



Why a master sintering curve model can be applied to the sintering of nano-sized particles?

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ABSTRACT

The master sintering curve model (*MSC*) has been widely applied to both the analysis and prediction of the sintering behavior of many powder materials, including nanocrystalline powder. However, since the conventional sintering theories are only true for submicron-sized or larger particles, it should not be applicable to the sintering of nano-sized particles. This work aims to provide an explanation as to why the *MSC* is capable of predicting nano-sized particle sintering. A comparison with another kinetic model, i.e., the master kinetics curve (*MKC*), which was derived from general chemical kinetic equation, reveals that *MSC* is almost identical except for a $1/T$ term in the equation. The analysis of sintering data also shows that the ability of both *MSC* and *MKC* are almost equal, and that the values of apparent activation energy provided by both two models are similar too. In previous researches, it is also found that the *MSC* can be applied to non-sintering systems. These results show that the ability of prediction of the *MSC* is strongly related to the integration of an Arrhenius type equation. However, because the *MSC* cannot determine the mechanism of the sintering process, the apparent activation energy Q_a may not represent any physical meaning. In summary, *MSC* may be a “universal” analytical tool for many reaction systems, and its success is definitely not due to its sintering origin but rather to its Arrhenius type form.

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1. Introduction

The master sintering curve model (*MSC*) was first developed by Su and Johnson [1,2] in 1996, and since then it has been widely applied to the sintering of various materials. The model was successfully applied not only to ceramics but also to powder metallurgy [3,4], and to the sintering of nano-sized particles [5,6]. Unlike other conventional sintering models, the construction of *MSC* is totally reliant on experimental data rather than on sintering stages and diffusion mechanisms. This feature makes the *MSC* more practical and convenient for the industry.

Although the construction of *MSC* is based on experimental data, the origin of *MSC* is strongly theoretical. The *MSC* is derived from the combined stage sintering model [7], which is a sintering model combining all three sintering stages and capable of describing the whole sintering process. The combined stage model, however, has a major problem in that it is extremely difficult to use. To use the model, the user needs to determine the geometric evolution of the powder particles, and this is especially difficult when each batch of powder has its own distinct evolutionary path. The *MSC*, however, avoided the problem by putting all the unknowns into a function

that can be determined by experimental data. Although the results indicate that the *MSC* is a very successful model, one should not forget that the *MSC* also inherited “all the assumptions” made by the conventional models.

Nanoparticles do not match the assumptions of conventional models. Due to their nanocrystalline sizes, the capillarity forces of nanoparticles, i.e. if applicable, would be so great that the particles should “explode.” Of course the nanoparticles do not explode, and this clearly shows that the conventional models, including the models derived from them, should fail in the analysis of the sintering of nanoparticles. Nevertheless, it is found that the *MSC* model is very successful in studying the sintering of nanoparticles. How could this happen? This paper aims to give a reasonable, plausible explanation for this seemingly unlikely phenomenon.

2. Derivation of the *MSC*

In order to compare the *MSC* with another similar kinetic model (see Section 3), a brief derivation of the *MSC* from the isotropic shrinkage rate (Eq. (1)) of the combined stage sintering model is given as follows:

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

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where ρ is relative density, t is time, γ is surface energy, Ω is the atomic volume, k is the Boltzmann constant, T is the absolute temperature, G is the mean grain diameter, Γ is the parameter related to the geometric feature of microstructure, n is the order related to the diffusion mechanism, R is the gas constant, and Q_a is the apparent activation energy.

By separating the parameters related to microstructure to the left side of the equation, and the parameters related to temperature and time to the right side, and then integrating both sides, the equation would become Eq. (2):

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

Then the left side of the equation becomes $\Phi(\rho)$, which is related to microstructural and material properties, and the right side of equation becomes $\Theta(t, T(t))$, which is related to Q_a and the time-temperature profile. Then from Eq. (2), we define Eqs. (3) and (4):

$$\Phi(\rho) = \frac{k}{\gamma\Omega D_0} \int_{\rho_0}^{\rho} \frac{(G(\rho))^n}{3\rho\Gamma(\rho)} d\rho \quad (3)$$

$$\Theta(t, T(t)) = \int_0^t \frac{1}{T} \exp\left(\frac{-Q_a}{RT}\right) dt \quad (4)$$

Thus the whole equation becomes Eq. (5):

$$\Phi(\rho) = \Theta(t, T(t)) \quad (5)$$

The relationship between ρ and $\log[\Theta(t, T(t))]$, i.e. an S-shape curve, is the master sintering curve. For more details, the assumptions and limitations of the MSC have been well discussed in the original MSC papers by Su and Johnson [1,2].

