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Cermet sphere-pac concept for inert matrix fuel

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Abstract

In the inert matrix fuel concept, plutonium reprocessed from spent fuel is burned in an inert matrix, e.g. yttria-stabilized zirconia. Coming from wet reprocessing, the internal gelation can perform an easy micro-spheres production. Utilization of these particles in a sphere-pac realizes a direct fuel production. Besides being economical, this direct usage offers an almost dustless fabrication. One disadvantage of yttria-stabilized zirconia as matrix is its low thermal conductivity. A further reduction by the macroscopic structure of a sphere bed seems unacceptable. This can be eluded by the insertion of a highly conducting phase. Similar to the cermet concept with the embedment of ceramic fuel into metal, the infiltration of a fine metal fraction into a coarse ceramic fuel fraction is studied here. The initial thermal conductivity shows much higher calculated values and the sintering behaviour is also clearly enhanced compared to the pure ceramic bed.

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1. Introduction

1.1. The inert matrix fuel

A zirconia-based ceramic has been selected as inert matrix fuel (IMF) in order to utilize reprocessed plutonium in light water reactors. The yttria-stabilized zirconia based matrix was chosen because of the small neutronic cross-section of its components, because of its high melting point and because of its low chemical reactivity with the Zircaloy cladding and with reactor water. This fuel form was extensively studied in e.g. [1,2]. A major disadvantage of this matrix is its relatively low thermal conductivity compared to UO₂ at room temperature, although this has to be put into perspective for reactor temperatures, where the difference becomes smaller.

1.2. The sphere-pac concept

The sphere-pac concept is investigated as an alternative fuel form for the economical re-fabrication of reprocessing products [3,4]. It enables a simple fuel fabrication method, where classified product particles are filled into the fuel pin. Compared to the classical processing of the materials to powders, which are then pressed and sintered into fuel pellets, this alternative is not only economical, but also has the potential of less contamination during production. The sphere-pac fuel, which originates from a wet reprocessing route, promises an almost dustless production. The ceramic particles are formed by an internal gelation process [5] resulting in micro-spheres. For reaching a good packing density (>80%), at least two size fractions are needed. The filling process is a simple infiltration method, where the coarse fraction is filled first and the fine sphere fraction is filled into the remaining space of the coarse fraction. An even distribution of the two fractions is easy to achieve resulting in a good density distribution over the whole fuel pin. In general, the thermal conductivity in particle fuel is lower than in pellet type fuel. The macroscopic

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structure of the particle arrangement with its small solid contact area hinders heat transfer. This is especially true at start-up, when the contact between the individual particles is small. During reactor operation sintering processes take place due to the elevated temperature. Particularly the centre region of the fuel is compacted to a porous-pellet-like structure. However, in the cooler region close to the cladding, the particle characteristic remains, although the absence of a gap helps to lower the fuel temperatures.

1.3. The combination of the IMF with the sphere-pac and the cermet concept

The combination of the IMF with the sphere-pac concept seems impossible, because it results in an even lower thermal conductivity. A possible solution of this problem is the combination with the ceramic–metal (= cermet) concept for enhancing the thermal conductivity. The combination is similar to the getter concept in the vipac fuel, where uranium–metal particles are added to the randomly shaped UO_2 (plus PuO_2) or MOX particles, mainly to serve as an oxygen sink, for minimizing corrosion of the cladding. The influence of the metal content on the thermal conductivity was also investigated [6,7]. However, in the case of the sphere-pac arrangement, the cermet combination is new and was previously only discussed by Van der Lindt [8] and by the authors [9,10]. A major difference to the getter concept in vipac fuel is the fixed structure and percentage of the metal component in the bed. In the case of vipac the metal component is randomly distributed, whereas in case of the sphere-pac, the metal component builds up a defined substructure between the ceramic spheres forming thermal conduction routes. During reactor operation and fuel sintering, the metal phase would convert to oxide. These processes, including advantages concerning thermal conductivity, are discussed

below. The experimental materials were partially yttria-stabilized zirconia (pYSZ) and zirconium metal.

