Modeling of Densification during Hot Pressing of Fe-Cu-Co-Ni-W-Sn Powder Mixture

Kyong Jun An
Korea Institute of Industrial Technology, Songdo-Dong 7-47, Yonsoo-Gu, Incheon, 406-840, Korea

The master sintering curve (MSC) is an effective method to predict densification during sintering or hot pressing. In MSC, the sintered density is a unique function of the integral of a temperature function over time, irrespective of the heating path. As a practical application of the MSC, the Fe-based powder mixture consisting of 6 different metallic materials was used since it is one of the most common soft metal-bonds of the diamond tool industry. The effective activation energy of sintering was found to be 200.2 kJ/mol. It suggests that the dominant densification mechanism for the present metallic powder was the diffusion of Cu since the effective activation energy was in good agreement with that of self diffusion in Cu from literature. Three data sets having different heating rates merged onto a single curve when the density was plotted as a logarithmic function of \( t \), the integral of temperature function over time. Thus, the density versus \( t \) profile can be used to predict the final density of Fe-based metallic powder at a given pressure regardless of heating history. The study was also extended to a range of pressures from 9.7 MPa to 58.1 MPa to generate the pressure-assisted master sintering surface (PMSS). [doi:10.2320/matertrans.M2011056]

(Received February 15, 2011; Accepted March 11, 2011; Published May 18, 2011)

Keywords: iron-based metallic powder, pressure-assisted master sintering surface, master sintering curve, self diffusion of Cu

1. Introduction

Diamond tools for cutting, grinding or polishing stone and concrete consist of a steel shank and a segment. The segment is made by sintering of metal-bond powder after mixing with diamond grits, and attached to the steel shank by brazing or laser welding. The wear resistance of the metal-bond has to be adjusted to the wear speed of the diamond to use the diamond capacity completely. If the metal-bond of the segment wears faster than the diamond, the diamond capacity is not completely used since the diamond grits are easily pulled-out. If it is too hard and wears more slowly, the available cutting edges of diamond grains became reduced. Thus, a relatively soft metal-bond was known to offer better diamond retention and be used for hard stone. Fe-based metallic powder is one of the most common soft metal-bonds of the diamond tool industry. The higher sintered density of diamond tools, comparing to W-based bond used as hard bond.

Besides materials parameter, the sintered density as a process parameter has also a significant effect on the performance of diamond tool. The higher sintered density at a given metal bond shows the greater bond strength, hardness and wear resistance. That can retard the exposure of new diamond cutting edges and make diamond grits dull. In contrast, the lower sintered density has not enough strength to retain the diamond grits that can be pulled-out before fully used. Since either case reduces the efficiency during grinding or cutting process, controlling density of metal-bond is one of the key issues to the commercial success of diamond tools.

Hot pressing is an effective method to fabricate the segments of diamond tools. Metal-bond powder can be densified at lower temperature and at shorter cycle time by hot pressing than those required by conventional sintering. Several mechanisms were suggested to model the densification during hot pressing.\(^1\)\(^-\)\(^4\) They reported that densification occurs by enhanced diffusion under the influence of effective stress. However, the effective stress was not precisely known with respect to the applied pressure and porosity. Due to this uncertainty, the models did not contain the time dependence of densification but could only approximate the instantaneous rate.

As an alternative to mechanistic modeling, the master sintering curve (MSC) was developed by Su and Johnson,\(^5\) to characterize the sintering behavior for a given powder regardless of the heating history. The formulation of MSC was derived from a combined stage sintering model which includes both volume and grain-boundary diffusion mechanisms.\(^5\)\(^,\)\(^7\) The instantaneous densification rate in the model is

\[
\frac{d\rho}{dt} = \frac{3\gamma\Omega k}{kT} \left( \frac{\Gamma_v D_v}{G^3} + \frac{\Gamma_g D_g}{G^4} \right)
\]

where \( \gamma \) is the surface energy, \( \Omega \) the atomic volume, \( k \) the Boltzmann constant, \( T \) the absolute temperature, \( G \) the mean grain diameter, \( D_v \) and \( D_g \) the coefficients of volume and grain boundary diffusions, respectively and \( \delta \) the width of the grain boundary. \( \Gamma_v \) and \( \Gamma_g \) are (non-constant) lumped scaling parameters that relate various geometric features, the driving force for sintering, and the mean diffusion distance to the grain size.

