Densification During Sintering of Formic Acid Treated Copper Powder

A. S. Reshamwala* and G. S. Tendolkar*

ABSTRACT

This paper attempts to investigate the mechanism associated with the densification of compacts made from (a) pure copper powder and (b) copper powder treated with aqueous formic acid prior to compaction. Isothermal sintering was carried out in hydrogen atmosphere in the temperature range 775° to 950°C. It has been proposed that densification in compacts made from formic acid treated powders occurs mainly by plastic flow aided by evaporation condensation mechanism. The conclusion is based on kinetic data supported by studies on linear shrinkage, variation in porosity and microstructural changes. For pure (untreated) powder compacts the mechanism associated with densification is confirmed to be volume diffusion.

INTRODUCTION

In an earlier publication1) the present authors have shown that the presence of copper formate on the surface of copper powder formed as a result of interaction with aqueous formic acid at room temperature and its subsequent decomposition during sintering results in improvement of physical and mechanical properties of the sintered compacts. The enhancement in properties was attributed to the formation of highly active copper atoms. It was suggested that the gaseous products of decomposition and the heat generated during decomposition might have supplemented the driving force for sintering.

In the present paper an attempt is made to establish the mechanism responsible for the enhancement of densification in aqueous formic acid treated powder compacts when sintered in hydrogen. Densification data on treated and untreated powder compacts are analysed by two procedures.

Studies on isothermal shrinkage, changes in porosity, loss in weight data and microstructural studies have been carried out to understand the densification process in treated powder.

EXPERIMENTAL PROCEDURE

50 g. of hydrogen reduced electrolytic copper powder of (−150+200) mesh fraction was equilibrated with 100 ml. of N/10 formic acid for a predetermined time of 4 hours. The concentrations of aqueous formic acid before and after treatment were determined spectrophotometrically using chromotropic acid reagent. It was established by a separate set of experiments that the species formed on the copper powder surface largely consisted of copper formate. Details of the powder preparation, analysis and identification of the species formed are given elsewhere1). The treated powder used in densification studies had 1500μg. of formic

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acid per gram of copper powder in the form of bulk salt on the surface of the powder. Table 1 presents certain important properties of treated and untreated copper powders.

Table 1 Characteristics of the powders used in the present investigation.

<table>
<thead>
<tr>
<th>Acid content</th>
<th>Apparent * density g/cc</th>
<th>Time for * flow of 50 g, (Sec.)</th>
<th>Specific surface ** cm²/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated powder</td>
<td>1.74</td>
<td>39.0</td>
<td>345.7</td>
</tr>
<tr>
<td>1500 µg formic acid per gram of copper</td>
<td>2.1</td>
<td>48.5</td>
<td>712.0</td>
</tr>
</tbody>
</table>

* A.S.T.M. B212-48 (1955) ** Lea and Nurse permeability method.

Samples, in the disc form, of about 16 mm dia and 5 mm thickness were pressed in a single action 50 ton hydraulic press in an unlubricated hardened steel die to a green density of 6.89 g/cc. It was noted that treated powder required slightly higher pressure than that required for untreated powder to attain an identical density. The specimens were sintered isothermally in a Kanthal wound resistance furnace in hydrogen, using a manually operated push-pull arrangement. The temperature was measured using a precalibrated Pt-Pt 10% Rh thermocouple. Temperature variation was maintained within ±3°C using a transistorized controller. Sintering time was measured from the instant the sample attained the desired temperature. After completion of the sintering cycle, samples were withdrawn to the cooler part of the furnace, which took about 15 minutes to reach room temperature. Green and sintered densities were determined by weighing and measuring the dimensions of the compacts. This was further checked occasionally by the ‘displacement’ method.

In order to minimize the effect of variation in green density on sintered density a normalized parameter called densification parameter-originally due to Jordon and Duwez is used. This is expressed as

\[ \sigma = \frac{\rho_s - \rho_G}{\rho_T - \rho_G} \]

were \( \sigma \) = densification parameter, \( \rho_G, \rho_s, \rho_T \) are green, sintered and theoretical densities respectively.

Isothermal dilatometric studies were carried out in a horizontal dilatometer which was similar to the one used by Tendolkar and Andrew.

Porosity measurements were carried out by vacuum xylene impregnation method used by Arthur.

**PROCEDURES ADOPTED FOR THE ESTIMATION OF ACTIVATION ENERGY IN THE PRESENT INVESTIGATION**

Two procedures are used in the present investigation for estimating the activation energy associated with material transport during sintering, resulting in densification of the compact.

The first one is that due to Jordan and Duwez. These investigators considered that densification is a rate process similar to that involved in chemical reactions. Such processes are characterised by the fact that if a given state is attained in a time \( t_1 \) at absolute temperature \( T_1 \) and if the same state can be attained in time \( t_2 \) at another temperature \( T_2 \) then these four quantities are related by the equation.

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where \( Q \) and \( R \) are activation energy and gas constant, respectively.

