

Master (Spark Plasma) Sintering Curve of UO_2 and UO_2 -10 vol% Mo Fuel Material

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Abstract

UO_2 -Molybdenum (Mo) composites are being considered for Accident Tolerant Fuel (ATF) applications in commercial nuclear reactors. In this study, UO_2 -10 vol% Mo was fabricated using Spark Plasma Sintering (SPS), where the particle size of Mo was varied between 30 nm, 60 nm, 100 nm and 150 μm , to study its effect on densification of UO_2 -10 vol% Mo. A decrease in Mo particle size was identified to cause a shift in densification peaks in UO_2 -Mo towards higher temperature, due to the Mo particles coating the bigger UO_2 particles. The *in situ* ram displacement data was used to construct a Master Sintering Curve (MSC), which was validated using additional SPS trials. The accuracy of the MSC was measured by the standard deviation between prediction and experimentally observed data, which varied from 0.7% to 4.8%.

Keywords: Spark Plasma Sintering, Nuclear fuel, Accident Tolerant Fuels, Molybdenum, Uranium dioxide, Master Sintering Curve

1. Introduction

The development of Accident Tolerant nuclear Fuel (ATF) shows great promise to reduce hydrogen generation, fission product release, Pellet Cladding Interaction (PCI) and steam-cladding reaction in comparison to commercially available pure UO_2 nuclear fuel during Loss Of Coolant Accident (LOCA) [1][2]. The enhancement of fuel thermal conductivity is often associated

with improving accident tolerance of nuclear fuel by reducing the Fuel Centerline Temperature (FCT) [2]. Hence, the most common ATF development strategy was doping high thermal conductivity additives such as SiC, diamond, Mo, CNTs, Graphene, etc. to fabricate a high thermal conductivity UO₂ composite [2][3][4][5][6]. However, these additives tend to deteriorate or oxidise during conventional sintering. Hence, alternative processing techniques, such as Spark Plasma Sintering (SPS) is primarily researched for fabrication of ATF material [2]. SPS is a novel powder consolidation technique with high heating rate and low process time compared to conventional sintering practice. The characteristic feature of SPS is the generation of heat applied during sintering internally by passing electric current through graphite tooling containing powder material. SPS has been effectively used for fabricating a wide array of materials including nuclear fuel over the past decade [2][3][4][5][6].

The use of METallic matrix CERamic (CERMET) materials as nuclear fuel material began with space applications such as Radioisotope Thermoelectric Generators (RTGs), Advanced Sterling Radioisotope Generators (ASRG), and General Purpose Heating Systems (GPHS), due to their high thermal conductivity and burn-up capabilities [2][7][8][9][10]. The metallic matrix is typically pure or alloyed refractory metals such as Tungsten (W), Molybdenum (Mo), Niobium (Nb), Tantalum (Ta) and Rhenium (Re)[10][11]. The selection of refractory matrix is based on various factors such as thermal conductivity, melting point, Coefficient of Thermal Expansion (CTE) mismatch and neutron absorption cross-section [12]. Among all the refractory metals, Mo has the least neutron absorption coefficient, hence has the least impact on the reactivity of the fuel [12]. Prior research on SPS of CERMET fuel was primarily focused on W as the metallic matrix for space applications, which showed near theoretical density densification and no interdiffusion between W and UO₂ [10][13][11][7][9]. UO₂-Mo CERMETS were also studied using SPS by *Buckley et al.* for 5 and 10 vol% addition [3]. Under the same sintering conditions, 10 vol% Mo addition was found to reduce sintered density by ~2% and increase thermal conductivity by 117% [3].

In order to support future research on SPS of UO₂-Mo fuel a good understanding of sintering behaviour is required. A Master Sintering Curve (MSC) could be used to predict density during

SPS experiments, to assist future studies. MSC is typically constructed using the data obtained by dilatometry, which could be used to predict density of conventionally sintered materials [14][15][16][17][18]. The inception of SPS as a rapid sintering technique, lead to studies targeted at MSC construction using in situ SPS data [19][20]. MSC was constructed using SPS by *Chen et al.* for UO₂ and UO₂-5 vol% SiC composite and the resultant prediction of as-sintered Relative Density (RD) was found to be within 1-2% of the experimentally measured value [19]. However, the ability of MSC to predict instantaneous RD during SPS, was not demonstrated in *Chen et al.*'s study, hence was addressed in this study [19].

The MSC theory was developed by *Su et al.* as a relation between the density (ρ) and the thermal history of the material ($\theta(t, T(t))$) during sintering, as shown in Equation 1 [21].

Equation 1: Thermal history relation to density

$$\phi(\rho) = \frac{k(G(\rho))^4 d\rho}{3\lambda D_0 \Omega(\Gamma(\rho))\rho} = \frac{1}{T} e^{\left(\frac{-Q}{RT}\right)dt} = \theta(t, T(t))$$

Where, k is Boltzmann's constant, R is the universal gas constant, G is the grain diameter, Ω is the atomic volume, γ is the surface energy, D_0 is the coefficient of diffusion, Γ is the scaling parameter for diffusion, T is temperature during sintering, t is time and Q is the activation energy. A MSC could be generated as a plot between ρ and thermal history ($\theta(t, T(t))$), using *in situ* sintering density data, provided the Q value is known. The estimation of the Q value requires ρ vs $\theta(t, T(t))$ data from multiple sintering trials. Subsequently, the Q value for which the magnitude of residual squares is the lowest from multiple sintering trial data, is assumed to be the Q value for the MSC. This MSC could be used to predict ρ for future sintering trials of same material at any given point in its thermal history.

In this study, the effect of Mo particle size on the densification of UO₂-10 vol% Mo ATF was studied during SPS. The in-situ sintering shrinkage data was used to construct MSC for UO₂ and UO₂-10 vol% Mo. The paper also focuses on validation of the insitu densification curves of UO₂-10 vol% Mo during SPS using MSC theory. In-depth characterisation of the sintered pellets has been discussed in a complementary publication by the authors [22].

