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REVIEW OF EXPERIMENTAL STUDIES  
OF ZIRCONIUM CARBIDE COATED FUEL PARTICLES  
FOR HIGH TEMPERATURE GAS-COOLED REACTORS

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Kazuo MINATO, Toru OGAWA and Kousaku FUKUDA

日本原子力研究所  
Japan Atomic Energy Research Institute

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Review of Experimental Studies of  
Zirconium Carbide Coated Fuel Particles  
for High Temperature Gas-cooled Reactors

Kazuo MINATO, Toru OGAWA and Kousaku FUKUDA

Department of Chemistry and Fuel Research  
Tokai Research Establishment  
Japan Atomic Energy Research Institute  
Tokai-mura, Naka-gun, Ibaraki-ken

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Experimental studies of zirconium carbide(ZrC) coated fuel particles were reviewed from the viewpoints of fuel particle designs, fabrication, characterization, fuel performance, and fission product retentiveness. ZrC is known as a refractory and chemically stable compound, so ZrC is a candidate to replace the silicon carbide(SiC) coating layer of the Triso-coated fuel particles. The irradiation experiments, the postirradiation heating tests, and the out-of-reactor experiments showed that the ZrC layer was less susceptible than the SiC layer to chemical attack by fission products and fuel kernels, and that the ZrC-coated fuel particles performed better than the standard Triso-coated fuel particles at high temperatures, especially above 1600 °C. The ZrC-coated fuel particles demonstrated better cesium retention than the standard Triso-coated fuel particles though the ZrC layer showed a less effective barrier to ruthenium than the SiC layer.

Keywords: Zirconium Carbide, Silicon Carbide, Coated Fuel Particles, HTGR,  
Fabrication, Characterization, Performance, Fission Products

高温ガス炉用炭化ジルコニウム被覆燃料粒子の研究  
(文献調査)

日本原子力研究所東海研究所燃料研究部  
湊 和生・小川 徹・福田 幸朔

(1995年2月7日受理)

炭化ジルコニウム (ZrC) 被覆燃料粒子について、燃料粒子の被覆形式、製造、特性評価、燃料挙動、及び核分裂生成物保持能の観点から、現在までの研究成果を調査・整理した。ZrCは、耐熱性に優れた化学的に安定な物質として知られており、Triso被覆燃料粒子の炭化ケイ素 (SiC) 層に代わり得る候補材である。数々の照射試験、照射後加熱試験、及び炉外実験により、ZrC層はSiC層よりも核分裂生成物や燃料による化学的腐食を受けにくいこと、及びZrC被覆燃料粒子はとくに1600°Cを超える高温においてTriso被覆燃料粒子よりも健全性に優れていることが明らかにされている。また、ZrC層は、ルテニウムについてはその保持能がSiC層より劣るものの、セシウムについては優れた保持能があることが確認されている。

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## 1. Introduction

The high temperature gas-cooled reactor (HTGR) uses coated fuel particles, which are dispersed in a graphite matrix to form fuel elements. In current HTGR designs the Triso-coated fuel particles are to be used [1-3]. The Triso-coated fuel particle consists of a microspherical kernel of uranium dioxide ( $\text{UO}_2$ ) or oxycarbide (UCO) fuel and coating layers of porous pyrolytic carbon (PyC), inner dense PyC (IPyC), silicon carbide (SiC) and outer dense PyC (OPyC). The function of these coating layers is to retain fission products within the particle. The SiC coating layer provides mechanical strength for the particle and acts as a diffusion barrier to metallic fission products which diffuse easily through the IPyC coating layer. Although SiC has excellent properties, it gradually loses mechanical integrity at very high temperatures, especially above  $1700^\circ\text{C}$  ( $1973\text{K}$ ), by thermal dissociation and transformation of  $\beta$ -SiC to  $\alpha$ -SiC [4-6]. The fuel temperatures are, therefore, limited to well below  $1700^\circ\text{C}$  during the design-basis accidents in the current HTGR designs [1-3].

Zirconium carbide (ZrC) is known as a refractory and chemically stable compound, having a melting point of  $3540^\circ\text{C}$ , and melts eutectically with carbon at  $2850^\circ\text{C}$  [7]; SiC sublimes at temperatures of about  $1800^\circ\text{C}$  [8]. ZrC is a candidate to replace the SiC coating layer of the Triso-coated fuel particles; the resulting particles are termed ZrC-Triso coated fuel particles. The ZrC-coated fuel particles are attractive not only to the HTGR but also to space reactors [9-11].

The evaluation of ZrC as a coating material for HTGR fuels is part of a recently published study prepared by Kasten et al. [8]. They summarized pertinent portions of the available literature on the ZrC coating layers and proposed R&D program for developing high quality ZrC-Triso coated particle fuels. It was mentioned that use of the ZrC-Triso coated particles has several potential advantages; a primary one is the potential for improved fission product retention at very high temperatures, such that the peak fuel temperature permissible under operating and accident conditions would increase while still retaining a very high degree of inherent safety. An associated feature would be the ability to operate at relatively high core power densities while maintaining a very high degree of safety. Also, use of ZrC coatings instead of SiC coatings could increase the temperature at which fuel matrix material can be carbonized during the fabrication process, result in increased thermal conductivity of the fuel matrix material, and reduce fuel operating temperatures for a given reactor-outlet coolant temperature [8].

## 2. Fuel particle designs

In the United States several coating designs have been tested [12,13]: ZrC-Triso coated particles, ZrC-Triso type coated particles without OPyC layer, ZrC-coated particles with ZrC-doped OPyC layer, and ZrC-coated particles with graded C-ZrC layer(s). In the graded C-ZrC layer, the compositions are changed gradually from the pure PyC through the C-ZrC alloy and into the pure ZrC. The graded layer was applied to either inside or outside of the ZrC layer. Propylene was used to produce the pure PyC and to provide the carbon for the graded portion of the co-deposited carbon and ZrC. Although most of the work reported on the use of ZrC in coated fuel particles has been directed toward the development of a replacement for the SiC barrier layer, ZrC was also tested as a fission product and oxygen getter [14,15], where ZrC was deposited over the fuel kernel or ZrC was dispersed throughout the buffer layer.

In Japan ZrC-coated fuel particles have been developed since early 1970s at JAERI [7]. The first generation of the ZrC-coated fuel particles was characterized by a thick ZrC layer with composition  $C/Zr > 1.0$  and by the absence of the OPyC layer. The ZrC was called "Zirconium-Carballoy" meaning ZrC-C alloy. Later it was found that the retention of metal fission products, especially  $^{90}\text{Sr}$ , by the Zr-Carballoy was rather poor [16], presumably owing to a short circuit through free carbon phase. And it was also felt from the irradiation experiences that the presence of the OPyC was essential for the mechanical integrity of the coated fuel particles. Hence, in the second generation, the emphasis was placed on the development of the ZrC-Triso coated particles with the ZrC composition  $C/Zr = 1.0$ .

