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(Received May 2, 1984)

A series of out-of-pile heating experiments has been carried out to study carburization of UO_2 kernels in cracked coated particles and its effect on xenon release. UO_2 kernels in cracked coating were carburized up to 80% in a week at 1300°C. Xenon release increased linearly with carburization. In an experiment of several hours heating at 1350°C, the amount of xenon released from completely carburized kernels was about 10 times larger than that from noncarburized ones.

Keywords: Coated fuel particles, UO_2, Carburization, Xenon, Cracked Particles

欠損粒子のUO_2核の炭化とキセノン放出への影響

日本原子力研究所東海研究所燃料工学部
飛田　勉・井川　勝市

（１９８４年５月２日受理）

被覆に亀裂をもつ燃料粒子を試料として一連の炉外加熱実験を行い，燃料核の炭化の現象を追跡した。比較のため，裸の燃料核を黒鉛粉末中に埋込んだ試料も用いた。前者の試料では，1300℃ ですでにかなり速い炭化が観察され，炭化速度は１週間で最高80％近くに達した。後者の試料では600時間でたかだか10－20％であった。これは非晶質炭素（バッファー層）の方が黒鉛より化学的に活性であるためと考えられる。いずれにせよ，実験炉の通常運転温度でも，破損粒子については核の炭化の現象を考慮に入れなければならないことがわかる。また，炭化した燃料核からのXe放出を放射化後加熱の方法で調べたところ，炭化によってXe 放出が大幅に増加することも明らかになった。これは炭化に伴うBET面積の増加によると考えられる。

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1. Introduction

UO_2 microspheres coated with pyrolytic carbon layers with or without silicon carbide interlayer is a form of fuel for HTGRs.

If a crack is generated through the coating layers, the UO_2 microsphere (called kernel) will be carburized by the reaction with the carbon layers. In the case that a crack is generated during fabrication, carburization occurs during compact baking at 1800°C, whereas in the case of irradiation-induced crack, carburization proceeds at temperatures of reactor operation. Change of the oxide to a carbide and consequent loss of rigidity of the microsphere will affect fission product release.

Although a large number of papers on the carburization of UO_2 have already been published in connection with the development of the carbothermic reduction process for carbide fuel production (see ref. 1 for example), most of the papers have been dealing with UO_2 powder. Lindemer et al.[2] studied carburization of UO_2 microspheres but the reaction partner was graphite, not pyrolytic carbon. The reaction between UO_2 kernels and carbon coating has been investigated in the framework of amoeba study[3,4]. In this case, however, the coatings are intact, which means that the system is closed and the UO_2 is not carburized significantly because carbon monoxide is not removed from the system.

Fission gas release from intentionally defected coated fuel particles (laser-failed, manually cracked, bare kernels, etc.) has been investigated in various countries[5-8]. Italian experiment[5] clearly demonstrated that the release is strongly influenced by the physical form of the free uranium. French

experiment[6] showed the dependence of the release on the material surrounding the kernel. Most of these experiments, however, deals with the effect of physical condition. Only a part of GA work[7] describe the effect of chemical reaction, namely hydrolysis of UC_2 kernels.

A series of out-of-pile heating experiments has been carried out to study carburization of UO_2 kernels and its effect on xenon release. Not only cracked coated particles but also bare kernels were used for comparison.

2. Carburization experiment

2.1 Specimen

TRISO-coated particles with UO_2 kernel (see Table 1) were gently pressed with a hand press to generate a crack through the coating layers. An example of the external appearance of the cracked particles is shown in Fig.1. Cracked particles were radiographed to select particles with a complete path through the coating layers as shown in Fig.2.

2.2 Procedure

Each cracked particle was embedded in graphite powder packed in a graphite container (10mm outer diam. and 15mm long) to simulate a condition in a fuel compact. Bare kernels were also used in place of the cracked particles. The graphite container was placed at the center of a graphite tube (14mm inner diam. and 180mm long), which served as a getter for oxygen leaked into the mullite furnace tube through a possible defect in the system. Graphite felt was inserted into the furnace tube for an additional getter. Commercially available argon

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of 99.999% nominal purity was supplied directly from a gas cylinder without further purification. Linear flow rate of argon in the furnace tube ranged 100-200cm/min.

After heating, the specimen particles (cracked particles or bare kernels) were dipped in 6N nitric acid for 2hrs at room temperature. Carburized portion was dissolved in the acid. The residue was collected on a paper filter and gamma counted for U-235 to determine the noncarburized portion. It was confirmed in advance that the kernels used in the present experiments remained undissolved in the acid for 88hrs at room temperature and that the carburized kernels were dissolved in less than 2hrs at room temperature.

2.3 Results and discussion

A partially carburized cracked particle was pulverized and analysed by X-ray diffraction. UO_2 and UC were detected as shown in Fig.3. UC_2 was not detected.

