
UO₂-BASED ACCIDENT-TOLERANT HYBRID FUEL: A COMPARATIVE STUDY OF HIGH THERMAL CONDUCTIVITY ADDITIVES

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ABSTRACT: *Lower fuel temperature than conventional pressurized water reactors (PWR) is strongly preferred for Autonomous, Transportable, On-demand reactor-Module (ATOM), an innovative small modular PWR concept under initial development phase in the Republic of Korea for the incoming six years. The conceptual design and material feasibility test of high thermal conductivity hybrid oxide fuel is thus an essential course of the development of the ATOM. Among a few additive candidates, uranium sesquisilicide (U₃Si₂) has been selected mainly due to high fissile density, high thermal conductivity, and acceptable chemical stability. This study first examined the fabricability of UO₂-U₃Si₂ hybrid fuel using surrogate materials, CeO₂ and Ce₃Si₂. Metallurgical and thermophysical characterizations of micro-wave sintered pellets of CeO₂-20%Ce₃Si₂ using SEM-EDS, XRD, and DSC suggested the formation of Ce₅Si₃ during high energy ball mill (HEBM) process for Ce₃Si₂ powder production. Achieved highest fractional density of the hybrid ceramic was ~87%TD and enhanced thermal conductivity was experimentally confirmed using LFA, which was comparable with that of 95%TD CeO₂ up to 500 °C*

KEYWORDS: *Accident-tolerant fuel, UO₂-based hybrid fuel, High thermal conductivity, Autonomous, Transportable On-demand reactor-Module(ATOM)*

I. Introduction

Accident-tolerant fuel (ATF) with lower centerline temperature than conventional pressurized water reactor (PWR) is a crucial, mandatory feature of Autonomous, Transportable, On-demand reactor-Module, or ATOM, to enable unmanned load-following operation. The *ab-initio* calculation on the core suggested that approximately 200 °C decrease of fuel centerline temperature is preferred to secure the aimed characteristics of the ATOM core. Furthermore, lowered fuel centerline temperature enables to increase thermal margin, mitigate degradation of mechanical properties caused by thermal stress from repeated thermal expansion, and delay the grain growth that can sustain fuel performance to high burnup range. To achieve this end, the concept of high thermal conductivity fuel is now under development in Ulsan National Institute of Science and Technology (UNIST).

The addition of high thermal conductivity additives to UO₂ fuel pellet is the effective way to increase the thermal conductivity of entire fuel pellet without decrease of neutron economy or corrosion resistance. Candidate additives materials for UO₂-based hybrid fuel were evaluated including uranium mononitride (U₃Si₂), beta-silicon carbide (β -SiC), and uranium sesquisilicide (U₃Si₂), which have high density or high thermal conductivity and melting point.

II. Comparative study on high thermal conductivity additives for UO₂-based hybrid fuel

Uranium mononitride (UN) has been actively studied as non-oxide fuel for fast breeder reactor (FBR), and recently researched as accident tolerant fuel (ATF) for light water reactor (LWR). UN has a high thermal conductivity, and quasi-metallic characteristic that increases in thermal conductivity with temperature¹. The distinction of thermal conductivity

behaviors from most other ceramic fuel materials enables to secure additional thermal margin by decreasing fuel centerline temperature or increase linear power rate by extending fuel pellet diameter. Also, the high fissile density of UN enables to reduce the fuel volume or enrichment that can increase expandability of fuel cycle. In addition, UN has high melting point and good dimensional stability² and has enough thermal cycle stress resistance to secure the integrity of load-following operation of ATOM. The disadvantage of UN is cause by ¹⁴N, accounting for 99.64% of the natural abundance of nitrogen, lead the formation of undesirable, radiotoxic ¹⁴C due to (n,p) reaction³ skyrocket the management cost of spent fuel. It can be solved by ¹⁵N enrichment but has difficulty due to low natural abundance and high enrichment cost. The other problem is relatively low compatibility with water coolant. In a case of transient situation, cladding failure might cause severe oxidation reaction between UN and water coolant that form brittle U₃O₈ and nitrogen gas. Alternatives method such as UN-UO₂ annular shape fuel, liquid phase sintering⁴, and ZrN additives⁴ enable to avoid continuous severe oxidation of fuel pellet, but further research is needed.