## 3. Fabrication and characterization

### 3.1 Coating processes

Coating layers of ZrC and ZrC-C alloy were prepared by the chemical vapor deposition, where the reaction of zirconium halide with hydrocarbon was used in principle. Two methods have been developed for supplying zirconium halide to the coater: sublimation of  $\text{ZrCl}_4$  [13,17-19] and in-situ generation of zirconium halide vapor [20-27].

At Los Alamos Scientific Laboratory (LASL) the chemical vapor deposition of ZrC

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At Los Alamos Scientific Laboratory (LASL) the chemical vapor deposition of ZrC



has been studied using a gas mixture of  $\text{CH}_4$ ,  $\text{H}_2$ ,  $\text{ZrCl}_4$  and Ar [13,17-19]. A key development in the ZrC coating project proved to be the  $\text{ZrCl}_4$  powder feeder for metering  $\text{ZrCl}_4$  into the coater.  $\text{ZrCl}_4$  is a solid at room temperature, and sublimates at  $352^\circ\text{C}$ . In this process the  $\text{ZrCl}_4$  powder was supplied from the powder feeder, whose rate was controlled by the auger speed and metered by the output of the load cell on which the powder feeder was hung. The powder was swept by Ar to the coater base where it was mixed with the other coating gases supplied from a gas manifold. The  $\text{ZrCl}_4$  powder in the gas stream was vaporized in the coater base before entering the coating chamber [18].

Wagner et al. [18] studied effects of varying  $\text{CH}_4$  and  $\text{H}_2$  concentrations and particle bed area on the coating rate, the appearance, and the composition of the ZrC, using the  $\text{ZrCl}_4$  powder feeder in which the mass flow rate of the powder could be varied and controlled accurately. Increases in  $\text{CH}_4$  and  $\text{H}_2$  concentration were effective in increasing the linear coating rate of ZrC. Increases in the ratio of  $\text{CH}_4$  to  $\text{ZrCl}_4$  in the coating gas resulted in a decreased metallic appearance of the coating and an increase in the C/Zr in the deposit. Increases in  $\text{H}_2$  inhibited these effects.

Hollabaugh et al. [19] have prepared ZrC coating using a gas mixture of  $\text{C}_3\text{H}_6$ ,  $\text{H}_2$ ,  $\text{ZrCl}_4$  and Ar with the same coater and  $\text{ZrCl}_4$  powder feeder as those used by Wagner et al. [18]. In general, ZrC coatings made with  $\text{CH}_4$  and  $\text{C}_3\text{H}_6$  were similar and were affected similarly by variations in the hydrocarbon and hydrogen concentrations. The coatings made using the  $\text{ZrCl}_4$ - $\text{C}_3\text{H}_6$  reaction were more sensitive to changes in hydrogen concentration than those made using  $\text{CH}_4$ .

At JAERI, on the other hand, the coating processes based on the in-situ generation of zirconium halide vapor have been investigated in order to avoid the handling of highly hygroscopic halide powder [7]. Ikawa et al. [20-25] and Ogawa et al. [26,27] studied several processes: the chloride process [20], the methylene dichloride process [21], the iodide process [22,23], and the bromide process [24-27]. Among these processes the bromide process proved to be the most convenient and reliable. Fig. 1 [28] shows experimental apparatus for depositing ZrC by the bromide process. In this process the bromine, which is liquid at room temperature, was carried by argon onto the heated zirconium sponge to generate the bromide vapor, and the vapor was mixed with methane and hydrogen to be fed into a spouted bed of fuel particles.

Ogawa et al. [27] studied effects of gas composition and temperature on the chemical vapor deposition of ZrC within a spouted bed by the bromide process. The feed gas was a

mixture of  $ZrBr_4$ ,  $CH_4$ ,  $H_2$  and Ar. The results of the deposition experiment were compared with the calculated chemical equilibria in the Zr-C-H-Br system. The thermochemical analysis predicted that the methane determines the deposition in the ZrC monophasic region and that the  $ZrBr_4$  concentration diminishes the C/Zr ratio of the deposit to 1.0. Fig. 2 [27] shows a map of deposition products predicted by the thermochemical analysis. It was found that the weight and composition of the deposit could be calculated by thermochemical analysis after correcting the supply of methane for its pyrolysis efficiency. Predominant reactions presumably occurring were derived by a mass balance consideration on the calculated equilibrium species. A simplified model of the ZrC deposition was proposed [27].

### 3.2 Characterization techniques

In the case of the SiC-Triso coated particles, the PyC layers are burnt off to recover the SiC fragments for characterization, such as density, composition, strength measurements, etc. However, it was almost impossible to separate the ZrC from the PyC layers by the same method, since ZrC, in contrast with SiC, does not form a protective oxide layer, resulting in oxidation of ZrC to  $ZrO_2$  when exposed to air at high temperatures [28].

Ogawa et al. [28] have developed the method for obtaining the ZrC fragments from the coating layers containing the PyC. They found that the ZrC is virtually unaffected by plasma oxidation. Fig. 3 [28] shows the plasma oxidation apparatus, where low-pressure oxygen is ionized by high-frequency induction coupling at 75MHz. Plasma reaction was monitored by a color analyzer and an optical power meter. The color changed from pale violet of pure oxygen to pale blue during vigorous oxidation of free carbon, and again to pale violet when the PyC was completely removed and a very thin oxide scale was formed on the ZrC. The brightness also changed dramatically during the reaction. It was confirmed by Raman spectroscopy and X-ray diffraction that the bulk of the ZrC remained unaffected by the plasma oxidation [29].

Plasma oxidation with emission monitoring was also applied to the quantitative analysis of free carbon in ZrC powder [30]. Analysis of the free carbon is important for the quality control of the ZrC coating. The emission was monitored with an optical color analyzer and was calibrated with standard samples of  $ZrO_2+C$  mixtures. Oxidation rates of the free and the combined carbons are so different that it is possible to estimate the amount of the former from the emission. With powdered ZrC of about 10mg, the free carbon of less than 1wt%

could be easily determined. Without this method the composition of the ZrC was estimated by burning the ZrC and PyC together, weighing  $ZrO_2$  and  $CO_2$ , and subtracting the contribution of PyC from the total amount of  $CO_2$  [28].