Data of percent carburization are summarized in Fig.4. The first point to be mentioned here is the fact that UO_2 in cracked particles was carburized up to 80% in a week at 1300°C. Therefore, even at fuel temperatures under normal operating conditions, carburization of UO_2 kernels in cracked particles should be taken into consideration. At 1400°C, kernels were carburized almost completely in a few days.

From a practical point of view, significant scatter of 1300°C data of cracked particles attracts our attention. At a heating time of about 170hrs, for example, carburization

ranged 10 to 80%. This scatter may be attributed, at least partly, to the different size of the opening of the crack (see Fig.2).

Another point of practical interest is the fact that, at 1300°C, kernels in cracked particles were carburized much faster than those in direct contact with graphite powder. In other words, reaction of UO_2 with buffer carbon is faster than that with graphite powder. The higher chemical reactivity of the noncrystalized pyrolytic carbon is easily understandable. At 1400°C, however, difference was not found, implying that graphite powder becomes well reactive at this temperature.

In an attempt to observe a preferred carburization around the crack as illustrated in Fig.5, microphotographs of polished sections were taken at various extent of carburization. But the attempt was unsuccessful. Carburization appears to proceed all over the kernel surface. This is probably because of the complete porous structure of the buffer layer. Carbon monoxide generated by the reaction may be easily removed from any part of the surface. Examples of the microphotographs are shown in Fig.6 and Fig.7 to enable better understanding of the carburization process.

3. Xenon release experiment

3.1 Specimen

Cracked particles carburized at 1400°C by the procedure described in section 2.2 and three compacts (10mm diam. and 10mm long), each containing one bare kernel at the center, were used as the specimens. Cracked particles were used to investigate the effect of carburization during reactor operation, whereas the compacts were prepared to simulate the condition of carburization during fabrication. The compacts were baked

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for 1hr in vacuum at three different temperatures, 1400°C, 1600°C and 1800°C for comparison.

3.2 Procedure

Each cracked particle was embedded in graphite powder packed in a graphite container as described in section 2.2. The graphite container was sealed in a quartz tube and irradiated in JRR-2 for 20min below 100°C at a thermal neutron flux of 5×10^{13} n/cm^2·sec. The compacts were also sealed in quartz tubes and irradiated in JRR-4 under the conditions identical to the case of cracked particles. All the specimens were cooled for more than a week.

Experimental apparatus is illustrated schematically in Fig.8. An irradiated specimen (a cracked particle in a graphite container or a compact) was placed in a graphite tube as described in section 2.2 to prevent oxidation during heating. Graphite felt was not used in this case because of relatively short heating time. Helium of 99.99% nominal purity was supplied from a gas cylinder without further purification. Heating temperature was 1350°C in all runs irrespective of the specimens carburization temperature. Released gaseous fission products was collected in a charcoal trap cooled in liquid nitrogen. Gamma activity of the trap was measured by a well-type NaI scintilator. The gamma activity was almost exclusively of Xe-133. Trace amount of I-131 and sometimes also of I-132 were detected in the trap.

After release measurement, percent carburization of the cracked particles was determined as described in section 2.2. In this case, however, fission product activity was used instead

of gamma activity of U-235. Percent carburization of the bare kernels in the compacts could not be determined because the compacts were rigidly consolidated and the carburized kernels could not be isolated without damage.

3.3 Results and discussion

An example of xenon release from cracked particles as a function of heating time (t) is shown in Fig.9. Xenon release at t=0 indicates the release during the time until the preset temperature was reached, which was about 80min. Replot against $\sqrt{t}$ (see Fig.10) dose not reveal the linearity which is expected when the release is controlled by diffusion in a uniform medium. GA experiment on laser-failed particles[9] did not reveal the linearity against $\sqrt{t}$, but the linearity against t was found. In the present case, neither linearity against t nor $\sqrt{t}$ was found. This is probably because of the sum of release from three different mediums, UC, UO_2 and inner surface of the coating into which Xe-133 precursor recoiled during irradiation. In a separate experiment[10] in which the specimen was noncarburized UO_2 kernels, the linearity against $\sqrt{t}$ was observed.

In order to clarify the quantitative effect of carburization, the total amount of xenon released from cracked particles in the first 4 hrs at 1350°C plus preceeding 80min (see above) was plotted against percent carburization as shown in Fig.11. It is clear that xenon release increases almost linearly with percent carburization. In other words, most of the released xenon came from the carburized portion.

Effect of baking temperature of the compacts is shown in Fig.12, indicating that the compact baked at higher temperature

releases larger amount of xenon. Although percent carburization of the kernels in these compacts could not be determined as described above, Lindemer's data[2] suggest that by baking at 1800°C more than a half of the kernel volume was carburized. Carburization by 1400°C baking can be roughly evaluated from Fig.4 to be a few percent.