Beta Silicon carbide(SiC) is mainly considered as cladding material for ATF due to high melting point, high corrosion resistance, and good mechanical properties. Thermal conductivity of single crystal SiC is very superior compared with other additive candidates, but high thermal conductivity of entire hybrid composite fuel is offset due to thermal conductivity degradation (TDC) with temperature increase and amorphization by irradiation⁵. Proper heat treatment at high temperature can mitigate irradiation induced thermal conductivity degradation (TCD) by recrystallization to form crystalline SiC. The fissile density of nuclear fuel decrease with SiC composition due to low density. Therefore, additional enrichment cost to compensate lowered fissile density is needed, Furthermore, G. C Allen et al.⁶ had shown that UO₂ and SiC react at 1377 °C to form silicon oxide (SiO) and carbon monoxide (CO) that can degrade fuel integrity for long fuel cycle.

Uranium sesquisilicide (U₃Si₂) has been limited used in research reactor with low power and coolant temperature until the 2000s, but several movements to utilize it as ATF for LWR has been existed after the Fukushima accident in 2011. Recently, Westinghouse Electric Company developed ATF concept with U₃Si₂ fuel combined with SiC cladding, so called EnCore, which has over than 5 times higher thermal conductivity, 16% greater fissile density⁷, and low fuel cycle cost. Overall good thermal performance might be obscured by competing effects of low thermal margin due to low melting point, but it can be offset by fuel centerline temperature decrease from high thermal conductivity. Theoretical modeling result from Metzger et al. showed fuel centerline temperature of light water reactor (LWR) using U₃Si₂ fuel was approximately 400 degrees lower than that of UO₂⁸.

This study focused on U₃Si₂ for additive material of UO₂-based hybrid fuel, due to the characteristic of high fissile density, high thermal conductivity, and acceptable chemical stability compared with other additive candidates. Experimental process with uranium compound in common university-scale laboratory environment is strongly restricted due to radioactivity and nuclear safety permission, so using a surrogate material for the early stage of fuel performance experiment might one of the alternatives. Cerium dioxide (CeO₂) and cerium sesquisilicide (Ce₃Si₂) were chosen of surrogate materials for UO₂ and U₃Si₂. Due to a difference valance state of cerium (3+, 4+) and uranium (3+, 4+, 5+, 6+), each element shows different stable oxide that makes concern to CeO₂ has non-similarity of thermophysical properties with UO₂. However, according to Nelson et al. measured thermophysical properties of CeO₂ are generally comparable to UO₂ below 1673 K⁹. Also, as seen TABLE I, UO₂ and CeO₂ has acceptable similar density and melting point and both are possessing same fluorite crystal structure. Ce₃Si₂ is one of the isostructural compounds of U₃Si₂ with similar density and melting point, and Ce-Si and U-Si system show reasonably similar^{10,11}.

TABLE I. Material data for the UO₂, CeO₂, U₃Si₂, and Ce-Si intermetallic compounds^{10,12,13,14}.

Compound	Theoretical density (g/cm ³)	Melting point (°C)	Space group	Thermal conductivity (W/m·K, at 298 K)
UO ₂	10.96	2865	<i>Fm</i> $\bar{3}$ <i>m</i>	7.08
CeO ₂	7.21	2400	<i>Fm</i> $\bar{3}$ <i>m</i>	6.22 (at 373 K)
U ₃ Si ₂	12.2	1665	<i>P4</i> / <i>mbm</i>	9.91
Ce ₅ Si ₃	6.08	1335	<i>I4</i> / <i>mcm</i>	~9
Ce ₃ Si ₂	5.97	1390	<i>P4</i> / <i>mbm</i>	-
Ce ₅ Si ₄	5.71	1440	-	-
CeSi	5.72	1470	<i>Pnma</i>	-
CeSi ₂	5.25	1620	<i>I4</i> ₁ / <i>amd</i>	14.5

III. Materials & methods

III. A. Powder preparation

Synthesis of Ce_3Si_2 was conducted by high energy ball milling (HEBM) in planetary ball mill. HEBM generally has been used to synthesize many silicide intermetallic compounds including Ti, Mn, Mg, and Mo¹⁴. Intermetallic compounds can be easily synthesized using HEBM with low temperature, pressure, power, and cost. The concern of HEBM method is due to impurity of synthesized powder from milling vessel and milling media.