2. Experimental and evaluation procedure

2.1. Sintering experiment

To investigate the fuel behaviour during reactor operation, sintering experiments were performed on behalf of the Japan Nuclear Cycle Development Institute at the Japan Fine Ceramics Center. Three particle bed types were investigated in different experimental series. The particle beds and the sintering parameters are presented in Table 1 where the different types are declared. Type (1) is a pure ceramic sphere-pac fuel. Type (2) is a cermet arrangements and type (3) is a special arrangement with the small spheres being composed of ceramic and metal spheres, so it is a cermet where the coarse spheres are all ceramic and 64% of the small spheres are also ceramic. At filling time the smear densities (relative space of the particles in the containing tube) of the different bed types were: (1) 83.2%, (2) 82.5% and (3) 81.58%.

The sintering was performed in a heated chamber with He gas at 1 atm pressure. Two ovens were used. Oven-A: To ensure a symmetric temperature distribution, the samples were placed in a cylindrical graphite cell. The sample holders had 3 cm height and 1.1 cm inner diameter. Up to 1270 K the temperature was controlled using a thermocouple placed on the outer wall of the graphite cell. Above this value, the temperature was measured using an infrared detector pointing at the graphite cell surface. A rate of 10^3 K h^{-1} characterized the heating and cooling procedures. Oven-B: For the lower temperatures normally a simpler oven was used, without an inner graphite cell and without measurement by infrared detector. The thermocouple was directly placed in the heated vertical tube in center-top

Table 1
Sphere-pac types and parameters for the sintering experiment

Types of sphere-pacs		Material – diameter (mm)			
Type		Fine fraction	Coarse fraction		
(1) Sphere-pac (cercer)		pYSZ – 0.08	pYSZ – 0.8		
(2) Sphere-pac (cermet)		Zr – 0.1	pYSZ – 0.8		
(3) Sphere-pac (cermet)		Zr – 0.1 & pYSZ – 0.08 (36% & 64%)	pYSZ – 0.8		
Experiments			Temperatures (K)	Times (h)	
Series	Bed type	Oven type			
s1	(1)	A	2070, 2170, 2270	3, 10, 50	
s2	(2)	B	1570, 1670, 1770	3, 20, 100	
s3	(2)	A	1770, 1870, 2070, 2270	3, 10, 20	
s4	(3)	A	1770, 1870, 2070, 2270	3, 10, 20	

position. The heating and cooling rate was 500 K h^{-1} . A scheme of the complex oven (Oven-A) set-up can be found in [10]. The helium gas was circulated and no oxygen getter was used. In case of the Oven-A, a vacuum was pumped before filling with He gas, the gas He flow was $2 \text{ cm}^3 \text{ min}^{-1}$. In case of Oven-B a direct filling with He gas was performed, the gas flow was with $50 \text{ cm}^3 \text{ min}^{-1}$ significantly higher (in both cases 99.9999% purity of the He gas). After the sintering experiment, the sphere beds were fixed with resin and cut with a diamond saw. The cross-sections were then analyzed with a laser microscope (wavelength 685 nm).

3. Results

3.1. Ceramographic pictures

Fig. 1 shows the sintering result for the pure ceramic sphere bed of type (1) in experiment s1. Here the specimen prepared with the longest sintering time and the highest sintering temperature is depicted (50 h at 2270 K). The compaction is rather low and a necking ratio (radius of contact area/sphere radius) ranging from 10% to 20% can be assigned.

Fig. 2 shows the sintering results for the type (2) cermet (pYSZ–Zr) sphere bed in the experimental series s2. Specimens were sintered in Oven-B, where the oxygen potential is higher than in Oven-A. The detail results

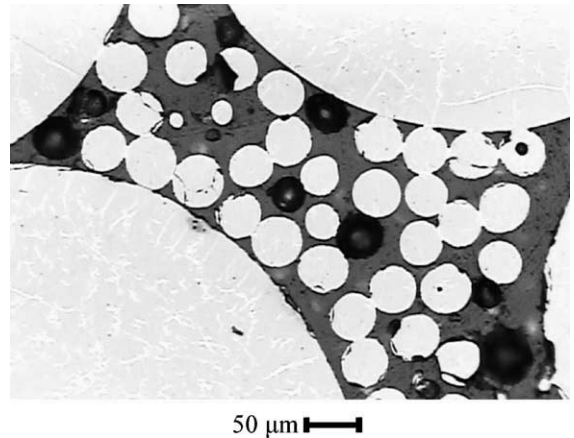


Fig. 1. Sintered pure ceramic particle bed (type 1). Only for the small spheres a necking ratio can be identified, it ranges from 10% to 20%.

