MASTER SINTERING CURVE CONSTRUCTION SOFTWARE AND ITS APPLICATIONS

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ABSTRACT

Sintering behavior can be modeled using the simple but powerful concept of master sintering curves both for relative density and for grain size. In this study, the computer software was developed for automatic construction of master sintering curves from experimental data such as dilatometery test, density and/or grain size measurement. This software consists of three steps for both for relative density and for grain size: (1) finding activation energies which governs master sintering curves, (2) automatically constructing the master sintering curves for given or calculated activation energies and (3) finding parameters for predicting relative density and/or grain size. Powders dealt with in this study include 17-4 PH stainless steel, 316L stainless steel, pure nickel, niobium, molybdenum, various tungsten heavy alloys and zirconia. In this paper, applications of master sintering curves will be discussed such as optimizing sintering cycles and furnace monitoring for consistent production.

INTRODUCTION

The master sintering curve model in densification is a recently developed sintering model with the assumption of only one dominant diffusion mechanism by Su and Johnson [1], which can adequately predict sintering results and is independent of the heating history. Basically this concept of master sintering curve can be applied to various material systems [2]. In master sintering curve model in densification, only one physical parameter, which is apparent activation energy, is used. Therefore the determination of this value is very important [3]. Several research works have been done recently especially on densification [4-7]. Even though the master sintering curve model has a big assumption and looks empirical, it has powerful potential on sense of database and field application.

In this study, we applied master sintering curve model of densification to various material system based on simple power law model. We extended the concept of master sintering curve into grain growth. Furthermore, we considered integration of two master sintering curves in densification and grain growth.

Finally, we proposed three beautiful applications of master sintering curves for powder metallurgy industry.

MATER SINTERING CURVE FOR DENSIFICATION

Three important parameters are used for constructing master sintering curve of densification: (1) densification parameter Ψ [2], (2) sinter density difference-ratio parameter Φ and (3) work of sintering Θ_ρ. The definitions of these two parameters are as follows:

$$\Psi = \frac{\rho - \rho_0}{1 - \rho_0} \tag{1}$$

$$\Phi = \frac{\rho - \rho_0}{1 - \rho} \tag{2}$$

$$\Theta_\rho = \int_0^t k_0 \exp\left[-Q_\rho / RT\right] dt \tag{3}$$

Simple power law model is introduced to explain the relation between sinter density difference-ratio parameter Φ and work of sintering Θ_ρ as follows.

$$\Phi = \frac{\rho - \rho_0}{1 - \rho} = \left(\frac{\Theta_\rho}{\Theta_{ref}}\right)^{n} \tag{4}$$

The following equation is logarithmic form of equation (4), which shows linear relation between $\ln\Phi$ and $\ln\Theta_\rho$.

$$\ln\Phi = \ln\left[\frac{\rho - \rho_0}{1 - \rho}\right] = n \ln\left(\frac{\Theta_\rho}{\Theta_{ref}}\right) = n\left(\ln\Theta_\rho - \ln\Theta_{ref}\right) \tag{5}$$

where n is a slop or power law exponent, that is rate of increment of $\ln\Phi$ during sintering process and $\ln\Theta_{ref}$ is logarithmic value of work of sintering $\ln\Theta_\rho$ at $\rho=(\rho_0+1)/2$, that is densification parameter Ψ of 0.5. Figure 1 shows an example for linear form of master sintering curve. The values for coefficient of determination, R^2 are almost one, which means that the proposed model can predict densification behavior during sintering very well.

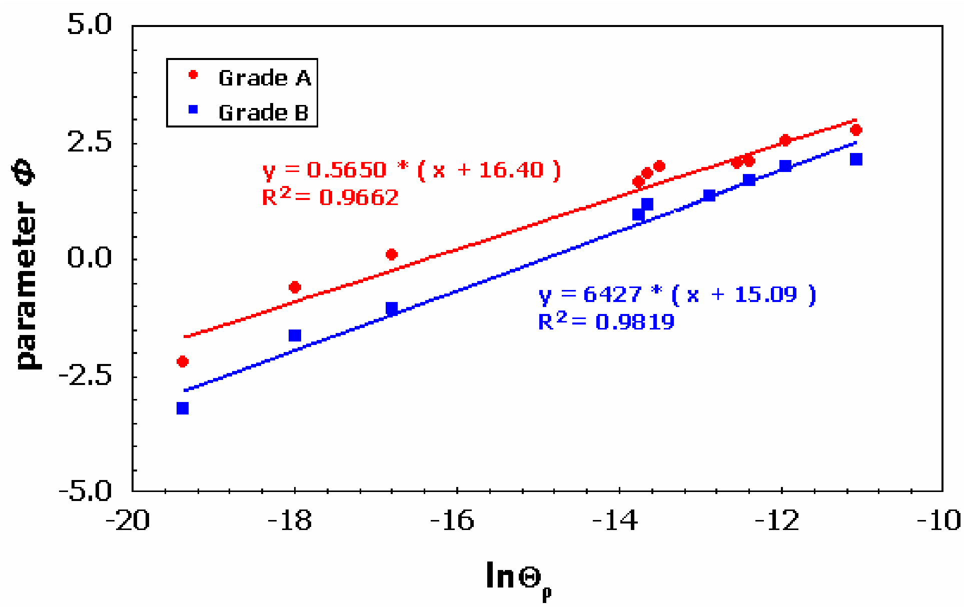


Figure 1. Linear form of master sintering curve with molybdenum

Based on linear form of master sintering curve, equation for densification parameter Ψ can be easily derived into the following form, which is exactly one of sigmoid function.