This equation can be rearranged for either grain boundary or volume diffusion such that all terms that are not explicitly functions of temperature are carried to the left hand side, and then integrated, as follows:

\[
\frac{k}{\gamma\Omega D_0} \int_{r_0}^{r} \frac{G^7}{3\rho T} \, dr = \int_{0}^{1} \frac{1}{T} \exp \left( -\frac{Q}{RT} \right) \, dr
\]

where \( Q \) is the apparent activation energy, \( D_0 \) is the pre-exponential term for the diffusion coefficient (including \( \delta \) in the case of grain boundary diffusion), \( R \) is the gas constant, and \( n = 3 \) or 4 for volume or grain boundary diffusion, respectively.

A mechanistic model would attempt to integrate both sides of this equation. For the MSC, the measured density is plotted as a function of the right hand side, hereafter denoted \( \theta \). If a single mechanism is responsible for densification, the sintered density can be predicted from the curve irrespective of the heating path.
However, empirical models of MSC in early studies were defined using a single kind of powder or a major powder with a little amount of sintering additives. It is of interest to see whether sintering behavior of more than 2 different powder mixtures can be predicted by MSC model.

The motivation of the present research was to provide MSC of Fe-based metallic powder to industrial users, since it is one of the most common metallic binders in the diamond tool industry. The objective of the present study was to determine whether the concept of the MSC can be applicable to the hot pressing of the powder mixture consisting of 6 different component materials and to establish the pressure-assisted master sintering surface (PMSS).

2. Experiments

For hot pressing, the powder of 6 different component materials included 35% Fe, 21% Cu, 15% Co, 14% Ni, 13% W and 2% Sn in weight, which is a metal bond used to make commercial diamond grinding wheels. Approximately 25 g of powder was loaded into the die assembly, and then a pressure was applied by a singly acting ram up to the desired level. The pellet in the die assembly was 25 mm in diameter and thickness, relatively, suggesting ~52% of green density. The chamber was evacuated by a mechanical pump to 50 mtorr and backfilled with high purity Ar gas (99.98%). The pressure of Ar gas was maintained between 30 and 50 kPa. A dilatometer determined the linear shrinkage from the motion of the pressing ram during hot pressing.

Two different heating and pressure schedules were used. First, 29 MPa pressure was applied at room temperature and then furnace was heated to 1000°C without an isothermal hold, in separate runs at different heating rates of 0.167, 0.333, and 0.5°C/s.

Secondly, hot pressing using applied pressures from 9.7 to 58.1 MPa were conducted. Pressure was applied at room temperature and a constant heating rate of 0.333°C/s was maintained from room temperature to 1000°C without an isothermal hold.

The microstructures of specimens were examined by scanning electron microscopy on fracture surfaces. Bulk and apparent densities were determined by the Archimedes method. For this measurement, specimens were immersed in water, boiled for 10 min and cooled to room temperature before determining the submerged and saturated masses.

3. Results and Discussion

A test of the applicability of the MSC to hot pressing of metallic powder mixture was made by comparing the densification curves hot pressed at 29 MPa with different heating rates of 0.167, 0.333, and 0.5°C/s. The density as a function of temperature is shown in Fig. 1. The densification curves were computed from the dilatometer trace during heating to 1000°C. Here the specimen hot pressed at higher the heating rate shows the lower densification at a given temperature. When the density is plotted as a function of $\ln(\Theta)$, where $\Theta$ is defined as the integral of the right hand side of eq. (2), the three data sets merge onto a single curve (Fig. 2), which is a constant pressure trace on the pressure-assisted master sintering surface (PMSS). Figure 2 indicates that the time-temperature integral values, $\Theta$, can be used to predict the density regardless of a heating path, since there exists a unique function between $\Theta$ and sintering density. Therefore, the MSC concept can be applied to metallic powder mixture of many different component materials.