Thus, by plotting the curves of \( \log_e(t) \) versus \( 1/T \) for a constant densification, it is possible to estimate the activation energy required for material transport during sintering.

The second procedure is purely empirical and is suggested by the nature of the curves of densification versus time. The densification parameter could be expressed as

\[
\sigma = Kt^n
\]

where \( \sigma \) = densification parameter, \( K \) = rate constant, \( t \) = sintering time and \( n \) = the time exponent.

If only one mechanism is responsible for the observed densification, then we have from the equation,

\[
\log_e(\sigma) = \log_e(K) + n \log_e(t)
\]

the condition that when \( \log_e(\sigma) \) is plotted against \( \log_e(t) \), a set of parallel lines should be obtained at various temperatures. In other words 'n' should be constant. These curves when extrapolated give intercepts on \( \log_e(\sigma) \) axis representing various values of \( \log_e(K) \).

Using these values of \( \log_e(K) \) in an equation of the type

\[
K = Ae^{-\frac{nQ}{RT}}
\]

'\( Q \)' can be determined.

RESULTS

Figs. 1 and 2 represent the relationship between densification and sintering time for various temperatures in the range 775°C to 950°C for (a) untreated (pure) and (b) treated powder. Figs. 3 and 4 represent \( \log(t) vs \frac{1}{T} \) for both types of powders as required by the Jordan & Duwez procedure to determine the '\( Q \) value.'

The data of Figs. 1 and 2 are replotted on log x log scale and are depicted in Figs. 5 and 6. Fig. 7 represents the Arrhenius plot for untreated powder. However, it was not possible to plot the same for treated powder.

DISCUSSION

Activation Energy for untreated (Pure) Copper Powder:

It may be noted from Fig. 3 that for a constant value of \( \sigma \), \( \log \) (time) vs. \( \frac{1}{T} \) yielded a straight line, suggesting that densification may be considered a rate process. The activation energy of 57.42 kcal/mole determined from these curves is in agreement with the reported value of activation energy associated with a volume diffusion process.

The alternative procedure as depicted in Fig. 5 indicated that the time exponent 'n' is not single-valued but varied monotonically, attaining a constant value after 120 minutes of sintering. This indicated that more than one mechanism is operative. The effect of faster mechanisms diminishes after 120 minutes. This can be seen in case of compacts sintered at 800° and 850°C. At higher temperatures, 'n' is almost constant, indicating that only one mechanism is operative. The activation energy of 55.91 Kcal/mole determined from Fig. 7 once again suggests that volume diffusion mechanism contributes significantly to densification. A point of interest is that the activation energy determined by the Jordan and Duwez method should be considered to represent an average value of activation energies for a number of
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Fig. 1 Densification vs. time for pure copper powder compacts.

Fig. 2 Densification vs. time for copper powder having 1500µg of formic acid in the form of bulk salt.

Fig. 3 Log (time) vs. 1/T for pure copper powder.

Fig. 4 Log (time) vs. 1/T for copper powder treated with aqueous formic acid (1500µg) in bulk form.
Fig. 5 Log (densification) vs. log (time) for pure copper compacts made from (-150+200) mesh fraction.

Fig. 6 Log (densification) vs. log (time) for copper powder having 150µg. of formic acid (in the form of bulk salt).

Fig. 7 Log K vs. 1/T plot for pure copper compacts.
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Activation Energy for Treated Powder:

Figs. 2 and 4 represent the data analysed by the Jordan and Duwez procedure which yielded a value of 50.58 Kcal/mole for activation energy. Fig. 6 represents the data of Fig. 2 on a log \( \times \) log scale. It may be of interest to note that these curves are very similar to those of Kingery's liquid phase sintering where \( \log (-\frac{dV}{dt}) \) is plotted against \( \log \) (time) for various temperatures. In the present investigation no liquid phase was observed to have formed. Because of the uncertain nature of these curves no attempt was made to determine activation energy for the rate determining mechanism. Nevertheless, it appears that densification occurred in three distinct stages. The initial 60 minutes of sintering contribute the first stage, where 'n' varies from 1/5 to 1/2 in the temperature range under study. This is very similar to the rearrangement stage in liquid phase sintering where the particles of residual solid phase rearrange themselves by viscous flow. A similar process can be postulated to have occurred here. Removal of chemically active layers due to decomposition or by chemical reaction between the layer and the ambient atmosphere may result in higher shrinkage. Formation of highly mobile copper particles brings about better binding and densification.

Densification occurs at a rather slower rate during 60 to 120 minutes of sintering. Evolution of gaseous products and water vapour is considered to be responsible for the decrease in densification.

The third stage commences from 120 minutes and extends up to 500 minutes. At higher temperatures 'n' becomes negative, indicating the expansion of the compact. It may be considered from the above discussion that at least in case of treated powder, information in addition to activation energy is required to establish the mechanism responsible for enhanced densification.

