ELSEVIER

Journal of Nuclear Materials 279 (2000) 253–258

journal of nuclear materials

www.elsevier.nl/locate/jnucmat

Reduction of the open porosity of UO_2 pellets through pore structure control

Kun Woo Song *, Keon Sik Kim, Young Min Kim, Ki Won Kang, Youn Ho Jung

Advanced LWR Fuel Development, Korea Atomic Energy Research Institute, P.O. Box 105, Yusong, Taejon 305-600, South Korea

Received 1 December 1999; accepted 12 January 2000

Abstract

A powder mixture was prepared by mixing uranium-dioxide (UO_2) powder ex-AUC with its milled powder and was pressed into compacts. The UO_2 pellets were sintered under hydrogen. The compact density increased with the content of milled powder, since the particles of the milled powder might fill the interstices between the particles of the UO_2 powder ex-AUC during pressing. A mechanism for the formation of flake-like pores was proposed on the basis of the microstructures of the powder, the compact, a partially sintered pellet and a final pellet. The open porosity of a sintered pellet decreased with increasing content of the milled powder, and the reduction of open porosity could be mainly attributed to the decrease in the number of flake-like pores whose shapes deviate greatly from roundness. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

Uranium-dioxide (UO_2) fuel pellets have been fabricated using UO_2 powder through the processes of mixing, pressing, and sintering, of which the conditions have been optimized in accordance with the properties of starting UO_2 powder. The manufacturing method of UO_2 powder from UF_6 determines largely the powder properties, and there are various manufacturing methods including ammonium uranyl carbonate (AUC), ammonium di-uranate (ADU), and dry conversion (DC) processes. UO_2 powder ex-AUC [1] is remarkably different in its properties from other UO_2 powders.

UO_2 powder ex-AUC has a large average particle size of about 17 μm, a round shape, and a good flowing ability. Owing to its good flowing ability, UO_2 powder ex-AUC has an advantage in that it can be directly pressed into compacts (green pellets) without granulation in the mass production of UO_2 pellets. Other UO_2 powders are usually granulated prior to pressing. Despite its large particle size, UO_2 powder ex-AUC has a high surface area of about 5 m^2/g compared to other UO_2 powders and includes a number of very small open pores [1,2]. However, UO_2 powder ex-AUC yields a somewhat lower pellet density than other UO_2 powders under normal sintering conditions at about 1700°C in a reducing atmosphere. This result is open to question since a rule-of-thumb presumes that the pellet density increases with the specific surface area of the powder. Thus, it is necessary to investigate further the densification behavior of a compact of UO_2 powder ex-AUC.

UO_2 pellets made from the UO_2 powder ex-AUC have a higher open porosity than those made from other UO_2 powders [3]. UO_2 pellets can absorb moisture through the open porosity from the environment during the period of handling and storage, and the moisture may cause a hydriding failure of fuel cladding during irradiation [3]. Thus, it is desirable to keep the open porosity of a pellet as low as possible.

The purpose of this work is to understand the pore structure development during sintering of UO_2 powder ex-AUC and to reduce the open porosity through pore structure control. This paper investigates the open porosity of pellets made from mixture of UO_2 powder ex-AUC and its milled powder, and the relationship between open porosity and pore shape is discussed. The

* Corresponding author. Tel.: +82-42 868 2579; fax: +82-42 868 2403.
E-mail address: kwsong@kaeri.re.kr (K.W. Song).

PII: S 0 0 2 2 - 3 1 1 5 (0 0) 0 0 0 0 4 - 0

paper proposes a mechanism for pore formation in the UO_2 pellet made from UO_2 powder ex-AUC.

2. Experimental

The UO_2 powders used in this work were UO_2 powder ex-AUC [1] and its milled powder. The latter was made by milling the UO_2 powder for 2 h with a ball mill. Both powders were mixed in a tumbling mixer to make powder mixtures, in which the contents of milled powder were 5, 10, and 20 wt%. The powder mixtures were pressed into compacts (green pellets) in the pressure range 200–350 MPa and sintered at 1680°C for 4 h under hydrogen to fabricate UO_2 pellets. The particle sizes of both UO_2 powders were measured by a laser light scattering method, and their morphology was observed by scanning electron microscopy.