## 4. Fuel performance

### 4.1 Fuel performance during normal operation

Although systematic irradiation experiments have not been completed on the ZrC-coated fuel particles, some promising data were obtained; the ZrC layer is less susceptible to chemical attack by fission products and fuel kernels, and the ZrC-coated fuel particles perform better than the SiC-Triso coated particles at high temperatures, especially above 1600°C. Some early irradiation tests showed poor performance of the ZrC-coated particles, which may be attributed to the fact that the fabrication conditions had not been optimized.

Irradiation tests on the LASL-made ZrC-coated particles [31-34] were carried out in the High Flux Isotope Reactor (HFIR) and the Oak Ridge Research Reactor (ORR). Table 1 summarizes the irradiation conditions [31-34]. Prior to the tests on the fuel-kerneled coated particles, carbon-kerneled inert coated particles were tested to determine the stability of the ZrC at high temperature and fluence [31,32]. The irradiation results of the inert coated particles were encouraging. In the tests of the fuel-kerneled particles, it was found that the graded coatings in the OF-2 capsule were cracked and it was postulated that the cracking was associated with the low PyC deposition rate and was not related to the ZrC [33]. Metallographic examination showed that the performance of the ZrC-coated particles in the HRB-12 capsule appeared to be poor by comparison with the SiC-coated particles. However, there was no evidence of palladium attack on any of the ZrC layers [34].

GAC-made ZrC-Triso coated fuel particles were irradiated in HFIR [35-37]. The irradiation conditions are listed in Table 2 [35-37]. The performance of the ZrC-Triso coated particles was very favorable. But there was evidence that ZrC may not be as effective in retaining fission products as SiC; microprobe analysis showed rare-earth fission products on the outside of the ZrC coating, whereas all cesium was retained within the coating [35]. The ZrC layers in the ZrC-Triso coated  $UO_2$  and  $UC_2$  particles in the HRB-15A capsule suffered no fission product attack, while the standard SiC-Triso coated fuel particles showed some

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degree of SiC-fission product interaction. The ZrC-Triso coated  $UC_2$  particles, however, showed poor retention of silver and europium, with large variety from particle to particle in this respect [36].

Reynolds et al. [38] performed irradiation test of the ZrC-coated fuel particles in the Siloe test reactor. Table 3 shows the irradiation conditions [38]. Postirradiation stereoscopic, metallographic and electron-beam microprobe examinations of the particles showed that the ZrC possesses exceptional resistance to chemical attack by fission products and good mechanical stability under irradiation. No chemical attack of the ZrC was found even in the case where the ZrC was adjacent to the  $UC_2$  kernel.

At JAERI irradiation experiments have been made on the ZrC-coated  $UO_2$  particles characterized by the Zr-Carballoy layer without the OPyC [7] and the ZrC-Triso coated  $UO_2$  particles [39].

The first generation of the ZrC-coated  $UO_2$  particles were charged into four capsules and irradiated in the Japan Materials Testing Reactor (JMTR), as summarized in Table 4 [7]. In all cases the particles were placed in a multi-hole graphite holder containing also the SiC-Triso coated particles as the reference. The particles in the 73F-12A and 73F-13A capsules experienced very high temperature exceeding  $1600^\circ C$ . The failure fractions of the ZrC-coated particles were rather high, though they were on a par with those of the SiC-Triso particles or below. Ceramographic examination showed the  $UO_2$  kernels came in contact with the Zr-Carballoy layers by the amoeba effect in the particles which experienced irradiation above  $1600^\circ C$ . However, there seemed to be no reaction except a little roughening of the inner surface of the Zr-Carballoy, showing better performance than the SiC layer against the chemical attack. The results of fission product inventory measurements suggested that the ZrC layer containing little free carbon could retain  $^{137}Cs$  better than the SiC layer.

The irradiation tests on the ZrC-Triso coated  $UO_2$  particles were done in JMTR and the Japan Research Reactor-2 (JRR-2). Irradiation conditions are summarized in Table 5 [39]. Except for the capsules denoted "VOF", the particles were irradiated in the form of annular compacts. The VOF capsules were designed to give a steep temperature gradient on the fuel particles. The release-to-birth ratio (R/B) of  $^{88}Kr$  was measured during irradiation in the 80F-4A capsule, which showed no failure through this irradiation test. After irradiation the particles were examined by the visual inspection with stereomicroscopy, X-ray microradiography, and acid leaching. No failure was detected for all samples using these inspection techniques. The particles in the VOF-14H capsule were irradiated at  $1600^\circ C$  for

3330h in the steep temperature gradient. The ceramographs of the particles from the VOF-14H showed carbon deposit at the colder end of the fuel kernel, which accompanied kernel migration up the temperature gradient. In the Triso coated fuel particles the palladium attack of the SiC was occasionally found at the colder side of the particle [40]. However, there was no indication of coating deterioration in the ZrC coating.

The better performance of the ZrC than the SiC against the chemical attack has also been demonstrated in the out-of-pile experiments [41]. The ZrC-Triso and SiC-Triso coated particles were heated in either vapor or powdered palladium. Morphology of the reaction was observed metallographically, and the reaction products were identified by X-ray diffraction and electron probe microanalysis. In addition, reactions in the mixture of SiC, ZrC, Pd and C, and the reaction of ZrC with an Ag-Pd alloy were studied. It is known that ZrC reacts with Pd to form  $ZrPd_3$  and C [42]. When the ZrC-Triso coated particles were heated in the palladium powder,  $ZrPd_3$  and C were formed, as expected. However, no reaction was found on the ZrC-Triso coated particles heated in Pd vapor at temperature ranging from 1557 to 1877°C, while the SiC layers were attacked severely and penetrated completely. The different reaction behavior of ZrC with Pd was discussed in terms of the Pd activity; if the Pd activity exceeded 0.12, ZrC should react with Pd. After heating of the mixture of SiC, ZrC, Pd and C at 1250°C for 7h, only  $Pd_2Si$  was formed as a reaction product but there was no formation of  $ZrPd_3$ . It was concluded that ZrC was less susceptible to Pd attack than SiC [41].

## 4.2 Fuel performance during accidents

### 4.2.1 Non-oxidizing conditions

Postirradiation heating test of the ZrC-Triso coated fuel particles has been performed at JAERI [39]. The heated particles were sampled from an irradiated fuel compact after electrolytic disintegration, which were irradiated to 4%FIMA at 1100°C. The postirradiation heating was made in a cold-wall furnace with a graphite heater, which has been used in the tests of the standard SiC-Triso coated particles [43]. The particles were contained individually in holes of thin graphite disks. The ZrC-Triso coated fuel particles were heated to 2400°C at 1°C/min. During heating radioactivity in flowing helium was monitored with an ionization chamber. The activity was due mostly to  $^{85}Kr$ . An activity burst occurred only after keeping the particles at 2400°C for about 6000s. The activity burst corresponded to one failure among 101 particles heated. This interpretation was confirmed by the X-ray radiographs of the

particles after heating. Fig. 4 [39] compares this result with the result on the JAERI standard SiC-Triso coated particles [43]; the figure shows the failure fraction at reaching the given temperature.

