Master Sintering Curves for UO_2 and UO_2 -SiC Composite Processed by Spark Plasma Sintering

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Abstract

Master sintering curve (MSC) theory has been applied successfully to UO_2 and UO_2 -SiC composite ceramics processed using spark plasma sintering (SPS). By applying the constant heating rate method, where the powder compact was heated at a constant rate to a specified maximum temperature and then cooled naturally, the apparent activation energies for sintering have been determined to be 140 KJ/mol for UO_2 and 420 KJ/mol for UO_2 -SiC composite. The ability of the derived MSCs to control and predict final density in the sintered compact was demonstrated by additional experimental runs using the isothermal heating method, in which the powder is held for a specified time at the maximum sintering temperature. It is shown that the master sintering curve is an effective tool to characterize the densification and sinterability behavior of a given nuclear powder compact during spark plasma sintering. The reason

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for significantly lower activation energy in SPS processed UO_2 pellets compared to conventional sintering has been rationalized on the basis of field activation in SPS process.

Key Words

UO_2 , $\text{UO}_2\text{-SiC}$, Master sintering curve (MSC), Spark plasma sintering (SPS), Activation energy

1. Introduction

Spark plasma sintering (SPS), also called field assisted sintering (FAST), has become a fairly promising approach for processing difficult-to-sinter powders. The advantages and importance of the SPS as a tool for consolidation of powders have been proven by a large number of publications and a variety of powder including metals [1], ceramics [2], polymers [3] and composite powders [4] have been compacted by the SPS technique. Recently, the application of SPS has been expanded to the area of nuclear fuel. Ge et al., [5-6] successfully fabricated uranium dioxide (UO_2) pellets with 96% of the theoretical density (TD) by SPS at a sintering temperature of 1050°C and a hold time as low as 0.5 minutes. These sintering conditions are significantly lower than the conventional sintering conditions of 1600°C for 4 hours [7]. Yeo et al. [8-9] later utilized SPS to fabricate $\text{UO}_2\text{-SiC}$ composite fuels with high density, which could not be sintered by conventional methods.

While these nuclear fuel pellets have been successfully fabricated, the sintering kinetics during SPS have not been investigated. The control of the sintering process and the reproducibility of sintered compacts are crucial for quality assurance and, therefore, it is essential to understand the densification kinetics during the SPS process. Based on the type of diffusion mechanism, many sintering models have been proposed to describe the sintering process. Coble [10] developed an intermediate-late stage sintering model for lattice diffusion. Johnson [11] derived the governing equations for calculating volume, grain boundary, and surface diffusion coefficients. Kang and Jung [12] modified Coble's model for final stage sintering and considered the influence of grain boundary diffusion. These theories were verified by experimental examinations; however, they are either just limited to a single sintering stage, i.e., either initial, intermediate or final stage, or only applicable to single-phase systems. The master sintering curve (MSC) concept, which was first proposed by Su and Johnson [13], describes the sintering process in a new perspective. It is an experimentally-derived model that regards sintering as a continuous process. Unlike the models mentioned above, MSC does not aim to describe sintering behavior in general, but describes the shrinkage behavior of a specific powder system. This makes MSC a useful engineering tool. In addition, MSC is applicable to multi-phase systems, both metals and ceramics. Su and Johnson [14] constructed the MSC for Al_2O_3 - TiO_2 and Al_2O_3 - ZrO_2 systems, and Park et al. [15] successfully applied this theory to tungsten heavy alloys. In addition, MSC has been introduced in industry to guide the manufacturing process. For example,

Deborah et al. [16] demonstrated the applicability of master sintering curve theory in an industrial furnace.

While MSC theory has been widely used to control and understand microstructure development in a conventional sintering process, to the author's knowledge, the theory is only recently beginning to be applied for SPS process [17-18] and has never been applied to nuclear materials. Field assisted sintering methods such as SPS and microwave sintering, have been known to utilize significantly lower processing times and temperatures compared to conventional methods. Therefore, the activation energy and the kinetics of densification are expected to be dramatically different. To further understand these issues, the current manuscript deals with the development of MSCs for nuclear materials fabricated by SPS. The primary goal of the present work is to investigate the applicability of master sintering curve theory to spark plasma sintering of UO_2 and $\text{UO}_2\text{-SiC}$ powders. The apparent activation energies for these two materials are determined and the MSCs are constructed. The approach has been validated by using isothermal heating methods. Finally, the activation energy of sintering UO_2 derived for SPS process is compared to that for the conventional sintering method and the difference in these values are rationalized.