The compact density (green density) was determined by a geometrical method, and the pellet density and open porosity were determined by the water immersion method [4]. In order to impregnate water in the open porosity, the pellets which had been put in water were evacuated for 30 min, and then the vacuum reverted to the atmospheric pressure.

Pore size and pore shape in the sintered pellet were analyzed quantitatively with the aid of the software Image Pro. About 8000 pores were counted for each specimen, and each pore was characterized two-dimensionally in its area and perimeter, which is the length of the line bounding a pore. The pore size was assumed to equal the equivalent diameter of a pore, which is defined by the following equation:

$$\text{Equivalent diameter} = 2\sqrt{(\text{area}/\pi)}. \quad (1)$$

The shape factor of a pore was determined by the following equation:

$$\text{Shape factor} = \frac{4\pi \times \text{area}}{(\text{perimeter})^2}. \quad (2)$$

A perfectly round pore has a shape factor of 1, and the shape factor of a pore decreases as the pore shape deviates from roundness.

3. Results and discussion

Fig. 1 shows the particle size distributions of UO_2 powder ex-AUC and the milled powders. Both powders had monomodal size distributions with different modes, which were 17.4 μm for the UO_2 powder and 2.5 μm for the milled powder. It can be deduced that the powder mixture of UO_2 and milled UO_2 has a bimodal size distribution with a large mode corresponding to the

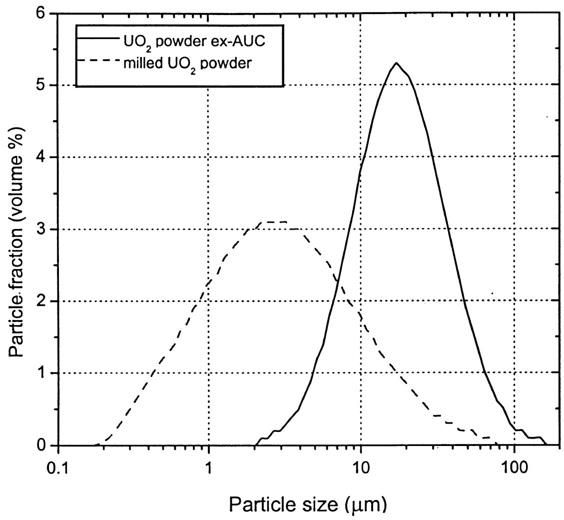

Fig. 1. Particle size distributions of UO_2 powder ex-AUC and milled UO_2 powder.

UO_2 powder and a small one corresponding to the milled powder.

The compact density of powder mixtures is plotted against the content of milled UO_2 in Fig. 2. The compact density increased linearly with the content of milled UO_2 and then remained almost constant above 10 wt% milled UO_2, suggesting that the degree of powder packing is enhanced by the addition of milled UO_2. This can be understood by assuming that small particles (milled UO_2) may fill the interstices between large particles (UO_2 ex-AUC) during the operation of pressing. Such a

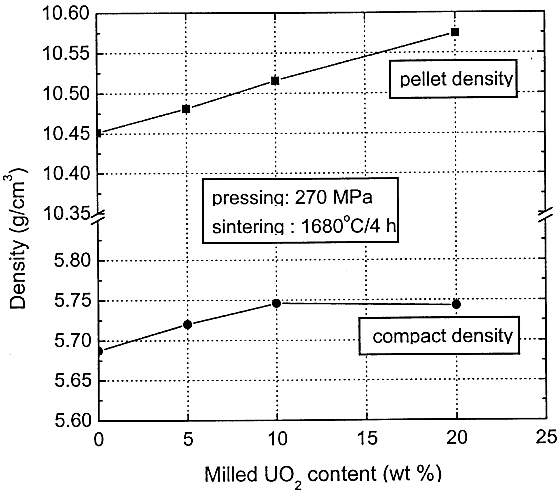

Fig. 2. Dependence of compact density and pellet density on milled UO_2 content.

filling effect of the milled powder on the powder packing appeared to have a maximum of about 10 wt% milled powder. Fig. 2 also shows that the pellet density increased linearly with the content of milled UO_2. Therefore, the mixing of UO_2 powder with milled powder gave rise to an increase in both compact density and pellet density.