The different behavior of the ZrC-Triso coated fuel particles at high temperatures from that of the standard SiC-Triso coated fuel particles was discussed with the postheating ceramographs [39]. There was a significant difference in behavior of the ZrC from that of the SiC at such high temperatures: while the SiC is brittle in nature, the ZrC can sustain a very large strain. The high plasticity is explained by the fact that resistance of the ZrC crystal lattice to the dislocation motion becomes very weak above 2200°C [44].

In this heating test, the particles have been heated in a loose condition without the mechanical support from the surrounding graphite matrix of fuel compact. The presence of graphite matrix could offset the coating expansion and would further reinforce the integrity of the ZrC-Triso coated fuel particles [39].

#### 4.2.2 Oxidizing conditions

No experimental work was found in the literature on the performance of the ZrC-coated fuel particles under accidental oxidizing conditions.

Thermodynamic analysis has been performed on the system of ZrC-C-(O<sub>2</sub> or H<sub>2</sub>O)-He at JAERI [45]. The analysis showed that there were two kinds of oxidation behavior of ZrC, which was similar to that of SiC, as shown in Fig. 5 [45]: active oxidation and passive oxidation. While a loss in mass occurs in the active oxidation, the passive oxidation results in a net mass increase. The active-to-passive transition of oxidation occurred depending on temperature and initial O<sub>2</sub> or H<sub>2</sub>O pressure.

Under most of the accidental air or water ingress conditions, the passive oxidation of ZrC was expected to occur. According to the experiment on the passive oxidation of ZrC at temperatures of 857–1887°C [46], protective layer of ZrO<sub>2</sub> would not be formed on the ZrC, in contrast with the case of SiC. The preferential oxidation along grain boundaries occurred in the ZrC. Between 857 and 1287°C this preferential oxidation resulted in intercrystalline fracture due to grain boundary stresses. At higher temperatures stresses were apparently sufficiently released so that the samples remained intact [46]. From this point of view, ZrC is not a retentive layer in air or water ingress accidents.

## 5. Fission product retentiveness

Several authors have investigated the potential of ZrC coating layer for retaining metallic fission products though the data is limited compared with that on SiC.

Stark [47] has performed cesium infusion experiments on ZrC powder and ZrC coated graphite. The diffusion coefficient of Cs in ZrC was estimated to be  $10^{-18}$ – $10^{-16}$  m<sup>2</sup>/s over the temperature range 1212–1623°C with the activation energy of about 50kJ/mol.

Fukuda et al. [16] have studied the diffusion behavior of <sup>137</sup>Cs, <sup>90</sup>Sr and <sup>144</sup>Ce in Zr–Carballoy (C/Zr=1.3) by measuring concentration profiles in the ZrC and PyC layers of the coated particles and the release from the particles during postirradiation annealing. The particles used were irradiated to 2.48%FIMA at 1260°C. The diffusion coefficient for <sup>137</sup>Cs obtained from the analysis of the concentration profiles in ZrC<sub>1.3</sub> was  $2.3 \times 10^{-7} \exp(-3.18 \times 10^5/RT)$  m<sup>2</sup>/s in the temperature range 1260–1600°C. The diffusion coefficients for <sup>90</sup>Sr and <sup>144</sup>Ce at 1600°C were estimated to be  $1.5 \times 10^{-15}$  and  $2.0 \times 10^{-16}$ , respectively.

Ogawa et al. [48] have made two types of experiments: strontium soaking experiments and postactivation annealing experiments. In the soaking experiments the ZrC–Triso coated UO<sub>2</sub> particles were annealed in graphite powder containing 0.2wt% Sr as nitrate tagged with <sup>85</sup>Sr. After annealing at 1400°C for 146h in flowing helium, the outer PyC layer was removed stepwise to measure Sr content. The diffusion coefficient of Sr in ZrC<sub>1.0</sub> was estimated to be  $2 \times 10^{-18}$  m<sup>2</sup>/s at 1400°C. In the postactivation annealing experiments short-lived fission products were generated within the ZrC–Triso coated UO<sub>2</sub> particles by short-term neutron irradiation. After annealing at 1400°C for 216h in flowing helium, the concentration distributions of fission products within the ZrC layer were determined. Based on these experiments, the diffusion coefficients were estimated to be  $1.2 \times 10^{-16}$  m<sup>2</sup>/s for <sup>103</sup>Ru and  $2.9$ – $4.6 \times 10^{-18}$  m<sup>2</sup>/s for <sup>140</sup>Ba in ZrC<sub>1.0</sub> at 1400°C.

Chernikov et al. [49] have investigated diffusion behavior of solid fission products in ZrC coating layer by annealing experiments. Nuclides <sup>133</sup>Ba, <sup>110m</sup>Ag and <sup>147</sup>Pm were deposited on the surface of unirradiated ZrC-coated particles from the solution. After annealing of the particles, the distribution of the nuclides in the ZrC coating layer were determined by removing the ZrC stepwise. Two kinds of diffusion coefficient for each nuclide were presented: the migration along short-circuit diffusion paths and the migration in the grain volume. The temperature range investigated was about 1700–2200°C. They [49] also



estimated the diffusion coefficients for  $^{133}\text{Ba}$  and  $^{144}\text{Ce}$  using irradiated ZrC-coated fuel particles. Based on the distribution of the nuclides in the ZrC measured by removing the ZrC stepwise, the diffusion coefficients were estimated to be  $1.3 \times 10^{-17} \text{m}^2/\text{s}$  for  $^{133}\text{Ba}$  and  $6.4 \times 10^{-18} \text{m}^2/\text{s}$  for  $^{144}\text{Ce}$  in ZrC at  $1500^\circ\text{C}$ .