2. Materials and methods

2.1. Precursor powders

Commercial grade UO_2 powder was obtained from Cameco. The particle size was $\sim 10\ \mu\text{m}$ and the powder particles had a polyhedral morphology, as seen in Figure 1a. Mo powder (purity >99%) of four different particle size was obtained from three different manufacturers: Sigma Aldrich ($150\ \mu\text{m}$, $100\ \text{nm}$), Alfa Aesar ($60\ \text{nm}$) and US Research Nanomaterials ($30\ \text{nm}$). The UO_2 -10 vol% Mo powder mixture was blended in a planetary ball mill using stainless steel balls in a Ball to Powder Ratio (BPR) 8:1 with isopropanol as Process Control Agent (PCA) at 200 RPM for 2 hours. A control material was also prepared with the $150\ \mu\text{m}$ Mo powder with no ball milling (referred to as “unmilled UO_2 - $150\ \mu\text{m}$ Mo”), to study the effect of milling process on the densification.

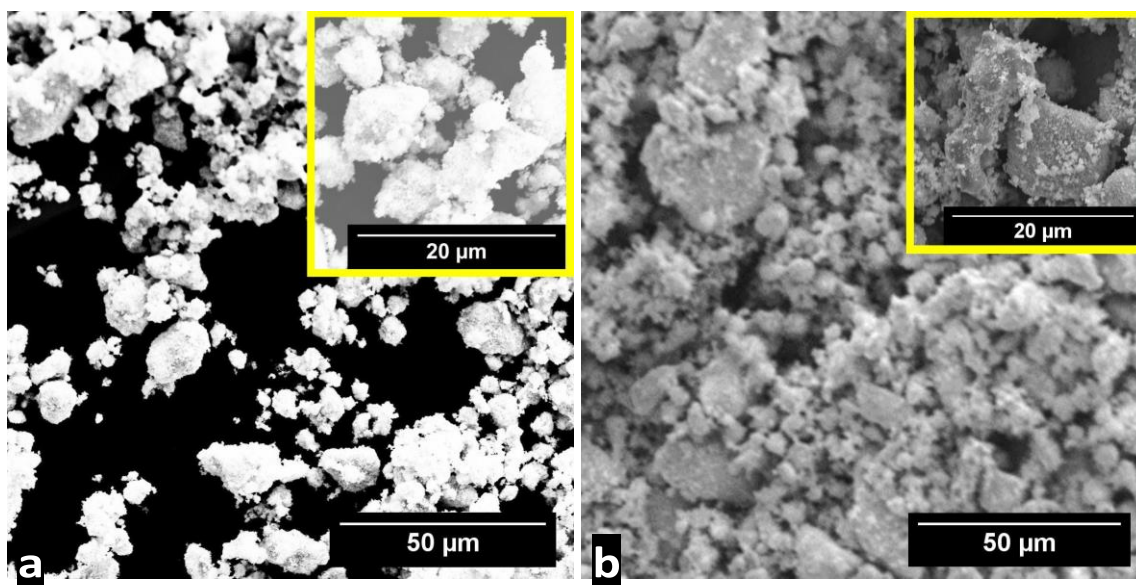


Figure 1: Precursor UO_2 powder particles observed using SEM.

2.2. Master Sintering Curve

The procedure used for MSC construction was based on the works of *Chen et al.* and *Pouchly et al.* [20][19]. A detailed step by step MSC construction procedure has been published elsewhere, but a brief description has been provided in this study [23]. The MSC construction was performed using data from three SPS trials and validated using a different MSC validation SPS trial. A software developed by *Pouchly et al.* was used to perform the MSC analysis using the Minimum Perpendicular Curve Distance (MPCD) method [20]. The constructed MSC was used to predict the

instantaneous density for a fourth SPS trial. The standard deviation between the predicted density curve and experimental data was used as a measure for the accuracy of the MSC model.

2.3. Spark Plasma Sintering

SPS experiments were performed using a Thermal Technologies 10-3 machine located at University of British Columbia - Okanagan. Graphite tooling was used, along with grafoil lining to impede contact between tooling and powder during SPS. The temperature during SPS was measured using a pyrometer hence temperature below 464 °C could not be measured. There were two types of SPS programs utilised for this study:

1. MSC construction experiments: The MSC was constructed using a model program as shown in Figure 2a. The maximum pressure (*i.e.* 60 MPa) was applied at room temperature before the start of thermal profile to ensure no pressure induced effects to the densification of the material during heating was imposed. A “holdback” step was included at 600 °C, to allow the optical pyrometer to re-calibrate to the program. The hold time at the sintering temperature (*i.e.* 1300 °C/1500 °C/1800 °C) for MSC construction experiments were set to 0.5 min. However, the difference between the three MSC construction programs was the imposed heating rate leading to the sintering temperature, which was varied between 50, 75, 100 or 125 °C/min. The cooling rate was kept same equal to the heating rate, as the displacement data obtained during cooling was used to calculate the thermal expansion contribution to densification.
2. MSC validation experiment: Figure 2b shows the SPS program used for validation of the constructed MSC. The difference was a lower peak temperature (*i.e.* 1000 °C/1300 °C/1500 °C). The dwelling time was increased to 5 min, with a secondary dwelling step at 1470 °C for 0.5 min. The heating and cooling rate was kept constant at 100 °C/min.

The as-sintered pellets were polished to remove grafoil adhering to the surface using silicon carbide papers. The density of the as-sintered pellets were measured using Archimedes principle in distilled water at room temperature. The theoretical density of pure UO₂ and Mo

were assumed to be 10.97 g/cm^3 and 10 g/cm^3 respectively and that of UO_2 -10 vol% Mo was calculated to be 10.89 g/cm^3 using rule of mixtures relationship [24].