The starting materials were elemental cerium ingot (99.5%, Avention) and amorphous silicon powder (99.9995%, ~1 μm , Avention). As-received cerium ingots with 1 ~ 10 mm were cut using diamond cutter to 1 ~ 2 mm specimen, and combined with silicon powder in a 3:2 molar ratio in a glove bag with argon atmosphere. Planetary ball mill (Fritsch PULVERISETTE 6, Germany), 80 mL ZrO_2 milling vessel, and 10 mm diameter ZrO_2 milling media were used for synthesis and initial milling parameters were referred to Gordon et al.¹⁵. Total 5.5 g of starting materials were loaded at ZrO_2 milling vessel with 55 g of ZrO_2 milling media and ball milled at 500 rpm for 6 hours.

After the synthesis process was completed, the milling vessel was moved into glove bag with argon atmosphere to separate adhered Ce-Si intermetallic powder. Approximately 30% of powder was freed in milling vessel, while the remainder was cold-welded to the milling vessel wall¹². The milling vessel and media were cleaned by filling 50 mL of isopropyl-alcohol (C_3H_7OH) to vessel and ball milled at 300 rpm for 30 minutes. The residual remainder was finally cleaned by ultrasonic cleaner. The cerium dioxide (CeO_2 , 99.9997%, ~10 μm , Avention) powder and the synthesized powder were blended in a turbula mixer with 8:2 weight ratio for 30 minutes to homogeneous dispersion. The morphology and characterization of mixed powder were analyzed by scanning electron microscopy (SEM), and energy-dispersive X-ray spectroscopy (EDS, Hitachi S-4800, Japan). As seen in Fig. 1, the morphology of pure CeO_2 powder is consisted of ~1 μm spherical shape particle with a porous structure. Fig. 3 show the SEM image and EDS analysis result of CeO_2 -based hybrid powder.

