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Embedding of HTR TRISO-Coated Particles into Reaction-Bonded Silicon Carbide

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Executive summary

An important part of the R&D carried out nowadays in nuclear science is the waste management of spent fuel. A promising advanced reactor system is the HTR reactor, which uses coated fuel particles dispersed in graphite spheres or blocks as fuel elements. One concept for the final disposal of HTR fuel is to remove the graphite matrix and then to encapsulate the coated particles in a stable SiC ceramics, increasing the stability of spent fuel and reducing the necessary storage volume. In this report the production of green bodies by filtrating slips consisting of coated particles in aqueous SiC/graphite powder suspensions is described, as well as their subsequent reaction-bonding with molten silicon. Basic solution and PEI were used for ceramic powder dispersion. The composites produced were of high quality and the distribution of coated particles in the composites was largely homogeneous. Dispersion in basic solution delivers better results and also the processing of the slips and green bodies is simpler. The matrix SiC forms a good junction with the SiC crucibles utilised for the reaction-bonding process. Investigation of the penetration depth of the molten silicon into the outer pyrocarbon layer of the coated particles reveals good adhesion of coated particles to matrix SiC provided by a layer of novel, reaction-sintered SiC of about 5 µm thickness. Furthermore, the high quality of the matrix SiC should enable to seal the crucible with a layer of SiC holding no coated particles and use the whole structure as durable waste matrix for direct disposal.

Revisions

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Contents

List of figures

List of tables

1 Introduction

1.1 General

High Temperature Gas Cooled Reactors (HTR) are a promising advanced reactor system due to their inherent safety and high efficiency. In consequence of the high burn-up and stability of the fuel matrix, direct disposal is the waste management option considered at present for HTR spent fuel. However, without further treatment the waste volume is enhanced needlessly by the large graphite amount harbouring the coated fuel kernels. In order to increase the spent fuel stability and reduce the waste volume, the graphite matrix can be removed and the remaining fuel particles immobilised in a durable matrix.

Owing to its favourable properties even at high temperatures, silicon carbide (SiC) is used as coating material for the HTR TRISO-fuel kernels and also considered as a possible matrix for final disposal. It is a material with extreme hardness (9.5–9.75 Mohs), high thermal conductivity, relatively low thermal expansion and chemical durability. SiC ceramics are widely used for structural and electrical applications. In general, SiC is not stable in oxidising environment, but the SiO_2-layer formed by oxidation largely passivates the surface for further oxidation [1,2]. Conventional methods for SiC production, such as liquid sintering or hot pressing are not applicable when processing spent coated particle fuel. These methods hold the danger of damaging the particles and release fission products, either due to the high temperature (1800-2000°C for liquid sintering) or the high pressure applied. In order to maintain integrity of the coated particles (CP), a mild processing method for the production of the composite material is required. Thence, the route envisaged in this report is the production of green bodies from well-dispersed aqueous SiC and graphite powder slips to which TRISO coated particles were added. These green bodies are subsequently infiltrated and reaction-bonded with molten silicon.

1.2 HTR fuel element and coated particle

The HTR distinguishes itself by its unique fuel element design. The German pebble fuel element consists of a graphite sphere filled with coated particles, randomly distributed in the graphite matrix and surrounded by a fuel-free graphite zone. In case of a block-type fuel element, graphite compacts filled with coated particles are inserted into boreholes of a prismatic graphite block. The proposed embedding procedure should be applicable both fuel types, the pebble fuel elements and the compacts, as well as for coated particles after removal of the matrix graphite. The coated particles are common for both fuel designs. The TRISO coated particle consists of a heavy metal oxide fuel kernel surrounded by a porous pyrocarbon buffer layer giving additional space for the fission products (FP), and a SiC layer sandwiched between two dense pyrocarbon layers as shown in Figure 1.

Their retention capability for fission products drastically minimises contamination in the primary circuit even at high temperatures. In earlier developed BISO coated particles the fuel is only covered with the buffer and one dense pyrocarbon layer and these particles cannot compete with the TRISO particles in terms of FP retention. TRISO particles are nowadays used in modern HTR designs. In the pebble-bed concept developed in Germany, about 30,000 of these coated particles are dispersed in a graphite sphere of about 60 mm diameter [3, 4].

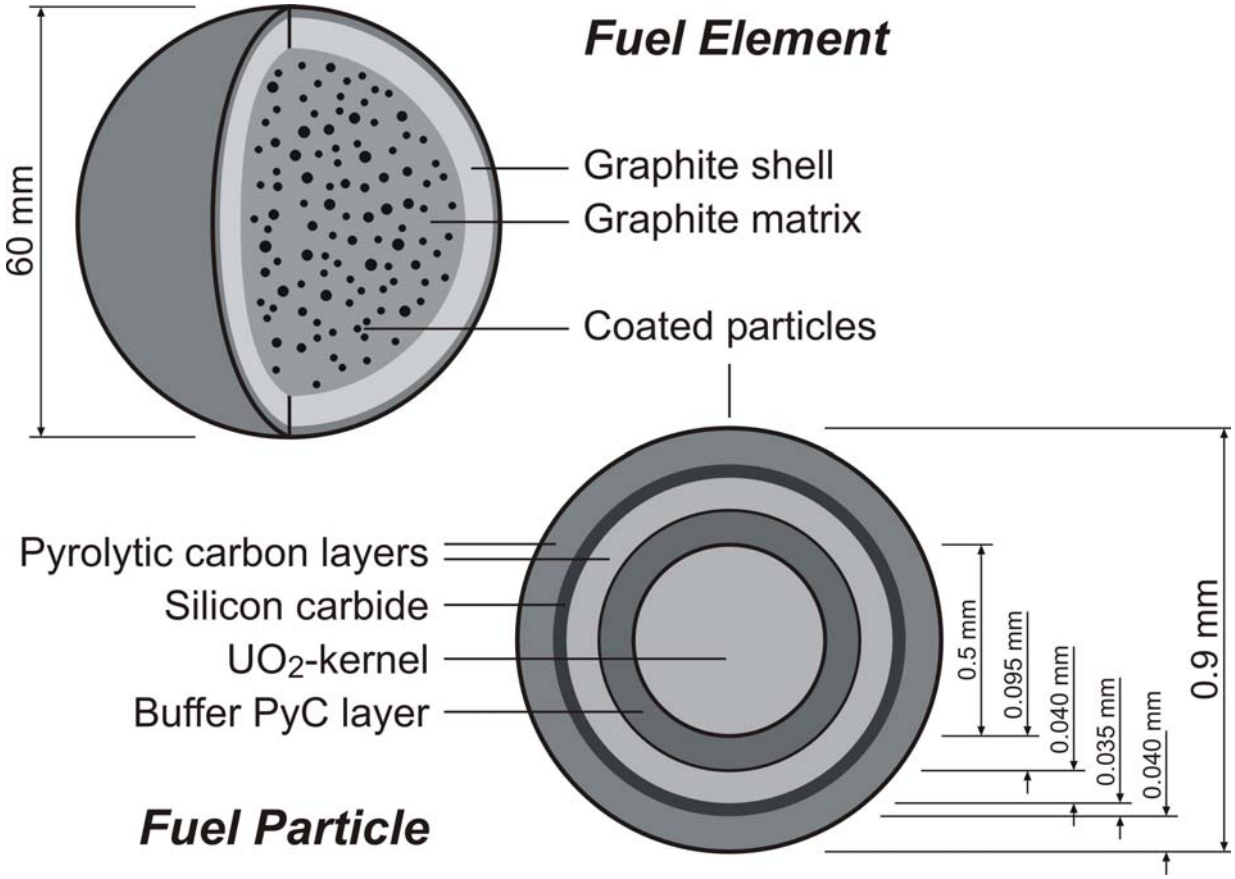

Figure 1: HTR pebble fuel element [4]