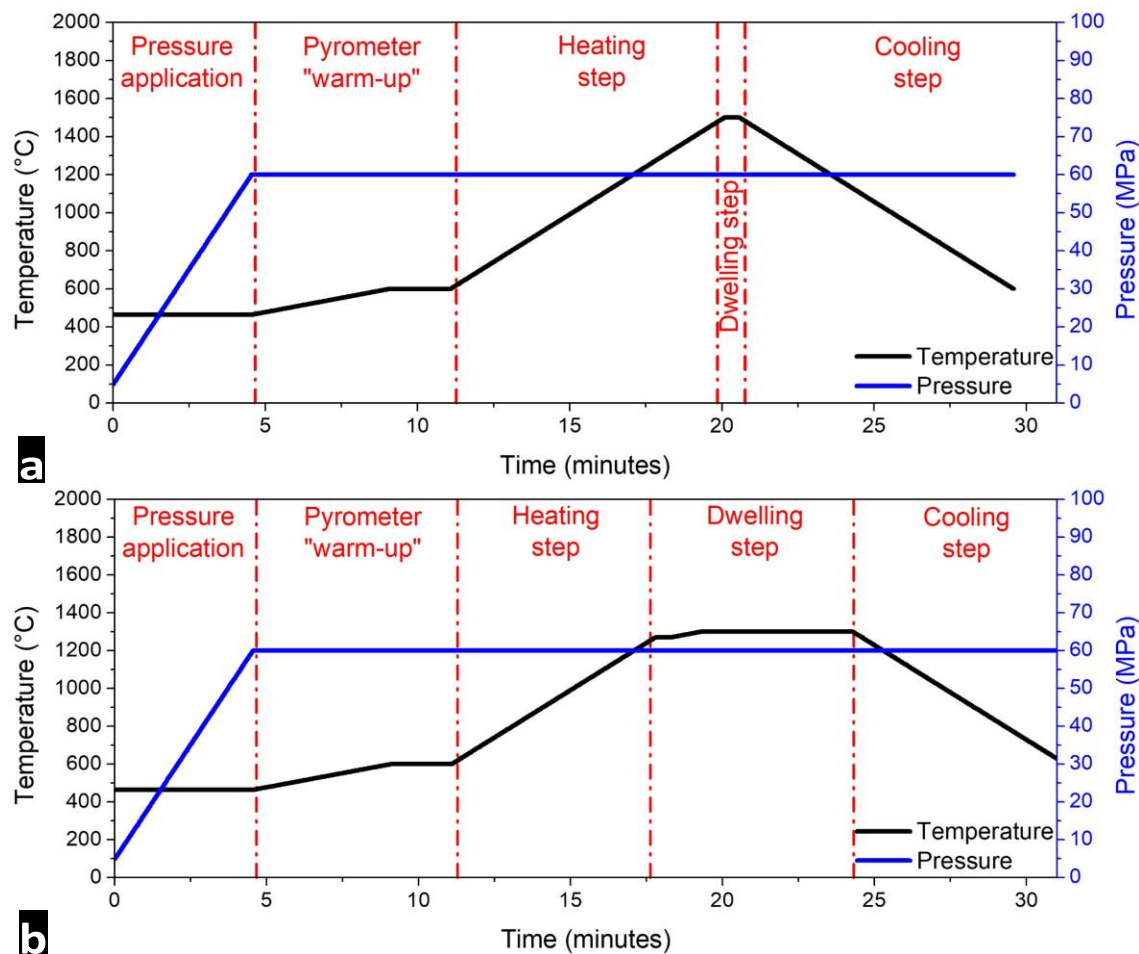


Figure 2: Representative temperature and pressure profiles from SPS trials used for a) MSC construction and b) MSC validation.

3. Results and discussion

3.1. Density results

Table 1 summarizes all the density measurements from this study. The peak sintering temperature was varied between the materials to achieve as-sintered RD of at least $\sim 90\%$. In the case of pure UO_2 , a peak temperature of 1300°C was sufficient to provide $\sim 99\%$ densification. A higher peak sintering temperature of 1500°C was used for UO_2 -10 vol% Mo composites, with the exception of $150 \mu\text{m}$ and 30 nm Mo were 1800°C was used. In all cases, the density of material

Table 1: Summary of SPS experiments of UO₂ and UO₂-10 vol% Mo

Material	Temperature (°C)	Holding time (min.)	Heating rate (°C/min.)	As-sintered density (g/cm ³)	As-sintered RD (%)
UO ₂	1300	0.5	50	10.82	98.7
			75	10.87	99.1
			125	10.84	98.8
	1000	5	100	10.32	94.1
UO ₂ -Mo (150 µm) unmilled	1500	0.5	50	10.36	95.2
			100	10.41	95.6
			125	10.57	97.1
	1300	5	100	10.43	95.7
UO ₂ -Mo (150 µm)	1800	0.5	50	10.47	96.1
			75	10.85	99.6
			100	10.77	98.9
	1350	0	125	10.63	97.6
UO ₂ -Mo (100 nm)	1800	0.5	50	10.23	93.9
			75	9.78	89.8
			100	10.36	95.1
	1400	0	100	10.38	95.3
UO ₂ -Mo (60 nm)	1500	0.5	50	10.50	96.4
			75	10.28	94.4
			100	10.35	95.1
	1300	5	100	10.48	96.3
UO ₂ -Mo (30 nm)	1500	0.5	50	10.19	93.6
			75	10.54	96.8
			100	10.89	100.0
	1300	5	100	10.30	94.6

A direct comparison of as-sintered RD between the six material variations was not possible, due to the difference in peak sintering temperature and holding time. Hence, the instantaneous RD at 1000 °C and 0 min dwelling time was back calculated from displacement data for comparison, as shown in Figure 3a. The addition of Mo reduced the density of UO₂, irrespective of Mo particle size. Further, the blending process using the ball mill for Mo and UO₂ powders seemed to have an impact on the densification of the UO₂-Mo composite. The unmilled UO₂- 150 µm Mo had a higher density than the milled UO₂- 150 µm Mo.