obtained for series s2 were described in [9]. Here only the most important results are depicted. At 1670 K and 20 h sinter time oxidation starts, after 100 h an important oxidation state is reached, at the highest temperature of this experiment 1770 K oxidation already can be observed after 3 h, at this temperature and 100 h sintering time not only a much advanced oxidation state of the metal spheres is reached, but also the smear density of the sintered bed has reached a remarkable state. As

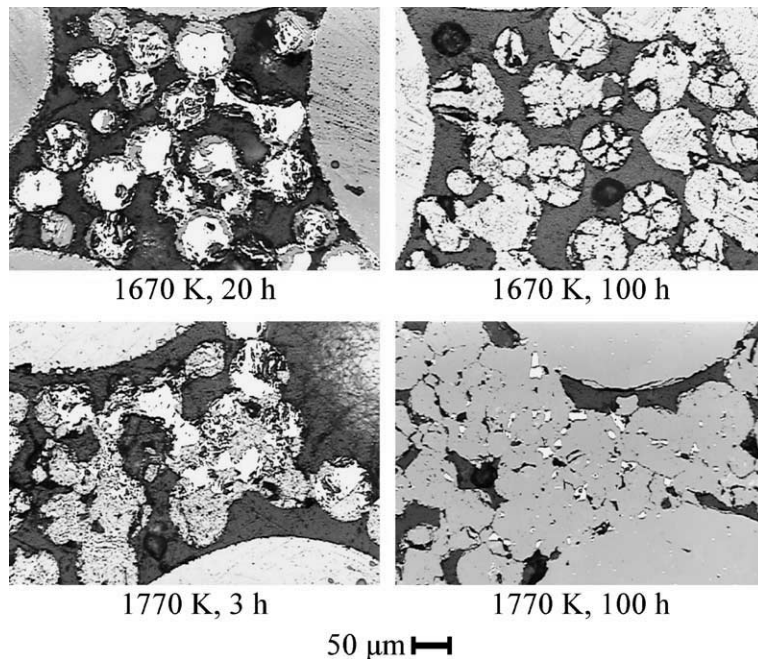


Fig. 2. Sintered cermet sphere bed (type 2) in the experimental series s2. The temperatures and times are noted in the graphic. White color identifies metallic phase, light gray identifies oxide phase and dark gray identifies the embedding resin.

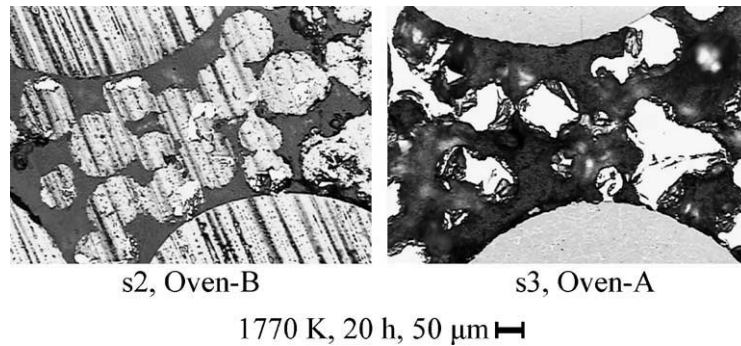


Fig. 3. Comparison between sintering of the cermet sphere-pac in Oven-A, and in Oven-B. Sintering was performed for 20 h at 1770 K. The same phase assignment to the gray values as in Fig. 2 can be made here. The exposures for the photographs were different, therefore the absolute grayscale values of the two pictures cannot be compared.

comparison of the oxidation behaviour in Oven-A and in Oven-B Fig. 3 shows cermet sphere beds from the s2 and s3 series, in both cases the sinter experiments were performed at 1770 K for 20 h. In case of Oven-B the oxidation seems to be much advanced, whereas in Oven-A no oxidation occurred.

In Fig. 3 it can also be seen that the smear density in the non-oxidized particle bed is lower than in the oxidized case. This observation can be explained with the lower density of zirconia compared to zirconium metal and the inbuilt of oxygen atoms. According to the Pil-

ling-Bedworth ratio of 1.56 for Zr, an oxidation expansion of 56% is implied, if full oxidation occurs.