1.3 Reaction-bonded SiC

Reaction-bonded SiC (RBSiC) is produced by infiltration of SiC/C-green bodies with molten Si. The SiC is thus formed out of the elements silicon (Si) and carbon (C) by the weakly exothermic reaction

$$Si + C \rightarrow \beta\text{-}SiC \qquad \Delta G^0 = -69\ kJ/mol \qquad \text{Equation 1}$$

The reaction needs about several minutes to complete and starts after the melting point of Si (1414°C) [5-9]. The reaction conditions of 1600°C for 20 minutes in vacuum

atmosphere as proposed by Paik et al. [10] were found suitable for the given application. Attention has to be paid to the temperature profile above the melting point of Si and while cooling in order to prevent tension resulting from the exothermic reaction between carbon and silicon and also due to the expansion of solidifying silicon. Annealing of the samples at 1200-1000°C during cooling may have a positive effect on the structure of the composite. The advantage of RBSiC is the little or no shrinkage of the composite, so near-net shaped green bodies can be produced. The green body has to hold the necessary amount of pores for the infiltration process. Molten Si has the favourable features of low viscosity, high surface tension and wettability, ensuring the short infiltration times of a few minutes. The driving force of the infiltration is capillary pressure within the pores of the green body. The infiltration process superposes with the reaction forming the SiC and leads to instantaneous SiC precipitation out of the Si/C-solution at the pore walls as illustrated in Figure 2.

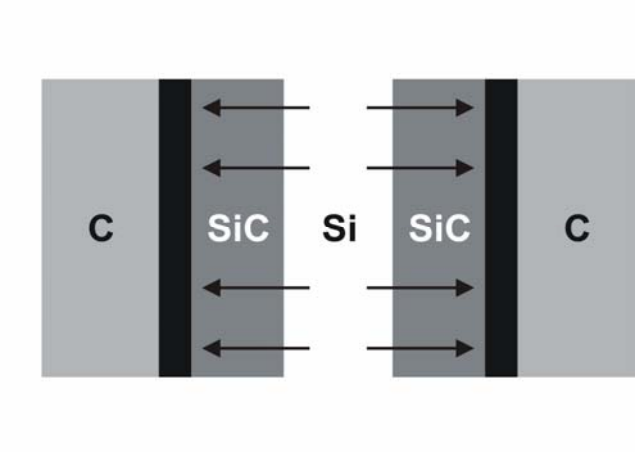

Figure 2: Si-infiltration & reaction-bonding

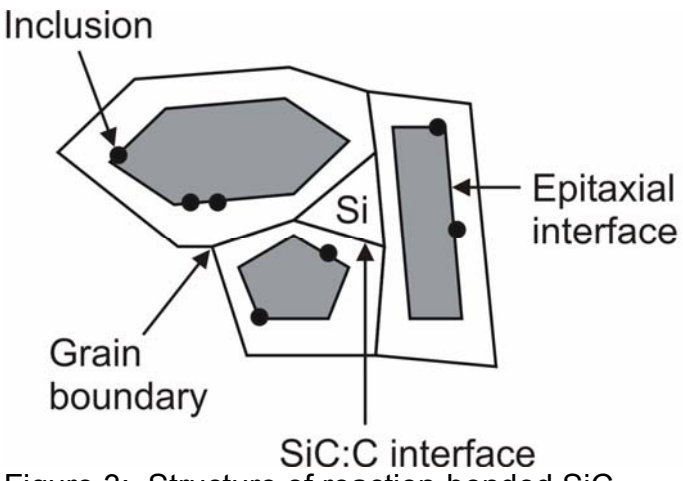

Figure 3: Structure of reaction-bonded SiC

Therefore, the reaction zone is at the Si-C interface and the chemical reaction needs to be maintained by the diffusion of Si-atoms through the novel SiC into the carbon. The added SiC powder initialises heterogeneous nucleation of novel β-SiC on the original α-SiC grains. This deposition preferably takes place on fine original SiC particles with high surface area [11, 12]. The coalescence of several novel SiC-nuclei binds the original SiC grains together and provides an epitaxial coating as shown in Figure 3. Due to the exothermic nature of the reaction, a brief temperature rise to about 2000°C induces the transformation of the novel β-SiC to the original α-SiC polytype resulting in a uniform structure [13]. Unreacted Si (usually around 2-12%) remains in the SiC as intergranular phase resulting in a non-porous body. [14] The SiC: Si is the weakest interface and hence the amount of free silicon determines the mechanical properties and reliability of the ceramics. Free silicon may be reduced in utilising smaller SiC-particle sizes and increasing the C/SiC ratio [15-17]. Nevertheless, the amount of free carbon in the green bodies should remain within the scope, as otherwise the formation of the SiC network proceeds too fast, which inhibits microstructural homogenisation and particle rearrangement and thereby leads to a less stable composite [11].

1.4 Aqueous SiC slips

Pursuing gentle treatment of the coated particles, the application of high pressure during production must be avoided. Therefore, axial and isostatic pressing of the SiC powder/CP mixture is not envisaged and the green bodies for infiltration are produced via slip casting of aqueous slips. The ceramic powder is suspensed in the solution. Special care has to be paid to this step, as the homogeneity of the green body largely determines the quality of the final product.

The production of dense and homogeneous green bodies depends on the following factors: interparticle potentials, particle size distribution, particle shape, solid loading, amount of dispersant and driving force. On the one hand, a high solid content and a high driving force (such as pressure or better said solvent elimination rate) favour aggregation of the particles that collide due to Brownian motion. Furthermore, they hinder spontaneous particle rearrangement to sites of lower energies leading to lower packing densities. On the other hand, they reduce segregation phenomena in bimodal systems, which depend on the degree of particle freedom [18, 19].

Inhomogenities in the green bodies, such as carbon islands, should be avoided and the colloidal processing of ceramic powders facilitates this. The use of bimodal SiC mixtures increases the packing density and provides narrow pore size distributions [18, 20]. In aqueous suspensions, SiC tends to oxidise at the surface, which might influence the infiltration and reaction-bonding process [1]. Wilhelm at al [17] propose to etch the original SiC powders with HF in order to eliminate the influence of SiO_2 on infiltration. However, a low oxygen content enhances complete infiltration by production of CO, which forms surface-near pores. Stopping the infiltration at 1300°C favours this process. The usually applied procedure for slip casting occurs with the aid of plaster moulds. The mould dehumidifies the slip via capillary action. As the green

bodies ought to be produced in the SiC crucibles utilised for reaction bonding, the water was largely removed by filtration.

