

Assessment of Thermal Conductivity of UO₂ pellets containing MoO₂ and Mo₂C

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1. Introduction

UO₂-based nuclear fuel pellets are a core component of commercial nuclear power plant fuels. Continuous efforts in performance improvement and development are underway to enhance the safety and economic efficiency of nuclear reactors. In particular, following the Fukushima nuclear accident in 2011, the safety of operating nuclear power plants worldwide has been comprehensively re-evaluated. To fundamentally enhance safety, the development of Accident Tolerant Fuel (ATF), which offers significantly improved safety compared to conventional zirconium (Zr) and UO₂ fuels has been actively pursued, and burnup tests in commercial reactors are currently in progress.

Furthermore, as increased enrichment and ultra-high burnup operations are being considered based on ATF technologies, numerous studies are being conducted to improve the inherently low thermal conductivity of UO₂ pellets. Notably, Westinghouse Electric Company (WEC) in US [1] is developing high density uranium pellets, such as U₃Si₂ and UN, while Framatome in France [2] is developing Cr-variant UO₂ pellets. Domestically, KAERI is developing Mo microcell pellets [3]. Concurrently, KEPCO NF is developing thermal conductivity enhanced pellets by mixing Molybdenum dioxide (MoO₂), Molybdenum carbide (Mo₂C) and Molybdenum metal powder with UO₂ powder, which precipitates Mo within the UO₂ matrix via a reduction reaction during the sintering process.

In this study, to improve the low thermal conductivity of UO₂ pellets, molybdenum dioxide (MoO₂) or Molybdenum carbide (Mo₂C) were individually added to UO₂ powder to fabricate thermal conductivity enhanced pellets. Subsequently, the thermal conductivity of the fabricated pellets was evaluated.

2. Experimental procedure

The fabrication of the thermal conductivity enhanced sintered pellets used in this study followed the same commercial manufacturing process utilized at KEPCO NF, proceeding in the order of mixing → compaction → sintering. In the mixing stage, the additives listed in table 1 and 0.25 wt.% Zinc stearate as a lubricant were added to virgin UO₂ powder. The mixture was blended in a tubular mixer for approximately 4 hours to ensure

uniform mixing. A measured quantity of the mixed UO₂ powder was placed into a die and uniaxially pressed at a compaction pressure of approximately 2,500 kgf/cm². The fabricated green pellets except for TF UO₂-1 to -2 were sintered at 1,700°C for 4 hours in flowing H₂ gas using an experimental furnace. Specifically, as shown in Fig. 1, the sintering conditions for TF UO₂-1 to -2 involved heating to 950°C at a rate of approximately 10°C/min, followed by an isothermal hold for 1 hour to completely 100% reduce the MoO₂ within the UO₂ green pellet into metal powder. Final sintering was subsequently performed at 1,700°C for 2 hours.

The sintered density of the fabricated TF UO₂ pellets was measured by the water immersion method. Also, to measure the thermal diffusivity, we prepared specimens with dimensions of 8mm x 8mm x 2mm by cutting along the axial direction of TF UO₂ pellets.

Table 1. Chemical composition of TF UO₂ pellets (Vol.%)

ID	MoO ₂	Mo ₂ C	Mo	TiO ₂	Al	UO ₂
TF UO ₂ -1	5.0	-	-	0.07	0.05	Bal.
TF UO ₂ -2	3.0	-	-	0.07	0.05	Bal.
TF UO ₂ -3	-	5.0	-	0.07	-	Bal.
TF UO ₂ -4	-	3.0	-	0.07	-	Bal.
TF UO ₂ -5	-	-	5.0	-	-	Bal.
TF UO ₂ -6	-	-	3.0	-	-	Bal.