The new data of this paper are the sintering behaviour of the cermet bed in an atmosphere with low oxygen potential at relatively high temperature. The experimental series s3 was performed in the Oven-A, where vacuum was applied before the He gas filling. The results can be seen in Fig. 4. At a temperature of 1870 K the metal phase remains for the experimented times. At 2070 K already after 3 h oxidation becomes visible and after 20 h a considerable sintering state with high oxidation of

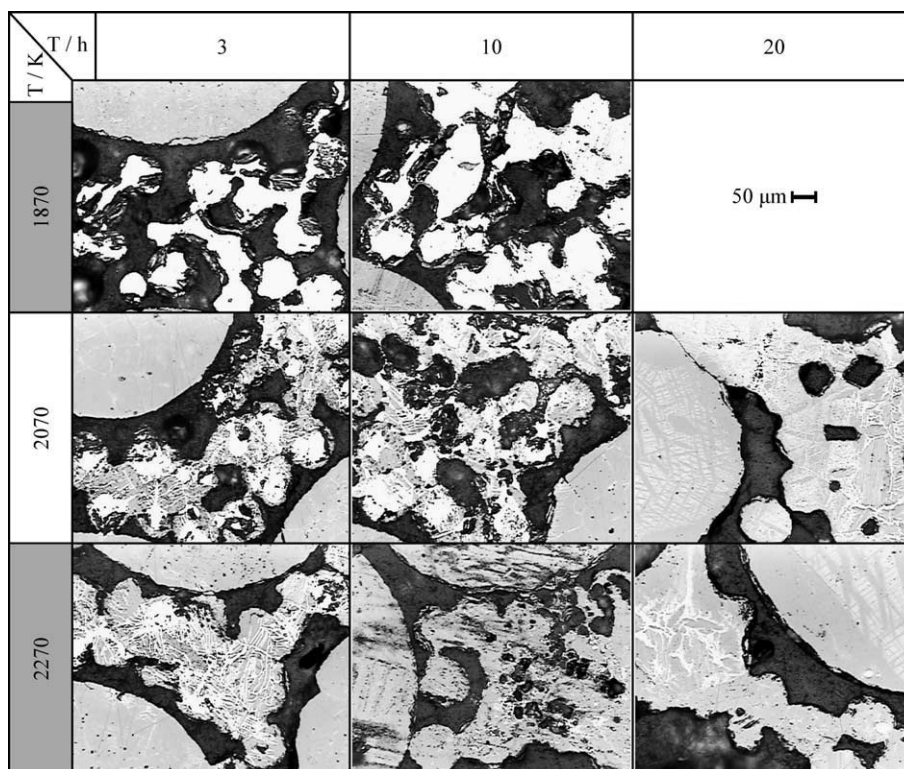


Fig. 4. Sintering of the cermet sphere-pac in the experimental series s3 with lower oxygen potential compared to series s2 (see Fig. 2).