It is important to note that the MSC is developed from models based on diffusional transport mechanisms and capillarity force, i.e. the curvature of particle surface. For submicron or larger particles the assumptions are adequate, because the surface of particles is nearly continuously smooth; but nano-sized particles rarely have a smooth surface; theoretically, the MSC should not be applicable to the sintering of nano-sized particles.

In reality, the MSC cannot only be successfully applied to sintering of nano-sized particles, but also to some non-sintering systems [8]. The model has also been applied to grain growth by German [9]. Our previous work showed that MSC can be applied to the kerogen-oil conversion system [10,11]. These results are surprising since these systems have nothing to do with sintering.

3. Arrhenius equation and the MKC

The MSC is actually more like a kinetic model because it describes the relationship between the densification and time (temperature is considered as a function of time). With this understanding, it is found that the MSC is very similar to another kinetic model derived from the chemical reaction rate equation. The reaction rate equation is given as Eq. (6):

$$\frac{dy}{dt} = k(T)f(y) \quad (6)$$

where the parameter y is reaction variation, or the percentage of chemical reaction. In the study on sintering, the parameter y can be replaced by relative density ρ . The constant k is reaction rate constant, which is often assumed to be Eq. (7), as proposed by Arrhenius in 1889:

$$k(T) = A \exp\left(\frac{-Q_a}{RT}\right) \quad (7)$$

The constant A is a pre-exponential factor or pre-factor, which differs according to different reactions. Eq. (7) is the Arrhenius

equation, and it gives the dependence of rate constant k on the temperature and activation energy; Eq. (7) has been widely applied to many fields of scientific study. Now the total equation would be as Eq. (8):

$$\frac{dy}{dt} = A \exp\left(\frac{-Q_a}{RT}\right) f(y) \quad (8)$$

If we do the same separating parameters treatment as with Eq. (1), we can simply get Eq. (9):

$$\frac{1}{A} \int_{y_0}^y \frac{dy}{f(y)} = \int_0^t \exp\left(\frac{-Q_a}{RT}\right) dt \quad (9)$$

The left side of equation has all of the terms related to the reaction percentage and constants, and the right side of equation is related to Q_a and the time-temperature profile. As in the MSC, the equation can be expressed as Eqs. (10) and (11):

$$\Phi(\rho) = \frac{1}{A} \int_{y_0}^y \frac{dy}{f(y)} \quad (10)$$

$$\Theta(t, T(t)) = \int_0^t \exp\left(\frac{-Q_a}{RT}\right) dt \quad (11)$$

And then the whole equation becomes Eq. (12):

$$\Phi(\rho) = \Theta(t, T(t)) \quad (12)$$

This model is called the master kinetics curve (MKC, a.k.a. the master curve model or MCM), and we will compare the model to the MSC in the following section. The MKC has been applied to several studies, such as the phase transformation of minerals [12,13]. The only difference between the mathematical equations of MSC (Eq. (4)) and MKC (Eq. (11)) is the $1/T$ term. Thus the unit of $\log \Theta$ in MKC is $\log(s)$, which is not the same as the unit $\log(s/K)$ in MSC. Otherwise, they are exactly the same.

4. Experimental results and analysis

Although the MSC and MKC were derived from different sources and differ by a $1/T$ term in their equations, their capabilities are very similar. To determine the differences in their prediction ability, we used both models to analyze three sets of sintering data: (1) 0.6–0.8 μm Al_2O_3 , (2) 80 nm TiO_2 , and (3) 35 nm TiO_2 . In the sintering of 0.6–0.8 μm Al_2O_3 powder, the green compacts were heated to 400 °C and held for half an hour to remove the binder, and then heated to 1600 °C at different heating rates. Fig. 1 shows that both MSC and MKC provide good prediction curves for sintering. It seems that the $1/T$ only translates the master sintering curve to the left side of the MKC by a constant. (For convenience sake, we use MSC and MKC interchangeably to represent the models and the curves determined by the model.) To compare the exact differences in the shapes of these two curves, we overlap the two curves, as shown in Fig. 2; there is little discrepancy between these two models.