2. Master sintering curve (MSC) theory

Master sintering curve theory is derived from a combined stage sintering model originally proposed by Hansen et al. [19]. In the development of MSC, two major assumptions were made [13]. First, the microstructural evolution depends on density

only; and second, one of the diffusion mechanisms, i.e, either volume diffusion or grain boundary diffusion, dominates the sintering process. It should be noted that another assumption, i.e., the sintering body undergoes isotropic linear shrinkage, was made in the original work of Su and Johnson [13], but this assumption was found to be unnecessary by Diantonio and Ewsuk [20]. As mentioned earlier, the MSC was derived from the densification rate equation of the combined-stage sintering model [19]. Based on the assumptions above, the sintering rate equation can be expressed in the following form [13]:

$$\frac{d\rho}{3\rho dt} = \frac{\gamma\Omega D_0 \Gamma(\rho)}{kT(G(\rho))^n} \exp\left(-\frac{Q}{RT}\right) \quad (1)$$

Where ρ is the relative density, t is the sintering time, γ is the surface energy, Ω is the atomic volume, D_0 is the diffusion coefficient, Γ is lumped scaling parameter that relates geometric features, G is the grain diameter, n is a constant which depends on the sintering mechanism, Q is the apparent activation energy, R is the gas constant, and T is the absolute temperature.

By separating all the micro-structural and material parameters from thermal parameters, Eq. (1) can be rearranged and integrated as

$$\frac{k}{\gamma\Omega D_0} \int_{\rho_0}^{\rho} \frac{G^n}{3\rho\Gamma(\rho)} d\rho = \int_0^t \frac{1}{T} \exp\left(-\frac{Q}{RT}\right) dt \quad (2)$$

The term on the left hand side represents the evolution of microstructure, which is independent of the thermal history of the powder compact, and can be expressed as a function of density, $\Phi(\rho)$. The right hand side represents the thermal history, which can be expressed as ‘work of sintering’, $\Theta(t, T)$. Therefore, Eq. (2) can be reduced to

$$\Phi(\rho) = \theta(t, T) \quad (3)$$

The above empirical relationship between ρ and $\Phi(\rho)$ is then defined as the master sintering curve (MSC), which is distinct for a given powder. For the construction of a MSC of a given powder, the experimental density evolution data, i.e., the integral on the left hand side of Eq. (2), should be known. This requires careful experimental measurement of the volume change of powder during the sintering process. The goal of this study is to develop MSC for two different powder systems, uranium dioxide (UO₂) and UO₂-SiC composite based on such experimental data. The experimental procedure and results will be discussed in detail in the following.

3. Experimental procedure

3.1 Starting powders

UO₂ powder, obtained from AREVA, Hanford, WA, was reported to have a bulk density of 2.3 g/cm³, a mean diameter of 2.4 μm and a BET surface area of 3.11 m²/g. The oxygen to uranium (O/U) ratio was determined to be 2.16 using ASTM C1430-07. The β-SiC powder, used as second phase to fabricate a UO₂-SiC composite, was obtained from Alfa Aesar Inc, Ward Hill, MA, and had a mean particle diameter of 1μm. Fig. 1 reveals micrographs of as-received UO₂ and SiC powders.

A 5 vol% SiC powder was blended with UO₂ powder in a SPEX 8000 shaker for 1 hour. The SPEX jar is of 38 mm (1.5 inch) internal diameter and 45.7 mm (1.8 inch) length, and is made of zirconium oxide. To disperse the second phase particles, a blending aid, 2,3-Dihydroperfluoropentane, which acted as a lubricant for powder

particles [21], was used. The blending aid evaporated in air after the mixing process, and no residual contamination was left in the final mixture [8].