In both cases of cracked particles and bare kernels, carburization caused significant increase of xenon release. This effect may be attributed to the porous structure of the carburized region as was observed by a stereo-microscope. The porous structure may have a larger BET area and hence a smaller equivalent sphare radius[11] than noncarburized UO_2 kernel. BET area and equivalent sphere radius of the noncarburized UO_2 kernel were found to be $39cm^2/g$ and $67\mu m$[12], respectively, but BET area of the carburized region could not be measured because sufficient amount of sample could not be obtained. If the so-called initial burst[11] is proportional to the BET area, the result of a separate experiment[13] suggests that the BET area of the carburized region is two orders of magnitude larger than that of the noncarburized UO_2 kernel.

4. Conclusion

Even at fuel temperatures under normal operating conditions, carburization of UO_2 kernels in cracked particles should be taken into consideration.

Irrespective of carburization conditions, slow carburization during reactor operation or rapid carburization during compact baking, fission gas release will be enhanced significantly.

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Acknowledgement

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Table 1 Nominal dimension of coated particle components
(unit: micron)

UO_2 kernel	600
Low density carbon	60
Inner high density carbon	30
Silicon carbide	25
Outer high density carbon	45

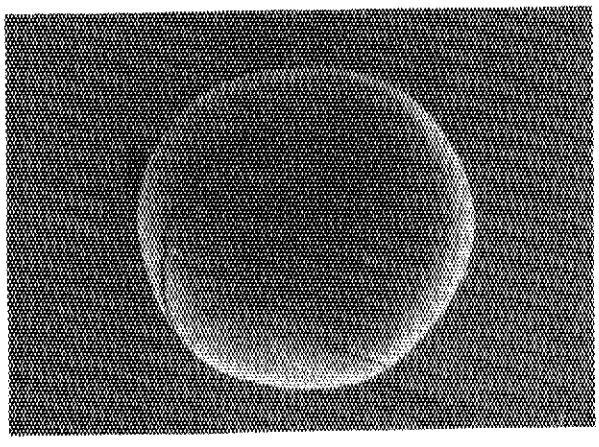


Fig.1 An example of the external appearance of cracked particles

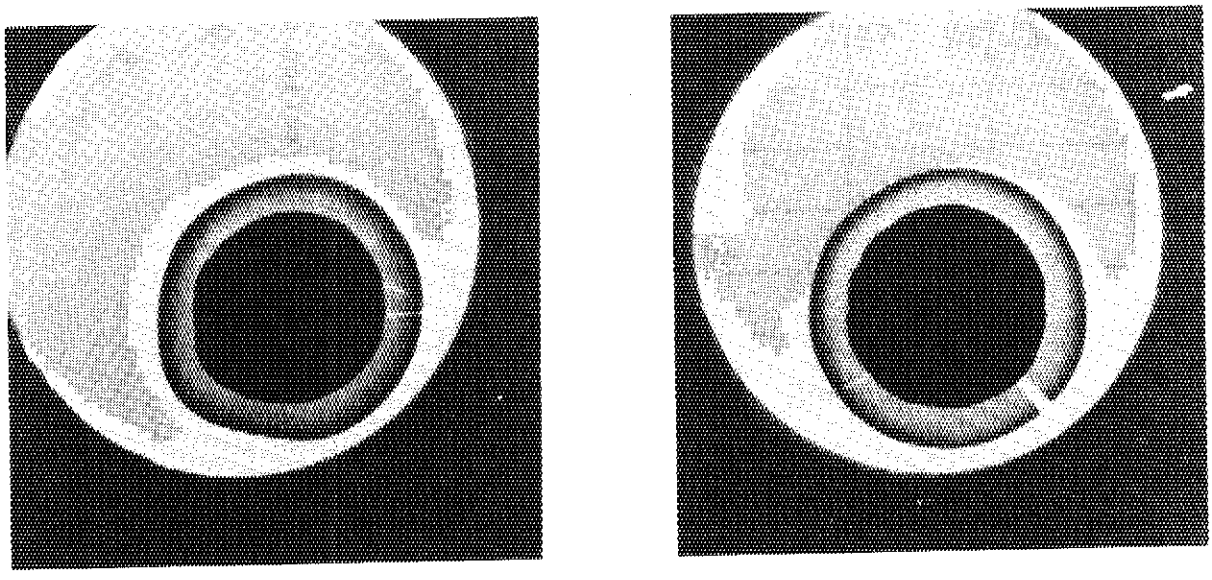


Fig.2 Examples of X-ray radiograph of cracked particles

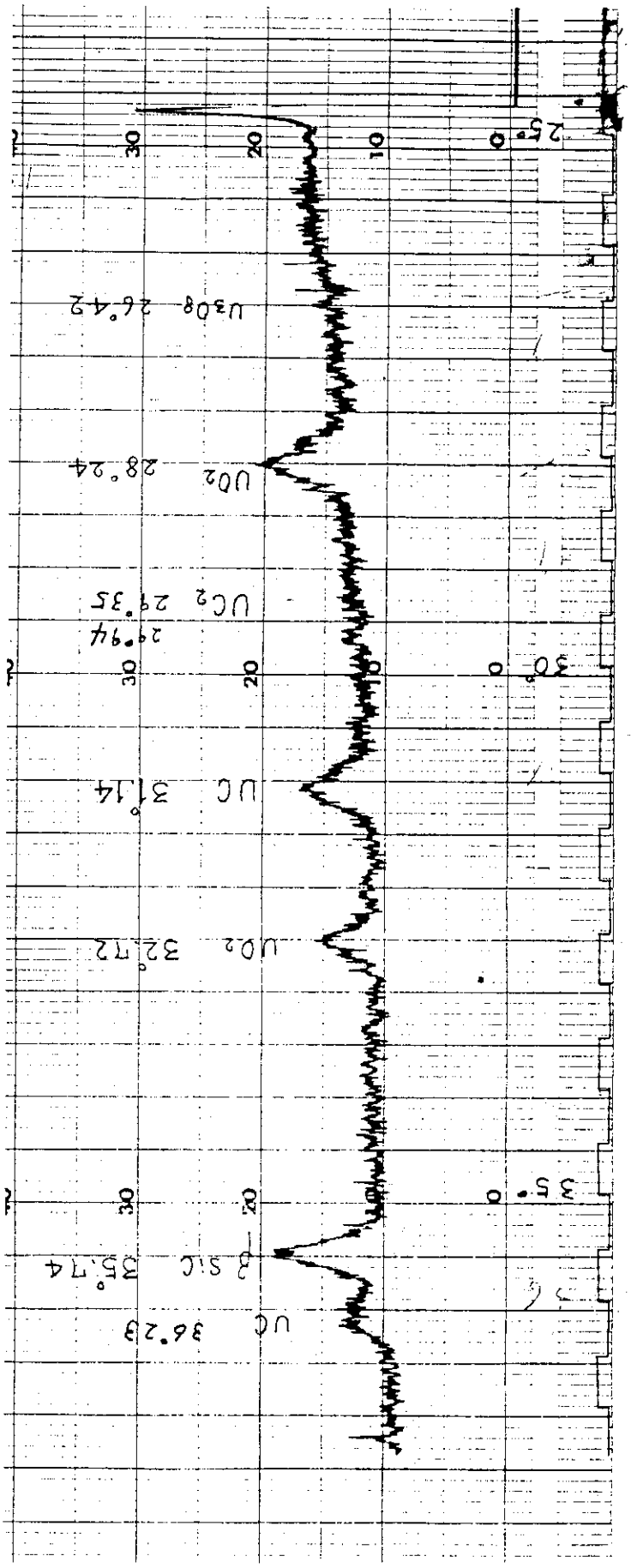


Fig.3 X-ray diffraction of a partially carburized cracked particle

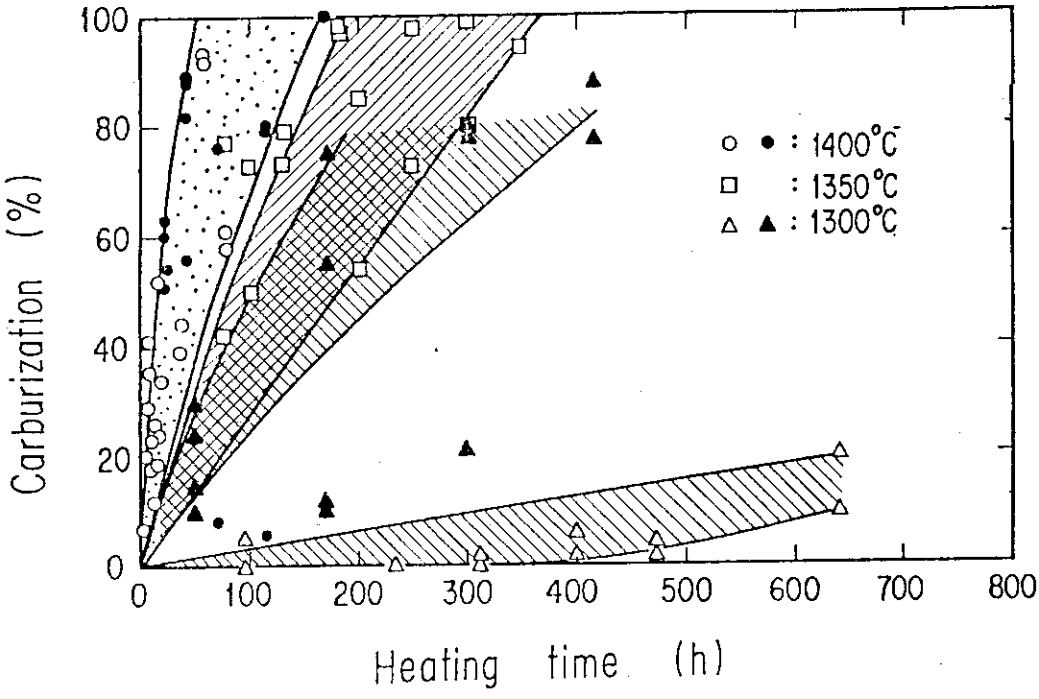


Fig.4 Carburization of UO_2 of broken TRISO-coated particles (black symbol) and of bare kernel in graphite powder (white symbol).