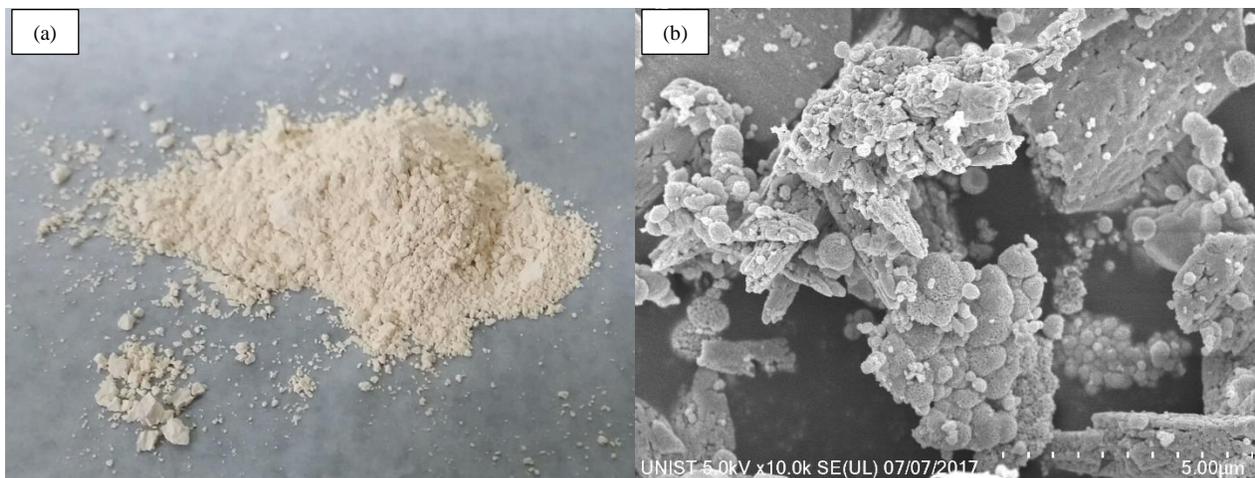


Fig. 1. (a) Macro image of CeO_2 powder, (b) SEM image of CeO_2 powder

III. B. Pellet preparation

The thermal conductivity of CeO_2 pellet and CeO_2 -based hybrid pellet were compared to investigate the increase of thermal conductivity by adding ball-mill synthesized Ce-Si intermetallic compound. For sintering green body pellets were made by cold pressing the CeO_2 -based hybrid powder at 350 MPa for 3 minutes holding time in a stainless steel die of 12.7 mm diameter. The green body pellets were microwave-sintered (UMF-04, Korea) with a constant power of 2 kW at 2.45 GHz. The sintering was carried out at 1500 °C with the microwave heating rate of 20 K/min to 1000 °C, 10 K/min to 1200 °C, 5 K/min to 1400 °C, and 2 K/min to 1500 °C and held 1 hour at air atmosphere. The pellet was natural cooled in the furnace after sintering. Fig. 2 shows the sintered CeO_2 -based hybrid pellets. The density of sintered pellet was determined by

Archimedes immersion. The X-ray diffraction (XRD, D/MAX2500V) analysis was conducted to determine the component of the sintered CeO₂-based hybrid pellet. Differential scanning calorimeter (DSC, Netzsch STA 449 F1 Jupiter, Germany) analysis was conducted to confirm intermetallic compound and chemical reaction between Ce-Si-O. DSC analysis was performed from 25 °C to 1500 °C with a ramping rate of 10 °C/min in argon atmosphere. The thermal conductivity was measured by laser flash analysis (LFA, Netzsch LFA 467 HT, Germany) method up to 500 °C at argon atmosphere. The LFA sample specimens were grinded to 10 mm diameter and graphite coated of 0.1 mm thickness to promote light absorption of sample and remove measuring noise.



Fig. 2. Figure of CeO₂-based hybrid pellets fabricated by microwave sintering at 1500 °C for 1 hour.

IV. Results & Discussion

Fig. 3 shows SEM image and EDS analysis graph performed to analyze the elemental composition of the selected area. The x-axis of EDS analysis graph is counting energy level and the y-axis is counting number. By comparing the SEM image shown in Fig. 3-a and composition analysis shown in Table II of selected area, the large black particle is expected as CeO₂ and white particle is expected as non-synthesized metal Ce particle. It seems due to large size and small specific volume of starting cerium ingot, that Si powder did not completely react with Ce ingot and cold-welded to ZrO₂ vessel that makes Ce-rich system. Table II shows that molar ratio of Ce is 54.50 at% and O is 45.48 at%. Due to Si or Zr was not detected, molar ratio of the residual metal Ce is ~31% if assume all O is existed in CeO₂ phase. Also, the area ratio of the white particle to the selected region in Fig. 3-a was determined as ~19.7% by using ImageJ program, and both result from EDS and image J show some relevant values of metal Ce composition.

As shown in Fig. 3-b, EDS analysis to determine the composition of the CeO₂-based hybrid powder was performed more wide range. The molar ratio of Si shown in Table II is 2.18 at%, which is 5.82 at% lower than calculated molar ratio of starting material. It reveals most of Si powder while ball milling was not completely synthesized but adhered to the ZrO₂ vessel wall and media. It is assumed that the detected Zr impurity was generated from removed ZrO₂ vessel wall and media.

CeO₂-based hybrid powders were fabricated using microwave sintering method. Unlike the conventional sintering method in which the heat source is externally present of heating chamber, the heat source of microwave sintering is material itself that absorbs microwave and emit the heat to the materials directly. Because microwaves can penetrate materials, heat can be generated throughout the volume of the material¹⁶. Measured density of sintered CeO₂ pellet was 6.45 g/cm³ (~90% TD) and CeO₂-based hybrid pellet was 6.21g/cm³ (~87% TD).