3.2 SPS sintering

A Dr. Sinter SPS-1030 system was used to perform the spark plasma sintering process. For SPS, 4 g of the mixture was loaded into a graphite die with a 12.7 mm inner diameter, and then graphite punches were inserted into both ends. The assembly was placed into the SPS chamber, and a vacuum of 10 Pa was maintained in the chamber throughout the sintering process. An axial pressure of 36 MPa was applied to the punches and sintering was carried out at prescribed conditions. The temperature was measured using a pyrometer that focused on the surface of the graphite die. The programmed heating schedule initiated at 600°C, as that is the lower detection limit of the pyrometer. More details of this method can be found in the work of Ge et al. [5].

Two different heating schedules were used: (i) the constant heating rate method and (ii) the isothermal heating method. The constant heating rate method was used to construct the master sintering curve. Three heating rates of 50°C/min, 100°C/min and 150°C/min were used to reach the maximum sintering temperature of 1200°C for pure UO₂ and 1400°C for UO₂-SiC composite. The current was then turned off at the maximum sintering temperature, and the pellets were naturally cooled down in the vacuum chamber. The isothermal heating method was employed to validate the constructed master sintering curve. The UO₂ and UO₂-SiC powders were sintered by heating at a rate of 75°C/min up to a maximum temperature of 750°C to 1050°C and

then held for 5 minutes at the prescribed maximum sintering temperature. Details on selection of maximum sintering temperature will be discussed later.

3.3 Determination of shrinkage curves

For the development of time-dependent relative density curves, actual shrinkage data of the given powder compact was required. In SPS, the axial displacement data of the bottom punch during sintering of the powder can be recorded. However, in order to take into account the thermal expansion of punches and the die blocks [22-24], the following procedures were adopted for each sample.

Initially, the powder was sintered in the graphite die and the axial displacement of the bottom punch was recorded. This displacement data was a combination of powder densification and the total expansion of graphite punches and die at high temperatures. To separate the graphite expansion, the entire die assembly was cooled down to room temperature and reheated to the same temperature with the sintered compact inside the die. As the length of sintered pellet is only about 3 mm, 30 times less than the length of punches, the thermal expansion of sintered pellets can be assumed negligible. Therefore, the displacement recorded in this second cycle corresponds only to the thermal expansion of the graphite punches and die. The length of the sintered sample was measured after the first and second run and found to be the same, indicating that no further densification of the sintered sample occurred during the second run. Finally, the powder shrinkage data were obtained by subtracting the thermal expansion of the graphite during the second run from the original displacement data in the first run.

Typical raw data for UO_2 and the graphite are shown in Fig. 2. In terms of the die displacement, positive values indicate shrinkage while negative values indicate expansion. The powder shrinkage curve (solid line) was obtained by subtracting the graphite expansion curve (dash line) from the original total specimen plus graphite shrinkage curve (dash-dot line).

With regard to the convention of shrinkage evolution being considered positive, it is extremely common in SPS literature to depict powder shrinkage as a positive quantity [2, 5]. However, most of these papers do not report the die expansion (which is opposite in sign for shrinkage) and hence no confusion was generated. However, the recent results by other authors [22, 24] which considered die expansion have followed the norm of powder shrinkage as positive and reported the die expansion as a negative quantity. Thus, the adopted sign convention confirms to the established norm.

The time-dependent relative density data was then calculated based on the following equations:

$$\rho_i = (\rho_f * l_f) / l_i \quad (4)$$

$$l_i = l_f - h_i \quad (5)$$

Where ρ_i is the instantaneous relative density, ρ_f is the final density which is measured by the Archimedes method, l_f is the final length of the sintered pellet, l_i is the instantaneous length, and h_i is the displacement difference between final state and instantaneous state, i.e., actual UO_2 shrinkage curve which can be read from Fig. 2.

4. Results

4.1 Construction of MSC

The time-dependent relative densities of the sintered powder versus temperature for different heating rates for both UO_2 and UO_2 -SiC composite are plotted in Fig. 3. The temperature started at 600°C , at which point no densification has taken place. It can be seen that at any temperature, the instantaneous relative density is dependent on the heating rate for a given powder, but all densification curves have the regular sigmoidal shape.