Variations in the open porosity of UO_2 pellets with pellet density are shown in Fig. 3, in which a large range of pellet density was controlled by varying the compact density. For all the powders the open porosity of UO_2 pellets declined with increasing the pellet density. It was found that the open porosity was significantly lower for the powder mixture with 10 wt% milled UO_2 than for the UO_2 powder ex-AUC. In the mass production of UO_2 pellets the open porosity of UO_2 pellets is usually controlled below some value by keeping the pellet density above some acceptable level. Fig. 3 shows that the value of pellet density, which the open porosity is lower than 1% by pellet volume, is about 94.3% TD for the powder mixture with 10 wt% milled UO_2 and 95.0% TD for the UO_2 powder. Mixing of UO_2 powder with milled powder leads to the reduction of the open porosity, and consequently it can decrease the acceptable level of density, which should be necessary to control the open porosity below some value.

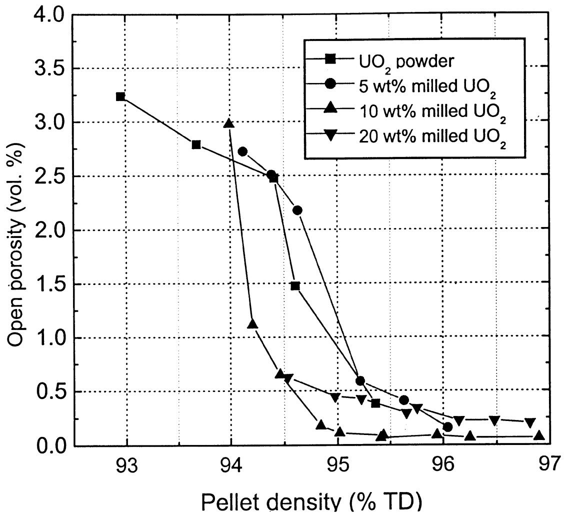

Fig. 3. Variations in open porosity with pellet density.