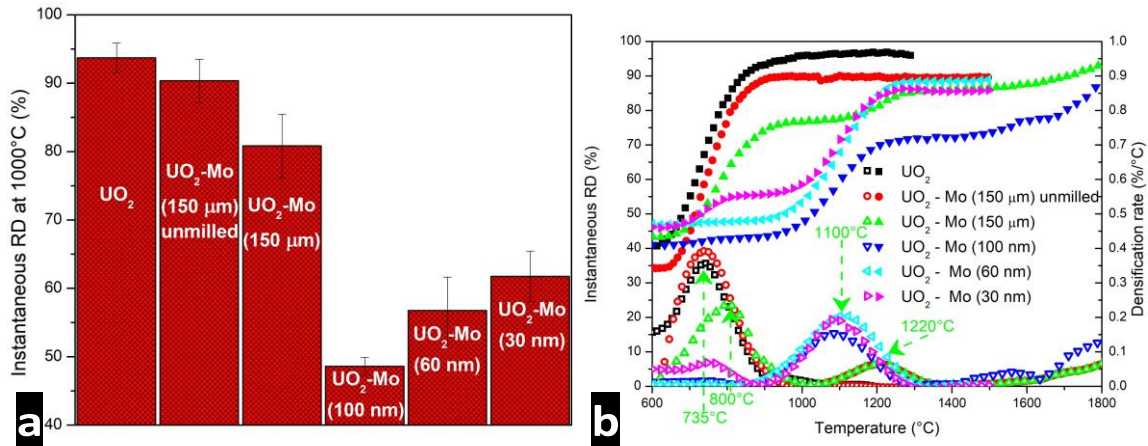


Figure 3: Effect of 10 vol% Mo addition to UO_2 : a) Averaged instantaneous RD at 1000°C, b) Densification curves (solid symbols represent instantaneous RD and open symbols represent densification rate).

The poor densification of UO_2 - Mo composites in comparison to pure UO_2 was also observed by Buckley *et al.* [12]. The deterioration of UO_2 densification by Mo addition was validated by the densification curves, where densification peaks were observed at higher temperatures for UO_2 Mo composites, as shown in Figure 3b. Previous studies have shown the densification regime of pure UO_2 and Mo to be 600 °C-1100 °C and 900 °C-1400 °C respectively [25][26][27]. Hence, the higher densification regime of Mo in comparison to UO_2 could be the reason behind the poor densification of UO_2 - Mo composites in comparison to pure UO_2 .

The fundamental mechanism causing this indifference in densification regime is unclear. In theory, the addition of Mo should enhance the densification of UO_2 , due to three factors: lower recrystallisation temperature, lower electrical resistance and higher ductility. Since UO_2 (~2880 °C) has a higher melting point (T_M) than Mo (~2600 °C), the recrystallisation temperature ($0.6T_M$) of Mo should be lower than UO_2 [12]. Also, Mo being a metallic material should have higher electrical conductivity and ductility than UO_2 . A higher electrical conductivity has been shown to enhance densification by causing more internal Joule heat generation, while a higher ductility should cause more deformation of powder particles during sintering.

A possible explanation for the enhanced densification of UO_2 in comparison to Mo could be electric field enhanced diffusion behaviour in UO_2 [28]. Tyrpekl *et al.* had observed that the densification of UO_2 during SPS was enhanced due to electric field assisted diffusion of O^{2-} ions [28]. A higher densification was observed near the positive electrode, which was credited to the

diffusion of O^{2-} ions. Hence, in this study the electric field enhanced diffusion could be the reason behind better densification in pure UO_2 in comparison to Mo.

Figure 3 also revealed the effect of Mo particle size on the densification of UO_2 - Mo composites. The second highest instantaneous RD after pure UO_2 was observed for the unmilled UO_2 - 150 μm Mo composite. The inhomogeneous distribution in unmilled UO_2 - 150 μm Mo blend might be causing the Mo particles to remain as agglomerates. These Mo agglomerates could be sintering independently at high temperature without hindering the UO_2 inter-particle bonding. In an evenly distributed milled UO_2 - 150 μm Mo blend, the Mo particles could be hindering inter-particle contact of UO_2 , causing poor densification. The densification curves also validate this conclusion as shown in Figure 3b. The densification curve of UO_2 and unmilled UO_2 - 150 μm Mo bear close resemblance, with no shift in peak positions, and UO_2 densification occurred at $\sim 735^\circ C$, as expected [25]. In the case of the milled UO_2 - 150 μm Mo, the UO_2 peak shifted to $\sim 800^\circ C$, probably due to Mo particles hindering UO_2 inter-particle contact. Additionally, a secondary peak corresponding to the densification of Mo was also detected at $1220^\circ C$ [26][27].

The Mo particle size also influenced the density of the UO_2 -Mo sintered composites, with the nanometric Mo addition reducing density further in comparison to micron Mo addition. This was evident in both average RD (Figure 3a) and densification curves (Figure 3b), where the UO_2 peak was absent for nanometric Mo additions. Nanometric Mo particles could be coating micrometric UO_2 particles, thus hindering UO_2 interparticle contacts [3]. However, the densification rate curves of UO_2 -(100 nm, 60 nm and 30 nm) Mo showed a singular peak at $1100^\circ C$. This could be due to the UO_2 peak shifting to a higher temperature and *vice versa* for the Mo peak, causing them to convolute into a single peak at $1100^\circ C$. The shifting of UO_2 peak to higher temperature could be due to the nanometric particles hindering inter-particle contact. The densification peak of nanometric Mo might be shifting to a lower temperature in comparison to 150 μm due to the higher surface energy of nano particles [29][30][6]. The lowering of sintering temperature due to nano Mo addition was also evident in the average instantaneous RD, wherein a decrease in Mo particles size from 100 nm to 30 nm was found to increase the instantaneous RD.

The above conclusions rely on the fact that the densification peak of UO_2 is at lower temperature than Mo during SPS [25][26][27]. The higher densification temperature of Mo in comparison to UO_2 was observed in literature on SPS of pure UO_2 and pure Mo [25][26][27]. In the case of SPS of UO_2 -Mo, Buckley *et al.* observed a decrease in the density of UO_2 -5 and 10 vol% Mo in comparison to pure UO_2 [3]. Since no studies focusing on direct comparison of densification mechanisms of UO_2 and Mo during SPS processing are available, an explanation was provided based on independent investigations with pure UO_2 and pure Mo.

3.2. MSC results

Figure 4a shows the MSC of UO_2 , with the inset showing the MPCD for various activation energies. The minimum MPCD was observed for an activation energy value of 645 kJ/mol for an MPCD value of 0.061. Chen *et al.* had reported an activation energy of 140 kJ/mol and 420 kJ/mol for pure UO_2 and UO_2 -5 vol% SiC respectively [19]. According to Frueh *et al.*, the "activation energy" from MSC construction is just a fitting parameter and could not be interpreted as sintering activation energy [31]. A comparison of activation energy of alumina was found to vary from 290 to 1064 kJ/mol between various published studies [31]. The observation by Frueh *et al.* was based on the fact that the powder characteristics and experimental conditions varied significantly between these individual studies. This could be the reason behind the difference in activation energy for current study and Chen *et al.*'s study. Additionally, there are also two other factors: Chen *et al.*'s study used MRS method in comparison to MPCD for MSC construction and the sintering pressure used by Chen *et al.* was 36 MPa in comparison to 60 MPa in the current study. Hence, a comparison of activation energy of UO_2 from this study to the past literature would be challenging.