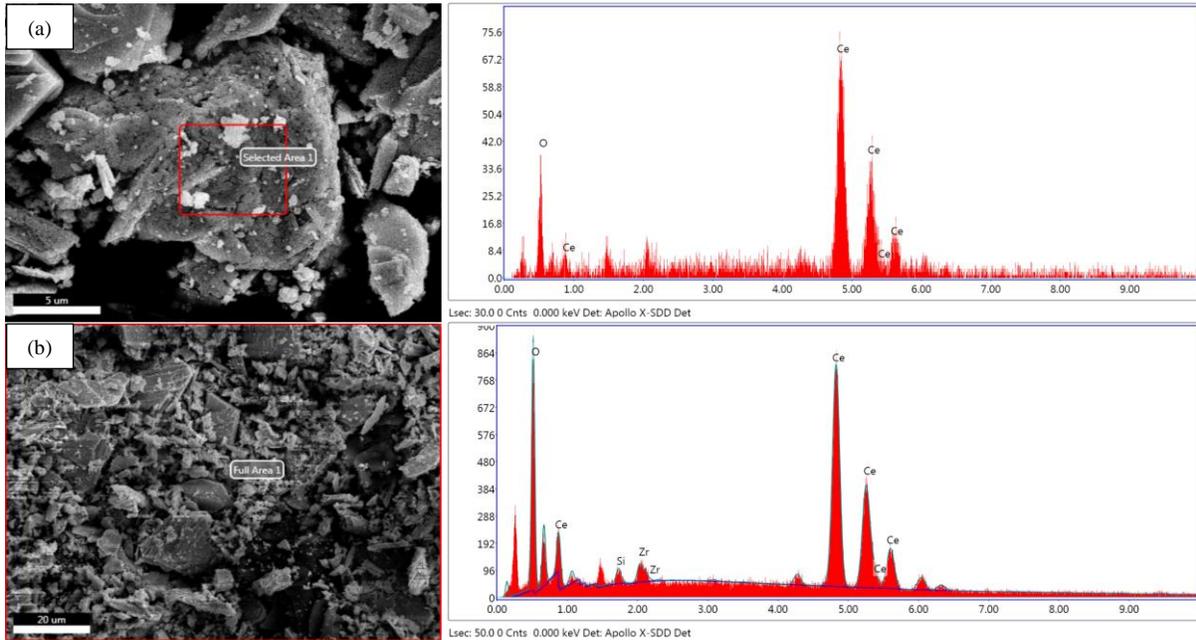


Fig. 3. SEM image and EDS analysis of CeO₂-based hybrid powder with 8:2 weight ratio of CeO₂ and Ce-Si synthesized powder by HEBM for (a) selected area and (b) full area.

TABLE II. EDS elemental composition analysis of CeO₂-based hybrid powder

Element (at%)	Ce	O	Si	Zr
Selected area	54.50	45.48	-	-
Full area	36.60	59.79	2.18	1.44

To analysis the chemical composition, the sintered pellet was pulverized and investigated by powder XRD analysis. Fig. 4 shows the XRD 2θ spectra of sintered hybrid pellet and phase identification. Phase identification was performed by comparison to data from Inorganic Crystal Structure Database¹⁷. The XRD result showed CeO₂, Ce-rich phase such as Ce₅Si₃ and Ce₃Si₂, and unexpected formation of cerium silicate (Ce_{4.67}Si₃O₁₃). The absence of metal Ce shown in Fig. 4 while presence in the EDS analysis shown in Fig. 3 means that oxidation reaction of the residual metal Ce during sintering process might occur. It was also verified by DSC analysis in the argon environment up to 1500 °C. The result of DSC scanning shown in Fig. 5 showed endothermic reaction occurred at 1106 °C and 1278 °C, and no phase transformation occurred at other temperature. In Ce-Si phase diagram, pure Ce has three times of phase transformation from room temperature to 798 °C that is β-phase to γ-phase to liquid phase¹⁰. The absence of those DSC peaks means that all metal Ce was oxidized during sintering process.

