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A COMPUTER PROGRAM OF MASTER SINTERING CURVE MODEL TO ACCURATELY PREDICT SINTERING RESULTS

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ABSTRACT

The Master Sintering Curve (*MSC*) model is a recently developed sintering model, which can adequately predict sintering results and is independent of the heating history. However, to develop the desired *MSC* from sintering data involves complicated and repeated calculations that may take several hours and may still result in some inaccuracies. We wrote a computer program (in *Excel VBA*) to facilitate the development of *MSC*, by which the users can easily transform their initial sintering data into *MSC* in minutes. We also improved the predictive accuracy of the model by redefining the *MSC* to be an S-shape curve, rather than the polynomial of the original work.

Key words: sintering model, simulation, prediction, computer program

INTRODUCTION

Sintering is a very complex process that involves several diffusional mass transport mechanisms, and is accompanied by the geometric evolution of powder throughout the whole process. As a result, it is generally not possible to quantitatively predict the sintering behaviors of a particular ceramic specimen even though its thermal history is known. A number of theoretical models (DeHoff, 1984; Wang and Raj, 1990; Chu *et al.*, 1991; Hansen *et al.*, 1992), however, had been developed trying to achieve this goal but with little success. Not until recently did a Master Sintering Curve (*MSC*) model (Su and Johnson, 1996; 1997), built on an earlier combined-stage sintering model (Hansen *et al.*, 1992), greatly simplify the process and make final-density prediction possible. The predictive accuracy, however, was not completely satisfactory. We usually found the curve fluctuated especially in both low- and high-density areas. Although the fluctuation was not extreme, it does not reflect the physical reality.

The long and tedious process to develop the *MSC* is another barrier to the practical application of the *MSC* model. In order to effectively use the predictive ability of the model, one has to conduct constant-heating-rate sintering experiments, and then use the data to construct and optimize the *MSC* following several repeated calculating procedures. It is a tedious process

and may take several hours, not to mention the possible human errors during the long process, especially to those who are not familiar with the model.

The purpose of this work was to improve the predictive accuracy of the *MSC* model, and to make the development and application of *MSC* easier. In order to achieve these, we redefined the shape of *MSC* and wrote a computer program that will do all the optimization automatically and, in addition, predict the sintering results of various heating profiles.

THE MASTER SINTERING CURVE (*MSC*) MODEL

The *MSC* model was derived directly from the final equation of combined-stage sintering model (Hansen *et al.*, 1992) :

$$-\frac{dL}{Ldt} = \frac{\gamma\Omega}{kT}\left(\frac{\Gamma_v D_v}{G^3} + \frac{\Gamma_b \delta D_b}{G^4}\right) \qquad (1)$$

where L = length of the sample (m)
t = time (sec)
γ = surface energy (J/m^2)
Ω = atomic volume (m^3)
k = Boltzmann constant = 1.38066×10^{-23} J/K
T = absolute temperature (K)
G = mean grain diameter (m)
D_v = volume diffusion coefficient (m^2/sec)
D_b = grain boundary diffusion coefficient (m^2/sec)
δ = width of the grain boundary (m)
Γ_v, Γ_b = scaling factors representing volume and grain boundary diffusion

Through a simple variable-separation and integration operation, assuming only one dominant diffusion mechanism and the geometry depends only on density, Su and Johnson (1996; 1997) rearranged Eq.(1) into two parts, thus:

$$\Phi(\rho) = \Theta(t, T(t)) \qquad (2)$$

Where $\Phi(\rho)$, as defined in Eq.(3), comprises all the geometric terms and is a function of density ρ; $\Theta(t, T(t))$, as defined in Eq.(4), comprises only the temperature, time, and an apparent activation energy Q_a.

$$\Phi(\rho) \equiv \frac{k}{\gamma\Omega D_0} \int_{\rho_0}^{\rho} \frac{[G(\rho)]^n}{3\rho\Gamma(\rho)} d\rho \qquad (3)$$

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

The beauty of this rearrangement is that now we can characterize the sintering behaviors of a given powder with specific green-body process regardless of the heating profiles, as long as the assumptions of the model hold. The only unknown parameter Q_a in Eq.(4), which includes many unknown factors in sintering (Su and Johnson, 1996), will have to be determined from sintering data by finding the one apparent activation energy that gives the minimum average residual square. Once we find the optimal Q_a, the master sintering curve, i.e. ρ vs $\log[\Theta(t, T(t))]$, can then be derived by Eq.(4). For more details, please refer to Su and Johnson (Su and Johnson, 1996; 1997).