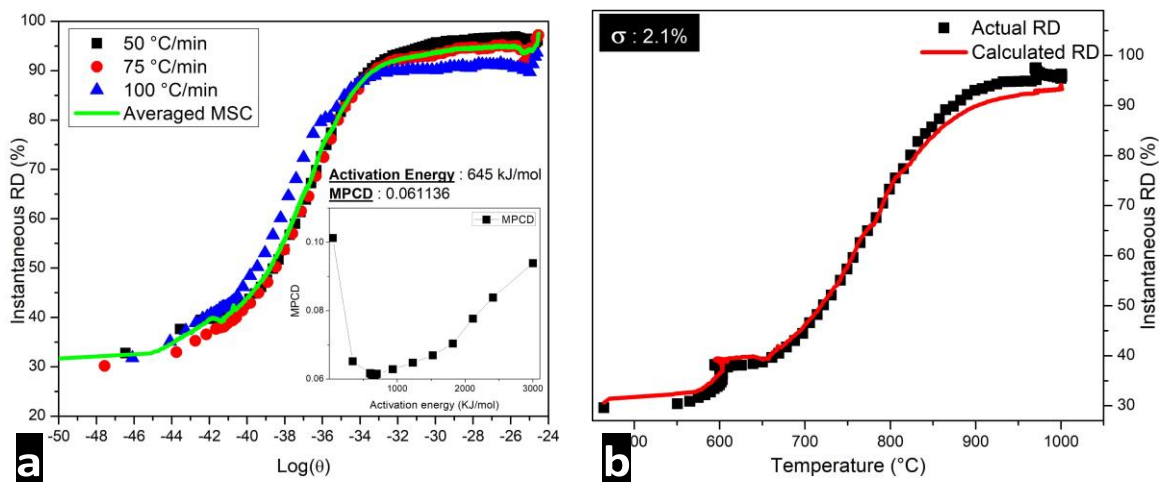


Figure 4: MSC analysis of pure UO_2 : a) Averaged MSC (inset shows activation energy vs MPCD), b) MSC validation experiment (inset shows temperature conditions for validation experiment).

The MSC of UO_2 was validated using an additional sintering trial for pure UO_2 as shown in Figure 4b, using the temperature profile shown in the inset. As shown in Figure 4b, the standard deviation (σ) between predicted densification curve and experimentally observed data was 2.1%, which could be decreased further by using data from more than 3 sintering trials for MSC construction.

Figure 5a shows the MSC of unmilled UO_2 - 150 μm Mo composite which showed an increase in activation energy to 980 kJ/mol. Similarly, the MPCD (0.11) was also higher in comparison to undoped UO_2 . However, the standard deviation between predicted densification curve and experimental data seemed unaffected at 2.1% as shown in Figure 5b. Figure 5a shows the MSC of UO_2 -150 μm Mo. The MPCD for MSC construction was 0.039 and activation energy was 660 kJ/mol. The temperature during holding period of the validation SPS trial was found to fluctuate by nearly $\pm 20^\circ\text{C}$ during the dwelling phase of the program. There are no explanations for this phenomena, however the temperature variation caused displacement to fluctuate due to thermal expansion and contraction, which could not be corrected by the thermal expansion correction. Hence, the dwelling part of program was not considered for MSC validation, due to which the standard deviation between predicted curve and experimental data was lower at 1.0% as shown in Figure 5b.