Minato et al. [50] have made postirradiation heating experiments on the ZrC-Triso coated  $\text{UO}_2$  particles at  $1600^\circ\text{C}$  for 4500h. The heated particles were irradiated to 1.5%FIMA at  $900^\circ\text{C}$ . The heating test was divided into 7 time steps, and the graphite components and the carbon insulators were removed from the furnace after each time step to identify and evaluate released fission products from the particles by  $\gamma$ -ray spectrometry. Based on the measured fractional release, the diffusion coefficients were estimated to be  $1-5 \times 10^{-18} \text{m}^2/\text{s}$  for  $^{137}\text{Cs}$  and  $3 \times 10^{-16} \text{m}^2/\text{s}$  for  $^{106}\text{Ru}$  at  $1600^\circ\text{C}$ . Ogawa et al. [48] previously pointed out that the diffusion coefficient for Ru in ZrC was somewhat larger than in SiC and discussed the fast diffusion of Ru by means of the atomic radius ratio of Ru/Zr. The values for fractional release of  $^{144}\text{Ce}$ ,  $^{154}\text{Eu}$  and  $^{155}\text{Eu}$  were larger than that for  $^{137}\text{Cs}$  though the diffusion coefficients for them were not obtained. This behavior was consistent with the electron probe microanalysis on the irradiated ZrC-coated particles observed by Valentine et al. [35] that Cs was retained inside the ZrC layer while Ce appeared to be both in the ZrC and outside the ZrC layer.

The diffusion coefficients for fission product species in ZrC are summarized in Table 6 [16,47-50] and plotted in Fig. 6 [50].

Hayashi et al. [51] have made postirradiation heating tests on the ZrC-Triso coated fuel particles to compare the results on the SiC-Triso coated fuel particles obtained under the same experimental conditions. The heated ZrC-Triso coated fuel particles were irradiated to 1.8%FIMA and their maximum irradiation temperature was  $1500^\circ\text{C}$ . The heating tests were performed  $100^\circ\text{C}$  stepwise from  $1400$  to  $2400^\circ\text{C}$ . The heating time was 2h at each temperature and the released fission products were measured by  $\gamma$ -ray spectrometry. The ZrC-Triso coated particle demonstrated better cesium retention than the standard SiC-Triso coated particle by up to one order of magnitude at temperatures  $<2000^\circ\text{C}$  and up to three orders of magnitude at  $2400^\circ\text{C}$ . In spite of better cesium retention, the ZrC layer showed a less effective barrier to  $^{106}\text{Ru}$  than the SiC layer.

## 6. Summary

Experimental studies of ZrC-coated fuel particles for HTGR were reviewed from the viewpoints of fuel particle designs, fabrication, characterization, fuel performance, and fission product retentiveness. ZrC is known as a refractory and chemically stable compound, so ZrC is a candidate to replace the SiC coating layer of the Triso-coated fuel particles; the resulting particles are termed ZrC-Triso coated fuel particles.

The ZrC coating layer was prepared by the chemical vapor deposition, where the reaction of zirconium halide with hydrocarbon was used in principle. Two methods have been developed for supplying zirconium halide to the coater: sublimation of  $ZrCl_4$  and in-situ generation of zirconium halide vapor. In the latter process the handling of highly hygroscopic zirconium halide powder can be avoided.

The plasma oxidation method has been developed to obtain the ZrC fragments from the coating layers containing the PyC for characterization, such as density, composition, strength measurements, etc. In the case of the SiC-Triso coated particles, the PyC layers are burnt off to recover the SiC fragments. However, it was almost impossible to separate the ZrC from the PyC layers by the same method, since ZrC, in contrast with SiC, does not form a protective oxide layer, resulting in oxidation of ZrC to  $ZrO_2$  when exposed to air at high temperatures. Plasma oxidation with emission monitoring was also applied to the quantitative analysis of free carbon in ZrC powder.

Some promising data were obtained on the fuel performance of the ZrC-coated fuel particles though systematic irradiation experiments have not been completed. The irradiation experiments, the postirradiation heating tests, and the out-of-reactor experiments showed that the ZrC layer was less susceptible than the SiC layer to chemical attack by fission products and fuel kernels, and that the ZrC-coated fuel particles performed better than the SiC-Triso coated particles at high temperatures, especially above  $1600^\circ\text{C}$ . Some early irradiation tests showed poor performance of the ZrC-coated particles, which may be attributed to the fact that the fabrication conditions had not been optimized.

Several authors have investigated the potential of ZrC coating layer for retaining metallic fission products though the data is limited compared with that on SiC. The ZrC-Triso coated particles showed better cesium retention than the standard SiC-Triso coated particle. In spite of better cesium retention, the ZrC layer showed a less effective barrier to ruthenium than the SiC layer.

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Table 1 Irradiation conditions of LASL-made ZrC-coated particles  
(prepared from refs. [31-34])

Capsule	Sample type	Temperature (°C)	Burnup (%FIMA)	Fast fluence (m <sup>-2</sup> , E>29fJ)
HT-28	C-kernel, without OPyC	900	0	3.5×10 <sup>25</sup>
	C-kernel, ZrC-Triso	900	0	3.5×10 <sup>25</sup>
	C-kernel, graded C-ZrC	1250	0	7.5×10 <sup>25</sup>
	C-kernel, double-graded	1250	0	7.5×10 <sup>25</sup>
HT-29	C-kernel, without OPyC	900	0	9.4×10 <sup>25</sup>
	C-kernel, ZrC-Triso	900	0	9.4×10 <sup>25</sup>
	C-kernel, graded C-ZrC	900	0	4.4×10 <sup>25</sup>
		900	0	9.0×10 <sup>25</sup>
		900	0	10.7×10 <sup>25</sup>
	C-kernel, double-graded	900	0	4.4×10 <sup>25</sup>
		900	0	9.0×10 <sup>25</sup>
900		0	10.7×10 <sup>25</sup>	
HT-31	C-kernel, ZrC-doped OPyC	1250	0	8.65×10 <sup>25</sup>
		1250	0	8.89×10 <sup>25</sup>
		1250	0	9.00×10 <sup>25</sup>
OF-2	UC <sub>2</sub> , double-graded C-ZrC-C	1150	73	5.6×10 <sup>25</sup>
		1350	80	8.4×10 <sup>25</sup>
HRB-12	UC <sub>4.6</sub> O <sub>1.1</sub> , ZrC-Triso	-	84	4.40×10 <sup>25</sup>
		1250	86	6.90×10 <sup>25</sup>
	UC <sub>4.6</sub> O <sub>1.1</sub> , ZrC-doped OPyC	1100	85	4.94×10 <sup>25</sup>
		-	87	7.14×10 <sup>25</sup>
		1260	85	5.40×10 <sup>25</sup>
	UC <sub>4.6</sub> O <sub>1.1</sub> , graded C-ZrC and ZrC-doped OPyC	-	87	7.36×10 <sup>25</sup>

Table 2 Irradiation conditions of GAC-made ZrC-coated fuel particles  
(prepared from refs. [35-37])