$$\Psi = \frac{\rho - \rho_0}{1 - \rho_0} = \frac{1}{1 + \exp\left[- \frac{\ln \Theta_\rho - a}{b} \right]} \tag{6}$$

where $a = \ln\Theta_{ref}$ and $b = 1/n$. Based on this sigmoid equation for densification parameter Ψ, CISP database for densification has 8 different materials including 17-4 PH stainless steel, 316L stainless steel, pure nickel, niobium, molybdenum, two different tungsten heavy alloys and zirconia. Figure 2 shows CISP database of eight different master sintering curves for densification.

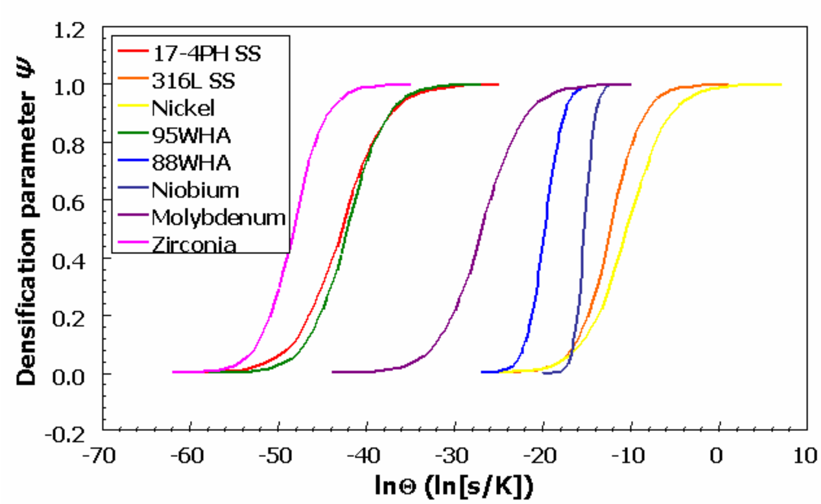
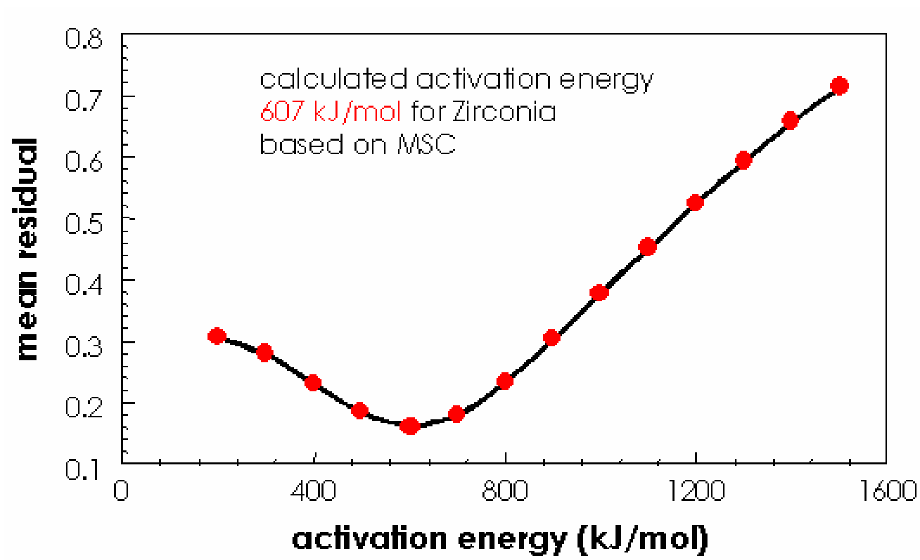