It is interesting to note that although both models yield almost the same apparent activation energies in this experiment, their values are much higher than those which Su and Johnson reported [1] (see Table 1). Although they used different Al_2O_3 particles, i.e., AKP-50 (particle size ranges from 0.1–0.3 μm) from our AKP-15 (0.6–0.8 μm), the particle sizes should not cause a very big difference in “real” activation energy. This big difference in apparent activation energies must be due to the characteristics of green body processes. Nevertheless, what is actually causing the differences in the values of activation energy is still hard to determine at present.

In the sintering of 80 nm and 35 nm TiO_2 powders, the compacts were heated to 350 °C and held for half an hour to remove the

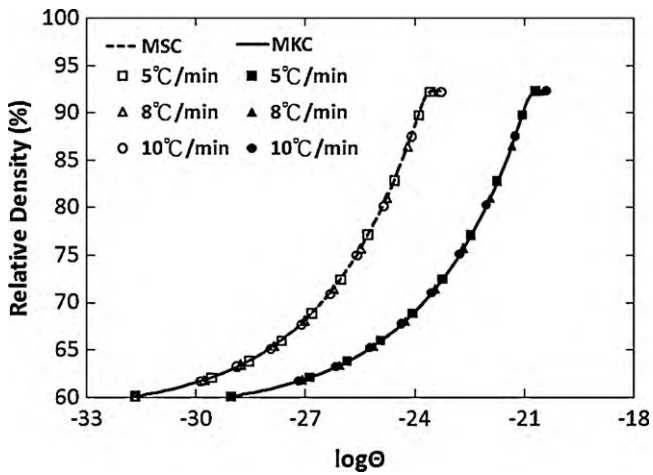


Fig. 1. The master sintering curve (MSC) and the master kinetics curve (MKC) derived from the sintering data of AKP-15 Al₂O₃ (0.6–0.8 μm) powder. The two curves are similar in shape, and both give good prediction results. Note that the unit of log Θ in MKC is log(s), which is not the same as the unit log(s/K) in MSC.

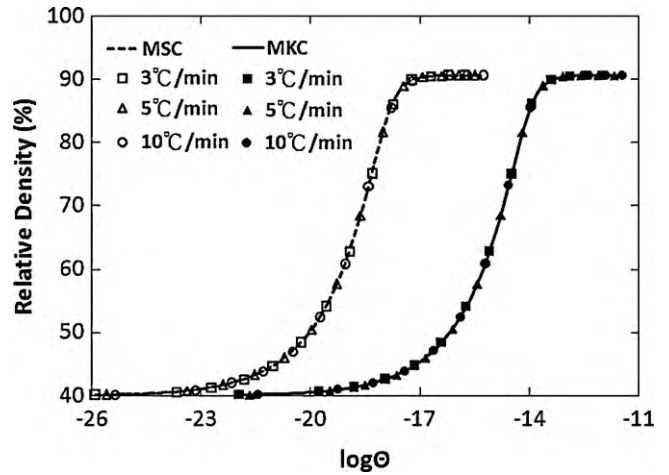


Fig. 3. The MSC and the MKC derived from the sintering data of 80 nm TiO₂ powder. In spite of the powder's nano-sized particles, the two curves yield good prediction results.

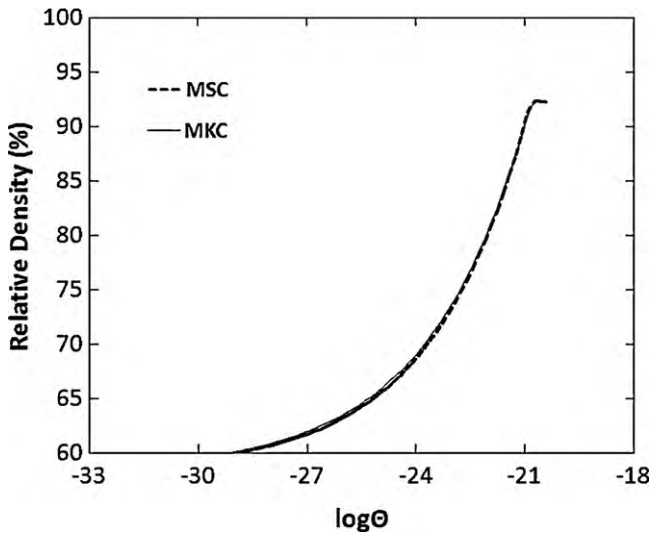


Fig. 2. Move the MSC in Fig. 1 and let it overlap with MKC. The two curves are almost identical in shape, showing that the 1/T term has little effect on the predictions of densification of AKP-15 Al₂O₃ (0.6–0.8 μm) powder.