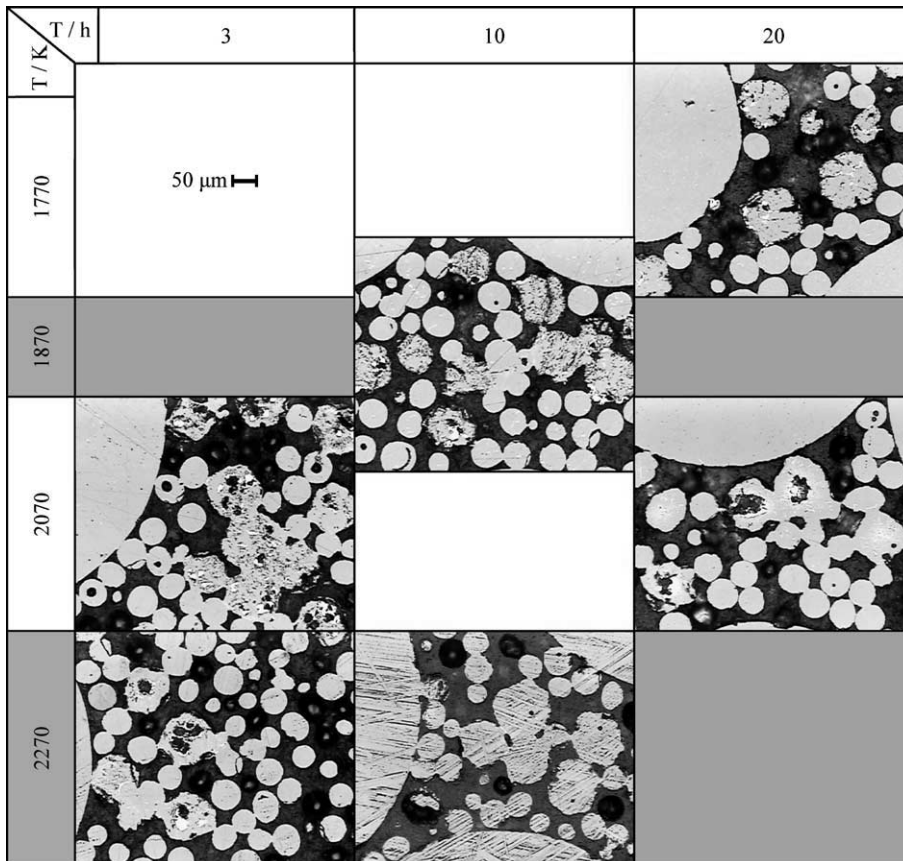


Fig. 5. Sintering of the cermet sphere bed with the small size fraction being composed of a metal and a ceramic component. Experimental series s4 with same oxygen potential of the atmosphere as in series s3.

the metal phase is realized. This effect is not very different for the case of the highest experimented temperature of 2270 K. However, the expansion seems to be less than in the case of the experimental series s2, where the oxygen potential was higher, this could indicate a remaining metal fraction and therefore a less important expansion of the original metal particles.

Fig. 5 shows another potential fuel form, where only a part of the fine fraction is composed of metal particles. Interestingly the oxidation of the metal particles seems to be much earlier than in the case of the pure metallic fine fraction. Already at 1770 K the metal spheres seem to have significantly expanded.

4. Discussion

4.1. Necking and sintering behaviour

An important initial necking of the cermet bed was observed [9] at already 1570 K and after 3 h sintering time (series s2, Oven-B). This means a clear enhancement of the heat transfer at start-up and confirms the

early necking of the metal spheres assumed in the calculation depicted in Fig. 6. In the experimental series s2 at 1770 K for 100 h sintering time, a significant densification occurred which was also influenced by the oxidizing and therefore expanding metal spheres. In the experimental series s3 where an oven with a much lower oxygen potential was used, the sintering seemed to be much retarded and similar densifications could only be observed at 500 K higher temperatures. At the highest experimented temperature of 2270 K a separation of the metal phase from the oxide can be observed, this effect has to be further investigated. Interesting are also the results of the experimental series s4, where the small size fraction was composed of both, metal and ceramic spheres. Here the expansion of the metal spheres seems to occur at lower temperatures again, the small ceramic particles could act as oxygen donors.

4.2. Oxidation behaviour

Two different ovens were used for the experiment; the atmospheric control was different as described in the

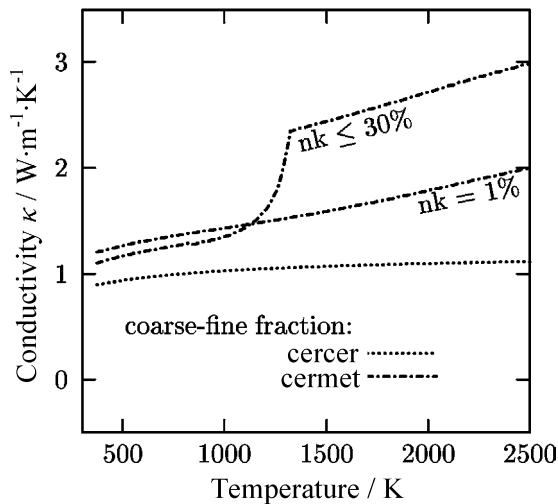


Fig. 6. Modeled thermal conductivity of the cermet sphere-pac as a function of the temperature. This result was calculated in [9] for YSZ fuel particles (cer) and Zircaloy particles (met). In this notation the first component represents the coarse fraction (0.8 mm) and the second the fine fraction (0.07 mm). The cercer is mainly displayed for comparison here. The necking is limited to 30% and for comparison a fixed necking of 1% is also depicted here.

Experimental section. A very different oxidation behaviour was found as illustrated in Fig. 3. Therefore it must be recognized that no conclusion with regards to the oxygen potential dependency of the metal particle oxidation can be made here. The results are very sensitive to the experimental set-up and the atmospheric control. A conclusion for the in reactor behaviour with regards to oxidation is very difficult, and, of course also very much depends on the fuel pin. An important point, which has to be clarified, is the diffusion of oxygen from the pYSZ into the Zr, and therefore the formation of hypostoichiometric regions in the ceramic material has to be further addressed. The final oxidation state in the former metal fraction has also to be addressed. With hypostoichiometric regions a potential decrease of the thermal conductivity must be investigated, and also the mechanical behaviour must be discussed. In case of the pYSZ–Zr mixture, the oxidation did not cause visible problems. However, this point must also be regarded, in order not to provoke a high stress towards the cladding.