Figure 2. CISP database of 8 different master sintering curves for densification

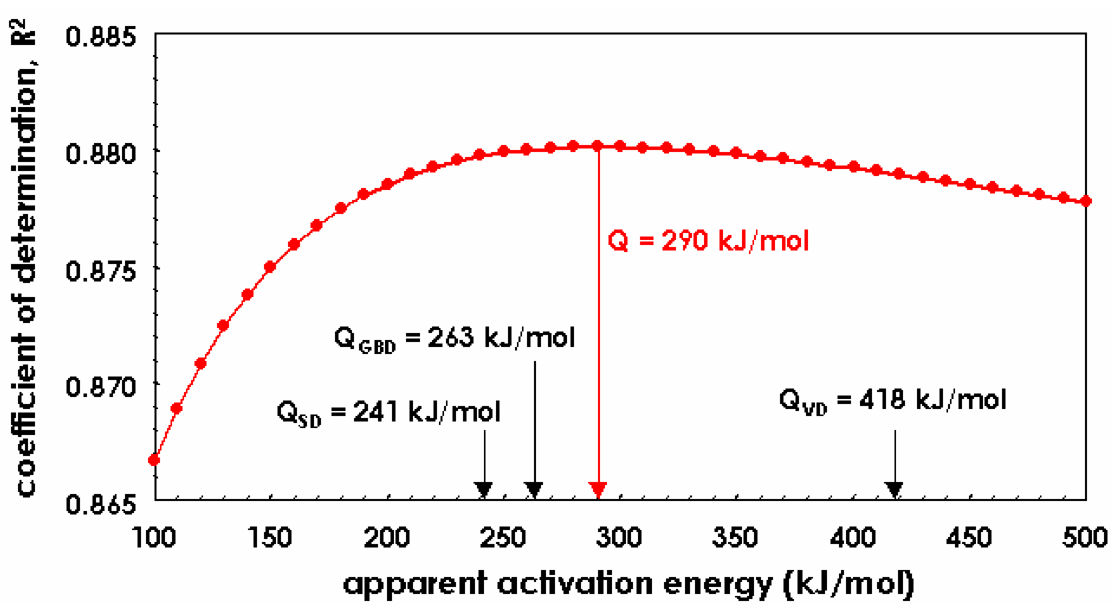
We proposed two different kinds of methods to determine apparent activation energy for master sintering curve of densification: (1) by minimizing mean residual and (2) by regression based on statistics. The mean residual used in method (1) is defined as follows

$$\text{Mean Residual} = \sqrt{\frac{1}{\rho_{\text{final}} - \rho_{\text{initial}}} \int_{\rho_{\text{initial}}}^{\rho_{\text{final}}} \frac{\sum_{i=1}^{N} \left(\frac{\Theta_i}{\Theta_{\text{avg}}} - 1 \right)^2}{N} d\rho} \tag{7}$$

Figure 3 shows two plots for determining apparent activation energies.



(a) Method by minimizing mean residual for zirconia



(b) Method of regression based on statistics for molybdenum

Figure 3. Two different methods for determining apparent activation energies

Figure 4 shows time-temperature-density plot for molybdenum. It will be useful for engineer to design initial sintering cycle to considering the final sinter density for given sintering system.

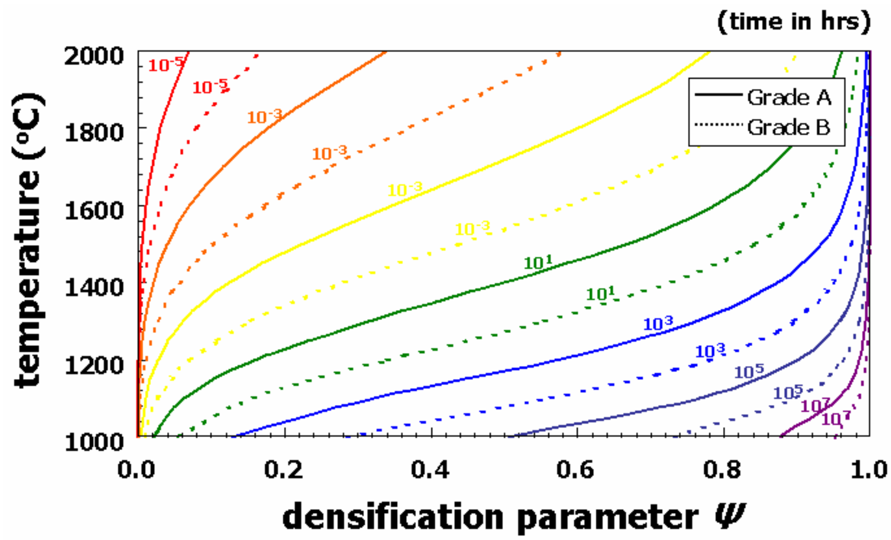


Figure 4. Time-temperature-density plot for molybdenum

MATER SINTERING CURVE FOR GRAIN GROWTH

One can develop the master sintering curve for grain growth from the classic grain growth model, which can be expressed three different equations: (1) differential form, [2]