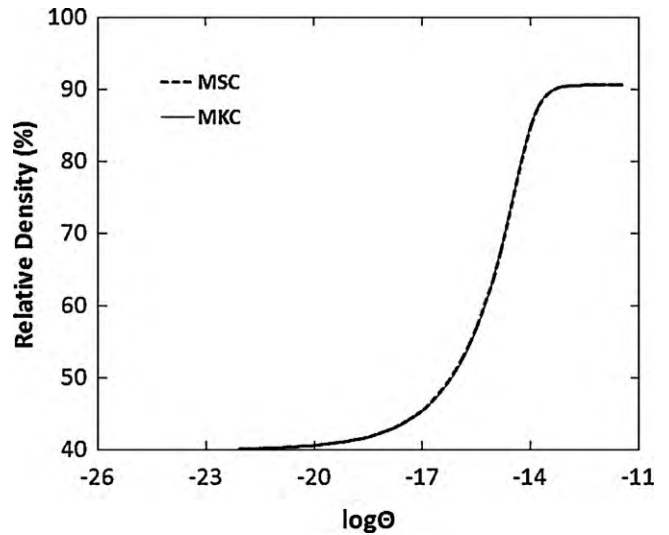


Fig. 4. Move the MSC in Fig. 3 and let it overlap with MKC. The two curves are identical in shape, showing that the 1/T term has little effect on the predictions of densification of the sintering of 80 nm TiO₂.

binder, and then heated at 5 °C/min to 850 °C, and finally heated to 1400 °C at three different heating rates. Figs. 3 and 4 show both the MSC and the MKC of 80 nm TiO₂; Figs. 5 and 6 show the results of sintering of 35 nm TiO₂. As the previous example has shown, there is little discrepancy between these two models in terms of curve shapes. The apparent activation energies (from 488.2 to 499.9 kJ/mol) are also very different from others, such as the 105 kJ/mol derived by Li et al. [14] (Table 1.)

Table 1
Apparent activation energies (kJ/mol) derived from several materials by MKC and MSC models.

	Model	Al ₂ O ₃ 0.6–0.8 μm	TiO ₂ 35 nm	TiO ₂ 80 nm
This work	MKC	824.9	488.2	490.7
	MSC	811.3	499.9	499.9
Other work	MSC	487.6 ^a	105 ^b	

^a Su and Johnson 0.1–0.3 μm Al₂O₃, AKP-50 [1].

^b Li et al. 50 nm TiO₂ [14].

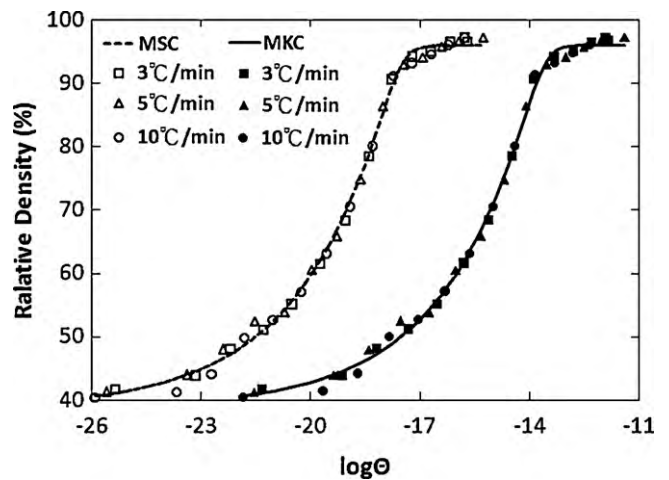


Fig. 5. The MSC and the MKC derived from the sintering data of 35 nm TiO₂ powder. In spite of the powder's nano-sized particles, the two curves also yield good prediction results.