1.4.1 Slip stabilisation

Particles have a tendency to agglomerate by virtue of the prevailing van der Waals forces. In order to stabilise a suspension, this interaction has to be prevented via *electrostatic* or *steric hindrance*. A combination of both is also possible.
SiC is usually oxidised at the surface forming a silica-like layer [21]. In water, this layer is hydrated to amphoteric e.g. relatively strongly acidic and weak alkalescent silanols (Si-OH). Their resulting reactions in acidic and basic environment are given in

$$SiOH_2^+ \xleftarrow{+H^+} SiOH \xrightarrow{+OH^-} SiO^- + H_2O \qquad \text{Equation 2.}$$

Si-O$^-$ formation results in a negative ζ-potential, a measure for the electrostatic repulsion forces between two particles. It can be measured by means of the electrophoretic mobility. The superposition of the attractive and repulsive potential energies between two particles (DLVO-theory) results in formation of an energy barrier preventing particle agglomeration and ensuring a stable suspension when the ζ-potential is higher than +/– 30 mV. The Si-OH$_2^+$ is obtained at pH < isoelectric point (IP) [22]. Reported values for the IP of SiC are in the region of pH 2-2.7, which is similar to the value reported for silica (pH 2.5) [20, 21, 10]. The ζ-potential obtained in highly alkaline solutions is usually higher than at strongly acidic solutions [22]. SiC oxidation may also lead to the formation of CO_2, which is absorbed on the surface. In strongly alkaline solutions, the CO_2 dissociates to CO_3^{2-}, which increases the ζ-potential [23, 24].
Electrostatic stabilisation of SiC suspensions usually can be achieved at a pH 10-11.5 and in this region the solutions have low viscosities [1, 22]. At pH > 11.5 reagglomeration may take place [25]. Basic SiC-slurries are in general strongly thixotrope, so the mixture should be continuously moved, e.g. with aid of an ultrasonic bath or jogging unit. Extensive vibrations, on the other hand, may lead to segregation of the particles [1].
More problematic is the proper dispersion of carbon present in the slips. Homogeneous mixing with the SiC particles and segregation prevention during drying process must be assured. Carbon is hydrophobic, badly wettable and has high homoflocculation tendencies [10,11]. Carbon does not react with water under normal conditions and not at all with alkaline solutions. However, the above for SiC described reaction with oxygen absorbed or in solution may occur and lead to CO_2 and high ζ-potentials in highly alkaline solution [24].
Furthermore, addition of dispersants may yield stable suspensions by charging the particle surface and/or steric hindrance. Polyethyleneimine (PEI) is a commonly used dispersant for ceramic colloidal processing. It is a weak basic secondary polyamine with a pK_a ~ 10.4. Commercially available (branched) PEI contains primary,

secondary and tertiary amine groups in the ratios 1:2:1. It consists of *-CH_2-CH_2-NH-* monomer units, which are branched every 3-3.5 units.

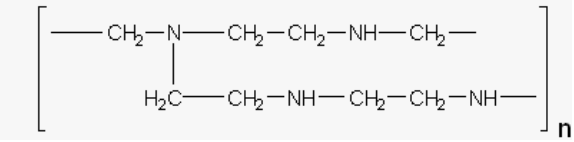

Figure 4: Structure of PEI

PEI dissolved in water will be protonated to [-CH_2-CH_2-NH_2^+-]$_n$. An aqueous solution containing 1 wt.% PEI has about pH 11, which is the IP of PEI. At the IP, adsorption occurs via hydrogen bonding. The underlying interaction is considered to occur with free surface silanol or siloxane and stabilisation of the suspension occurs by steric hindrance by the polymer branches. Adsorbance onto SiC powders shifts the IP of the SiC to pH 10.5. In acid and weak basic region PEI is a positively charged polyelectrolyte and adsorption on the SiC surface might lead to charge reversal, the stabilisation takes place by electrosteric hindrance [26-28]. A positively charged polyelectrolyte is considered to yield a strong absorption at neutral or slightly acidic pH, as the surface of the SiC powders is then negatively charged. Thence it was decided to disperse the SiC powder with PEI that is protonated in a solution of about pH 3. According to Sun et al. [26], this yields a positively charged SiC powder. Zhang et al. [27] consider dispersion at pH 10.5 –11.5 to be most suitable. This was concluded from sedimentation studies performed.

1.4.2 Binder

Binders are commonly used in ceramic industry in order to obtain stability of the green bodies during manufacturing. For production of reaction-bonded SiC, it is assumed that the addition of binder and its subsequent burn-out may provide the necessary pores for the infiltration. A binder should be compatible with the system, have a low glass transition temperature and be effective at low concentration. Polyvinylalcohol (PVA) was chosen as binder, as it is commonly used for aqueous ceramic processing. Furthermore, it is compatible with the dispersant used. [29] PVA is produced via transesterification of Polyvinylacetate with alcohols, so they are partially saponied Polyvinylacetates, as shown in Figure 5. The properties of PVA largely depend on the molecular weight and the degree of hydrolysation. Commercially available PVA has molar masses in the range of 20,000-100,000 g/mol and the acetate groups are hydrolysed to 98-99, resp. 87-89 mol%.

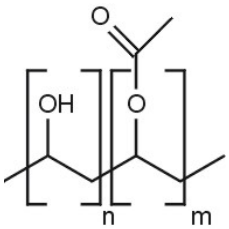

Figure 5: Structure of PVA

Water is not an ideal solvent for PVA and the higher the degree of hydrolysation (e.g. the cristallinity), the more insoluble it is [30, 31]. The PVA used in the following

experiments is soluble in hot water at about 70°C. The problems that might be involved with usage of binder are flocculation and interaction between the different components in the system, both leading to lower packing densities of the green bodies. Zhang et al. [29] added 7.3 wt.% dry weight powder based (dwb%) PVA to the mixture.

2 Experimental

2.1 Chemicals

Bidistilled water (specific resistance of 18.2 mΩ)
NaOH pellets, GR, Merck
Unirradiated UO_2-TRISO coated particles (pilot series of HTR fuel production);
Silicon powder, -100 mesh (149 µm), 99.9%, Alfa Aesar
α-Silicon carbide, 99.8%, 2 µm, Alfa Aesar
Silicon carbide, 99%, -325 mesh (44 µm), Alfa Aesar
Graphite flakes, median 7-10 µm, 99%, Alfa Aesar
PVA, 86-89% hydrolysed, medium molecular weight (57,000-66,000), Alfa Aesar
Polyethyleneimine (PEI), branched, M.W. 70,000, Alfa Aesar
Nitric acid 65% puriss., Riedel de Haën; for production of concentrated subboiled 14.2 N and 3 N nitric acid

2.2 Equipment

DSC	Netzsch STA 449C
High Temperature Graphite Oven	Gero HTK 8
Scanning Electron microscope	Jeol JSM 840 with EDX unit Tracor Northern 5502
Optical microscope	Karl Zeiss KS300 with image processing software (KS300)
pH-meter	Metrohm 780
Glass electrode	6.0232.100, Metrohm
Analytical balance	Kern 870-13
Ultrasonic Bath	Bandelin Sonorex Super RK103H
BET	Junior Quantosorb, Quantochrom
Heating oven	Heraeus T-6200
Centrifugal Ball Mill	Type S2, Retsch
Membrane Filter	ME 24, 0.2 µm, Schleicher & Schuell RC 55, 0.45 µm, Schleicher & Schuell
SiC crucibles	EKasic® F, Wacker Ceramics inner diameter: 10 mm outer diameter: 20 mm height: 25 mm

2.3 pH-measurements of additives

For the pH-measurements, 1 and 3 wt.% solutions of PEI and 11 wt.% PVA-solution in water and sodium hydroxide (pH 11) were produced. The PVA was dissolved for several hours in a desiccator at 95°C. The PVA-solutions were then diluted to about 1.1 wt.%.