$$G' = \frac{k_0 \exp[-Q_G/RT]}{G^2} \tag{8}$$

(2) integral form

$$G^3 = G_0^3 + 3\int_0^t k_0 \exp[-Q_G/RT]\, dt \tag{9}$$

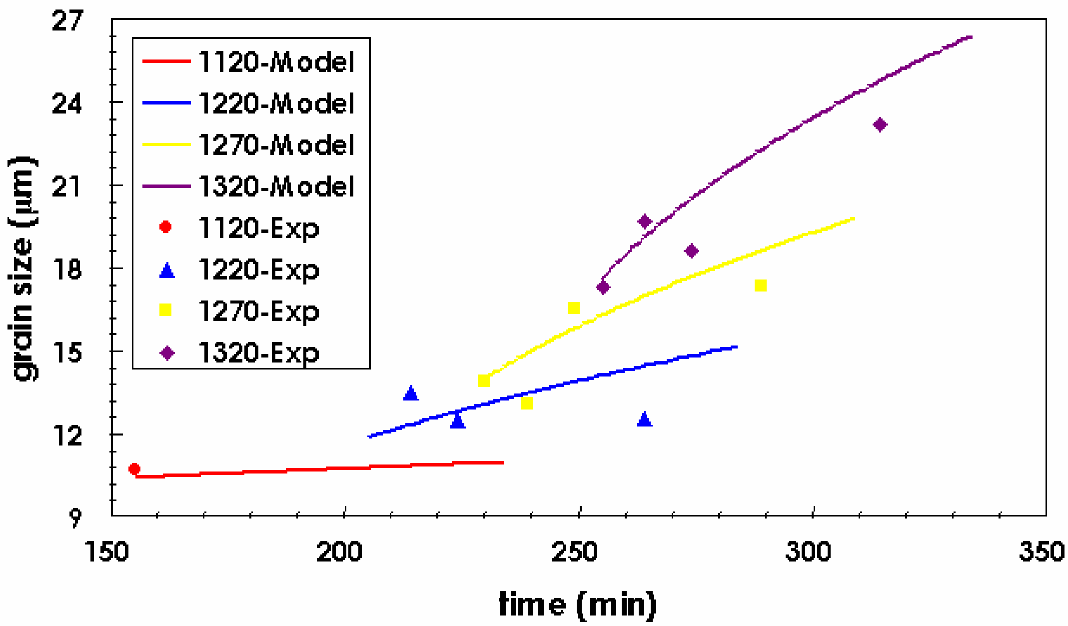
and (3) master sintering form

$$G = \sqrt[3]{G_0^3 + 3\Theta_G} \tag{10}$$

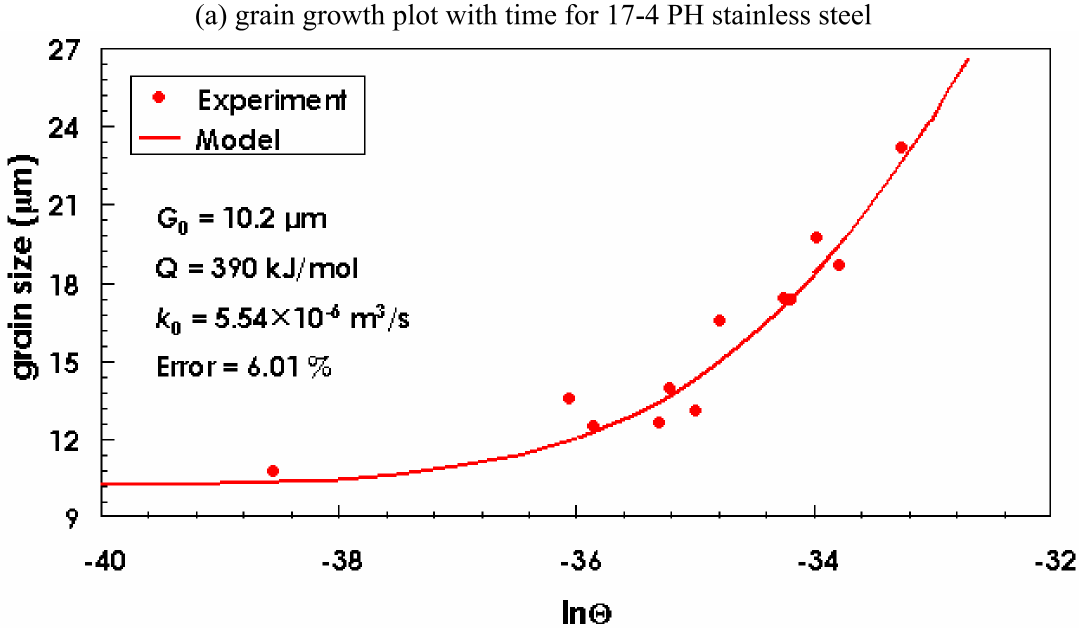
where

$$\Theta_G = \int_0^t k_0 \exp[-Q_G/RT]\, dt \tag{11}$$

Two parameters k_0 and Q_G can be determined by curve fitting from experimental data. Figure 5 shows two different plots of grain growth for 17-4 PH stainless steel. This master sintering curve is fitted with maximum relative error of 6.01 % for grain growth.



(a) grain growth plot with time for 17-4 PH stainless steel



(b) grain growth plot with master sintering form for 17-4 PH stainless steel

Figure 5. Two different forms of grain growth plots for 17-4 PH stainless steel

CISP database for grain growth has 5 different materials including 17-4 PH stainless steel, molybdenum and 3 different tungsten heavy alloys. Figure 6 shows time-temperature-grain size plot for 17-4 PH stainless steel. It will be useful for engineer to design initial sintering cycle to considering the final grain size for given sintering system.