Fig. 4 showed that the Ce-rich system due to the absence of Si during ball milling produced Ce₅Si₃ as well as Ce₃Si₂. It is also verified by DSC scanning data shown in Fig. 5 that endothermic reaction at 1278 °C is consistent with the eutectic reaction of Ce₅Si₃ and Ce₃Si₂ to liquid phase occurs at 1270 °C¹⁰. Phase transformation from tetragonal/cubic structure to cubic structure of CeO₂-ZrO₂ system¹⁸ might be one possible candidate to explain the DSC peak result at 1106 °C shown in Fig. 5 is expected to be. No noticeable phase transformation or chemical reaction occurred other than the above reaction to the temperature up to 1500 °C.

Thermal conductivity analysis results performed by LFA are shown in Fig. 6. The thermal conductivity of ~87% TD CeO₂-based hybrid pellet was measured at room temperature up to 500 °C. Despite the lower density of hybrid pellet compared to the CeO₂ pellet, the thermal conductivity values were slightly higher in the temperature range, seems to be due to high thermal conductivity of Ce-Si intermetallic compounds. It seems unintentional formation of Ce_{4.67}Si₃O₁₃ did not affect significantly on the overall thermal conductivity of sintered hybrid pellet but additional investigation should be performed.

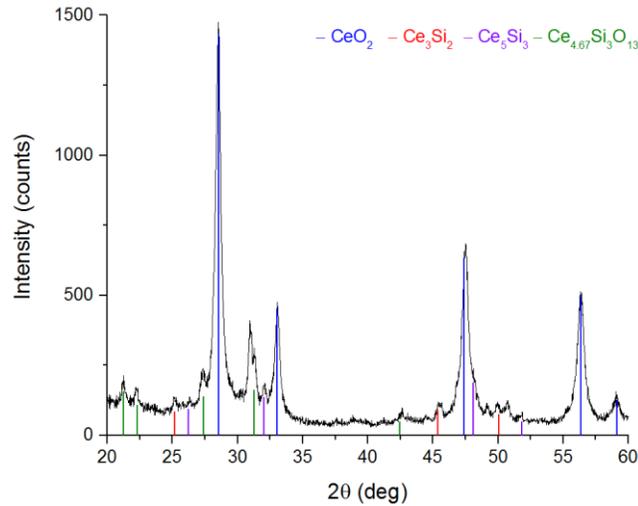


Fig. 4. X-ray diffraction analysis of microwave sintered CeO₂-based hybrid pellet at 1500 °C. Expected peak position for CeO₂ (blue line), Ce₃Si₂ (red line), Ce₅Si₃ (purple line), and Ce_{4.67}Si₃O₁₃ (green line).