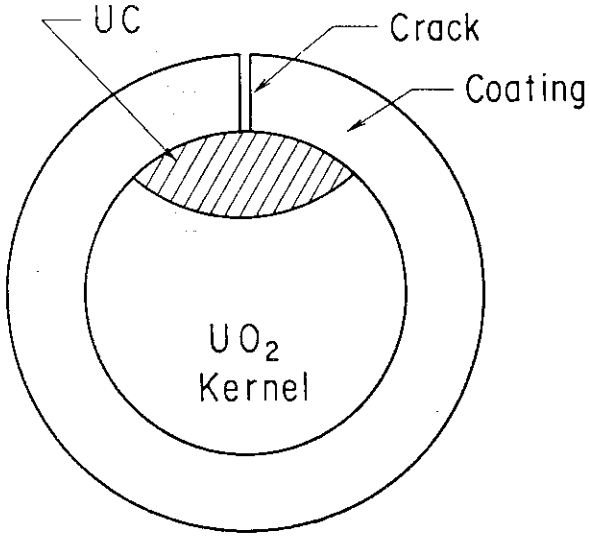
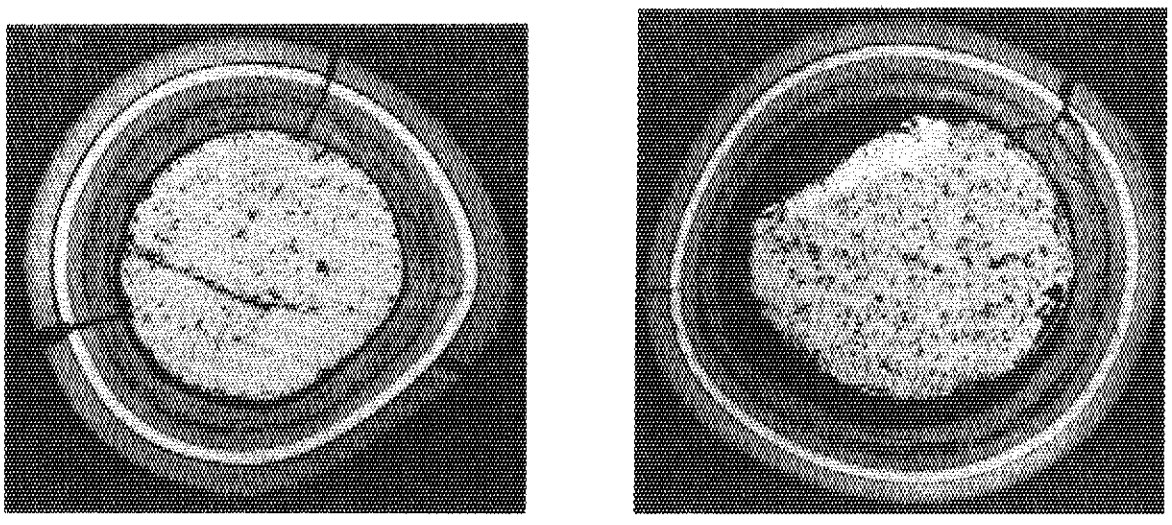


Fig. 5 Illustration of preferred carburization around the crack.