2.4 Preparation of stock solutions

The pH of the PEI-solution was adjusted by usage of nitric acid to pH 3. In order to prevent the denaturation of the organic dispersant by pH-gradients, the acid was first diluted with the appropriate amount of water. Finally, the dispersant was added and the solution mixed thoroughly.
The PVA-solution was produced by adding the PVA grains to the appropriate amount of water and dissolved in the desiccator for several hours at 95°C.

2.5 Preparation of bimodal SiC-slips

As from now, the 44 µm SiC powder will be named 'coarse' and the 2 µm SiC powder 'fine', respectively. Bimodal SiC mixture was used to increase the packing density and provides narrow pore size distribution. The conditions used for the experiments described in this report were set according to literature studies of comparable systems.

Following ratios were fixed for all slips prepared:

Ratio coarse/fine SiC:	60/40 by weight
Ratio SiC (total)/graphite:	2 by weight

Variable conditions were:

Electrostatic stabilisation with NaOH:	pH 10-11
(Electro)Steric stabilisation with PEI:	1-3 dwb% at pH 3
PVA-addition:	7.3 dwb%; 43% of carbon weight

2.5.1 Preparation of the slip in basic media

Three different slips with solid load 35, 37.5 and 40 wt.% were produced by weighing the appropriate amounts of solids and NaOH at pH 10.8 followed by thorough mixing. An amount of 2.251 g of the 37.5 wt.% slip was then mixed with 1.260 g of coated particles, corresponding to about 56% of the slurry weight or 1.5 times the amount of solid substance. This mixture was subsequently filtered in a device specially designed for this purpose- a cylindrical die with a water outlet at the bottom, using a 0.2 µm membrane filter. Thereafter, the green body was dried in the desiccator at 95°C in the SiC crucible.

2.5.2 Preparation of the slip with PVA

We assumed that the compacted powder already contains 20% of the pore volume needed for the SiC formation and the rest of the pores needed have to originate from

the binder burn-out. Given that carbon, novel SiC and binder have their theoretical densities and the binder can be burned-out totally, the necessary quantity of binder was determined from the amount of added carbon powder and the novel SiC originating from it. Earlier calculations had already shown that the transformation of the outer PyC layer of the coated particles into SiC can be neglected. As PVA-solutions have a high viscosity even in relatively low concentrations, the slip was prepared according to a solid load of 35 wt.%. The exact amounts of PVA stock solution, water and powder mixture (see Chapter 2.7) needed for the slip were weighed and mixed thoroughly. Two gram of this slip were now mixed with about 0.5 g coated particles and subsequently filtered. Another slip was prepared with 7.3 dwb% PVA and a solid load of 37.5 wt.% in a similar manner.

2.5.3 Dispersion of the slip with PEI

The first slip was prepared having a solid load of 37.5 wt.% and 3 wt.% PEI. It contained 3.756 g of the powder mixture (see Chapter 2.7), 3.601 g of the PEI solution and 2.642 g of water. Other slips were prepared with about 0.8-1 wt.% PEI, corresponding to 1.0-1.21 g of PEI solution for 3.78 g powder mixture, and a higher solid load of 43 (4 g water), 55 (2 g water) and 65 wt.% (1 g water) respectively.

2.6 Analysis of the reaction between silicon and coated particles

2.6.1 DSC-analysis

The reaction of liquid silicon with the outer PyC layer (OPyC) of the coated particles was studied with aid of a Differential Scanning Calorimeter (DSC). 0.073 g UO_2-TRISO coated particles were filled into a small alumina crucible with diameter of about 5-6 mm. These were then covered with 0.034 g silicon powder and the crucible subsequently closed with an alumina lid. The sample was heated in the calorimeter to 1600°C with 600°C/h in argon atmosphere. Simultaneously, a thermogravimetry (TG) was performed.

2.6.2 Determine the thickness of the novel SiC layer

The sample after DSC analysis was used to determine the reaction depth of OPyC with molten Si. For better handling, the sample was consequently embedded in epoxy resin in order to grind and polish it with abrasive paper and diamond paste. SEM as well as EDX analyses were performed. Optical micrographs were taken of the polished sample in order to estimate the penetration depth of the liquid silicon into the OPyC layer. The mean diameter of a CP and the mean thickness of the layer that has reacted to SiC were determined from about 20 measurements. A second experiment with a dwelling time of 60 minutes at 1600°C in the oven under vacuum serves to determine, if the reaction time has an influence on the thickness of the reacted layer.

2.7 Production of coated particle-/RBSiC-composites

These experiments were conducted with a stock mixture prepared of silicon carbide and graphite powders. The powders were weighted and consequently mixed for 3 hours in the ball mill.
Two samples were prepared with NaOH (pH 9.8) as dispersant. The slips with a solid load of 37.5 wt.% were prepared by mixing the appropriate amounts of powder mixture and NaOH-solution. The homogenisation was performed by ultrasonic treatment for 10 minutes. The two slips differed in the amount of coated particles added. Sample 7-1 was produced from 2 g slip and 0.5 g coated particles. Sample 8-3, in contrast, contained about 1 g of coated particles for about the same amount of slip.
Sample 7-6 contained 1 wt.% PEI as dispersant for a solid load of 65 wt.%. The amount of coated particles added was analogous to the above described sample 8-3.
In all three cases, the slips containing the coated particles were mixed thoroughly and then filtered in the die with aid of a 0.45 µm membrane filter. The green compacts were pressed in silicon carbide crucibles and consequently dried several hours in the desiccator at 95°C. SiC crucibles are utilised in order to avoid side-reactions. The first millimetres of sample 7-6 do not contain coated particles and are removed before reaction-bonding. Si powder (0.7 g) was added above the green compacts in the crucible. Then the samples were reaction bonded in the oven under vacuum (2 mbar). The program was as follows: heating with 400°C per hour to 1600°C, dwell for 0.5 hour at 1600°C and cool down to room temperature with 200°C per hour.
The fracture surface of sample 7-1 was analysed by means of optical microscope and SEM were taken.
Sample 8-3 and 7-6 were cut lengthwise with aid of a diamond saw, embedded in epoxy resin, ground and polished with abrasive paper and diamond paste. The samples were analysed by optical microscopy.

3 Results and Discussion

3.1 pH-measurements of additives

	pH	Temperature (°C)
1.1 wt.% PEI-solution	10.9	22
3.2 wt.% PEI-solution	11.1	21
~1.1 wt.% PVA solution (water)	4.84	22
~1.1 wt.% PVA solution (NaOH)	4.85	22

Table 1: pH-determination of additives

3.2 Preparation of bimodal SiC-slips

3.2.1 Determine the solid and coated particle load when dispersing with NaOH

The experiments have shown that the slip with solid load of 37.5 wt.% posesses the most suitable properties for the production of SiC/C green bodies with the applied method.
The distribution of coated particles in the final product produced from this slip appears widely homogeneous. The diameters before and after drying can not be compared, as the green compact is too fragile, but to all appearances it has not changed significantly. It is difficult to pour out all the coated particles present in the slip into the filtering die, an alternative might be to fill in the coated particles first and subsequently pour the slip on top.

3.2.2 Preparation of the slip with PVA

Assuming 20% pores, the amount of binder used is about double of the amount used 7.3 dwb% PVA. Both slips cause difficulties while filtering. Only a small part of the liquid can be removed, as the lower part gets compacted too much preventing further filtration. Due to the attempt to filter a slip without coated particles, that caused the same difficulties, it can be inferred that the presence of the binder ‘gluing’ the particles together leads to the high compaction of the bottom part of the slip ceasing the filtration process. The usage of binder was thus not pursued further.