At the same heating rate, both UO_2 and UO_2 -SiC started to densify at about the same temperature, but the densification rate of UO_2 -SiC composites was much lower than that of UO_2 . For a constant heating rate of $50^\circ\text{C}/\text{min}$, 95% of the TD could be achieved at 1100°C for sintering a pure UO_2 pellet, whereas a 1350°C temperature was required for sintering a UO_2 -SiC pellet. This difference can be quantified by the MSC, and will be discussed later. Ge et al. [5] reported that the densification range for UO_2 (where rapid increase of densification occurred) was around 720°C to 1000°C , whereas from Fig. 3, obvious further densification could still be seen until 1100°C . It is more appropriate to modify this range to 1100°C , as the shrinkage curve in the present study also accounts for punch and die expansion at high temperature, which was not considered in the previous study [5]. Thus, the current study provided more accurate limits for the densification process.

A typical microstructure for sintered UO_2 and UO_2 -SiC pellets at a rate of $150^\circ\text{C}/\text{min}$ is shown in Figs. 4(a) and 4(b) respectively. Low levels of porosity (95.5% of TD for UO_2 and 96.0% of TD for UO_2 -SiC) are seen in both images, revealing that high density pellets can be achieved under the current sintering conditions. It is instructive to

note here that no more than 96.5% of TD is needed in the UO_2 pellet used in nuclear industry [25]. Therefore, the curves in Fig. 3 can represent the entire densification evolutions of the given powder and can be used to construct the MSC.

Another important parameter for constructing the master sintering curve is the apparent activation energy Q in Eq. (2). As discussed earlier, for a given powder compact, with the appropriate value of Q , the densification behavior becomes independent of thermal history, which means that the data with different heating rates can converge to a single curve. To accomplish this, various values of activation energies were chosen, and $\theta(t, T)$ values were calculated from Eq. (2). The $p\text{-ln}\theta$ curves of UO_2 with selected activation energy values for all heating profiles are shown in Fig. 5. It is seen that the three curves do not converge when Q equals 50 KJ/mol and 250 KJ/mol, whereas they tends to almost collapse into a single curve for all three heating rates when Q is around 150 KJ/mol.

To obtain more precise values of activation energy, detailed analyses were performed on UO_2 and $\text{UO}_2\text{-SiC}$ powder systems for a range of Q values. To quantify the convergence, various statistical analysis methods and tools have been used by many researchers. Teng et al. [26] performed a sigmoidal curve fit for the data and developed a Visual Basic macro in Microsoft Excel and automated the computation. Pouchly and Maca [27] stated an alternative criterion, the so-called Mean Perpendicular Curve Distance (MPCD), and developed specific software for calculation. In our study, a polynomial curve fit was made to all the data points by Origin, and the mean of residual

squares of all points with respect to that line were calculated. Fig. 6 reveals the mean residual squares with different assumed values of Q , from which the minimum is identified when $Q=140$ KJ/mol for pure UO_2 , and $Q=420$ KJ/mol for $\text{UO}_2\text{-SiC}$ composite.

Once the activation energy was obtained, the master sintering curves for pure UO_2 and $\text{UO}_2\text{-SiC}$ composite were reconstructed as shown Fig. 7. Although there was a 3-fold difference in heating rates, a single curve has been obtained by converging individual curves reasonably.

4.2 Validation and application of MSC

Before applying MSC to guide a manufacturing process, the validity of the constructed curves should be verified with various experimental runs. To accomplish this, a new set of experiments in which pellets were sintered by isothermal hold at maximum sintering temperature was conducted. With a heating rate of $75^\circ\text{C}/\text{min}$, which was chosen randomly, pellets were heated up to a selected temperature and held for 5 minutes. Compared with the constant heating rate method used previously, lower maximum sintering temperatures were used here to guarantee that the powders were in the sintering range during the 5-minute hold time. According to the densification curves in Fig. 3, the densification range (where rapid increase of densification occurred) was around 720°C to 1100°C for UO_2 , and 750°C to 1350°C for $\text{UO}_2\text{-SiC}$ composite. Therefore, in the isothermal sintering method, 750°C , 800°C and 850°C were selected as the maximum sintering temperatures for UO_2 , and 900°C , 1000°C and 1050°C were

selected for $\text{UO}_2\text{-SiC}$ composite. After sintering, the final densities were measured by the Archimedes method. The results are shown in Fig. 8, where the relative densities of pellets made in this method are now plotted on the MSC obtained from the previous method. It can be seen that the relative densities of the pellets made using these new conditions fall right on the constructed MSCs, confirming the validity of the MSCs derived from the earlier experiments.