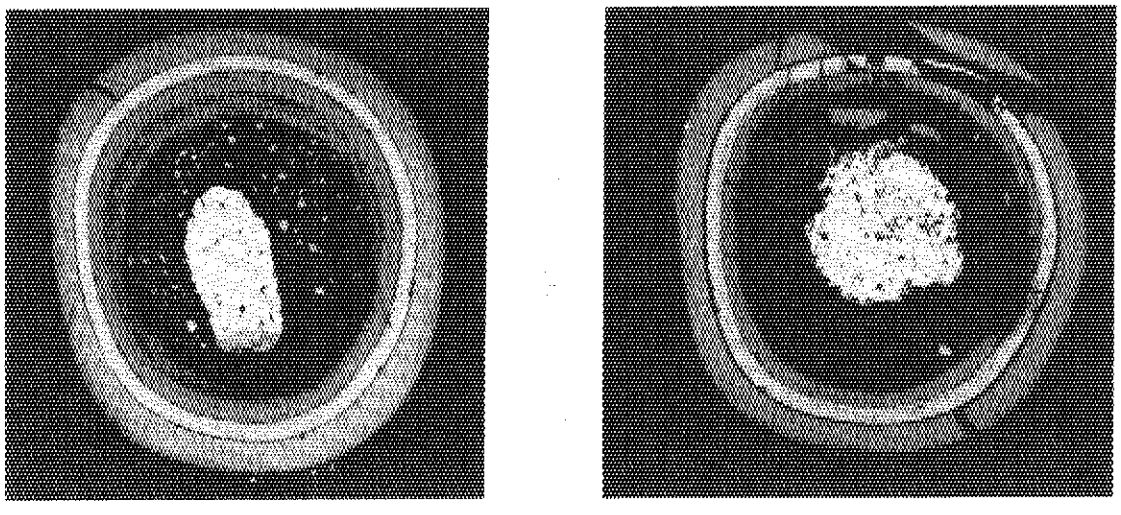
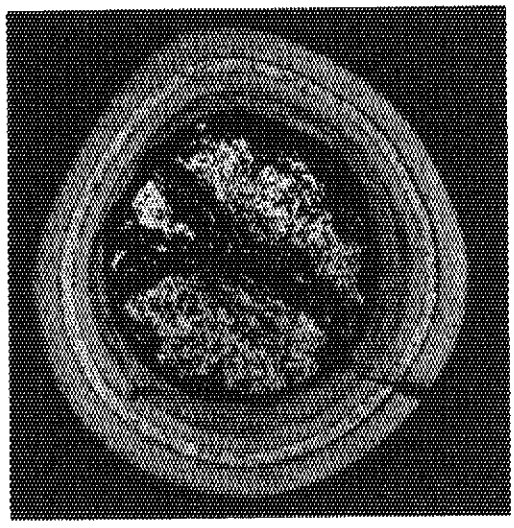
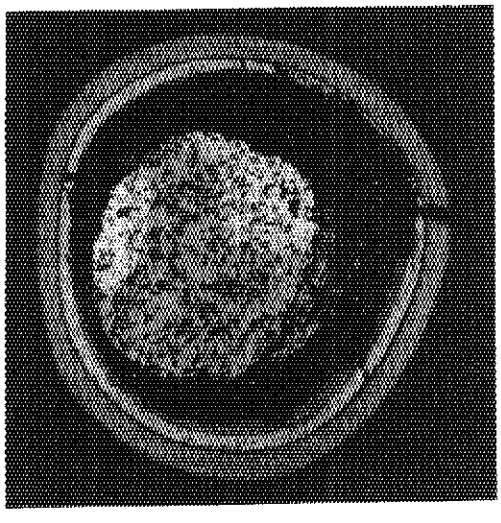


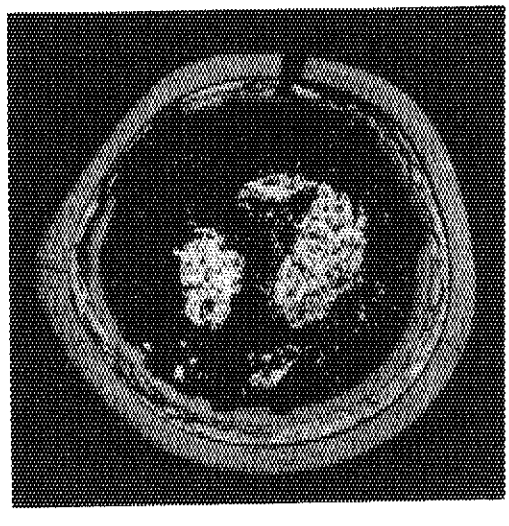
Fig. 6 Cross-section of cracked particle after heating at 1300°C.



1400°C 71 hrs.



167 hrs.



217 hrs.

Fig. 7 Cross-section of cracked particle after heating at 1400°C.