To correct "the fluctuation problem" of the original *MSC* model, we redefined the *MSC* to be a sigmoidal (S-shape) curve (rather than the polynomial of the original paper):

$$\rho = \rho_o + \frac{a}{\left[1 + \exp\left(-\frac{\log(\Theta) - \log(\Theta_o)}{b}\right)\right]^c} \qquad (5)$$

where a, b, c are constants, ρ_o is the green density, and $\log(\Theta_o)$ is the abscissa coordinate of the reflection point of the curve. The five parameters, a, b, c, $\log(\Theta_o)$, and ρ_o, determine the exact form of the S-curve, which gives a smooth *MSC* and is obviously a better fit to the data. Except for the redefined shape of the *MSC*, we basically followed the original procedures of Su and Johnson (1996; 1997) to develop the computer program for *MSC*.

THE MASTER CURVE PROGRAM

The Master Curve computer program (or *MSC* program) was written using Visual Basic for Application (*VBA*), which can be found in *Microsoft Office*® applications (such as *Word*, *Excel*...etc.). We took advantage of the powerful numerical calculation ability of *Excel*, and let the written program became a VBA macro attached to an *Excel* file (file name: **Master_Curve_V.1**; for a copy of the program please contact mhteng@ccms.ntu.edu.tw). (Chen, 2000)

Figure 1 shows a simple user flow chart that demonstrates what the user will do when using the program. Once open the *Excel* file **Master_Curve_V.1**, the users are required to type in at least three sets of sintering data (Table 1 and Figure 2), each represents a sintering path of unique thermal history, which could be either constant-heating-rate or any other designed heating profile. Each data set should comprise at least five to as many as one hundred data rows, and in each row the sintering temperature, time, and corresponding relative density should be clearly specified as shown in Table 1. In this paper we'll take the sintering of yittria stabilized tetragonal zirconia powder (with 5% Y_2O_3, particle size 0.13 ~ 0.46 μm) as an example, and all the following results shown will be based on this experiment.

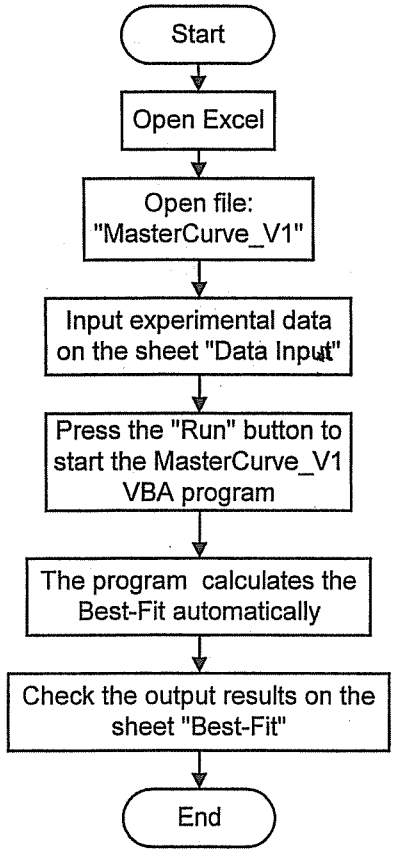

Figure 1. The user flow chart demonstrating the simple procedures of how to use the *MSC* computer program.

Table 1. An example of the input of sintering data (see Figure 2) in Excel worksheet "Data Input" before starting the *MSC* program. Each row of data includes temperature, sintering time (starting from room temperature), and the relative density.

2°C/min			5°C/min			8°C/min		
temp (°C)	**time (sec)**	**density (%)**	**temp (°C)**	**time (sec)**	**density (%)**	**temp (°C)**	**time (sec)**	**density (%)**
1050	9975	54.43	1050	12360	53.86	1050	7725	53.75
1100	11475	55.70	1110	13080	55.69	1100	8100	54.82
1150	12975	60.15	1150	13560	58.01	1150	8475	57.14
1200	14475	67.53	1200	14160	64.06	1200	8850	61.05
1250	15975	76.40	1250	14760	72.50	1250	9225	69.43
1300	17475	85.35	1300	15360	81.44	1300	9600	77.40
1350	18975	92.71	1350	15960	90.69	1350	9975	87.34
1400	20475	96.42	1400	16560	94.67	1400	10350	93.01
1450	21975	97.63	1450	17160	96.46	1450	10725	95.10
1500	23475	98.79	1500	17760	97.31	1500	11100	97.51
1500	25275	98.89	1500	19560	98.40	1500	12900	99.03

