally at a single temperature only. The results at 1465, 1600 and 1750° C obtained from different samples are shown in Fig. 5. In the former figure, it is seen that the release at 1075° C i.e. during the initial step of annealing, is higher than that at 1144 and 1199° C, but the rate of the increase is gradually reduced with time. The release in the temperature range 1144 to 1399° C, is linear with the square root of the annealing time. Above 1449° C, however, the linear relationship is held except in the initial short period of annealing. In Fig. 5, the initial rapid release is not observed.

From the ^{133}Xe fractional release, the apparent diffusion coefficients of ^{133}Xe (except at 1073° C)

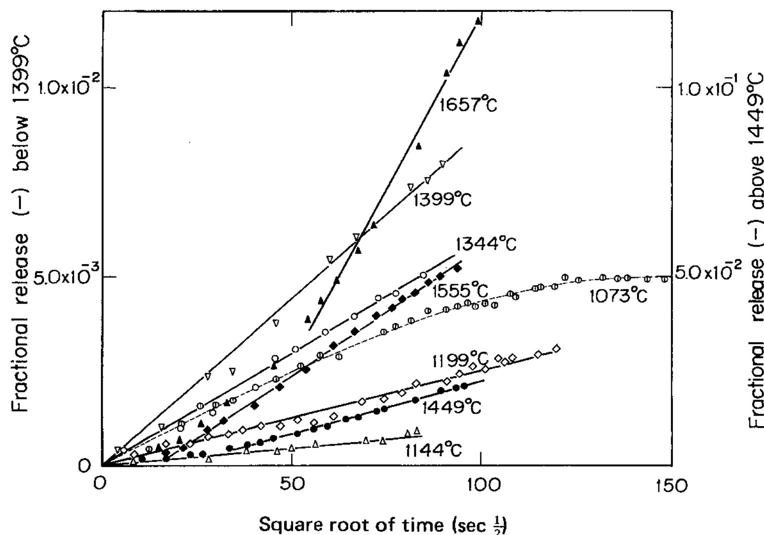

Figure 4 Fractional release of ^{133}Xe in isothermal annealing; radius of powder sample is 10.2 μm.

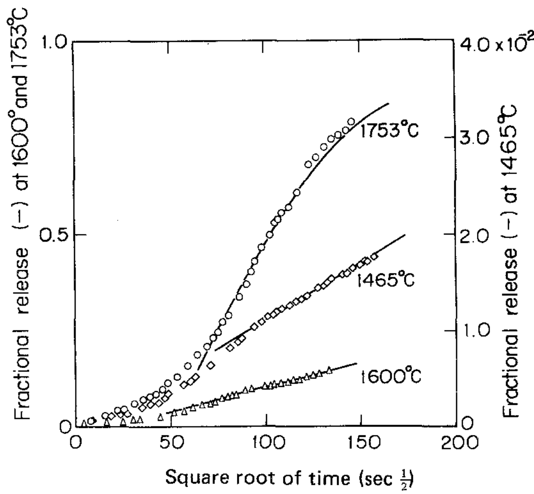

Figure 5 Fractional release of ^{133}Xe in isothermal annealing; radii of powder samples are 16, 26 and 10.2 μm in annealing at 1465, 1600 and 1753° C, respectively.

were estimated by the equation [24]:

$$F = 1 - \frac{24}{\nu^2(12-\nu^2)} \sum_{n=1}^{\infty} \left\{ \frac{\nu(2+\nu)}{(n\pi)^2} - \frac{2\sin(n\pi\nu)}{(n\pi)^3} - \frac{2[1-\cos(n\pi\nu)]}{(n\pi)^4} \right\} \times \exp(-Dtn^2\pi^2/a^2) \quad (1)$$

and for approximate solution in low fractional release ($F < 0.3$),

$$F = \frac{24(\nu+2)}{\nu(12-\nu^2)} \left(\frac{Dt}{\pi a^2}\right)^{0.5} \quad (2)$$

where F is the fractional release from the sphere, ν the ratio of the fission recoil range to the sphere radius a, D the diffusion coefficient and t the time. The apparent diffusion coefficients were obtained either from the slope of linearity seen in Figs. 4 and 5 by using Equation 2, or by choosing the coefficient so as to fit the results using Equation 1. The values of the coefficient obtained are plotted against the temperature in Fig. 6. The temperature dependence of the coefficients is expressed by two steps: the coefficients at higher temperatures (>1400° C) are expressed as

$$D = 3.7 \times 10^6 \exp(-157 \times 10^3/RT) \text{ cm}^2 \text{ sec}^{-1}. \quad (3)$$

and at lower temperatures (<1400° C)

$$D = 8.6 \times 10^{-6} \exp(-78 \times 10^3/RT) \text{ cm}^2 \text{ sec}^{-1}.$$