Capsule	Sample type	Temperature (°C)	Burnup (%FIMA)	Fast fluence (m <sup>-2</sup> , E>29fJ)
HRB-7	UC <sub>2</sub> , ZrC-Triso, rod	1225	84.4	4.50×10 <sup>25</sup>
HRB-8	UC <sub>2</sub> , ZrC-Triso, rod	1225	84.4	5.92×10 <sup>25</sup>
HRB-15A	UC <sub>2</sub> , ZrC-Triso, rod	1125	28.1	6.2×10 <sup>25</sup>
	UC <sub>2</sub> , ZrC-Triso, tray	1130	26.7	5.8×10 <sup>25</sup>
		1055	24.9	4.9×10 <sup>25</sup>
	UC <sub>2</sub> , ZrC-Triso, wafer	1125	28.3	6.3×10 <sup>25</sup>
		1065	27.4	5.7×10 <sup>25</sup>
	UO <sub>2</sub> , ZrC-Triso, rod	1075	27.2	6.0×10 <sup>25</sup>
	UO <sub>2</sub> , ZrC-Triso, tray	1125	27.6	6.1×10 <sup>25</sup>
	UO <sub>2</sub> , ZrC-Triso, wafer	1100	27.6	6.1×10 <sup>25</sup>
		1125	28.8	6.2×10 <sup>25</sup>
HRB-16	UC <sub>2</sub> , ZrC-Triso, tray	1080	20.9	4.1×10 <sup>25</sup>
	UC <sub>x</sub> O <sub>y</sub> , ZrC-Triso, tray	1160	20.3	3.8×10 <sup>25</sup>

Table 3 Irradiation conditions of ZrC-coated fuel particles by Reynolds et al.  
(prepared from ref. [38])

Sample type	Temperature (°C)	Burnup (%FIMA)	Fast fluence (m <sup>-2</sup> , E>29fJ)
UC <sub>2</sub> /buffer/ZrC/PyC	1200	70	5×10 <sup>25</sup>
UC <sub>2</sub> /ZrC/buffer/PyC	1200	70	5×10 <sup>25</sup>
(8Th,U)O <sub>2</sub> /buffer/ZrC/PyC	1200	8	5×10 <sup>25</sup>
(8Th,U)O <sub>2</sub> /ZrC/buffer/PyC	1200	8	5×10 <sup>25</sup>

Table 4 Irradiation conditions of JAERI-made Zr-carballoy coated fuel particles (prepared from ref. [7])

Capsule	Sample type	Temperature (°C)	Burnup (%FIMA)	Fast fluence (m <sup>-2</sup> , E>29fJ)
72F-6A	UO <sub>2</sub> , ZrC-Triso type, without OPyC	1197-1427	2.5	1.4×10 <sup>25</sup>
72F-7A	UO <sub>2</sub> , ZrC-Triso type, without OPyC	1287	0.1	0.06×10 <sup>25</sup>
73F-12A	UO <sub>2</sub> , ZrC-Triso type, with thin OPyC	697-1177	2.0	0.8×10 <sup>25</sup>
		927-1807	3.2	1.4×10 <sup>25</sup>
	UO <sub>2</sub> , ZrC-Triso type, without OPyC	927-1807	3.2	1.4×10 <sup>25</sup>
73F-12A	UO <sub>2</sub> , ZrC-Triso type, with thin OPyC	647-1197	2.5	1.9×10 <sup>25</sup>
		957-1627	4.1	3.1×10 <sup>25</sup>
	UO <sub>2</sub> , ZrC-Triso type, without OPyC	957-1627	4.8	3.1×10 <sup>25</sup>

Table 5 Irradiation conditions of JAERI-made ZrC-coated fuel particles (prepared from ref. [39])

Capsule	Sample type	Temperature (°C)	Burnup (%FIMA)	Fast fluence (m <sup>-2</sup> , E>29fJ)
78F-4A	UO <sub>2</sub> , ZrC-Triso, compacts	1100	4.0	2.2×10 <sup>25</sup>
80F-4A	UO <sub>2</sub> , ZrC-Triso, compacts	900	1.5	1.2×10 <sup>25</sup>
ICF-26H	UO <sub>2</sub> , ZrC-Triso, compacts	1400-1500	1.8	1.0×10 <sup>25</sup>
VOF-8H	UO <sub>2</sub> , ZrC-Triso, disks	1370 (15°C/mm)	1.6	(<1×10 <sup>24</sup> )
VOF-14H	UO <sub>2</sub> , ZrC-Triso, disks	1600 (15°C/mm)	1.6	(<1×10 <sup>24</sup> )

Table 6 Diffusion coefficients for fission product species in ZrC  
(prepared from refs. [16,47-50])

Species	Temperature range (°C)	Diffusion coefficient <sup>*)</sup> (m <sup>2</sup> /s)	Reference
Cs	1212-1623	$1 \times 10^{-18} - 1 \times 10^{-16}$	[47]
Cs	1260-1600	$2.3 \times 10^{-7} \exp(-3.18 \times 10^5/RT)$	[16]
Sr	1600	$1.5 \times 10^{-15}$	[16]
Ce	1600	$2.0 \times 10^{-16}$	[16]
Sr	1400	$2 \times 10^{-18}$	[48]
Ru	1400	$1.2 \times 10^{-16}$	[48]
Ba	1400	$2.9 - 4.6 \times 10^{-18}$	[48]
Ag	1700-2200	$2.6 \times 10^{-10} \exp(-2.25 \times 10^5/RT)$	[49]
Ba	1700-2200	$2.3 \times 10^{-9} \exp(-3.01 \times 10^5/RT)$	[49]
Ba	1500	$1.3 \times 10^{-17}$	[49]
Ce	1500	$6.4 \times 10^{-18}$	[49]
Cs	1600	$1 - 5 \times 10^{-18}$	[50]
Ru	1600	$3 \times 10^{-16}$	[50]

<sup>\*)</sup> R is gas constant (8.314J/mol·K)  
T is temperature (K)