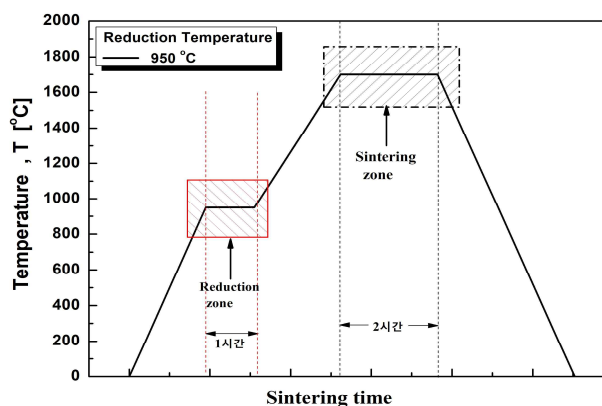


Fig. 1. The sintering condition of the TF UO₂-1 and TF UO₂-2 pellets.

3. Results and discussion

3.1 Microstructure

Fig. 2 shows the microstructures of fabricated TF UO₂ pellets. As shown in Fig. 2, the fabricated TF UO₂-1 to -2 clearly exhibit the dispersed precipitation of metallic Mo within the UO₂ matrix. In particular, the precipitated metallic Mo possesses a plate-like morphology with a length of approximately 10~20μm establishing a microstructure capable of transferring the thermal energy of the UO₂ to the exterior. Also, in case of TF UO₂-3 to -4 pellets, spherical metallic Mo precipitated within the matrix of UO₂. This difference in Mo precipitate morphology, compared to the TF UO₂-1 to -2 pellets, is attributed to the varying melting points of additives mixed into the UO₂ powder. In other words, MoO₂ of TF UO₂-1 to -2 pellets liquefy at 1,100°C before precipitating as plate-like Mo via reduction. Meanwhile, because the melting point of Mo₂C of TF UO₂-3 to -4 pellets far exceeds the sintering temperature, it reduces directly without melting, thereby forming spherical Mo precipitates.

In contrast, TF UO₂-5 to -6 pellets differed from the other pellets by exhibiting a non-uniform distribution of relatively large spherical Mo, along with observed agglomeration of the additive.

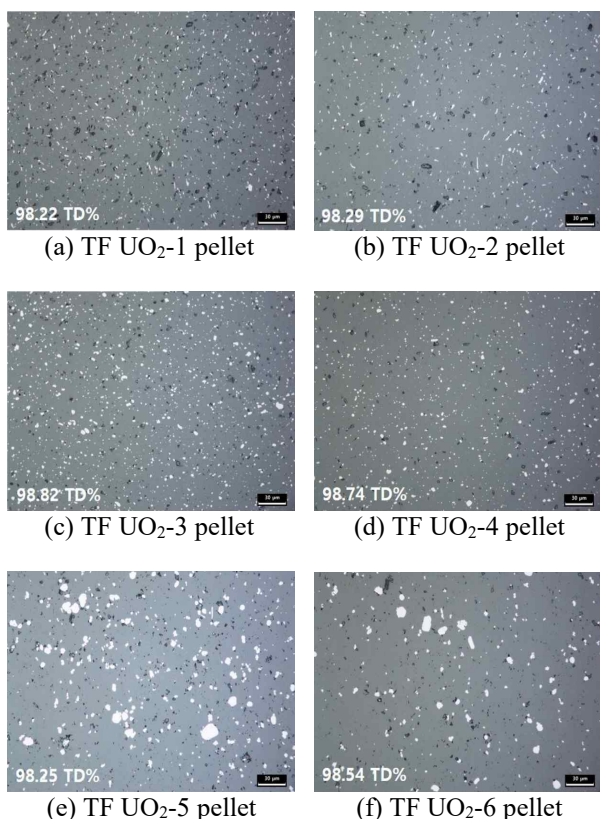


Fig. 2. The Microstructure of fabricated thermal conductivity enhanced UO₂ pellets