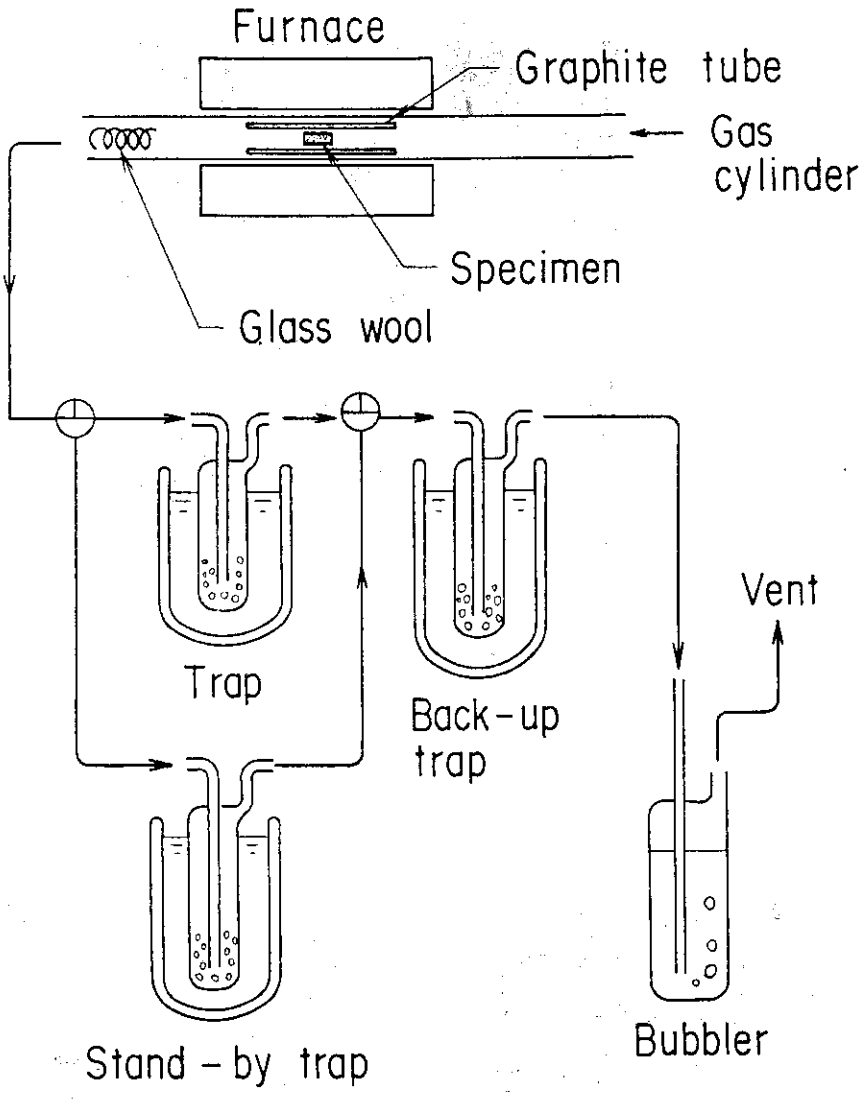


Fig. 8 Schematic illustration of the apparatus for xenon release experiment.

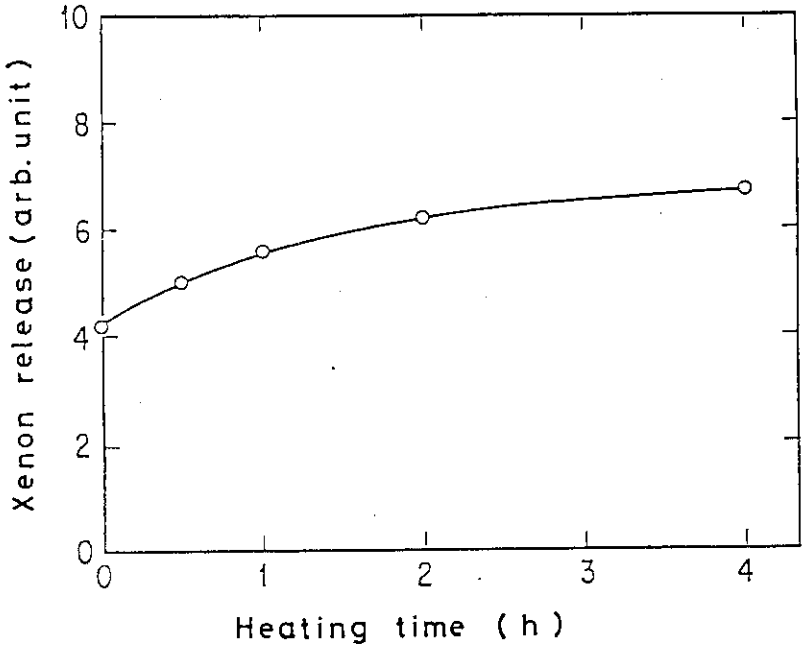


Fig.9 An example of xenon release from carburized cracked particles as a function of heating time at 1350°C.

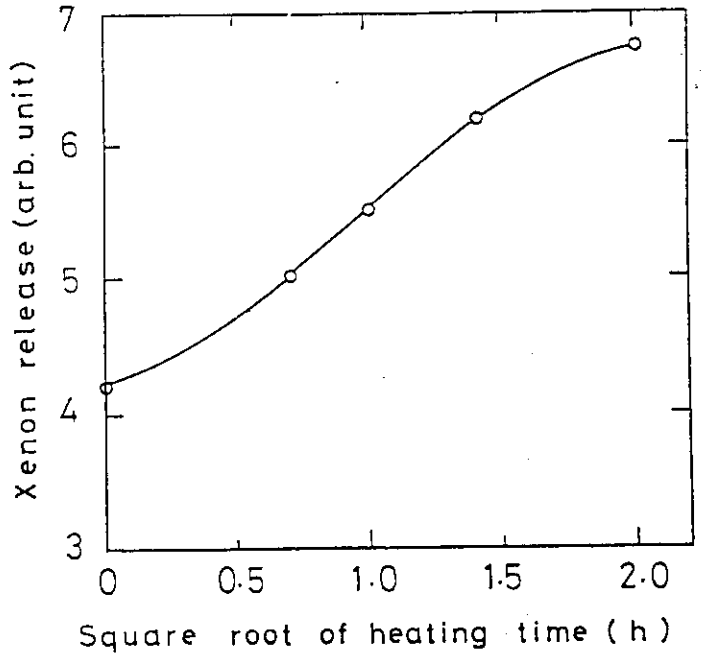


Fig.10 Replot of Fig.9 as a function of square root of heating time.