4.3. Influence of the sphere dimension – potential of three size fractions

In the cermet concept, the dimension of the included ceramic fuel particles within the metal matrix plays an important role concerning the centre temperatures of each fuel sphere. The thermal conductivity of the metal matrix and the ceramic fuel particles is so different that

the thermal gradient within the fuel particles is most important. Therefore a dimensional increase of the ceramic fuel particles leads to importantly higher peak temperatures within the fuel. In the cermet sphere-pac concept, the thermal conductivity of the whole sphere arrangement is increased by the interjacent small metal particles. This is especially true at start-up, because of the more advanced necking state of the metal particles compared to the ceramic particles. This effect can be observed in Fig. 6, where at 1250 K necking of the metal spheres initiates and the conductivity curve shows much higher values for cermet than for the pure ceramic bed (Cer–Cer). At about this temperature the thermal conductivity of the cermet sphere-pac reaches about the same values as for the pure ceramic material of 1.9 $\text{W K}^{-1} \text{m}^{-1}$. With the realization of a necking of 30%, higher thermal conductivity values can be expected, however, the thermal conductivity remains in the same range, and if oxidation of the spheres can be expected, the thermal conductivity of the bed will not exceed the conductivity of the dense ceramic material (no pores or gaps). It can be concluded that the size of the ceramic fuel particle will not importantly influence peak temperatures in the fuel, because the thermal conductivity corresponds to the thermal conductivity of its surrounding. If considering importantly larger particles for the realization of three size fractions, where the coarse fraction would be in the range of 5 mm diameter, we would have a locally higher fuel density because of the missing voids and metal particles. For a homogeneous heat production the fissile content would have to be adjusted in these spheres.

The irradiation damage caused in the sphere arrangement is another parameter to be addressed. Especially stabilized zirconia shows very good irradiation behaviour [11], however, because of rim effects especially the surface of other potential inert matrices might undergo radiation damages. If this radiation damages will cause a swelling of the surface (not taking into account sintering or necking mechanisms), the total swelling of the bed will be reciprocally proportional to the sphere diameter. But even if sinter mechanisms will compensate any swelling, the volume of the totally damaged fuel region will be proportional to the surface of the fuel component, and therefore reciprocally proportional to the sphere diameter squared. A larger surface also means a larger interface to a region, where fission products will easily propagate, if the fission gas can be retained by the ceramic matrix and no cracks are formed due to high pressure, the total fission product release will also be proportional to the surface of the ceramic fuel component. For all these reasons, and because the increase of particles does not seem to provoke higher peak temperatures, a larger sphere size seems favourable. Because the cladding imposes important boundary conditions, a two-size fraction bed with larger coarse and fine spheres

leads to a smaller packing density. The formation of a third fraction might offer a good solution. With a very large coarse fuel fraction, which could be in the range of 5.0 mm, a middle fuel fraction and a fine metal fraction, which would correspond to the common coarse (0.8 mm) and fine (0.01 mm) fraction, the total surface of the fuel component could be significantly decreased to 46% (of two size fraction beds surface) at start-up. Additionally the total filling density could reach 86% compared to 81% in the case of two size fractions [12].

5. Conclusion

The suggested cermet sphere-pac fuel shows promising properties. The initial enhancement of the thermal conductivity was already shown earlier [9]. A clearly improved sintering behaviour was observed for the cermet fuel, this leads to a further enhancement of the thermal conductivity in a later state, when the metal is oxidized. Also the cermet with a mixed fine fraction, being composed of metal and ceramic spheres, shows a clearly enhanced sintering behaviour compared to the pure ceramic bed. However, these are only first investigations, and many aspects should be clarified. The potential of this concept, to control the fuel pin atmosphere during reactor operation, the oxidation behaviour, the effective thermal conductivity in hypostoichiometric regions and mechanical behaviour must be investigated. There is also a potential to initiate a three-size fraction fuel type with one very large coarse fraction. The advantage of such a system would be a clearly smaller fuel surface with potentially less fission product release, less radiation damage and increased smear density of the whole sphere bed. The fission product

release must be relativized, because larger fission gas retention could lead to cracks in the sphere.

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