Typical microstructures of the selected pellets produced under isothermal conditions are shown in Figs. 9(a) and 9(b). Note that significantly lower temperatures were used in this method, and hence the densities obtained in these pellets were lower than what were obtained previously. Compared with Fig. 4, it is clearly seen that the levels of porosities, especially the inter-granular porosities, are much higher.

5. Discussion

The constructed MSC can be a useful tool to model and control the spark plasma sintering process. First, as any given heating profile corresponds to a specific value on the MSC, the final density is predicted. Second, if a desired density is given, the way to design various heating profiles for this objective is achievable. An example of designing the heating profiles which can be utilized to achieve a UO_2 pellet with 90% of the TD is discussed here. With the goal of 90% of the TD, the corresponding value of work of sintering, $\ln\theta$, can be easily found to be -16.6 through Fig. 7. Then, a combination of heating rate, maximum sintering temperature and hold time can be determined by

Equation (2), to achieve the required Θ . The data corresponding to these heating profiles are shown in Table 1.

In addition to the ability to predict processing conditions for a given theoretical density, the presence of the rapid grain growth regime can also be detected by the MSC. Note that in Fig. 7, the curves of sintering UO_2 with different heating rates do not converge well in the high density range ($>95\%$ of the TD). Recall that MSC is valid only when one sintering mechanism dominates the process. It is reasonable to conclude that when the density exceeds 95%, rapid grain growth occurs during sintering, and the dominant diffusion mechanism is different. Ge et al. [6] studied the microstructure evolution of UO_2 during SPS process, and concluded that the grain size remains nearly the same ($0.4\text{ }\mu\text{m}$ to $1\text{ }\mu\text{m}$) in the medium density range (70% TD-95% TD), while it increased rapidly ($3\text{ }\mu\text{m}$ to $9\text{ }\mu\text{m}$) in the high density range (96% TD-97% TD), which is consistent with the statement here. On the contrary, the curves for UO_2 -SiC composites fit well in the entire density range, which shows that no exaggerated grain growth occurred in UO_2 matrix due to the pinning effect of SiC particles. This result was also consistent with the work of Yeo et al. [8], where very small grain sizes were observed even in a pellet with 97.8% of the TD of UO_2 -SiC pellet.

The MSC is unique for a given powder, as clearly seen in Fig. 7. With the addition of 5 vol% SiC particles, the apparent activation energy increases dramatically from 140 KJ/mol to 420 KJ/mol, and the MSC is drastically different. The MSCs for both UO_2 and UO_2 -SiC give a quantitative description on the sinterability and densification of these

two materials. Table 2 shows an example of the density results of UO_2 and $\text{UO}_2\text{-SiC}$ pellets sintered at 850°C and held for 2 minutes. Under the same heating profile, the extent of densification of different materials can be easily compared. Due the presence of the SiC particles, the grain boundary diffusion path of UO_2 grains was diminished and thus led to the poor densification of the composite. Similar behavior was also seen in Si_3N_4 based ceramics as well [28]. In other words, compared to UO_2 , more energy, either higher sintering temperature or longer hold time, was required for sintering the $\text{UO}_2\text{-SiC}$ composite to the desired high density. Thus, MSC provides a quantitative analysis to characterize the effect of second phase particles on the densification during the sintering process.