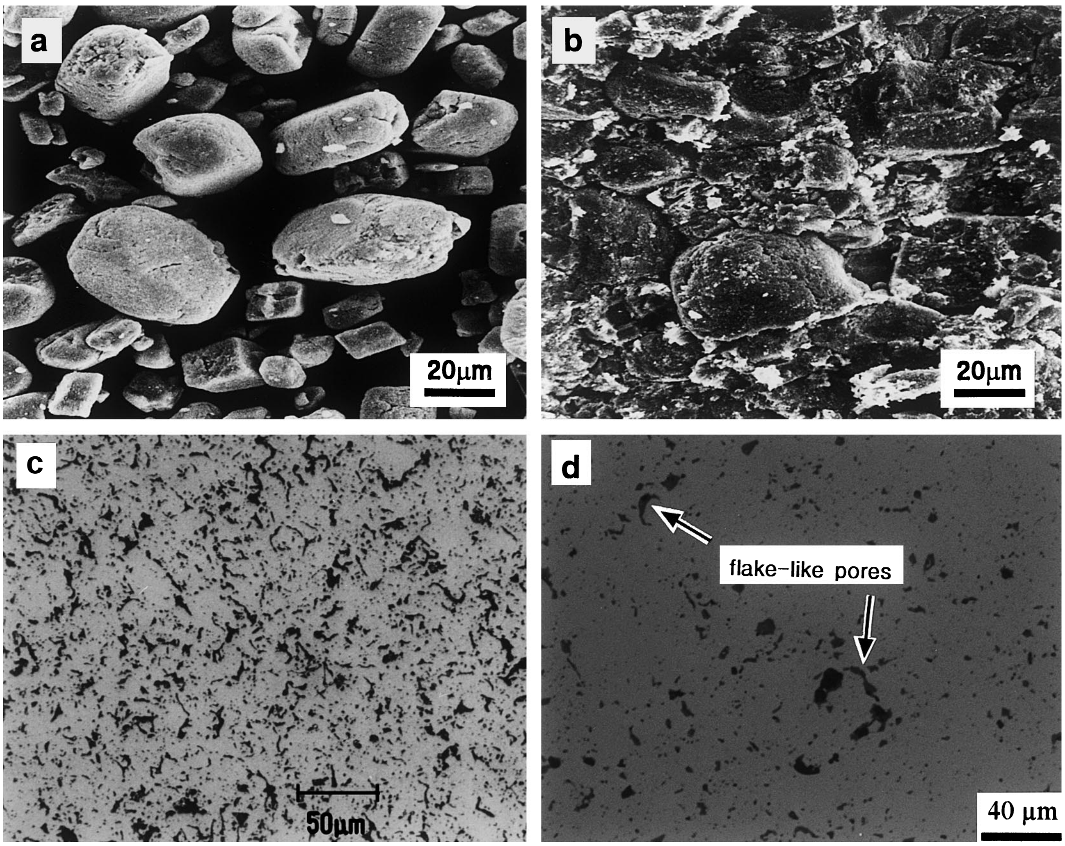

Fig. 4. Microstructures of intermediate products associated with the UO_2 pellet fabrication from UO_2 powder ex-AUC: (a) UO_2 powder; (b) compact; (c) partially sintered pellet; (d) sintered pellet.

Fig. 4(a)–(d) illustrates the microstructures of intermediate products associated with the pellet fabrication using UO_2 powder ex-AUC. Fig. 4(a) and (b) shows the morphology of UO_2 powder and the cross-section of a compact, respectively. Fig. 4(b) shows that most UO_2 particles remain in a compact with their original shapes and slightly deformed or broken, and that interstices appear to form between the intact UO_2 particles. It can be inferred that the UO_2 particles ex-AUC are too hard to be broken or deformed notably by the operation of pressing [5]. Fig. 4(c) illustrates the microstructure of a partially sintered pellet, which has many long pore channels. The shapes of pore channels suggest that they might be formed along the surfaces of round UO_2 particles, i.e., at the interstices in a compact. Fig. 4(d) shows that some of such pore channels remain as pores even in a final pellet. These pores will be called 'flake-like pores' in the next part of this paper.

Fig. 5(a)–(d) shows a series of schematic diagrams illustrating the formation of a flake-like pore, based on the findings in Fig. 4. Fig. 5(a) shows that an interstice is formed between UO_2 particles in a compact. In the initial stage of sintering (see Fig. 5(b)), individual UO_2 particles may sinter all alone rather than one another because each of them has a number of very small pores that are primarily to shrink [2,3]. Thus, UO_2 particles shrink whereas the interstice between particles may come to expand slightly. In the intermediate stage of sintering (see Fig. 5(c)), the UO_2 particles may sinter one another and the interstice starts to shrink. The interstice may shrink very slowly because of its relatively large size, and it eventually becomes a flake-like pore (see Fig. 5(d)).

Fig. 6(a) and (b) shows the microstructures of UO_2 pellets made from UO_2 powder and the powder mixture with 10 wt% milled UO_2, respectively. It can be readily seen that the flake-like pores are less formed in Fig. 6(b) than in Fig. 6(a). The size of the flake-like pores is larger than that of the round pores, so it is expected that they are difficult to shrink during the sintering cycle. This may be one of the reasons why UO_2 powder ex-AUC can be sintered up to a lower density than the powder mixture with 10% milled UO_2.

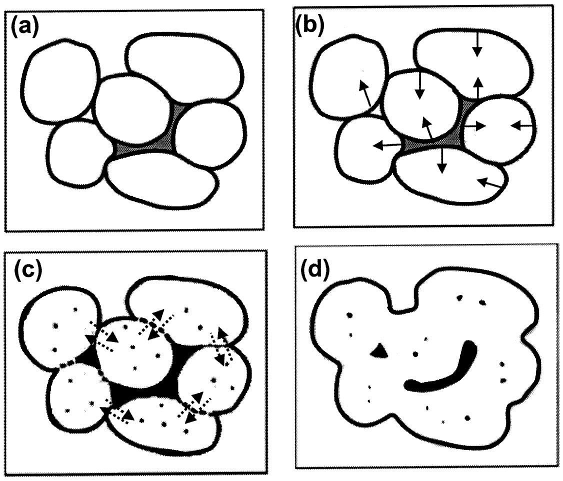

Fig. 5. A series of schematic diagrams illustrating pore development in the UO_2 pellet made from the UO_2 powder ex-AUC: (a) formation of an interstice between particles; (b) a slight expansion of an interstice due to the primary self-shrinkage of particles; (c) sintering between particles; (d) formation of a flake-like pore.