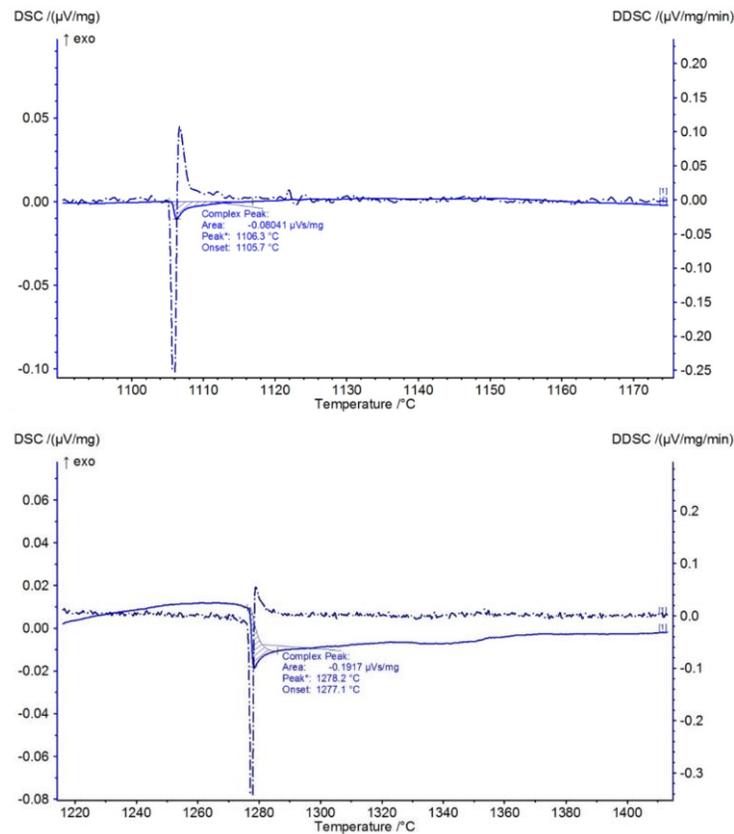


Fig. 5. Differential scanning calorimeter scan of sintered CeO₂-based hybrid pellet.

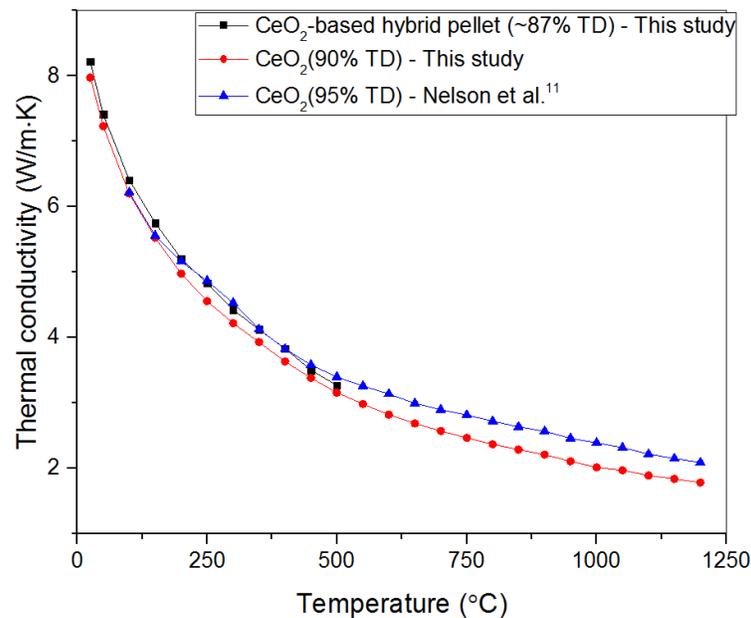


Fig. 6. The thermal conductivity of CeO₂ and CeO₂-based hybrid pellet.

V. Summary

At the first stage of research, three additive candidates with high thermal conductivity for UO₂-based hybrid fuel for ATOM core were selected and evaluated based on material properties and fuel performance. UN has high thermal conductivity, fissile density, and melting point, but excluded due to relatively low compatibility with water coolant and undesirable ¹⁴C formation issue. β -SiC has very high thermal conductivity but excluded due to low uranium density, severe irradiation induced-TCD, and secondary phase formation. U₃Si₂ was selected because of high thermal conductivity, density, and acceptable chemical stability. The fuel performance of UO₂-U₃Si₂ hybrid fuel was investigated using surrogate material that has similar thermophysical properties and phase diagram. Ce₃Si₂ was synthesized using HEBM but 20 ~ 30% amount of starting cerium was not synthesized completely due to large size and small specific volume of starting cerium ingot. Chemical composition analysis conducted by SEM-EDS, XRD, and DSC showed Ce₅Si₃, Ce₃Si₂, and Ce_{4.67}Si₃O₁₃ were co-existed in synthesized powder. DSC analysis of sintered hybrid pellet showed that chemical reaction did not occur between CeO₂ and Ce-Si intermetallic compounds up to 1500 °C. Microwave-sintered CeO₂-based hybrid pellet at 1500 °C for 1 hour in air atmosphere showed ~87%TD but has comparable thermal conductivity with 95%TD CeO₂.

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