Finally, a brief discussion on the apparent activation energy Q of UO_2 by SPS is warranted. As master sintering curve is a model that describes the whole densification process, the Q value calculated in this study can be seen as an average value for the entire temperature range. It is noted that compared with the Q value calculated for conventional sintering methods (299 KJ/mol-429 KJ/mol) [29], the activation energy during SPS (140 KJ/mol) is significantly lower, which could possibly be attributed to the presence of coupled direct current field and pressure field in SPS. The effect of the current field has been noted and discussed most recently by many researchers. Cologna et al. [30] proposed that an avalanche of Frenkel point defects, both anions and cations, can be nucleated under an electric field, and this phenomenon has been observed in ceramics, such as yttria [31] and titania [32]. The aggregation of these point defects accelerates the diffusional transport rate and lowers the activation energy. Second, the

pressure is also a significant factor that distinguishes SPS from conventional sintering methods. The presence of pressure could increase the number of grain-grain contacts and change the grain shape [33]. This effect has also been observed in SPS by Ge et al. [6] during their studies on densification and grain growth. All of these effects could lead to a lower activation energy. However, it is still difficult to quantify the effect of current field and pressure on activation energies. Raj et al. [34] stated that the current field, as compared with the applied pressure, cannot significantly influence activation energy for diffusion during ceramic sintering in SPS. The above studies clearly indicate that further study is required on the role of pressure and electric field in SPS.

6. Conclusion

MSC theory has been applied successfully to UO_2 and UO_2 -SiC composite ceramics sintered by SPS. Utilizing just one temperature and time dependent parameter (θ), the densification process was quantified. The activation energy for SPS has been determined to be 140 KJ/mol for UO_2 and 420 KJ/mol for UO_2 -SiC composite.

The master sintering curve is proven to be an effective tool to describe the densification behavior of UO_2 and UO_2 -SiC powder compact during SPS. The ability of MSC to control and predict density has been demonstrated by a few experimental runs using the isothermal method. In addition, it is shown that the MSC can be used to compare the sinterability of different powder compacts in SPS.

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Table 1. Parameters of the heating profiles to sinter a UO_2 pellet with 90% of the TD in SPS

Goal:	Sintering profile	Heating rate ($^{\circ}\text{C}/\text{min}$)	Maximum sintering temperature ($^{\circ}\text{C}$)	Hold time (min)
90% of the TD	1	75	800	6.0
	2	75	850	2.6
	3	125	850	3.0

Table 2. Density comparison of UO_2 and $\text{UO}_2\text{-SiC}$ pellets under the same heating profile in SPS

	Heating rate ($^{\circ}\text{C}/\text{min}$)	Maximum sintering temperature ($^{\circ}\text{C}$)	Hold time (min)	Predicted density (% of TD)	Experimental density (% of TD)
UO_2	100	850	2	88.8	89.8 $\pm$ 0.4
$\text{UO}_2\text{-SiC}$	100	850	2	69.0	70.8 $\pm$ 1.0

Fig. 1 SEM images showing morphologies of a) UO₂ powder and b) SiC powder

Fig. 2 Shrinkage curves of UO₂ and the graphite during SPS. The actual shrinkage curve for UO₂ is obtained by subtracting graphite expansion from total shrinkage curve.

Fig. 3 Evolution of relative density as a function of temperature for UO_2 and $\text{UO}_2\text{-SiC}$ composite

Fig. 4 SEM images of polished surfaces of a) UO_2 and b) $\text{UO}_2\text{-SiC}$. Sintering conditions are shown on the top left of each image.

Fig. 5 ρ - $\ln\theta$ curves for selected value of activation energy. Note that for $Q=150$ KJ/mol, the relative density values tend to almost collapse into a single curve for all three heating rates.

Fig. 6 Mean residual squares for various estimated activation energy values. The minimum value provides the true activation energy for a given powder.

Fig. 7 Master sintering curve for pure UO_2 with activation energy of 140 KJ/mol and $\text{UO}_2\text{-SiC}$ with activation energy of 420 KJ/mol

Fig. 8 Comparison of MSC predicted relative density and experimental value of UO₂ and UO₂-SiC pellets using isothermal heating method

Fig. 9 SEM images of the microstructures of isothermally produced a) UO₂ and b) UO₂-SiC compacts. Sintering conditions are shown on the top left of each image.