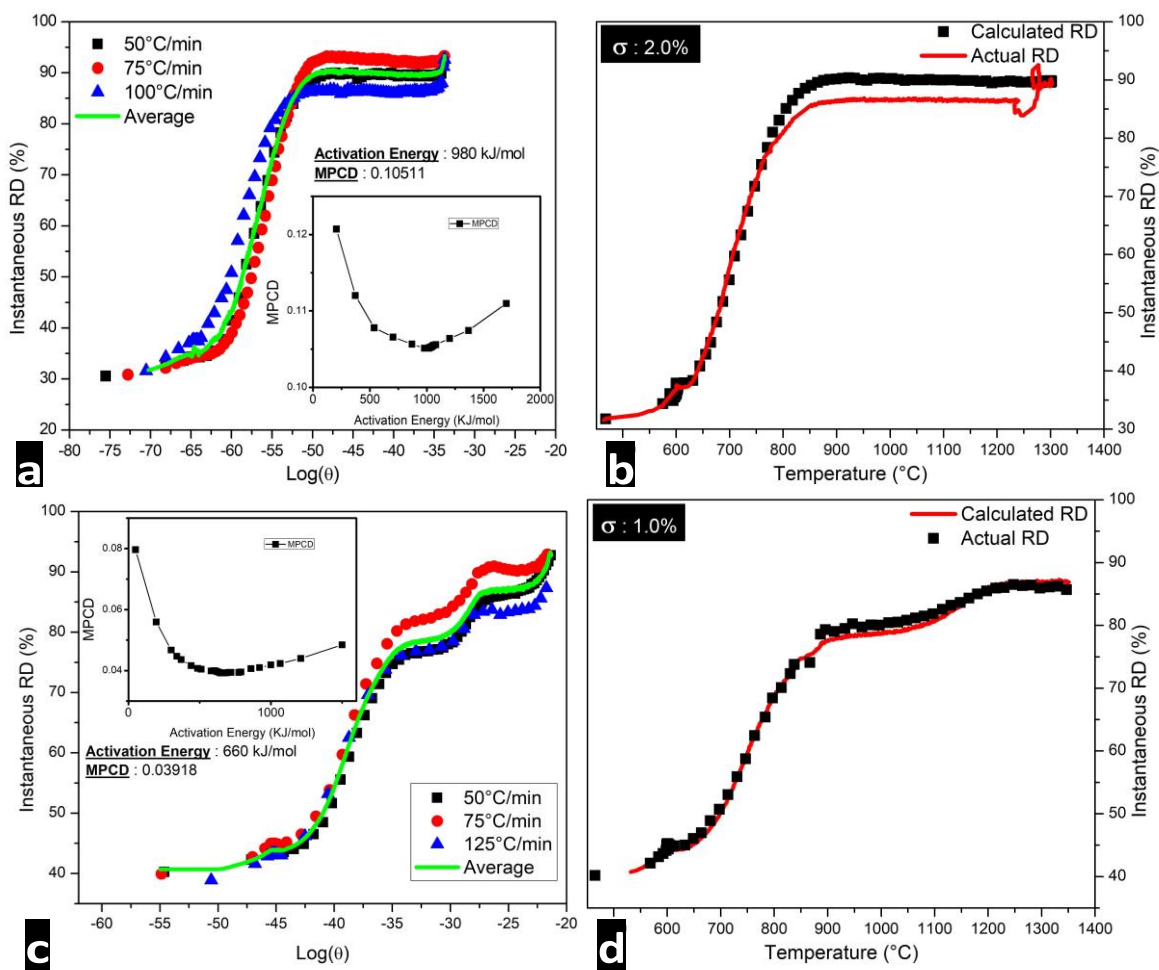


Figure 5: MSC analysis of unmilled (a & b) and milled (c & d) UO_2 -10 vol% 150 μm Mo: a & c) Averaged MSC (inset shows activation energy vs MPCD), b & d) MSC validation experiment.

Figure 6a shows the MSC of UO_2 -100 nm Mo. The MPCD for MSC construction was 0.054 and activation energy was 1050 kJ/mol. Similar to the UO_2 -150 μm Mo, the UO_2 -100 nm Mo also had a temperature fluctuation during dwelling phase, hence removed for MSC validation. Similarly, the standard deviation between predicted curve and experimental data was the least for all the predictions in this study at 0.7% as shown in Figure 6b.

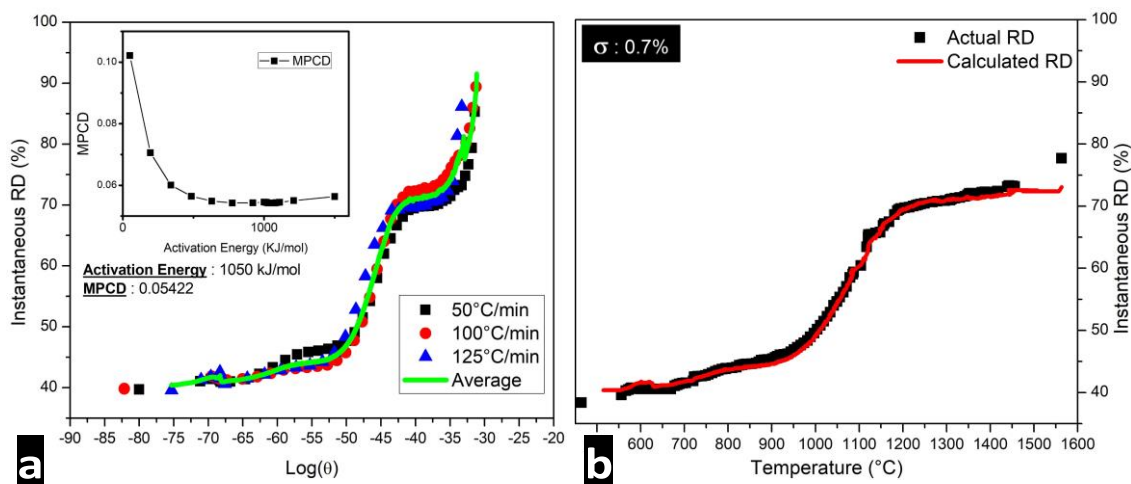


Figure 6: MSC analysis of UO_2 -10 vol% Mo (100 nm): a) Averaged MSC (inset shows activation energy vs MPCD), b) MSC validation experiment (inset shows temperature conditions for validation experiment).

Figure 7a shows the MSC of UO_2 -60 nm Mo. The MPCD for MSC construction was 0.078 and activation energy was 1190 kJ/mol. The standard deviation between predicted curve and experimental data was 3.5% as shown in Figure 7b.

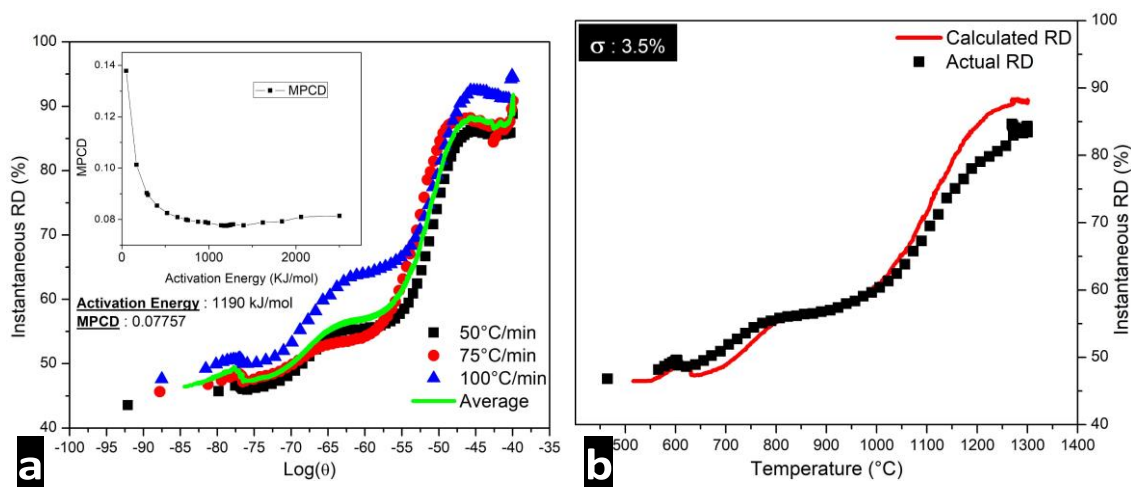


Figure 7: MSC analysis of UO_2 -10 vol% Mo (60 nm): a) Averaged MSC (inset shows activation energy vs MPCD), b) MSC validation experiment (inset shows temperature conditions for validation experiment).