Fig. 7 shows the pore size distributions in the UO_2 pellets made from UO_2 powder and from the powder mixture with 10 wt% milled UO_2. The former had a pore size distribution with a maximum porosity at the pore size of about 4 μm. This size distribution is in good agreement with the other works [6,7]. It can be noticed that the pellet made from the powder mixture has a slightly lower porosity in the pore size range larger than 4 μm. In the light of the microstructures in Fig. 6, this lower porosity is mainly ascribed to the decrease in the number of flake-like pores.

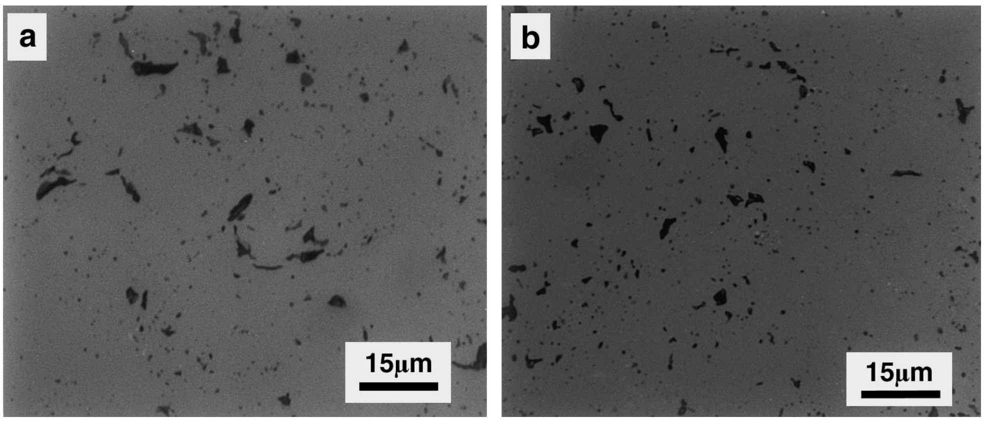

Fig. 6. Microstructures of UO_2 pellets made from: (a) UO_2 powder; (b) powder mixture with 10 wt% milled UO_2.

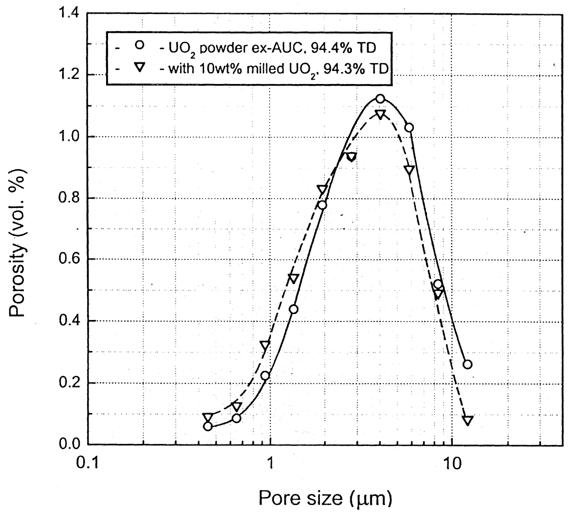

Fig. 7. Pore size distributions of UO_2 pellets.

Fig. 8 shows the variations in the number of pores with the shape factor of the pores. For the pellets made from UO_2 powder and from the powder mixture with 10 wt% milled UO_2, about 85% of the total number of pores had a shape factor of 1. The pellet which was made from the powder mixture had a lower fraction of the total number of pores in the shape factor range less than 0.5, but it had a higher fraction in the shape factor range 0.6–0.9. The flake-like pores were found to have the shape factors less than 0.5. In a compact made of the powder mixture, the milled UO_2 particles may fill the interstices between UO_2 particles ex-AUC, so the interstices formed are less in number. Accordingly, a relatively small quantity of flake-like pores may be formed in a pellet after sintering.

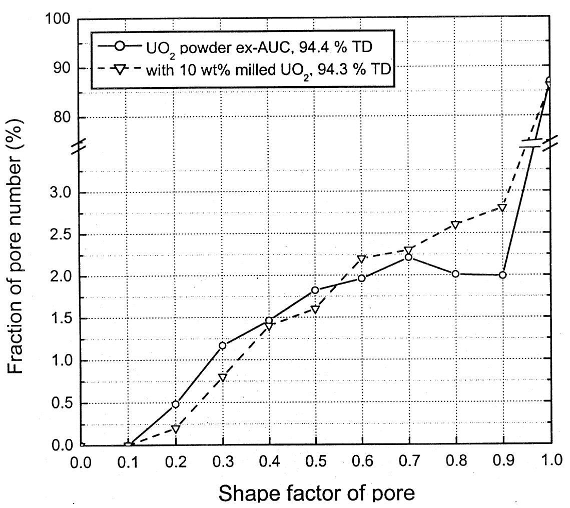

Fig. 8. Variations in the number of pores with shape factor.