The activation energy, $Q$ was also estimated using the right hand side of eq. (2). When the best estimation of $Q$ was made, the relative density profiles versus $\ln(\Theta)$ converge into a single curve as shown in Fig. 2, as well as the mean of residual squares (sum of residual squares divided by total number of data points) becomes a minimum. The estimated activation energy was found to be 200.2 kJ/mol in Fig. 3. This was in good agreement with that of self diffusion in Cu from literature, where it was reported as 197 kJ/mol. This suggests that the dominant densification mechanism for the
powder mixture (35% Fe, 21% Cu, 15% Co, 14% Ni, 13% W and 2% Sn in weight) was the self diffusion of Cu. It should be noted that the activation energies of the self diffusion in the other materials are far different from that in Cu. For instance, those from literature\textsuperscript{11,12} are 251 kJ/mol for α-Fe, 268 kJ/mol for Co, 284 kJ/mol for Ni, 585 kJ/mol for W, and 107 kJ/mol for Sn.

Sn is one of the well known sintering additives in practical application of powder metallurgy due to its wettability and liquid-phase sintering property.\textsuperscript{13} It was also reported that the effective activation energy decreases with increasing the amount of adding liquid-phase element.\textsuperscript{14,15} However, the effective activation energy for the present research was equivalent to that of self diffusion in Cu and no further decrease was found by adding Sn. This might be due to the fact that the 2 mass% Sn was not enough to make measurable difference of the apparent activation energy.

Although the concept of MSC originally developed\textsuperscript{5} for the densification of pure materials, it was also found to be applicable to powder mixture for the present research, which agreed well with the literature.\textsuperscript{9,10} S. J. Park et al. found that the grain growth during sintering of W-Ni-Fe alloys can be successfully transformed into MSC form.\textsuperscript{9} K. J. An et al. developed PMSS using SiN-Y\textsubscript{2}O\textsubscript{3}-Al\textsubscript{2}O\textsubscript{3} powder mixture.\textsuperscript{10} It might be due to the fact that the MSC concept is based on the single value of activation energy in order to make all the data placed on a single curve regardless of heating path. As long as a dominant mechanism does not vary during the whole sintering process even using a powder mixture, there exists a single value of activation energy, and therefore MSC can be applicable.

Figure 4(a)–(c) are the fracture surfaces of the specimens made at the constant heating rate of 0.5°C/s, 0.333°C/s and 0.167°C/s. Peak temperature was 1000°C with no hold.

Sn is one of the well known sintering additives in practical application of powder metallurgy due to its wettability and liquid-phase sintering property.\textsuperscript{13} It was also reported that the effective activation energy decreases with increasing the amount of adding liquid-phase element.\textsuperscript{14,15} However, the effective activation energy for the present research was equivalent to that of self diffusion in Cu and no further decrease was found by adding Sn. This might be due to the fact that the 2 mass% Sn was not enough to make measurable difference of the apparent activation energy.

Although the concept of MSC originally developed\textsuperscript{5} for the densification of pure materials, it was also found to be applicable to powder mixture for the present research, which agreed well with the literature.\textsuperscript{9,10} S. J. Park et al. found that the grain growth during sintering of W-Ni-Fe alloys can be successfully transformed into MSC form.\textsuperscript{9} K. J. An et al. developed PMSS using SiN-Y\textsubscript{2}O\textsubscript{3}-Al\textsubscript{2}O\textsubscript{3} powder mixture.\textsuperscript{10} It might be due to the fact that the MSC concept is based on the single value of activation energy in order to make all the data placed on a single curve regardless of heating path. As long as a dominant mechanism does not vary during the whole sintering process even using a powder mixture, there exists a single value of activation energy, and therefore MSC can be applicable.

Figure 5(a)–(c) are the fracture surfaces of the specimens made at the constant heating rate of 0.5°C/s, 0.333°C/s and 0.167°C/s. Peak temperature was 1000°C with no hold.