Figure 8a shows the MSC of UO_2 -30 nm Mo. The MPCD for MSC construction was 0.072 and activation energy was 1190 kJ/mol. The standard deviation between predicted curve and experimental data was 4.8% as shown in Figure 8b.

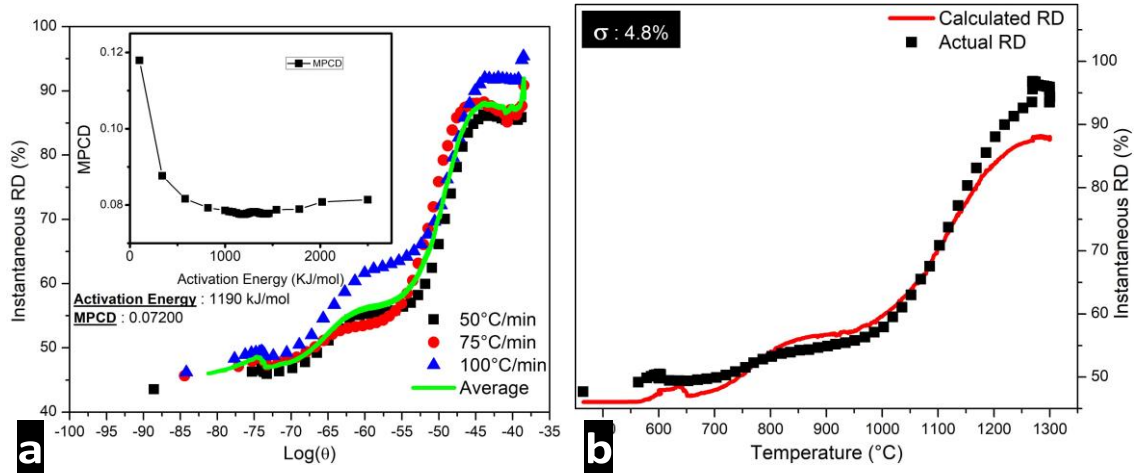


Figure 8: MSC analysis of UO_2 -10 vol% Mo (30 nm): a) Averaged MSC (inset shows activation energy vs MPCD), b) MSC validation experiment (inset shows temperature conditions for validation experiment).

The summary of MSC analysis is shown in Figure 9. Figure 9a compares the MPCD for pure UO_2 and UO_2 -10 vol% Mo composites. MPCD is a quantitative representation of deviation between the three trials used for MSC construction. The variation of MPCD could be merely experimental variation between these trials. If the densification curves were dependent on heating rate that could also influence the MPCD values as sintering data from varying heating rates were used for MSC construction.

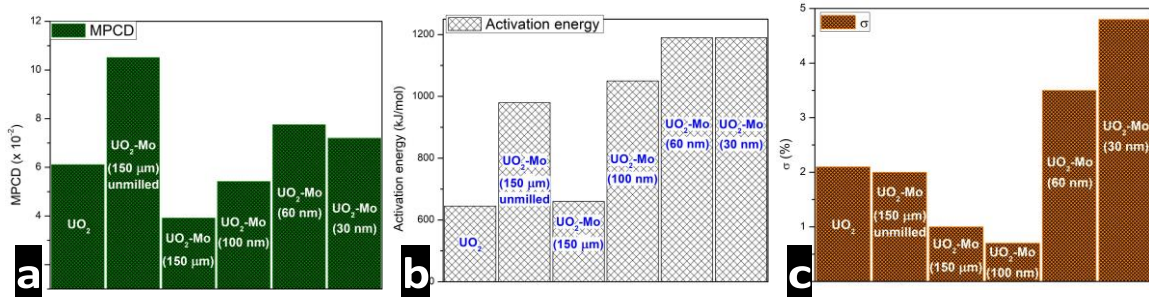


Figure 9: Summary of MSC analysis: a) MPCD, b) Activation energy and c) Standard deviation of prediction.

The comparison of activation energy for MSC is shown in Figure 9b. *Frueh et al.* had proven that the comparison of MSC activation energy between studies might be unreasonable for the same material, due to variation in powder characteristics and experimental conditions [31]. However, the same UO_2 powder and experimental conditions were used for all six materials, the variation in activation energy should be only dependent on the Mo doping. Since the activation energy is derived from Arrhenius relationship as shown in Equation 1, an increase in activation

energy should indicate the densification process required more energy for its inception (i.e. higher temperature or more time at higher temperature).

The nanometric Mo additions had the highest activation energy, specifically 30 nm and 60 nm additions. The next highest activation energy was observed for 100 nm addition. As Mo particle size decreases, the population of individual particles increase, hence there are more Mo particles that need to be joined to each other, resulting in an increase in activation energy of UO_2 -nanometric Mo composites. Also, the nanometric particles could be coating the bigger UO_2 particles changing the densification behavior to joining of Mo particles rather than UO_2 particles, which are barricaded by Mo particles coating them. The pure UO_2 and UO_2 -150 μm Mo had negligible difference in activation energy. The 150 μm Mo particles might be well dispersed, causing less occurrences of bonding between Mo particles. This might be the reason behind the unmilled UO_2 -150 μm Mo having a higher activation energy (980 kJ/mol) than UO_2 -150 μm , since there could be Mo particles agglomerated together. In these Mo agglomerates there might be inter-particle Mo sintering causing an increase in activation energy.

The standard deviation in prediction appeared to lowest for UO_2 -100 nm Mo and highest for UO_2 -30 nm Mo as shown in Figure 9c. The dwelling part of these two trials were ignored causing the standard deviation of prediction to be lower. Apart from this, the variation of standard deviation could be experimental deviation, however the standard deviation could be reduced in future by adding more trials for MSC construction.

3.3. Characterisation of as-sintered pellets

A detailed complimentary article will be published comprising of detailed microstructural, structural and thermophysical characterisation of as-sintered pellets. Some supplementary results from characterisation of UO_2 -150 μm Mo composite have been included in this section. Micrographs from polished UO_2 -150 μm Mo is shown in Figure 10. The low magnification micrograph showed a uniform distribution of Mo particles in UO_2 matrix as shown in Figure 10a. However, such a distribution would be undesired in comparison to the UO_2 particles distributed in a Mo matrix that would enhance thermal conductivity by forming a conductive metallic matrix.