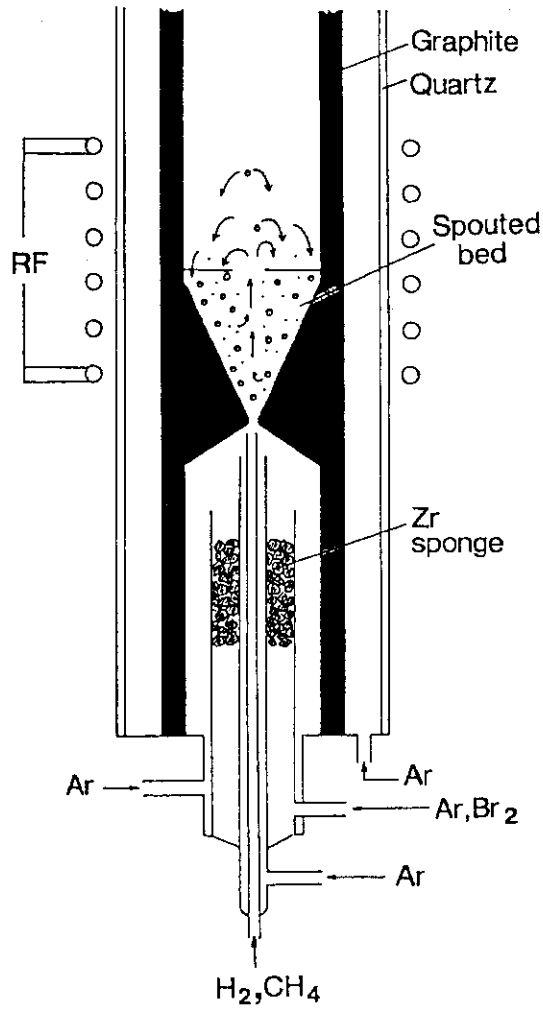


Fig. 1 Experimental apparatus for depositing ZrC by the bromide process.  
(reproduced from ref. [28])

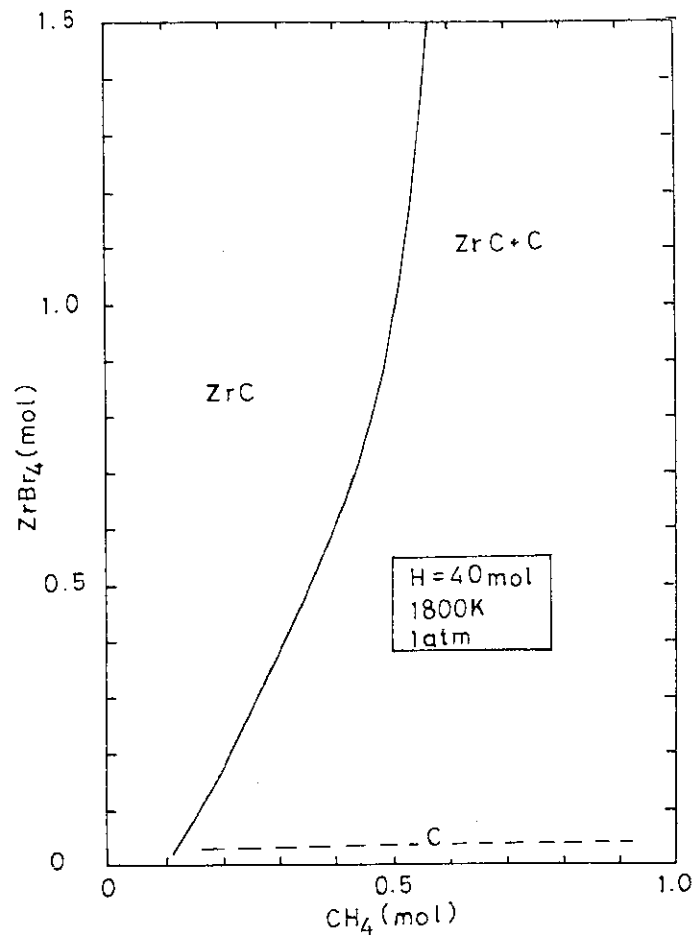


Fig. 2 A map of deposition products predicted by the thermochemical analysis.  
(reproduced from ref. [27])

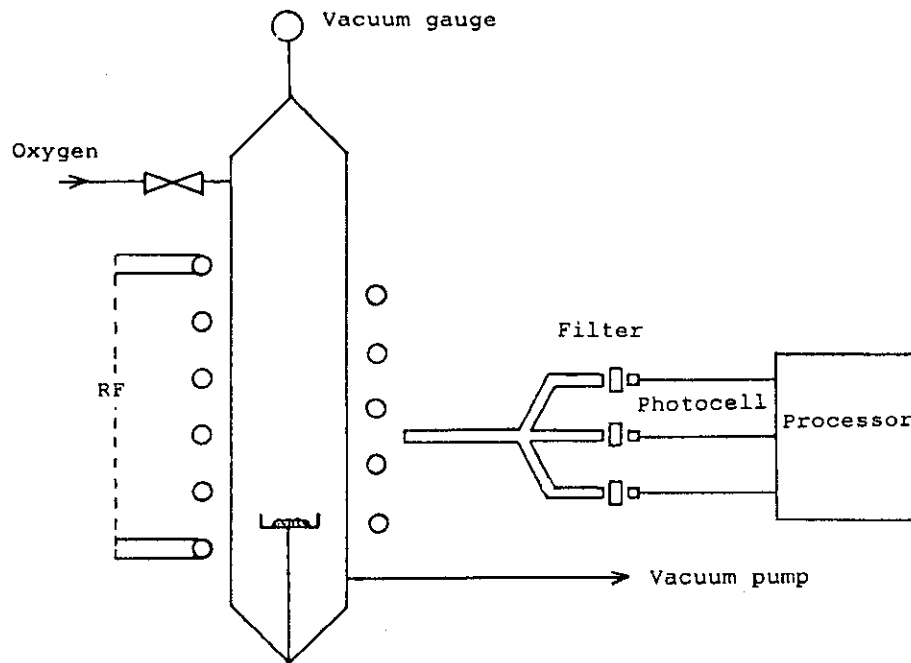


Fig. 3 Plasma oxidation apparatus for removing PyC layers from ZrC.  
(reproduced from ref. [28])