Although the concept of MSC originally developed\textsuperscript{5} for the densification of pure materials, it was also found to be applicable to powder mixture for the present research, which agreed well with the literature.\textsuperscript{9,10} S. J. Park et al. found that the grain growth during sintering of W-Ni-Fe alloys can be successfully transformed into MSC form.\textsuperscript{9} K. J. An et al. developed PMSS using SiN-Y\textsubscript{2}O\textsubscript{3}-Al\textsubscript{2}O\textsubscript{3} powder mixture.\textsuperscript{10} It might be due to the fact that the MSC concept is based on the single value of activation energy in order to make all the data placed on a single curve regardless of heating path. As long as a dominant mechanism does not vary during the whole sintering process even using a powder mixture, there exists a single value of activation energy, and therefore MSC can be applicable.

Figure 4(a)–(c) are the fracture surfaces of the specimens made at the constant heating rate of 0.5°C/s, 0.333°C/s and 0.167°C/s. Peak temperature was 1000°C with no hold.

Figure 5(a)–(c) are the fracture surfaces of the specimens made at the constant heating rate of 0.5°C/s, 0.333°C/s and 0.167°C/s. Peak temperature was 1000°C with no hold.

Although the concept of MSC originally developed\textsuperscript{5} for the densification of pure materials, it was also found to be applicable to powder mixture for the present research, which agreed well with the literature.\textsuperscript{9,10} S. J. Park et al. found that the grain growth during sintering of W-Ni-Fe alloys can be successfully transformed into MSC form.\textsuperscript{9} K. J. An et al. developed PMSS using SiN-Y\textsubscript{2}O\textsubscript{3}-Al\textsubscript{2}O\textsubscript{3} powder mixture.\textsuperscript{10} It might be due to the fact that the MSC concept is based on the single value of activation energy in order to make all the data placed on a single curve regardless of heating path. As long as a dominant mechanism does not vary during the whole sintering process even using a powder mixture, there exists a single value of activation energy, and therefore MSC can be applicable.

Figure 4(a)–(c) are the fracture surfaces of the specimens made at the constant heating rate of 0.5°C/s, 0.333°C/s and 0.167°C/s. Peak temperature was 1000°C with no hold.

Figure 5(a)–(c) are the fracture surfaces of the specimens made at the constant heating rate of 0.5°C/s, 0.333°C/s and 0.167°C/s. Peak temperature was 1000°C with no hold.
plotted as a function of temperature for a constant heating rate of 0.333°C/s using different applied pressures of from 9.7 to 58.1 MPa. The densification curves exhibit a significant increase with pressure. Figure 7 shows the constant pressure contours of the PMSS constructed from the densification data displayed in Fig. 6. To develop other view, points were picked at the relative density levels of 0.7, 0.75, ..., 0.9 for each of the constant pressure curves and multiple regressing analysis was done to obtain an empirical model of the PMSS. The resulting surface is shown in Fig. 8. Figure 9 shows a constant density contour plot of the PMSS, along with the data points from which it was obtained, projected onto the pressure-ln(\theta) plane. Having determined the PMSS, it now is possible to predict the density of a specimen hot pressed at any pressure from 9.7 MPa to 58.1 MPa if the temperature-time trajectory is known. Also, one can specify the time-temperature excursion at any pressure in this range to achieve a given density.

4. Conclusions

The concept of MSC was applied to the hot pressing of metallic powder mixture that consisted of 6 different component materials including 35% Fe, 21% Cu, 15% Co, 14% Ni, 13% W and 2% Sn in weight. When the density was plotted as a logarithmic function of \theta, the three data sets merged onto a single curve, in which the activation energy was estimated as 200.2 kJ/mol. This was in good agreement with that of self diffusion in Cu from literature, suggesting that the dominant densification mechanism for the present powder mixture was the self diffusion of Cu. Thus, the density versus \theta profile can be used to predict the final density at a given pressure regardless of heating history. The study was extended to a range of pressures 9.7 MPa to 58.1 MPa to generate the PMSS. This surface enables the prediction of the final density at a fixed pressure and an arbitrary heating history.

Acknowledgement

A major part of this research was supported by a subcontract of the ‘Components and Materials Technology Development Project’. The author would like to thank the Korea Evaluation of Industrials Technology (KEIT) as well as LG Innotek for the financial assistance and their encouragement throughout this work.

REFERENCES