3.2.3 Dispersion of the slip with PEI

The 3 wt.% slip appears much too liquid and so it was decided that further slips will be produced with 1 wt.% PEI. The solid load of the slip was adjusted in order to obtain the desired viscosities of the slips. Among the 1 wt.% PEI dispersed slips, the one with 65 wt.% solid load seems to have the most suitable properties. This indicates that PEI is more suitable to disperse the SiC slips than NaOH and its usage reduces the viscosity of the slips drastically.

3.3 Analysis of the reaction between silicon and coated particles

3.3.1 DSC-analysis

DSC analysis performed on CP/Si mixture shows a virtually constant mass during heating (Figure 6). At about 1410°C the endothermic melting of silicon is visible. The subsequent small exothermic peak at 1424°C indicates the reaction of silicon with carbon leading to formation of β-SiC.

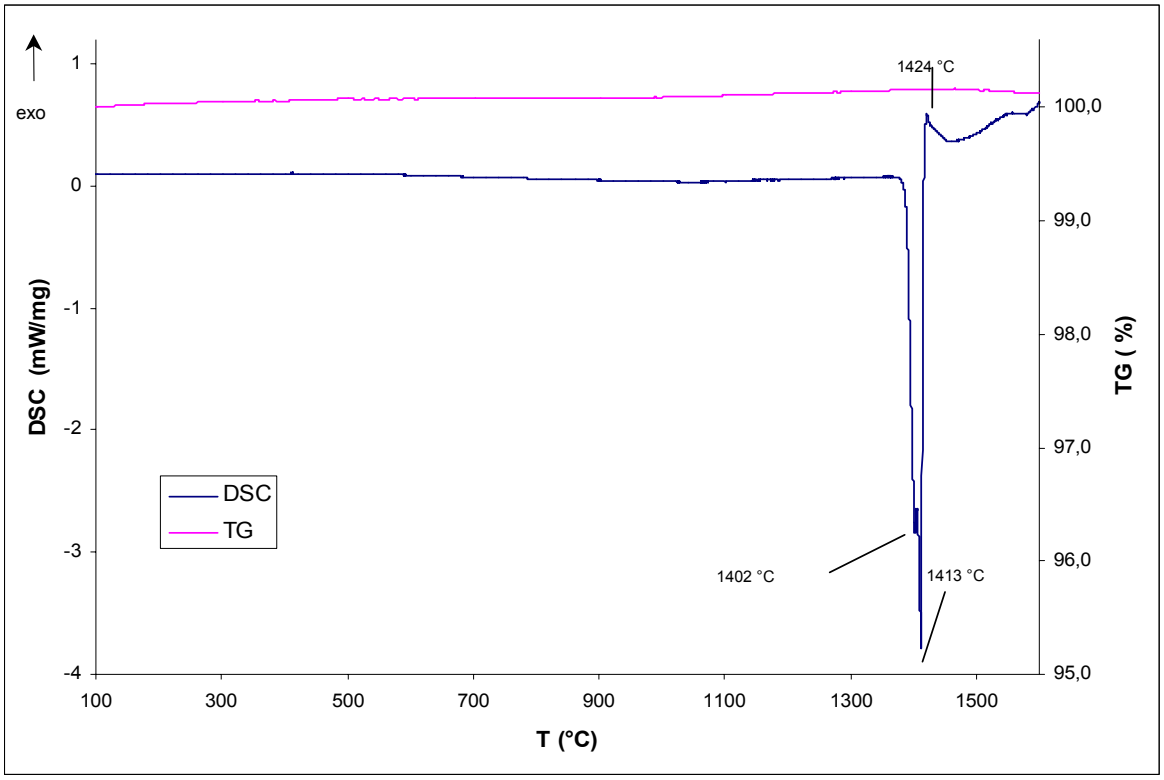

Figure 6: DSC analysis

The reaction between silicon and carbon starts after the melting of silicon, which is in agreement with literature [5]. The shape of the endothermic peak indicates that it may originate from two events, one at 1402 and one at 1413°C, the underlying processes were not investigated further. In addition to the main process, silicon melting, it could be a reaction of the PyC-layer with the aluminium oxide crucible or buffer with UO_2 kernel [32].

3.3.2 Determine the thickness of the novel SiC layer

In Figure 7 a SEM image with its respective EDX-line is shown. The decrease of the Si-signal at the Si/OPyC-interface clearly indicates that a reaction must have taken place between silicon and carbon. Analysis for carbon could not be performed, as the EDX system of the electron microscope has a Be-window.