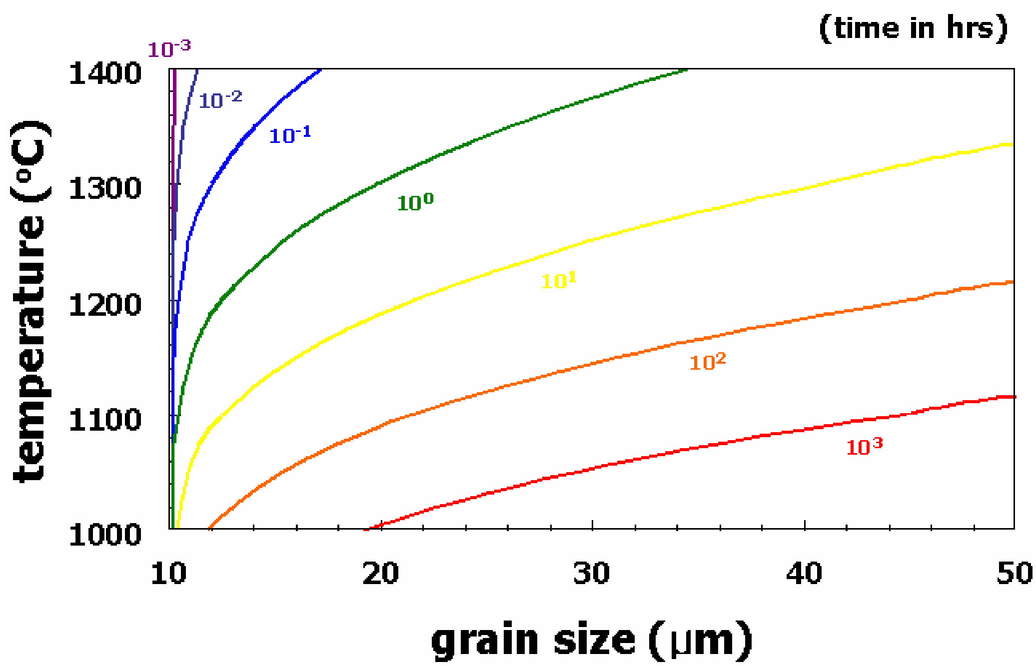


Figure 6. Time-temperature-grain size plot for 17-4 PH stainless steel

INTEGRATION OF TWO MATER SINTERING CURVES

It is very interesting to integrate two master sintering curves for densification and grain growth. Figure 7 shows an example of integration for 17-4 PH stainless steel. In this integration, upper and lower curves are obtained from upper and lower sintering temperatures, which envelopes the possible area of the final sinter density and grain size pair after sintering process. This plot will be useful for engineer to design the pair of sinter density and grain size for given sintering system.

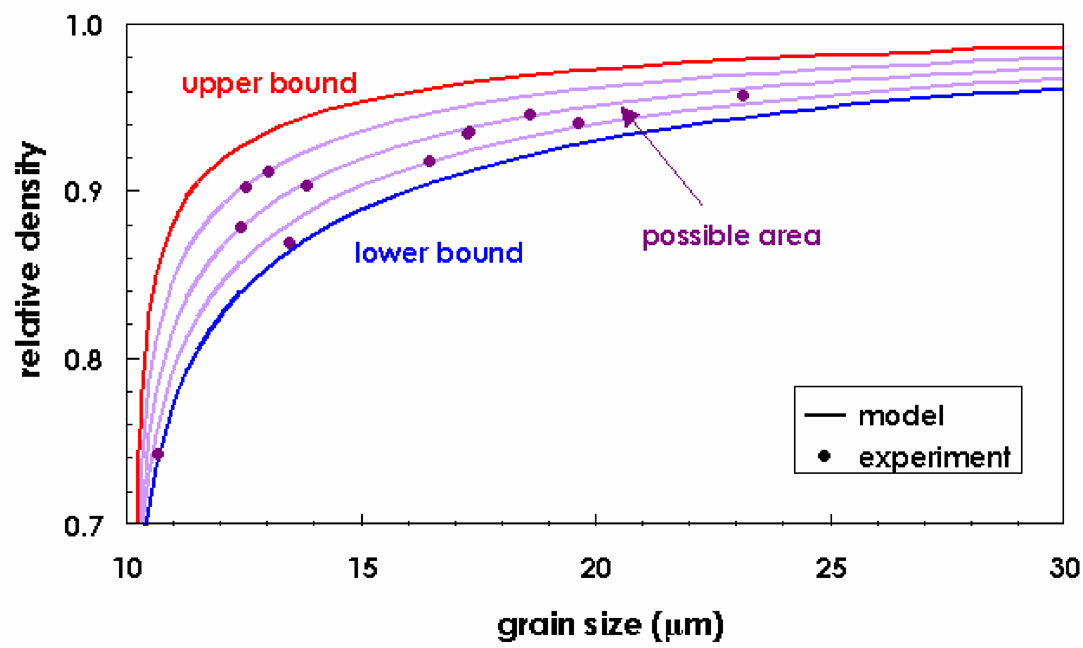
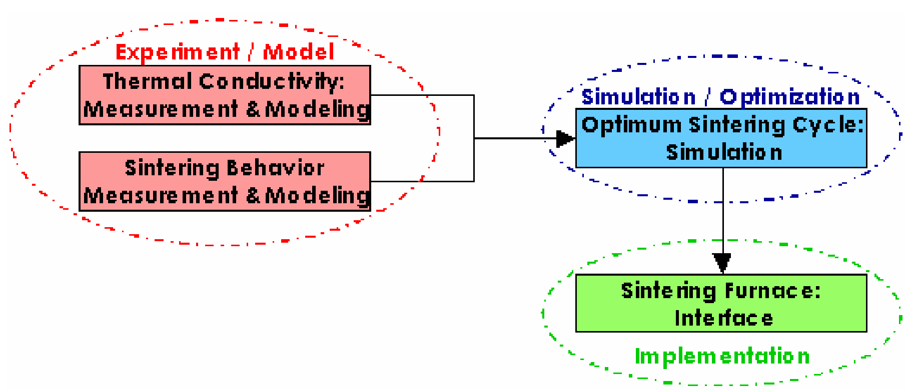