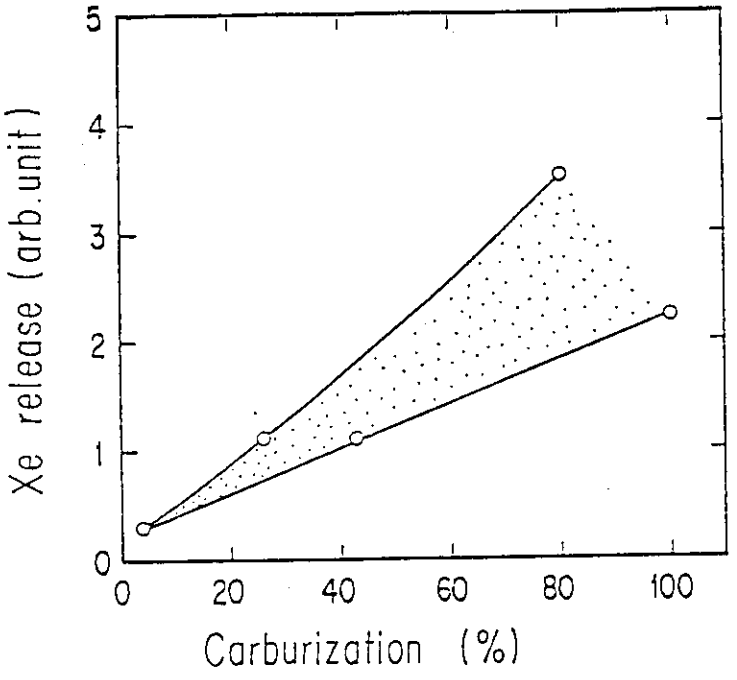


Fig.11 Correlation between xenon release and percent carburization of cracked particles.

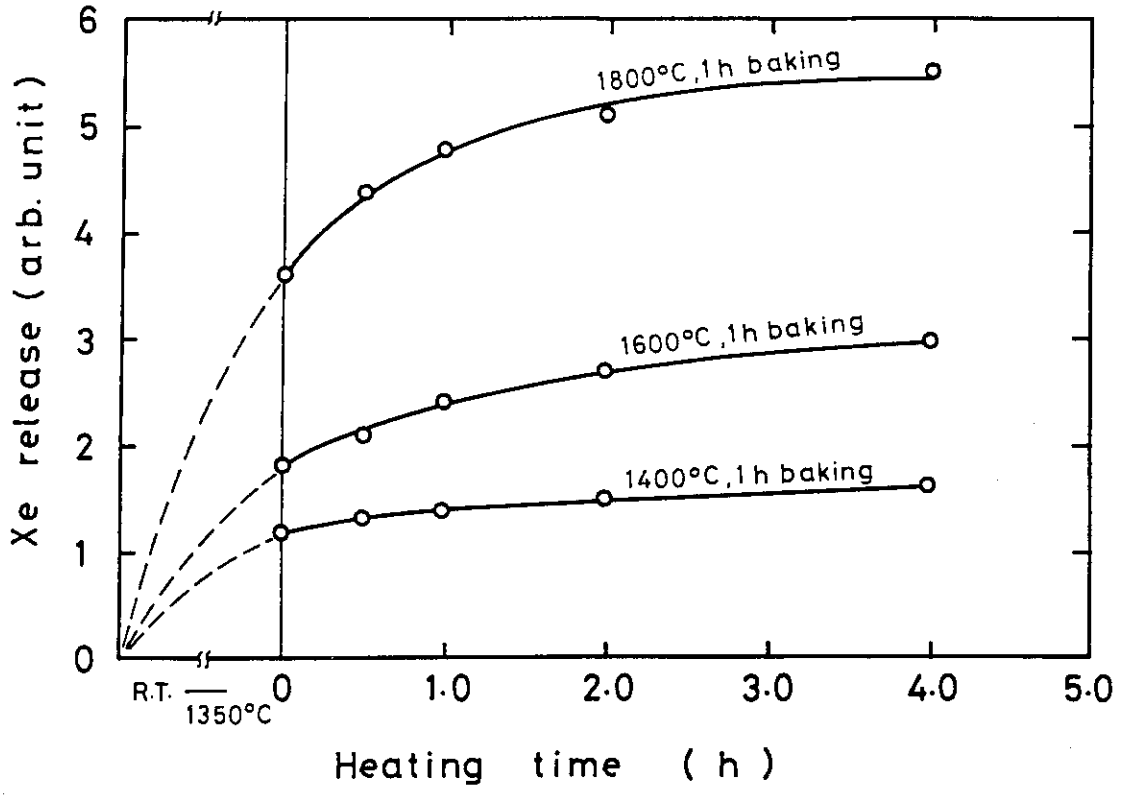


Fig. 12 Effect of baking temperature on xenon release at 1350°C