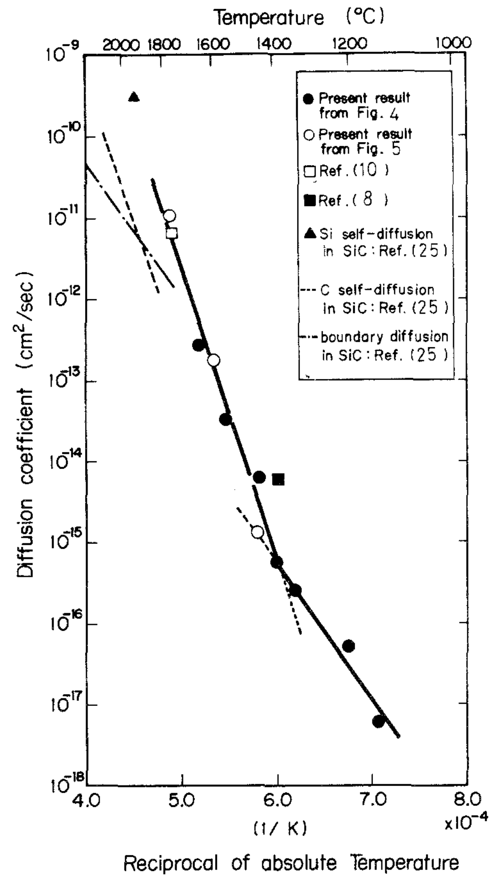

Figure 6 Temperature dependence of apparent diffusion coefficients of ^{133}Xe in SiC.

where R is the gas constant and T the temperature.

The activation energy of diffusion at higher temperatures is nearly the same as that of carbon self-diffusion in SiC, 140 kcal mol^{-1} [25]. In the case of Xe release from ZrC powder [23], high activation energies of Xe diffusion from 158 to 190 kcal mol^{-1} are reported in the composition of ZrC, 0.75 > C/Zr > 0.91, where the diffusion is better correlated with that in covalently bonded material than in metallic materials. As shown in Fig. 6, the present results are in good agreement with those in previous works [8, 10], which were obtained by measuring the release from coated fuel particles. Also the extension of diffusion coefficients to higher temperature is in accord with the silicon self-diffusion in SiC [25].

4. Discussion

In several studies on fast neutron irradiation [26, 27], electron bombardment [28] and ion bombardment [14] of SiC, it is reported that point defects or dislocation loops are produced at 400 to 625° C, while steady disorder or an amorphous

structure is produced nearer to room temperature. Furthermore, Hart *et al.* [29] showed in the luminescence experiments that lattice defects in SiC induced by ion bombardment were almost completely annealed at about 1000° C. Therefore, the peaks in the release rate below about 1200° C in the present isochronal annealing shown in Fig. 3 are considered to be related with recovery of such defects induced by fission recoil of rapid cooling, or located naturally in the SiC sample. Patrick *et al.* [16] have described how H atoms induced into SiC and trapped in Si vacancies, were ejected from Si lattice sites to the interstitial sites during the vacancy annealing at 800 to 1000° C. As for the interstitial mechanism of diffusion, although there is no report about the mechanism in SiC, interstitials in covalent materials such as Si, Ge and diamond are mobile at very low temperature [30]. The interstitial mechanism of Xe diffusion in UC is reported to occur at room temperature or lower [31], and the vacancy mechanism at high temperatures [32]: also, Cu atoms undergo rapid interstitial diffusion in polycrystalline Pb [33]. Thus, it is arguable that the release below 1200° C is due to the interstitial mechanism of diffusion combined with the ejection of Xe from trapping sites. The appearance of the peaks in the release rate below 1200° C suggests that the release is controlled by the ejection from the trapping sites rather than by the diffusion only.

In an additional experiment carried out using SiC plates as samples, the release in the second annealing after slow cooling (cooling rate, 5.3 $^\circ C\,min^{-1}$) was somewhat different compared with the release after more rapid cooling: the peak in the second annealing after the slow cooling was hardly noticeable (except a very small one around at 600° C), the fractional release was lower than that in the first annealing through the whole temperature range examined, whilst the appearance of the peaks after the rapid cooling was almost the same as that shown in Fig. 3. This suggests the possibility of re-trapping of Xe atoms in defects produced during the rapid cooling, and if so, the peaks in the second annealing after the rapid cooling would be due to annihilation of such defects, in the same manner as the appearance of the peaks in the first annealing. Further studies are required to confirm the above possibility.