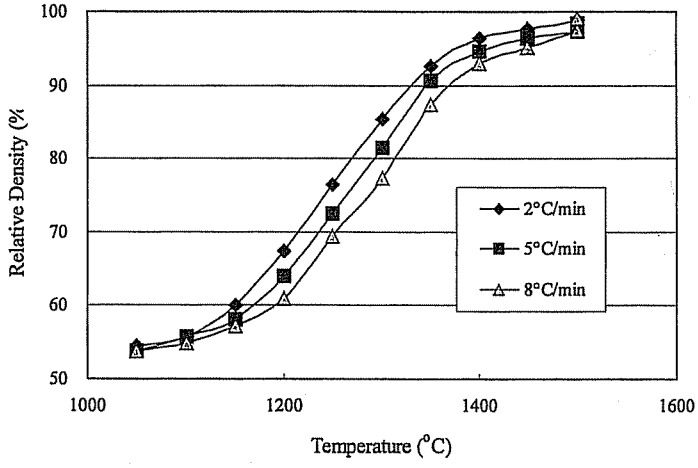

Figure 2. The results of three constant heating-rate sintering experiments (2°C/min, 5°C/min, and 8°C/min) of zirconia. The experimental data are listed in Table 1 and will be used as an example in this paper.

Next, the user can click a "RUN" button letting the program find the best Q_a automatically (Fig. 3). After the program is completed, two useful figures will be generated on separate worksheets, one is the average residual square vs Q_a (Fig. 4), where the activation energy 660.1 kJ/mol that gives the minimum average residual square value is found to be the best Q_a; another one is the final *MSC* (Fig. 5), where the variation of ρ vs. $\log(\Theta)$ and the equation of the *MSC* are shown. On the worksheet "Predictions", based on the newly derived *MSC*, the program lists the predictions of the sintering time required to reach certain relative densities at some constant temperatures (Tab. 2). Part of the predictions listed in Figure 6, excluding those with impractically long sintering time, had been confirmed in later experiments with errors of less than one percent (Chen, 2000). In addition, users can also input their own custom designed sintering profiles, and the program, by using the newly derived *MSC* equation, will calculate the predicted density variations accordingly. Table 3 is a simple summary of the worksheets and their contents generated by the *MSC* program.

Table 2. The predictions of the sintering time (sec) required for a zirconia sample to reach a particular density at a constant temperature. The predictions are shown in *Excel* worksheet "Predictions". Note that the heating rate is not considered.

Temp (°C)	Relative density								
	60%	65%	70%	75%	80%	85%	90%	95%	98%
1000	4.5E+05	2.0E+06	5.8E+06	1.4E+07	3.4E+07	8.5E+07	2.5E+08	1.4E+09	1.5E+10
1100	5.2E+03	2.3E+04	6.6E+04	1.6E+05	3.9E+05	9.7E+05	2.9E+06	1.6E+07	1.7E+08
1200	1.1E+02	4.8E+02	1.4E+03	3.5E+03	8.3E+03	2.1E+04	6.2E+04	3.4E+05	3.7E+06
1300	3.8E+00	1.7E+01	4.9E+01	1.2E+02	2.9E+02	7.2E+02	2.1E+03	1.2E+04	1.3E+05
1400	2.0E-01	8.7E-01	2.5E+00	6.3E+00	1.5E+01	3.7E+01	1.1E+02	6.1E+02	6.6E+03
1500	1.5E-02	6.4E-02	1.8E-01	4.6E-01	1.1E+00	2.7E+00	8.1E+00	4.4E+01	4.8E+02

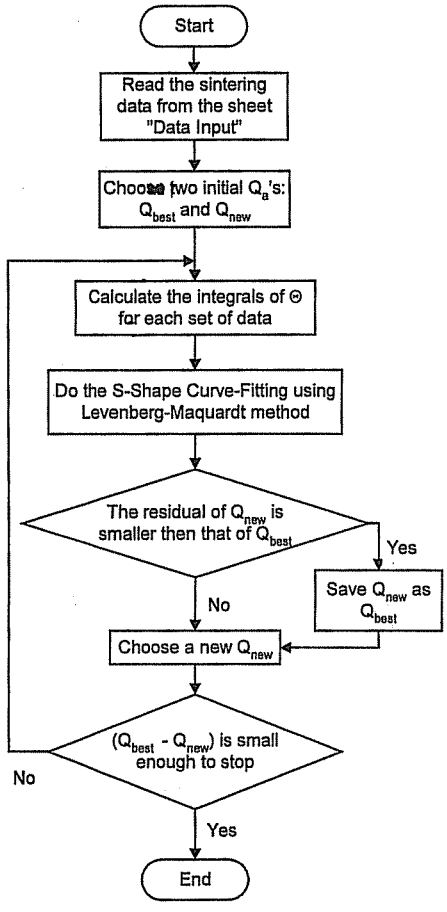

Figure 3. The flow chart of the *MSC* program. Where Q_{best} is the best apparent activation energy at the moment, and Q_{new} is the possibly better new apparent activation energy during iteration process.