Fig. 8 represents isothermal shrinkage for untreated and treated powder compacts in hydrogen atmosphere at 800°C. It can be seen from these curves that as the formic acid content increases, rate of shrinkage also increases. In case of compacts made from powders with 1500 µg. of formic acid, the shrinkage in the first 100 minutes is fast after which it progresses at a rather slower rate.

Fig. 9 (a) and (b) represent the variations in total and interconnected porosity as a

Fig. 8 Shrinkage isotherms for compacts made from pure powder as well as powders having various amounts of formic acid in the form of bulk salt.
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Fig. 9 a and b. variation of total and interconnected porosity as a function of sintering time for compacts made from powder having 1500 µg of formic acid.

Fig. 10 Microstructures of compacts made from copper powder treated with aqueous formic acid and sintered in hydrogen at 950°C. Formic acid content: 1500 µg/g. Cu (×225).
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function of time for various temperatures in the range 750 to 900°C. It may be noted that the rate of removal of interconnected porosity and decrease in total porosity is very fast for treated powder compacts as compared with those in case of untreated powder compacts. Secondly, a desired level of porosity could be attained at much lower temperature and in lesser time by the above discussed treatment of powder prior to sintering.

Fig. 10 represents microstructures of treated powders compacts sintered in hydrogen at 950°C for various length of time. It can be seen from these microstructures that in addition to spheroidization of pores a large number of twins are present. Pores are found to exist at the twin boundaries. These probably could be understood in the following way.

Decomposition of metal formates, according to Dollimore and Tonge\(^3\), occurs by one of the following routes.

\[
\begin{align*}
M(HCOO)\_2 & \rightarrow MO + CO + CO\_2 + H\_2 \\
M(HCOO)\_2 & \rightarrow MO + 2CO + H\_2O
\end{align*}
\]

The formation of oxide particles is considered to impede material transfer by flow process where the crystallite unit as a whole moves. The presence of twins can perhaps be explained in this way. Presence of microscopic pores along and on the twin boundaries can be explained as being due to the reduction of fine oxide particle under sintering atmosphere which in the present case is hydrogen.

Table 2 presents the data on percentage loss in weight of treated powder compacts when sintered in hydrogen atmosphere for one hour at various temperatures.

<table>
<thead>
<tr>
<th>Sintering temperature °C</th>
<th>Formic acid content % (1500µg./g of Cu)</th>
<th>Loss in wt. after sintering %</th>
</tr>
</thead>
<tbody>
<tr>
<td>600</td>
<td>0.15</td>
<td>1.55</td>
</tr>
<tr>
<td>700</td>
<td>0.15</td>
<td>1.69</td>
</tr>
<tr>
<td>800</td>
<td>0.15</td>
<td>1.73</td>
</tr>
<tr>
<td>850</td>
<td>0.15</td>
<td>1.77</td>
</tr>
<tr>
<td>900</td>
<td>0.15</td>
<td>1.73</td>
</tr>
</tbody>
</table>

The formation of an organic salt on the metal powder by interaction with an aqueous organic acid, constitutes a surface under stress. This was evident from the difficulty in compacting the treated powder. It was stated earlier that treated powder required higher pressure as compared to untreated powder to attain identical density. The stress concentration results from the noncoherency of crystallite lattice. Copper formate is monoclinic while copper is face centered cubic. Increase in stress on the surface of the powder is believed to have enhanced evaporation condensation.

Several investigators\(^7\)\(^4\) have stated that decrease in porosity can come only from volume diffusion or plastic flow mechanism.

Volume diffusion is considered to be rather a slow process where material transfer occurs by atom to atom movement. In the present investigation, therefore, it is difficult to account for the large linear shrinkage and high rate of decrease in porosity on the basis of a diffusional process. The essential features of a diffusional process from the point of view of microstructural changes, is the gradual decrease and elimination of small pores with simultaneous increase.
in the size of pores which are bigger than a certain critical diameter. In the present work, however, it can be seen that shrinkage of pores was rather uniform. There has been segregation of pores and formation of a large number of twin boundaries. Thus the kinetic data when considered with dilatometric studies, porosity measurement, loss in weight data and microstructural evidences suggest that in the case of aqueous formic acid treated powder, densification occurs by a plastic flow mechanism aided by evaporation condensation.

**CONCLUSIONS**

1) Densification studies on pure copper powder confirmed that more than one mechanism contributes to densification. The contribution of volume diffusion mechanism is significant and the same mechanism is rate controlling.

2) Densification in formic acid treated powder compact occurs in three stages. The mechanisms responsible for material transport in that case is plastic flow aided by evaporation condensation.

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**REFERENCES**

1) A. S. Reshamwala and G. S. Tendolkar: 'Activated Sintering of Copper' accepted for publication in 'Planseeber Pulvermet' (Austria).
3) G. S. Tendolkar and J. H., Andrew: J. Scientific and Industrial Research, 913 (10), 244 (1950).
8) I. Jenkins: 'Powder Metallurgy', 7 (13), (1964) 68-92. (Received July 2, 1969)