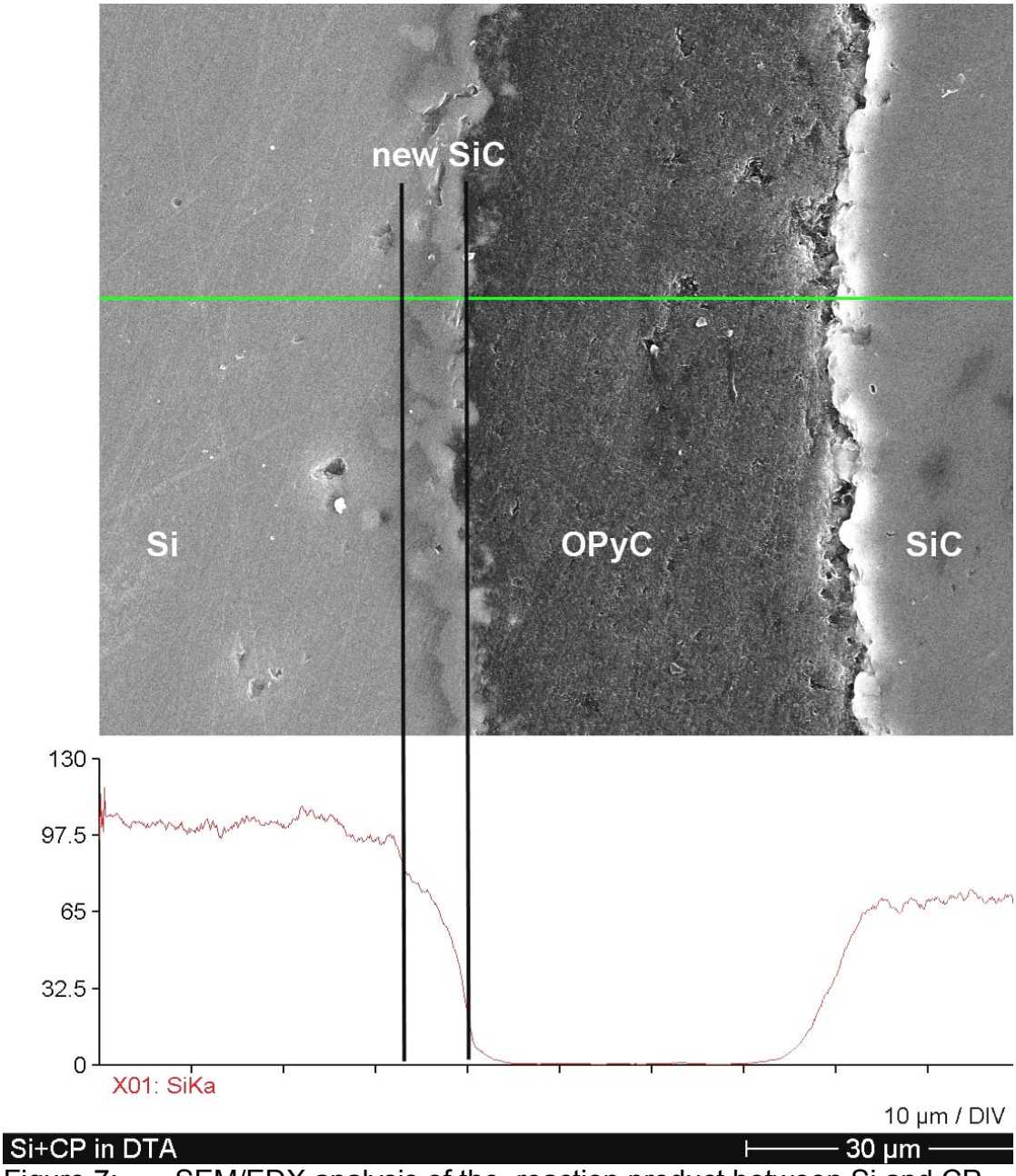

Figure 7: SEM/EDX analysis of the reaction product between Si and CP

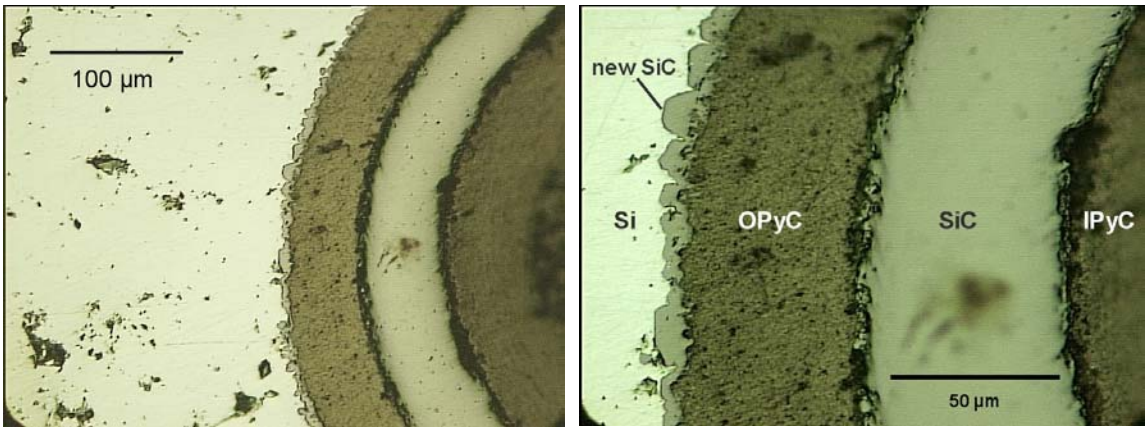

Figure 8: Optical micrographs of the reaction product between Si and CP

The penetration depth and thickness of the novel SiC layer amounts to about 5 µm. The measurements were performed on optical micrographs such as shown in Figure 8, and were corrected to sample over- and under polishing. The penetration depth does not change significantly even with a dwelling time of 60 minutes. It is assumed that the reaction of silicon with the outer dense pyrocarbon layer prevents the further infiltration with silicon and extinguishes the reaction. However, a reaction layer of a few micrometers is more than adequate to produce a stable composite.

3.4 Production of coated particle-RBSiC-composites

Several test samples with different coated particle loads at dispersing conditions were successfully fabricated by the slip casting / reaction bonding route. During fabrication it was observed that the slips in basic media (NaOH) are easily filterable, whereas the slips containing PEI are a little bit problematic. The macromolecular dispersant prevents the water removal. When PEI is present, the coated particles are more wettable. The usage of an ultrasonic bath leads to segregation between fine and coarse particles and is therefore not recommended.

Figure 9: Sample 7-1

A comparison of sample diameter before and after reaction bonding does not reveal any valuable dimension changes. This shows, that near-net shape production is possible via reaction bonding.
The surprisingly high quality of the novel SiC implies that possibly an excess amount of pores is present for infiltration. This would make the usage of binder, also considering the problems evolving for further processing, unnecessary and the amount of carbon should be increased. A proof of this assumption is the presence of free Si in the ceramics. However, with the analyses methods applied here, a reliable statement is not possible. The distribution of the coated particles in the matrix seems largely homogeneous.

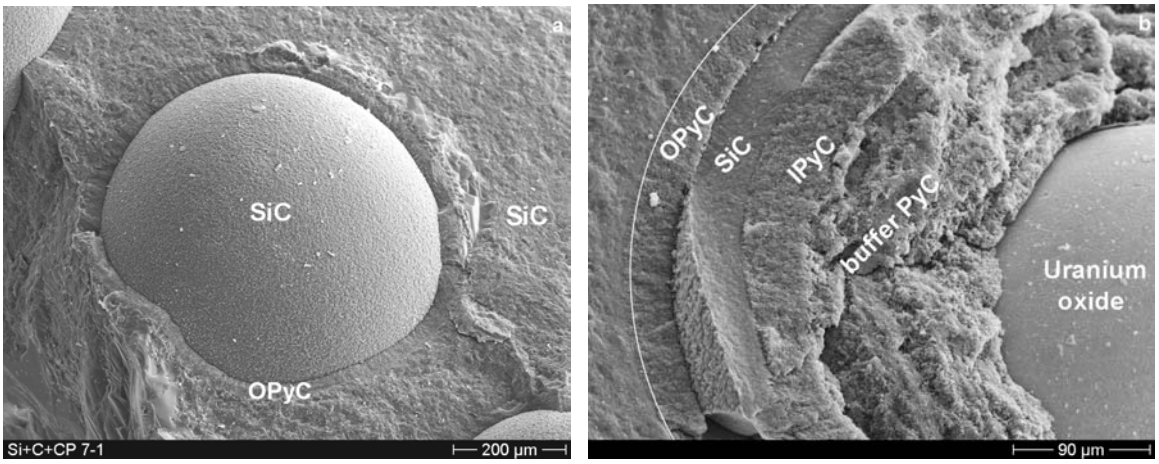

Figure 10: a) SEM of CP embedded in RBSiC with intact SiC-coating
b) SEM of CP embedded in RBSiC with broken SiC- and IPyC-coating

Sample 7-1 (Figure 9) was analysed with SEM/EDX (Figure 7), the resulting layer identification is given in Figure 10 a. Upon mechanical influence on the composite, the sample fractures at the SiC/OPyC- interface. This indicates that the method chosen is suitable to join the outer PyC layer of a coated particle with the SiC matrix via novel, reaction-bonded SiC. And this joint is actually more stable than the coated particles themselves.
Figure 10 b shows a fractured coated particle embedded in the matrix, next to the white line is the interface between the particle and the SiC matrix. Also here the good junction is evident. It is possible to produce high quality composites with the applied procedure.