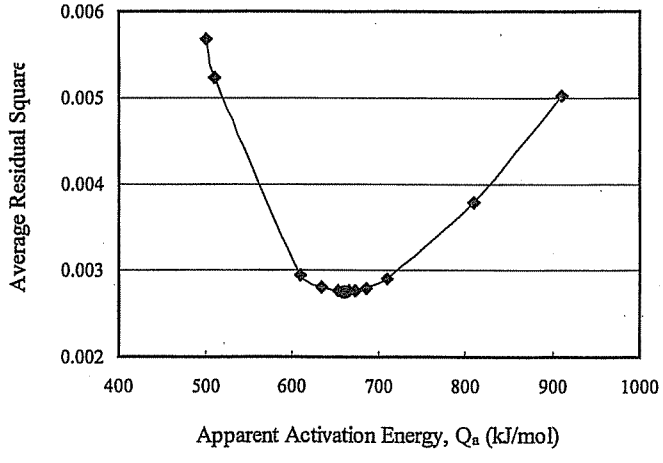

Figure 4. The average residual square vs apparent activation energy, calculated and displayed on the worksheet "Residual" by the Master Curve computer program. The optimum activation energy is 660.1 kJ/mol, which gives the minimum value of the average residual square in the figure.

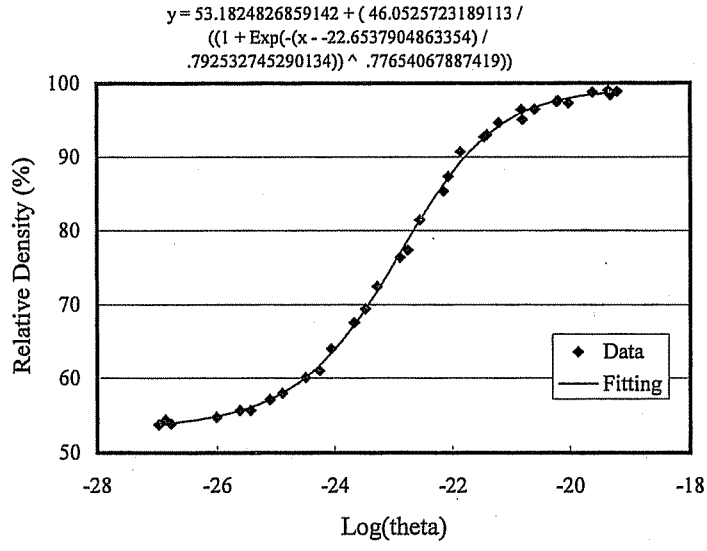

Figure 5. The Master Sintering Curve (*MSC*) of the zirconia samples, calculated and displayed on the worksheet "*MSC*" by the Master Curve computer program. The equation of the fitted S-curve is listed on the top of the plot.

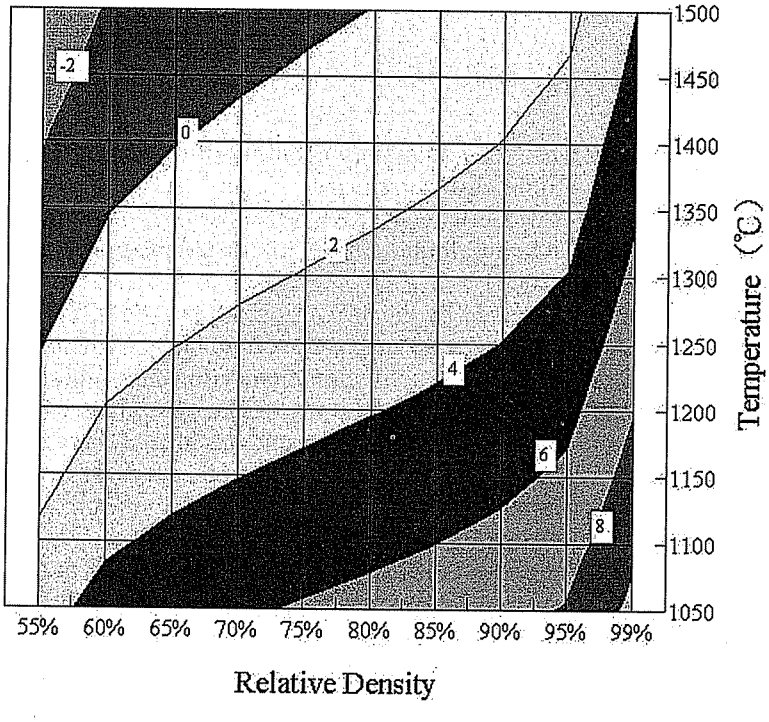

Figure 6. The contour map of the predictions of the sintering time (see Table 3) for a zirconia sample. The time is in logarithmic scale; for example, the line labeled 2 in the middle of the map indicates 10^2 seconds.