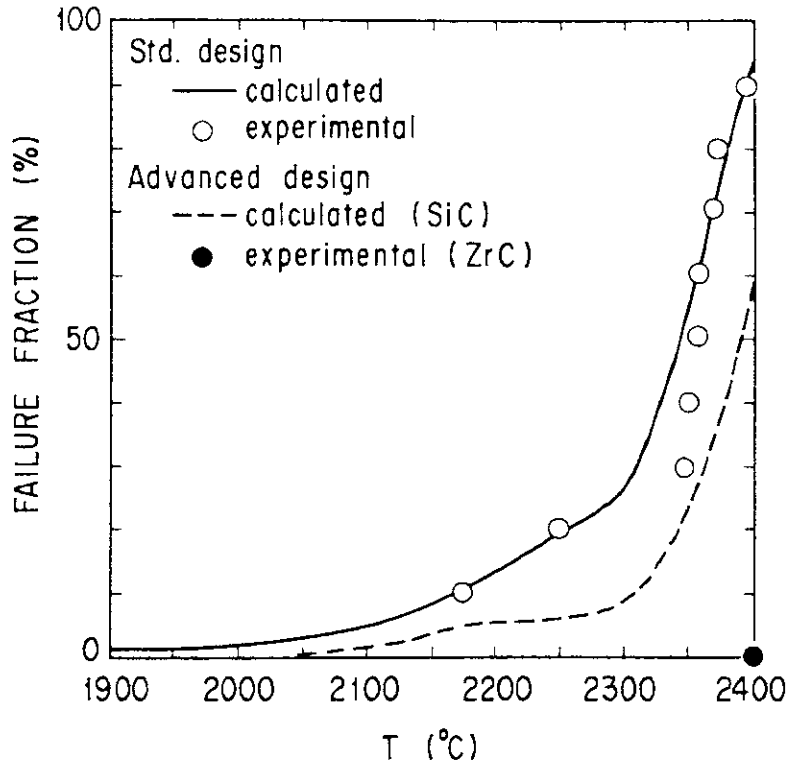


Fig. 4 Comparison of failure fraction of the ZrC-Triso coated fuel particles with the reference SiC-Triso coated particles. Dashed line gives model prediction for the SiC-Triso coated particles, which have the same dimensions as the ZrC-Triso coated particles in this study.  
(reproduced from ref. [39])



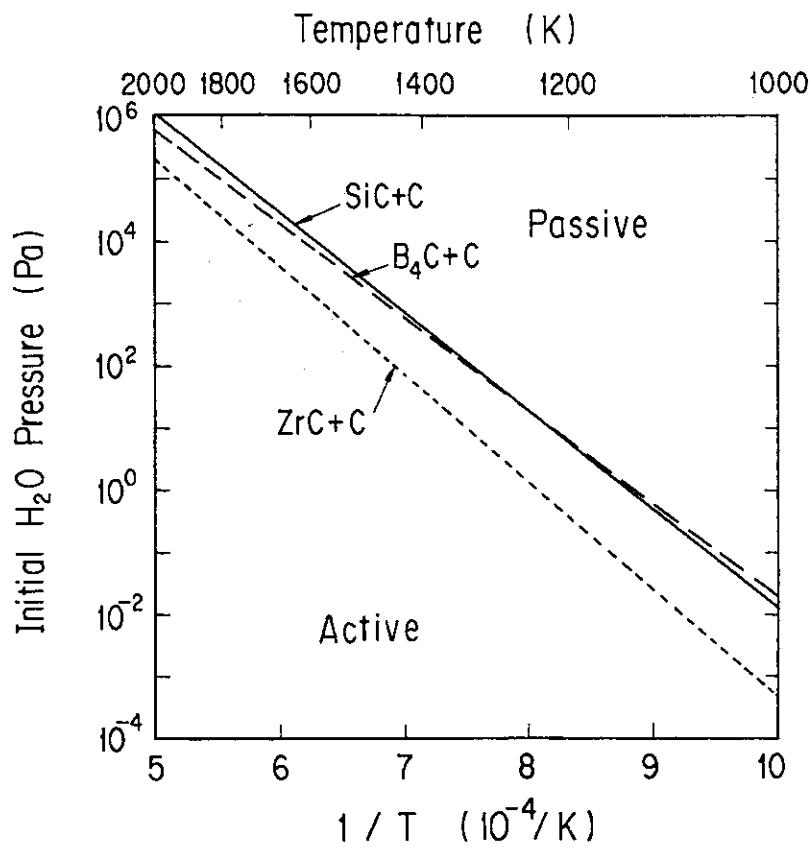


Fig. 5 Active-to-passive oxidation transitions for ZrC+C, B<sub>4</sub>C+C and SiC+C calculated in the (ZrC, B<sub>4</sub>C or SiC)-C-H<sub>2</sub>O-He system as a function of temperature and initial H<sub>2</sub>O pressure.  
(reproduced from ref. [45])

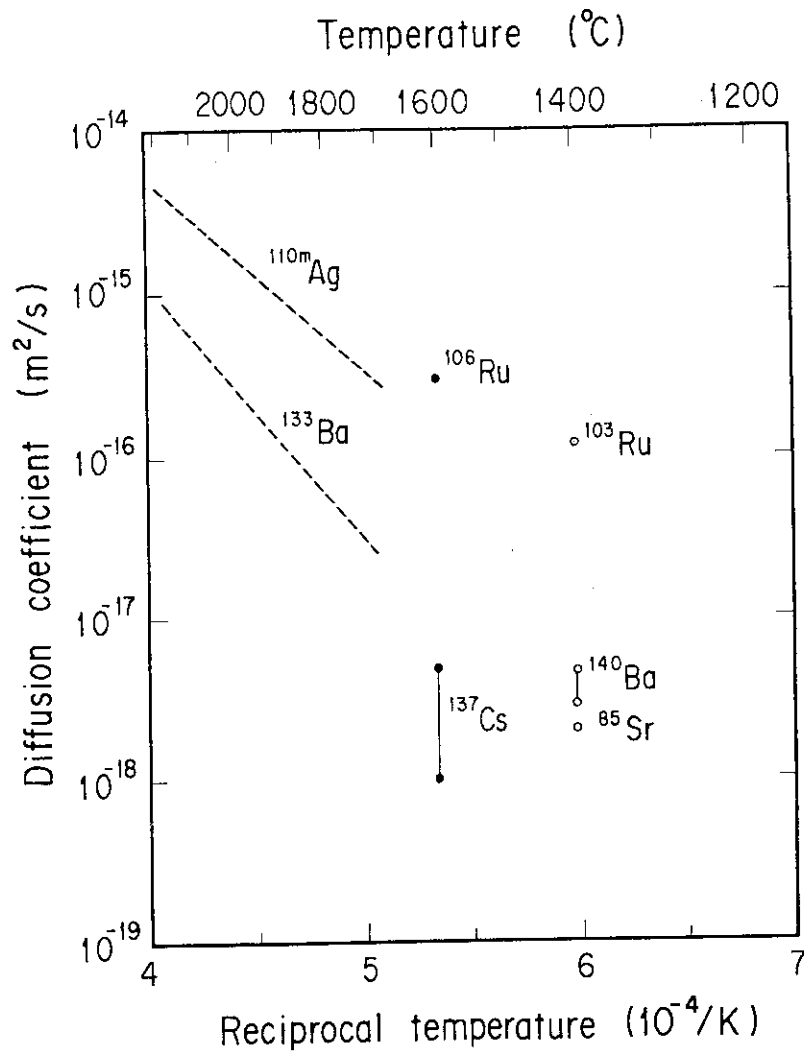


Fig. 6 Diffusion coefficients for fission product species in ZrC. Data of solid circles are from ref. [50], open circles from ref. [48], and broken lines from ref. [49]. (reproduced from ref. [50])