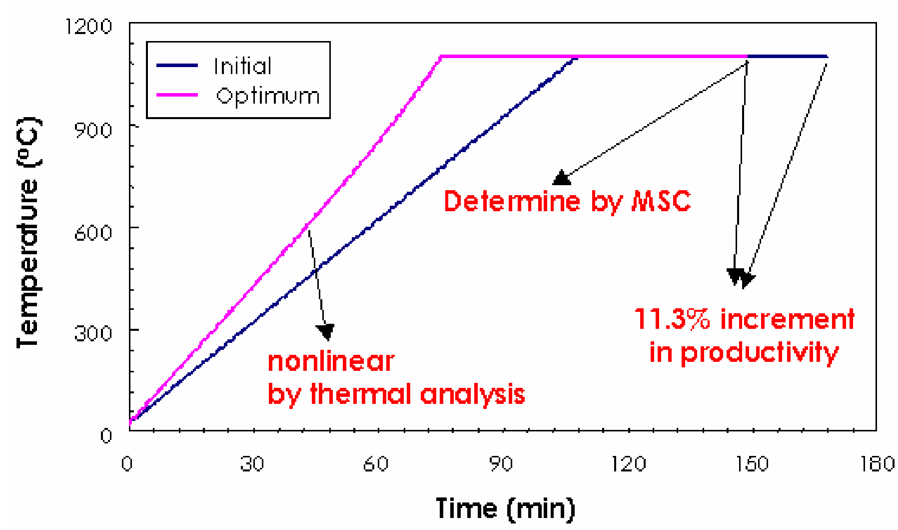
Figure 7. Integration of two master sintering curves for 17-4 PH stainless steel

APPLICATIONS

Optimum Sintering Cycle: For given specification for final sinter density, the productivity can increase based on thermal analysis and master sintering curve. The overall algorithm for this optimization consists of (1) calculation of density based on master sintering curve, from thermal history during sintering process, (2) calculation of thermal conductivity based on density dependent model for thermal conductivity, (3) calculation of maximum ramp speed to get uniform temperature distribution within part based on thermal analysis and (4) calculation of holding time to obtain the given specification for final sinter density based on master sintering curve. Figure 8 shows the schematic diagram for algorithm for optimum sintering cycle and its example with nickel. In this case, the productivity can increase by 11.3 %.



(a) Algorithm for optimum sintering cycle



(b) Example for optimum sintering cycle with nickel

Figure 8. Algorithm and example with nickel for optimum sintering cycle

Monitoring System: Towards goal of consistent density and grain size after sintering process, the following monitoring system can be applied to sintering furnace: (1) establishment of database for master sintering curves of density and grain size and thermal conductivity, (2) collection of thermal history data from furnace by data acquisition, (3) calculation of work of sintering, density, grain size and thermal conductivity based on database, and (4) control of ramp speed and starting and ending times for holding temperature. Figure 9 shows the algorithm, monitor panel and sintering cycle for monitoring system based on master sintering curve.