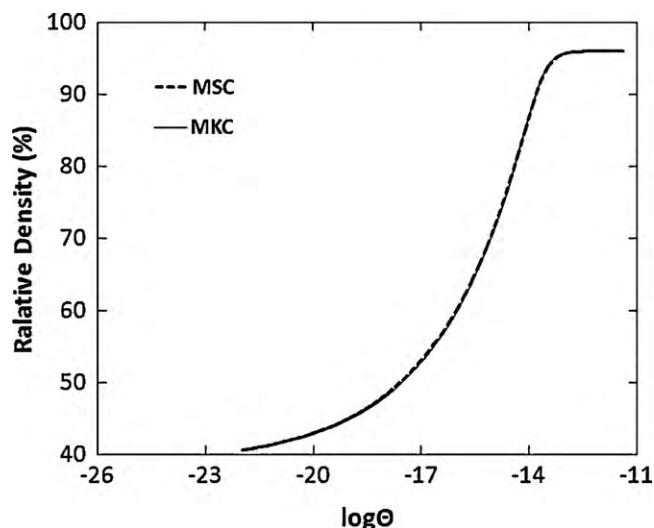


Fig. 6. Move the MSC in Fig. 5 and let it overlap with MKC. The two curves are identical in shape, showing that the $1/T$ term has little effect on the predictions of densification of the sintering of 35 nm TiO_2 .

5. Discussion

We have demonstrated in previous sections that both *MSC* and *MKC* yield almost the same results in the analysis of three powders, i.e., one submicron Al_2O_3 , and two nano-sized TiO_2 powders. The two models are identical except for the $1/T$ term difference in their mathematical equations. Considering the temperature range in a typical sintering experiment, the $1/T$ term of the *MSC* will contribute a factor from about 0.001 to 0.0006 to each exponential term, and translate the fitted curve about three units smaller than *MKC* in logarithmic scale. While one may argue that the *MSC* is a sintering model, and it is thus not surprising that the model can be used to interpret any sintering experiments, i.e. including nanoparticles, *MKC* is a different story. The *MKC* has nothing to do with conventional sintering models, yet it can be used to analyze sintering behavior. Obviously a deeper common reason lies behind the success of the two models.

The main reason may be the Arrhenius type equation. The exponential term in the Arrhenius equation results from Boltzmann's law. The probability of an atom having certain energy Q is proportional to $\exp(-Q/RT)$. Thus, by ignoring the exact (maybe very complicated) mechanisms of sintering, if we can assume the probability to represent some kind of "driving force," we can calculate the accumulated value of the effort. Progress, however, does not depend linearly on how much effort is exerted, but rather is determined by the system status. At any specific status, say either 50% or 80% relative density, the same "effort" will lead to different progress, i.e., different densification rates in sintering. What then can help us decide upon the progress? Both models tell us that the answer lies in the experimental data.

Since a sintering system is so complicated (e.g. a 200 ppm impurity may change the sintering path), it is almost impossible to develop a practical model for every sintering system. The closest one may be the combined stage sintering model [7]. Yet it contains the almost unattainable Γ parameters (see Eq. (1)), which represent a specific feature of the microstructure that influences

the kinetics of sintering. Now we have the *MSC* derived from the combined stage sintering model, and it not only works for sintering but also for many other kinetic reactions. Therefore, it is more like a "universal" kinetic model, and that is why it is not necessary to understand the mechanism in order to predict the sintering result.

However, the value of the apparent activation energy yield by the *MSC* method may not represent any physical meaning due to a lack of understanding of the mechanism. In Table 1, we can see that the values of apparent activation energy are made to differ by several factors. This awkward situation is especially apparent in the study of the *MSC* analysis on kerogen-oil conversion [10]. When the conventional models, which have been used by the oil industry for years, assumed that several organic chemical reactions had combined and given activation energy for each reaction, the predictions of the conversion were less accurate than that given by the *MSC* [11]. In summary, we think the *MSC* (as is the *MKC*) is a very powerful tool in the analysis and prediction of many kinetic reactions, and its success is definitely not due to its sintering origin but rather to its Arrhenius type form.

6. Conclusions

The master sintering curve has been applied in many fields of scientific research. In this work, we found that the reason why the *MSC* can be applied to the sintering of nano-sized particles is due to its Arrhenius type form. By comparing the *MSC* to a model derived from a chemical kinetic reaction equation, i.e. *MKC*, it has been demonstrated that both models work equally well on the sintering of nano-sized particles. Since the *MSC* cannot determine the sintering mechanism of the system, the value of the apparent activation energy cannot represent any clear physical meaning. Especially in regard to the non-sintering applications, the value of the apparent activation energy is more like a fitting parameter rather than a meaningful energy barrier. Overall, the *MSC* may be a "universal" analytical tool for many systems, but its success is due not to its sintering origin but rather to its Arrhenius type form.

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