3.2 Thermal conductivity

The thermal conductivity of the TF UO₂ pellets is calculated as the product of density, specific heat and thermal diffusivity. In this study, the thermal diffusivity was measured using the Netzsch LFA 427 model and the Improved Cape Lehman model[4] was used as the numerical analysis model for the thermal diffusivity measurement. And the theoretical density of the TF UO₂ pellets, calculated from the volume fractions of UO₂ and Mo, was assumed to be approximately 10.9396 g/cm³, with all fabricated TF UO₂ pellets achieving a sintered density exceeding 98 TD.%. However, for a conservative estimation in this study, the sintered density of the fabricated TF UO₂ pellets was set to approximately 97.5% of the theoretical density. Also, we calculated the specific heat for this study by applying the Neumann-Kopp rule for mixtures [5], multiplying the specific heat of each constituent by its volume fraction.

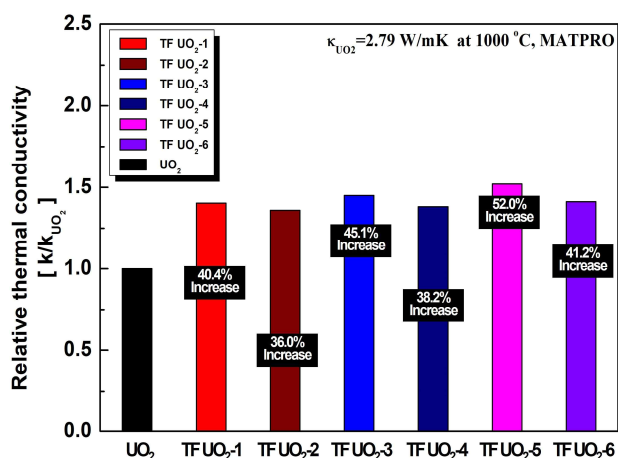


Fig. 3. The relative thermal conductivity of fabricated TF UO₂ pellets

Fig. 3 shows the thermal conductivity of the TF UO₂ pellets. As shown in Fig. 3, the TF UO₂-5(Mo-dispersed) exhibits the highest thermal conductivity, showing an increase of over 50% compared to commercial UO₂ pellet. Also, the TF UO₂-1 to -4 pellets precipitating Mo via a reduction reaction also showed an approximately 36% to 43% increase in thermal conductivity(depending on the residual amount of precipitated Mo within the UO₂ pellets). Consequently, the actual amount of Mo precipitated within the UO₂ matrix varies in the order of Mo-dispersed > Mo₂C > MoO₂. Therefore, it is concluded that not only the shape of the precipitates but also the amount of Mo present in the UO₂ matrix significantly affects the thermal conductivity.

4. Conclusions

In this work, to improve the low thermal conductivity of UO_2 pellets, we fabricated the thermal conductivity enhanced UO_2 pellets by incorporating Mo metal powder, MoO_2 and Mo_2C , and subsequently measured their thermal conductivity. Based on microstructural observations, the fabricated TF UO_2 -1 to -2 pellets clearly exhibit dispersed precipitation of metallic Mo within the UO_2 matrix. In particular, the precipitated metallic Mo has a plate-like morphology with a length of approximately 10-20 μm . Furthermore, in the TF UO_2 -3 through TF UO_2 -6 pellets, spherical metallic Mo precipitated within the matrix of UO_2 . Additionally, thermal conductivity measurements revealed that the TF UO_2 -5(Mo-dispersed) pellet exhibits the highest thermal conductivity, showing an increase of over 50% compared to conventional UO_2 pellets. Moreover, the TF UO_2 -1 through TF UO_2 -4 pellets, in which Mo precipitated via a reduction reaction, showed an approximately 36% to 43% increase in thermal conductivity (depending on the residual amount of precipitated Mo within the UO_2 matrix). Therefore, we conclude that not only the shape of the precipitates but also the amount of Mo present in the UO_2 matrix significantly affects the thermal conductivity.

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