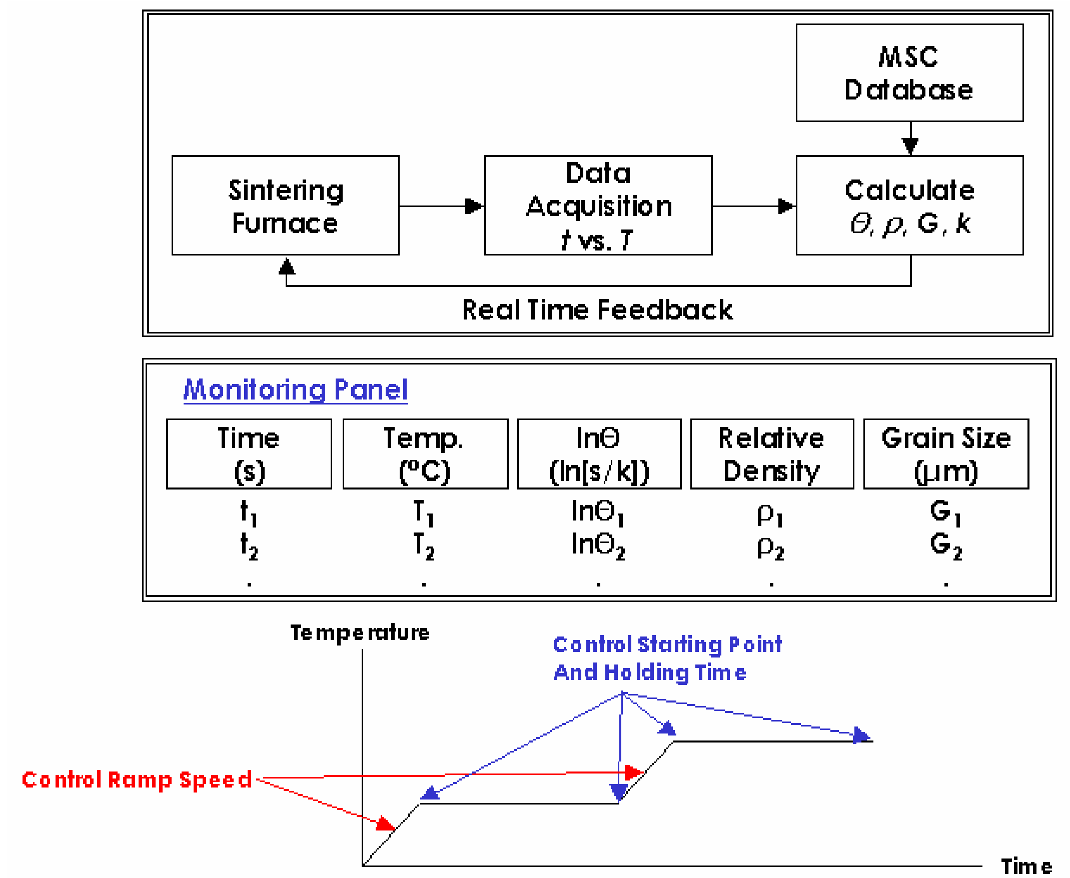
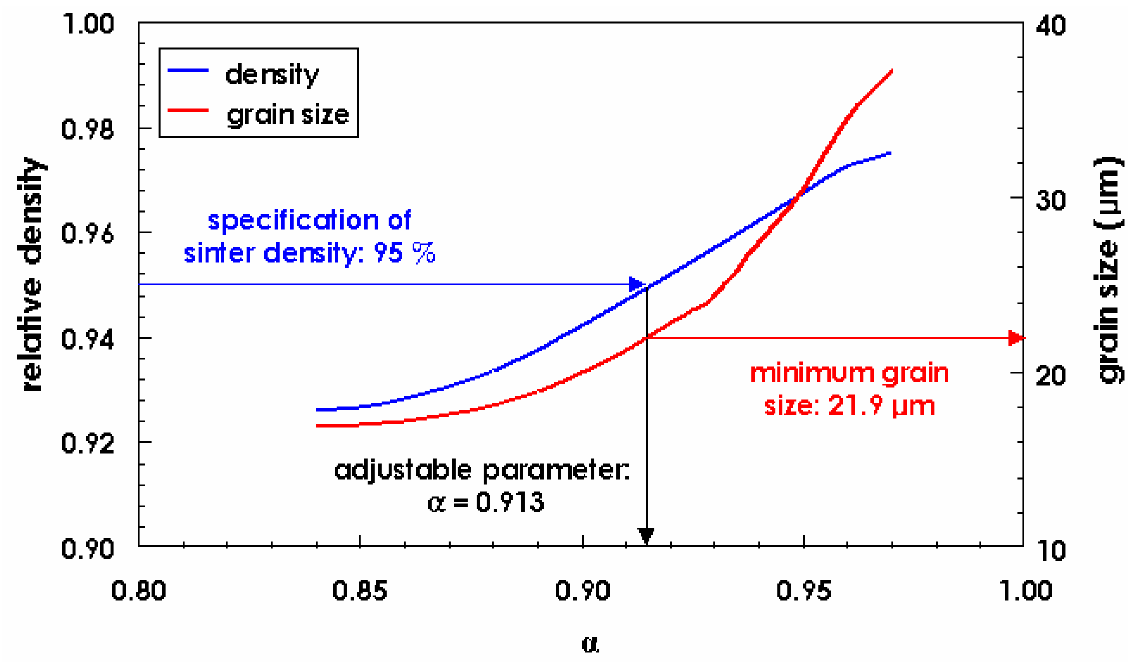


Figure 9. Schematic diagram for monitoring system based on master sintering curve