Table 3. The worksheets and their contents generated by the *MSC* program in *Excel*. The corresponding figures of the example (zirconia) in this paper are also listed.

Worksheets	Contents	Example
Data Input	Where users input the sintering data	Figure 2
Best Fit	Where program stores the results	—
Best Fit Tmp	Where program stores temporary data	—
Residual	Where shows the plot of average residual square vs several activation energies	Figure 4
MSC	Where shows the plot and equation of the final *MSC*	Figure 5
Predictions	Where program shows the predictions of sintering times needed for the samples to reach certain densities at various constant temperatures.	Table 2

DISCUSSIONS

Master sintering curve model had been proven adequately accurate in describing and predicting solid state sintering behavior of simple pure ceramics by Su and Johnson (1996, 1997). Independently, after redefining the shape of the *MSC*, we've worked on several common ceramic materials, such as Al_2O_3, ZnO, and TiO_2, and found that the modified model indeed worked very well as claimed (Teng and Chen, 2002).

Note that the apparent activation energy obtained by the *MSC* program will be different from that which is derived from the same sintering data by the original polynomial *MSC* method. For example, Su and Johnson (1996) found the apparent activation energy for their alumina sintering data was 487.6 kJ/mol, but for the same data we found it was 450 kJ/mol. However, the difference will only change the distribution of the $\log(\Theta)$ function, and has much less effect on the predicted density variation. In other words, the two apparent activation energies are the results of two models with different definitions of the shape of the *MSC*; although they both will predict the sintering results, but it's the modified one that gives the better predictions.

The curve-fitting algorithm was probably the most difficult part during the writing of the computer program. We chose to use the Levenberg-Marquardt method (Press *et al.*, 1992), the most popular and powerful algorithm of nonlinear curve-fitting, to derive the desired nonlinear S-shape curve (with five parameters, see Eq.(5)) based on the input data. It's not surprising that the number of data points will affect the final results dramatically. In the case of three sets

of data and each with only five to six data rows, the resolution of the *MSC* will be relatively poor, i.e. error > 1%, and the predictions will also be less accurate. In principle, the more data rows, the better the final results will be; but the running time of the program, however, will be much longer. By using the program, running on a standard Pentium II 300 PC for example, the time needed to construct a *MSC* has been reduced from a couple of hours down to less than five minutes, and without any human errors.

The input errors will lead to mistaken results. These include wrong data from experimental errors, typing errors, or from the breakdown of the *MSC* model when the assumptions are no longer correct, e.g., low temperature sintering (when surface diffusion becomes important), etc. Any deviations from the established *MSC* of a particular system will indicate the occurrence of some abnormal events, either in the sintering process or in the handling of data.

Another important application of the *MSC* computer program is that it can be a very helpful tool to design the best heating profile, in terms of efficiency and economy, to reach the desired final density. For example, Figure 6 is a contour map constructed by the prediction data in Table 2. In Figure 6 we know that in order to have a 98% relative density zirconia, we'll have to sinter the sample for 8 minutes at 1500°C, or 110 minutes at 1400°C, or 36 hours at 1300°C; while a sinter at 1200°C will be totally unacceptable, because it will take 42.8 days. Thus, in order to save time we may want to heat up the sample to over 1400°C as fast as possible; or in order to save money we may want to use a lower temperature. Similarly, we may use the program to design a special non-linear heating profile, so that the densification gradient is a constant, and so on.

CONCLUSIONS

The development of the master sintering curve model, specifically its predictive ability, is an important step toward the realization of the concept of "materials by design", i.e. to create the desired materials through designs based on our understanding of materials. The *MSC* computer program is a helpful tool; it not only accelerates the construction of *MSC* based on real sintering data, but also solves the fluctuation problem of the original model, and greatly improves the predictive accuracy of the model. The program saves time, eliminates possible human errors, and more importantly makes the designing of the best heating profile of sintering possible.

ACKNOWLEDGMENTS

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