Both changes in the activation energy at 1400° C (Fig. 6) and the release rate in the isochronal annealing at that temperature (Fig. 3), suggest that two mechanisms are involved in the release above 1200° C. On the assumption that the release above 1400° C in the first isochronal annealing (in Fig. 3) is due to the normal volume diffusion, the activation energy of diffusion is estimated. The fractional release, F, in the volume diffusion can be solved by the usual diffusion equation for a sphere [34], and the following is given in case of $F = 0.1$:

$$\Delta H/T_{10} = 89.3 + 4.6 \log [t_{\min} \cdot k_0/(a^2 \cdot 10^{15})]$$

and $k_0 = 2D_0/d_2$, where $D = D_0 \exp(-\Delta H/RT)$ is the diffusion coefficient for the volume diffusion, R the gas constant ($cal\,mol^{-1}\,K^{-1}$), T the absolute temperature (K), T_{10} the temperature of 10% gas release (K), ΔH the activation energy ($cal\,mol^{-1}$), $t_{\min}$ the time (min) and a the spherical radius in units of mean atomic spacing d. Using the value of $3.7 \times 10^6 (cm^2\,sec^{-1})$ as D_0 from Equation 3, 2.2×10^{-8} cm as λ (half of the lattice parameter 4.3596×10^{-8} cm [35]) and 1.02×10^{-4} cm as a, ΔH is calculated to be 181 kcal mol^{-1}. This is fairly close to the activation energy of the apparent diffusion coefficient above 1400° C (157 kcal mol^{-1}). It may, therefore, be that the release above 1400° C is due to the volume diffusion. Furthermore, from the report [14] that 90% of In atoms induced in β–SiC are substitutional after 1200° C annealing, and the agreement of the activation energies between Xe diffusion in the present experiment and carbon self-diffusion [25], it is suggested that the diffusion of ^{133}Xe is due to the vacancy mechanism.

From the ion bombardment experiments, some defects such as di-vacancies [11, 12], impurity-vacancies complex [13] and small amount of disorder [14] in β–SiC can survive in the annealing above 1600° C. If these defects act as trapping sites for ^{133}Xe diffusion, the trapping effect offers a problem. According to Elleman [36], the trapping effect lowers the diffusion coefficient without deviation from the diffusion kinetics. Lowering of the coefficient due to the trapping effect is studied in the Xe release from irradiated UC [32] and that from CsI [36]. In the case of CsI, however, when the fission density is low (3×10^{12} fissions/cm^2), the effect is negligibly small [36]. In the present experiment, the density is 4×10^{10} fissions/cm^2, which is almost two orders of magnitude less than the above value in CsI. Also, as the displacement energies of C and Si from the SiC lattice are reported to be very

large (~106 eV) [28], it is considered that the trapping effect is not sifnificant for the Xe diffusion at high temperatures above 1400° C.

A possible mechanism for ^{133}Xe release in the temperature range from 1200 to 1400° C is now discussed. As already described, a large proportion of defects which act as the trapping sites for diffusing Xe atoms would be annihilated below 1200° C, so the volume diffusion controlled by the trapping effect would be disregarded. The gas-bubble migration mechanism is also ruled out because ^{133}Xe concentration is too low to form the gas bubbles (2×10^{-6} ppm after a week's decay). In the case of CsI [36], for example, the release due to gas-bubble migration occurs at a concentration of 1 ppm or more. Here, it is noteworthy that the activation energy of the apparent diffusion coefficient, 78 kcal mol^{-1}, in that temperature range is nearly the same as that of C or Si grain-boundary diffusion, 73 kcal mol^{-1} [25]. This would imply that the release is due to grain-boundary diffusion related to the migration of C or Si atoms in the boundary region. It is, thus, considered that the marked decrease of the accumulated fractional release from 1% in the first isochronal annealing, to 0.5% in the second in that temperature range, is caused by sweeping out of Xe atoms initially located in the grain boundaries (cf. Fig. 3).

5. Conclusions

From experiments on ^{133}Xe release from SiC, the following are concluded:

(1) The release behaviour below 1200° C is considered to be due to interstitial diffusion coupled with the ejection of ^{133}Xe trapped in the defects. Recovery of the defects causes several peaks in the release rate.

(2) The release in the temperature range 1200 to 1400° C is probably due to the grain-boundary diffusion of ^{133}Xe, which is activated by the migration of C or Si in the boundary. The temperature dependence of the apparent diffusion coefficients is expressed as

$$D = 8.6 \times 10^{-6} \exp(-78 \times 10^3/RT) \text{ cm}^2 \text{ sec}^{-1}.$$

(3) The release above 1400° C would be due to normal volume diffusion without hindrance of trapping effect, and the apparent diffusion coefficient are expressed as

$$D = 3.7 \times 10^6 \exp(-157 \times 10^3/RT) \text{ cm}^2 \text{ sec}^{-1}.$$

The results obtained from the diffusion of Xe in SiC would be useful for anlysis of the Xe release from HTGR coated fuel particles. However, more basic experiments are required to interpret the mechanisms more quantitatively because of their complexity.

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