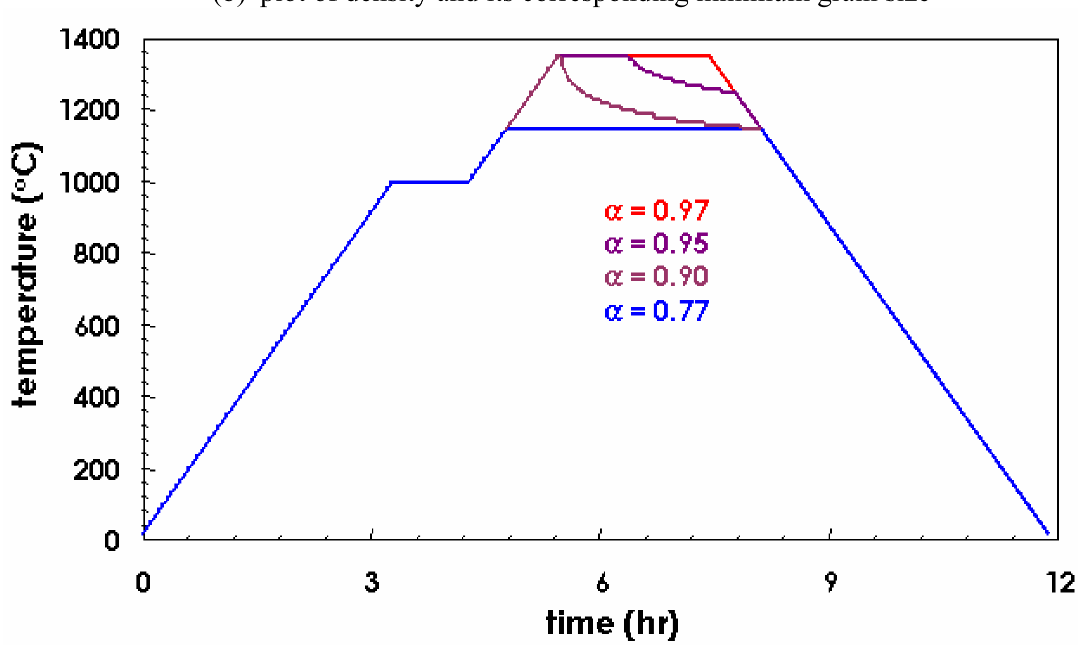
Minimum Grain Size: Usually minimum grain size is required for given specification of sinter density. To obtain maximum density and minimum grain size, the following objective function F is proposed.

$$F = \alpha\left[\frac{\Delta\rho}{\rho}\right] + (1-\alpha)\left[-\frac{\Delta G}{G}\right] \tag{12}$$

where α is adjustable parameter. Figure 10 shows an example for maximum density and minimum grain size with 17-4 stainless steel. For example, the minimum grain size will be 21.9 μm if the specification of density is 95 %. Figure 10(b) show the corresponding sintering cycle by matching the value of adjustable parameter α.



(b) plot of density and its corresponding minimum grain size



(b) Corresponding sintering cycle

Figure 10. Minimum grain size for given specification of the final sinter density and corresponding sintering cycle with 17-4 PH stainless steel

CONCLUSION

In this study, the computer software was successfully developed for automatic construction of master sintering curves for densification and grain growth. This software consists of three parts: (1) finding activation energy, conduction of master sintering curve and sigmoid function plot for densification, (2) finding activation energy and conduction of master sintering curve for grain growth and (3) optimization of sintering cycle for maximizing productivity and minimizing grain size for give specification of sinter density. Powders dealt with in the developed software included 17-4 PH stainless steel, 316L stainless steel, pure nickel, niobium, molybdenum, various tungsten heavy alloys and zirconia. Applications of master sintering curves proposed in this paper will be useful in powder metallurgy industry. Figure 11 shows the overall flow chart for developed software.

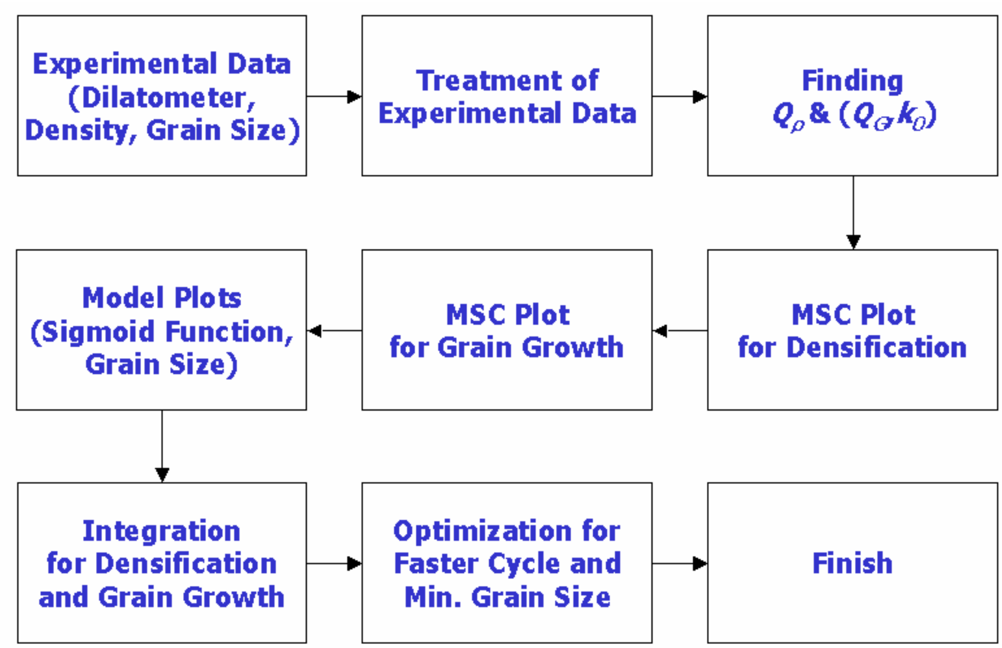


Figure 11. Overall flow chart of construction software for master sintering curve

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