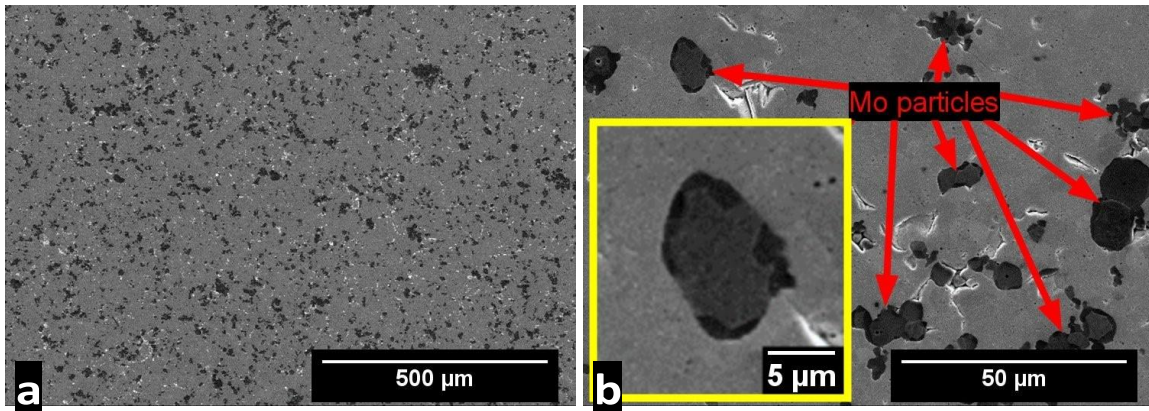


Figure 10: SEM micrographs from as-sintered UO_2 -150 μm Mo pellet: a) Low and b) High magnification.

Figure 10:

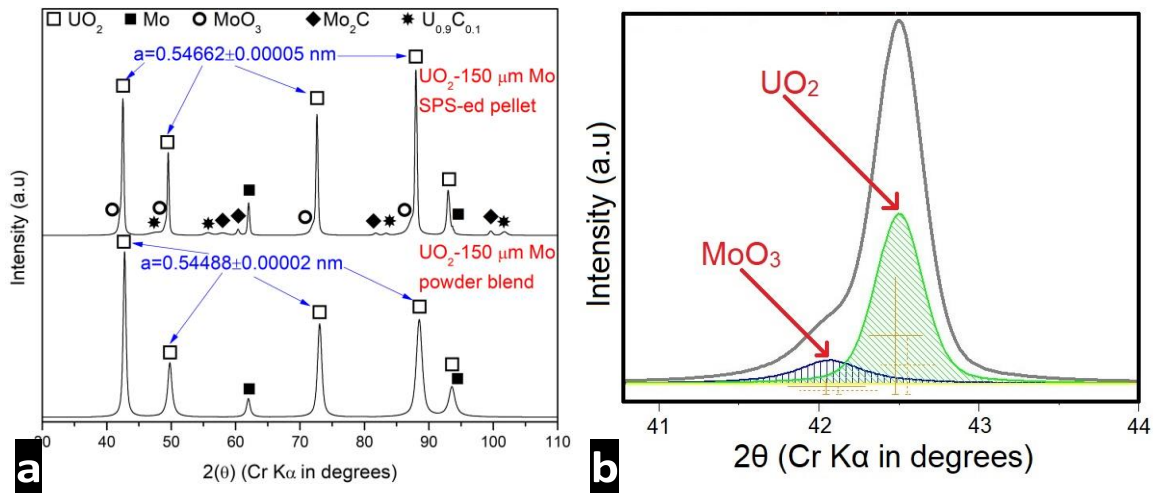


Figure 11: XRD analysis of UO_2 -150 μm Mo composite: a) XRD scans from before and after SPS and b) Deconvoluted peak profile showing UO_2 and MoO_3 peaks.

4. Acknowledgements

5. Conclusion

Accident Tolerant Fuels are gaining attention due to their improved ability to disperse heat evenly throughout a pellet. The study of densification behavior of pure UO_2 compared to Mo doped UO_2 through Spark Plasma Sintering found that the density of UO_2 decreased with Mo addition, due to the hindering of UO_2 interparticle contact by Mo particles. The densification rate peak for UO_2 was observed at $\sim 735^\circ\text{C}$ for pure UO_2 and unmilled UO_2 -150 μm Mo. The milling process increased densification rate peak of UO_2 -150 μm Mo mixture to $\sim 800^\circ\text{C}$. The milling

process would be causing Mo to distribute uniformly causing them to hinder UO_2 interparticle contact. A secondary densification rate peak was observed at $\sim 1220^\circ\text{C}$, for milled UO_2 -150 μm Mo, corresponding to densification of Mo. The densification rate peak might be at lower temperature for pure UO_2 due to electric field enhanced diffusion of UO_2 .

The primary densification rate peak was absent for nanometric (100, 60 and 30 nm) Mo addition, due to Mo nanoparticles coating UO_2 particles. UO_2 -(100, 60 and 30 nm) Mo had a single densification rate peak at $\sim 1100^\circ\text{C}$. The densification rate peak corresponding to UO_2 could be shifting to higher temperature, due to UO_2 interparticle contact hindered by Mo particles. Additionally, the densification rate peak of Mo might be shifting to lower temperature due to higher surface energy of nano particle. These two phenomenons might be causing the UO_2 and Mo peak to coalesce into a single peak. The RD of UO_2 -10 vol% Mo increased from 100 nm to 30 nm addition validating the previous conclusion. The activation energies were 645, 980, 660, 1050, 1190 and 1190 kJ/mol for pure UO_2 , UO_2 - unmilled 150 μm Mo, UO_2 -150 μm Mo, UO_2 -100 nm Mo, UO_2 -60 nm Mo and UO_2 -30 nm Mo respectively. The higher activation energies could have been caused by more occurrences of Mo interparticle sintering, which occurs at higher temperature. The standard deviation in prediction using MSC was as low as 0.7% and as high as 4.8%. The post sintering characterisation of pellets have been discussed in a different publication [22].

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