The porosity of a sintered pellet consists of open and closed porosities. The open porosity of a pellet is representative of the pore volume, which is connected to the pellet surface. A higher value of open porosity implies that the pores which are directly connected to the pellet surface extend longer into the interior of a pellet. Such morphology of open porosity can be scarcely observed in the plane microstructure since a really interconnected pore in three dimensions might appear to be two or more separated pores in the plane microstructure. It is reasonable to assume that the open porosity of a pellet increases with the number of such interconnections. The possibility that a pore can be interconnected with other pores may be estimated from the pore shape in the plane microstructure.

If only the round pores that have a shape factor of 1 are found in the plane microstructure, almost all the pores can be regarded as spherical pores in three dimensions. In this case, each pore has the lowest value in the surface area-to-volume ratio, and thus it is supposed that a round pore is scarcely interconnected with other round pores. However, if the plane microstructure has some fraction of pores whose shape factor is much less than 1, those pores should have higher values in the surface area-to-volume ratio, so that they have a greater chance to be interconnected with one another. Thus the open porosity of a pellet may decrease as the number of the pores, which have low shape factor decreases. As shown in Fig. 8, the number of pores having shape factor less than 0.5 decreased when the powder mixture with 10 wt% milled UO_2 was used. Therefore, the reduction of open porosity in the UO_2 pellet made from the powder mixture can be explained by the decrease in the number of flake-like pores, which have shape factor less than 0.5.

4. Conclusions

Compared to UO_2 powder ex-AUC, the powder mixture of the UO_2 powder and its milled powder improved the properties of compact and pellet. The compact density increased with the content of milled UO_2, mainly because small particles (milled UO_2) might fill the interstices between large particles (UO_2 ex-AUC) during the operation of pressing. The powder mixture gave rise to the decrease in the open porosity of a sintered pellet.

It was found that the UO_2 particles ex-AUC have slightly deformed or broken during pressing so that the interstices between them have formed in a compact. A relationship between the interstice in a compact and the flake-like pore in a pellet is proposed; the interstices initially expand slightly as a result of the primary self-shrinkage of individual UO_2 particles and then shrink slowly due to relatively large sizes, and finally some of them remain as flake-like pores in a pellet.

In a compact of the powder mixture with milled powder, the number of the interstices might decrease due to the filling effect of milled UO_2 particles, and consequently, the number of flake-like pores which have shape factor less than 0.5 was decreased in a pellet after sintering. It is assumed that the open porosity may increase with the number of pore interconnections in three dimensions, which in turn may increase with decreasing the shape factors of pores in the plane microstructure. The reduction of open porosity, which was achieved by using the powder mixture with milled UO_2, can be mainly ascribed to the decrease in the number of flake-like pores.

Acknowledgements

This work has been carried out under the nuclear R&D program supported by the Ministry of Science and Technology. The authors would thank Mr J.H. Kim for assisting experiments.

References

[1] C.S. Choi, J.H. Park, E.H. Kim, H.S. Shin, I.S. Chang, J. Nucl. Mater. 153 (1991) 148.
[2] Y.W. Lee, M.S. Yang, J. Nucl. Mater. 178 (1991) 217.
[3] H. Assmann, H. Stehle, in: P. Vincenzini (Ed.), Material Science Monographs 6, Energy and Ceramics, Elsevier, Amsterdam, 1980, p. 893.
[4] W. Doerr, H. Assmann, G. Maier, J. Steven, J. Nucl. Mater. 81 (1979) 135.
[5] K.W. Song, D.S. Sohn, W.K. Choo, J. Nucl. Mater. 200 (1993) 41.
[6] H. Assmann, W. Doerr, M. Peehs, J. Am. Ceram. Soc. 67 (1984) 631.
[7] K.W. Song, K.S. Seo, D.S. Sohn, S.H. Kim, J. Korean Nucl. Soc. 23 (1991) 49.