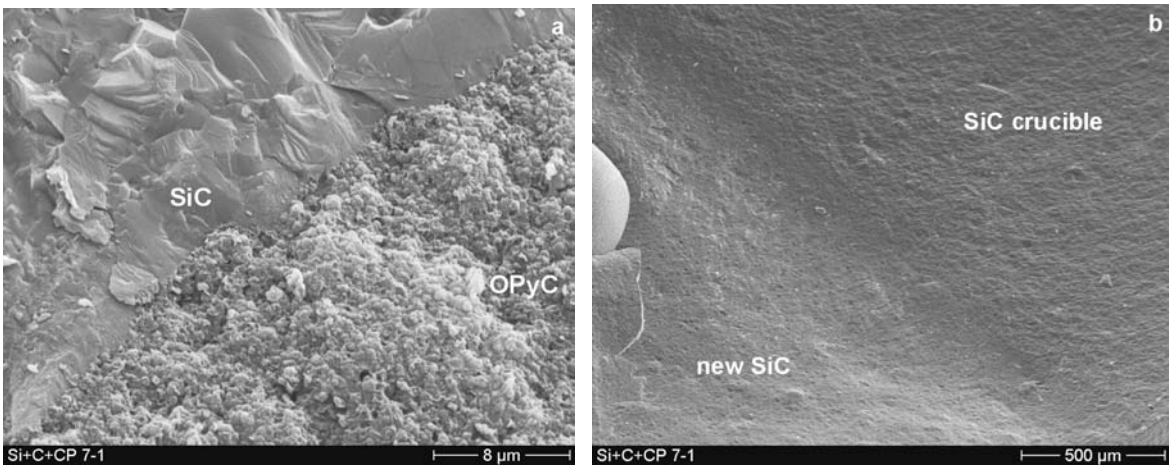

Figure 11: a) junction between RBSiC and OPyC b) junction between RBSiC and the crucible

In Figure 11 a the interface between the coated particle and the matrix is shown. As it is not possible to distinguish between novel and matrix SiC, this indicates that they form a homogeneous structure. Figure 11 b shows the good quality of the joint between the matrix SiC and the SiC crucible, which opens the option to perform production of the green bodies, reaction-bonding and final disposal of the HTR-waste in one and the same SiC crucible. This is a means to avoid contamination and loss of material during the production process and furthermore reduces production costs. Due to the high quality of the matrix SiC, a sealing for the crucible can be performed by the same procedure, using a pure SiC/C slip without coated particles. The crucible can also be sealed (additionally) with a SiC lid using silicon paste as proposed by Alkan et al. [7]. A sketch of such a waste matrix is shown in Figure 12.

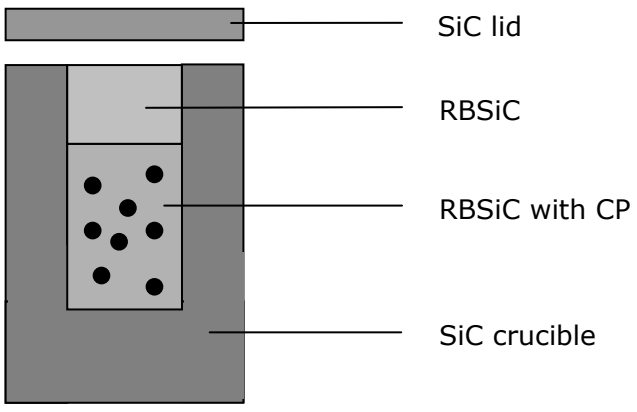

Figure 12: Waste matrix for HTR fuel

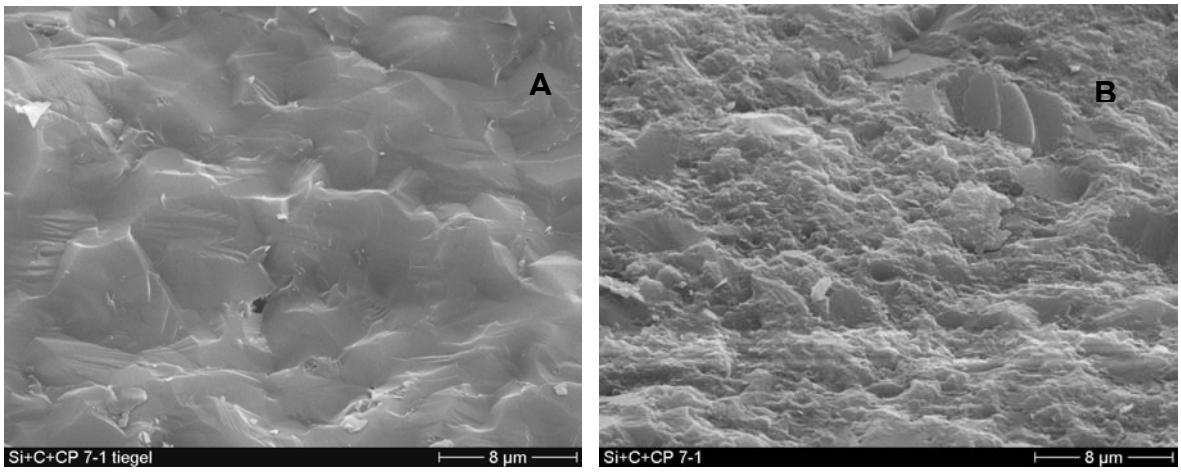

Figure 13: a) SiC crucible b) RBSiC

Figure 13 shows the difference between the SiC structure of the crucible and the novel reaction-bonded SiC at the same magnification. The grain structure does not vary significantly from bottom to top of the sample. However, the grain size distribution of the crucible SiC is more homogeneous. Furthermore, the grains of the RBSiC are much smaller.

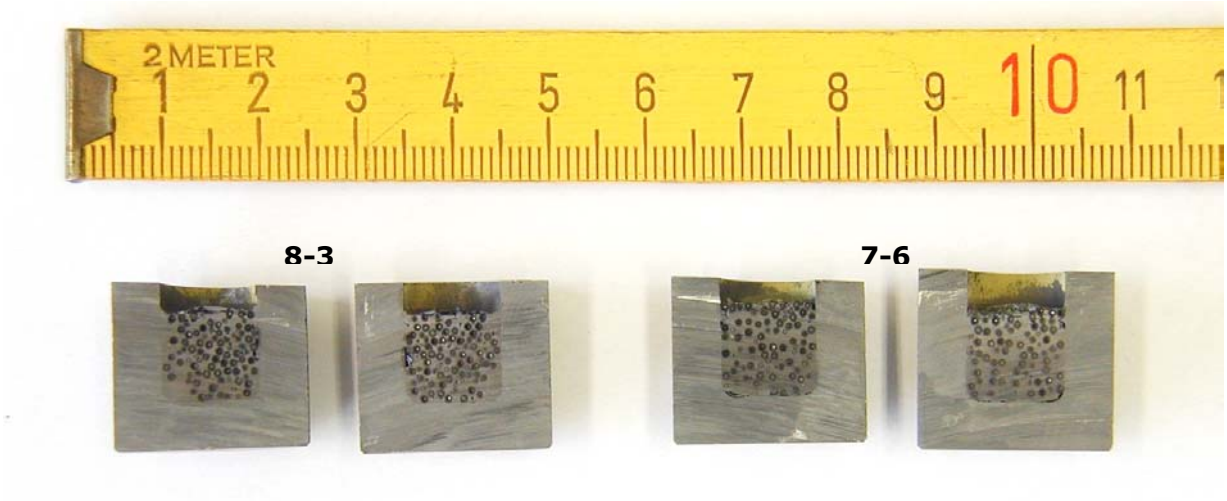

Figure 14: Section of samples 8-3 & 7-6

The height of the green body is then 9 mm and does not change during reaction bonding. Figure 14 shows the cut samples 8-3 and 7-6. Both show a quite homogeneous distribution of coated particles throughout the sample section, the coated particle load is lower in sample 7-6. It should be possible to increase the coated particle load in samples with PEI. Sample 7-6 shows some greenish deposits after reaction bonding. This is most probably originating from the evaporation and decomposition of the dispersant. It was assumed earlier, that the heating process will

already remove the organic polymer before the reaction bonding takes place. A careful removal of the dispersant is necessary and the procedure should be revised.
Figure 15 shows the optical microscopies of the samples 8-3 (a-c) and 7-6 (d-f). In both samples either pores, excess carbon or metallic inclusions (at tilted angle) are present indicated by the dark dots. In the figures b, d and e bottom and wall parts of the crucible are shown for comparison. The bad quality of sample/ crucible bottom interface is connected with rough green body bottom surface. In contrast to the crucible, the RBSiC contains more pores/inclusions. It is clearly visible that the dispersion with PEI results in compacts with less quality. Sample 8-3 has a much better quality and can be produced more easily than the samples dispersed with PEI. Thus, from the present point of view, dispersion at pH 10-11 seems to be most appropriate.
The experiments conducted until now indicate that the following solid/ coated particle loads are suitable for the production of RBSiC/coated particle compacts:

Table 2: Amount of solid load and coated particles

	Solid load w.r.t. dry powder amount:
NaOH as dispersant:	37.5 wt.%
PEI as dispersant:	65.0 wt.%

	Amount of coated particles:
NaOH as dispersant:	1.5 times the solid amount
PEI as dispersant :	> 0.77 times the solid amount

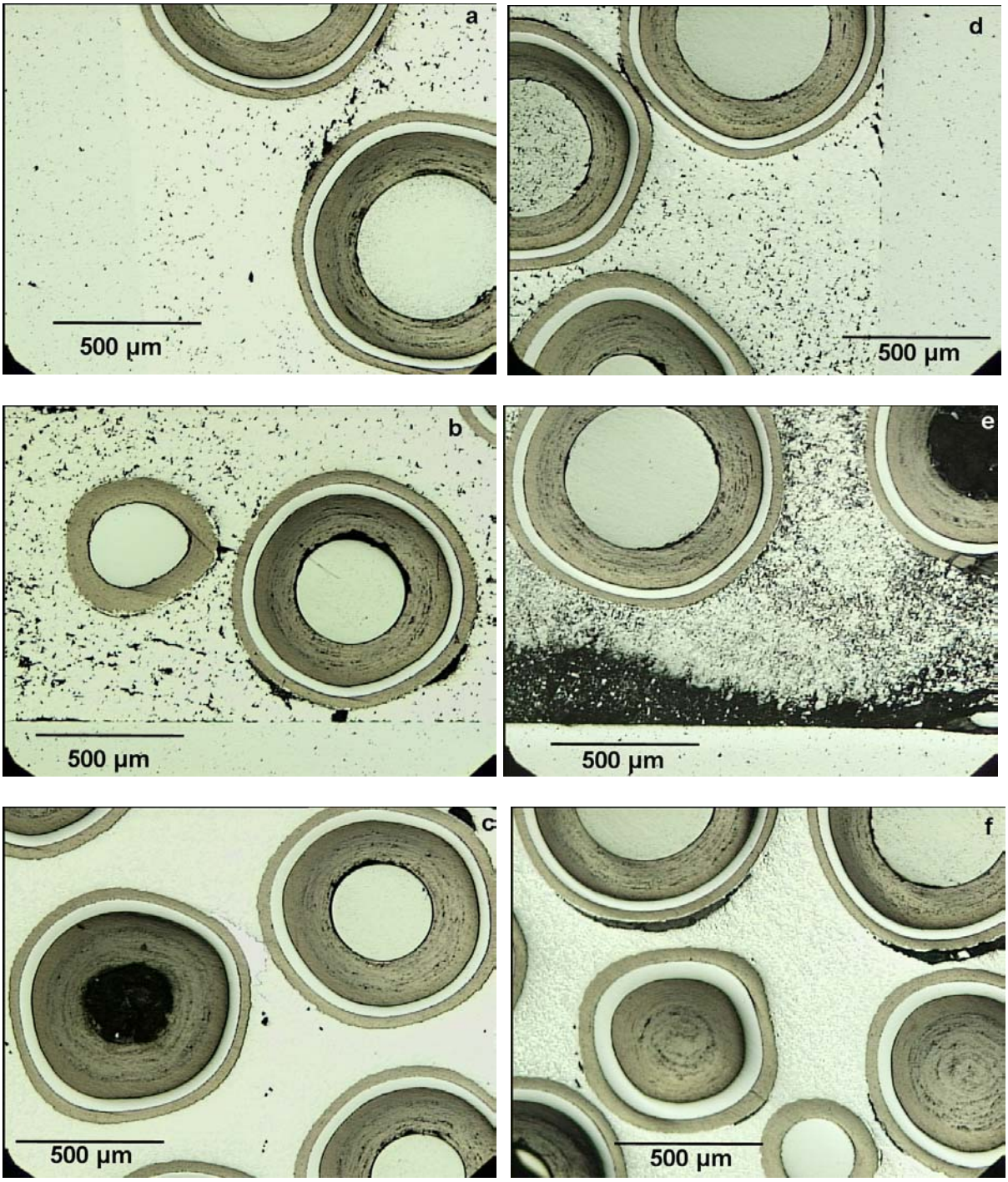

Figure 15: Optical microscopies of sample 8-3 (a-c) and sample 7-6 (d-f)

4 Conclusions & Recommendations

The experiments conducted show that it is possible to produce high-quality ceramic composites of coated particles and silicon carbide via the reaction-bonding route. However, further research needs to be carried out in order to improve the features and quality of the composite and develop a procedure, which is suitable for a large-scale application. This should provide a reliable option for the final disposal of HTR waste.

In general, there is a good junction between the coated particles and the matrix SiC, which originates from the reaction of the outer pyrocarbon layer with the liquid silicon. Dispersion in basic media (NaOH) delivers the better results for the production of SiC/coated particle composites. The problems involved with PEI-dispersion originate due to the inability to burn-out the PEI properly. It was assumed that organic additives should decompose at temperatures higher than 500°C. In order to understand the decomposition of PEI better, a DSC analysis is a useful tool. If the problems with PEI during processing are solved, composites of even higher quality might be produced.

Addition of PVA to the slips makes further processing impossible, therefore its utilisation is not considered. However, the high quality of the matrix SiC leads to the assumption that the non-ideal packing of the original SiC powders already results in the necessary amount of pores.

The optimum pH for dispersion and the amount of eventually added dispersant depends on particle size and isometry and should be determined for each system. The measurement of the pH dependency of the viscosities (should be minimum) and ζ-potential of the solution for different dispersants and dispersant concentrations is an important prerequisite for the optimisation of the slip stability and thus the quality of the composite.

As the experiments performed shall only give a first insight how SiC/ coated particle-compacts can be produced, further examinations and possibly adaptations of the chosen parameters are necessary. The solid load with coated particles can be increased, especially with PEI-dispersion. The focus in future experiments should be on improvement of the structure of reaction-bonded SiC by variation of the original SiC (e.g. ratio fine/coarse, other particle sizes), C/SiC-ratio, reaction conditions, such as temperature, duration. Adjusting the C/SiC ratio is always a compromise between the amount of residual Si and dispersability. In order to obtain a mechanically stable ceramics, the amount of residual Si should be reduced. Determination of the residual Si can be carried out by vaporising the Si at a temperature higher than 1600°C, possibly also etching with HF leads to success, followed by Hg-porosimetry.

Very interesting results may be obtained when the experiments are performed with dummy kernels for comparison. These dummies lack the outer PyC layer. Also in case of a later large-scale production, when the coated particles are burned out of the graphite sphere, the coated particles might miss their outer carbon layer. Therefore, it is of huge importance if this is of influence for the ceramic composite formed.

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