MEASURING DEGREE-OF-SINTER USING METALLOGRAPHIC METHODS

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Abstract

The determination of degree-of-sinter in P/M materials historically has been difficult. Past attempts have been subjective and lacked the quantitative results that could be used in correlation studies to improve properties or monitor manufacturing processes. An attempt is made to develop a test technique using quantitative microscopy to evaluate pore structures in pressed and sintered materials. For this initial phase of the study, a F-0005 material was sintered at times ranging from 5 to 45 minutes in the heating zone. Specimens were removed, prepared by metallographic methods, and tested using quantitative microscopy techniques. The preparation procedures and results of the testing are presented along with a brief historical background.

Introduction

Evaluating the effectiveness of sintering in pressed and sintered materials historically has been a challenge to the P/M community. The techniques and methods used were primarily subjective and prone to inconsistencies and inaccuracies due to variable levels of operator skill and experience. Most of the methods relied on the ability of an operator to both prepare and recognize regions within the microstructure where sintering was incomplete or where evidence of prior particle identity remained. The tests were effective in determining when materials were sintered to different degrees, but there was no avenue to use the results in a quantitative manner. The framework for many of these efforts was an accurate assessment of the number of prior particle boundaries and angular pores present in a metallographically prepared section of a sintered compact. The problems with this approach resulted in a lack of correlation between the numbers of the features of interest with mechanical properties and coordination of the results between and within testing facilities. Usually, the parameters used to describe the degree-of-sinter (DOS) were relative in nature and consisted of comparative terms such as good, fair, or poor.

Two approaches using light microscopy techniques will be presented in this paper in an effort to make the evaluation process more objective and quantitative. The well documented and rigorously proven stereological methods
and a lesser-known, fractal-like technique known as the box-counting dimension (BCD) will be used to describe the changes in microstructure observed as the sintering process progresses. Examples will be used to show how use of the stereological methods can be accomplished with both manual methods and automated image analysis (AIA) while the BCD will be demonstrated using AIA. It should be noted that, even though the BCD will be determined by automated methods in this work, the process is straightforward and may be used successfully with proper manual techniques and operator patience.

Background

The steps used in the manufacture of P/M components are usually separated into three or four distinct operations. These include preparation of the powder mixture, compaction, sintering, and any secondary operations. Each has an effect on the pore structure and consequently, on the properties attained by the finished part. Both the compaction and sintering portions of the manufacturing process will be discussed briefly to provide basic information for understanding formation of the pore structure.

Compaction and Sintering

During compaction, adjacent particles are forced into intimate contact as pressure is applied through movement of the punches. In the initial stage of compaction, particle rearrangement occurs followed by deformation of the particles as the density is increased. The amount of particle-to-particle contact is controlled by the amount of applied pressure and particle characteristics such as hardness, size, and shape.

The sintering process causes the particles in contact to form metallurgical bonds, alloy by diffusion, and improves the mechanical and physical properties by creating a coherent compact. In general, the bonding occurs through two means of material transport. At the particle contact areas, the boundaries are lost and bonds are formed through mass transport. Along the pore edges, the surfaces become smoother through vapor phase transport.

Visually, the results of these transport mechanisms appear as a loss of the particle boundary edges and a rounding or smoothing of the pore edges. The particle-to-particle and pore surface areas are decreased as sintering progresses. The outcome of the particle bonding and the reduction in internal surface area is an improvement in mechanical properties to levels needed to fulfill the requirements for the application of the part. It is the measurement of these reductions in particle contact and pore surface areas that the test methods used in this study are designed to quantify.

Many prior studies were designed to investigate the sintering process including how the time at sintering temperature changed the microstructure and resulted in
the desired improvements in properties. Stereological techniques were used extensively in these studies. However, applying the results from these studies to the typical pressed and sintered production operations was difficult. Models, idealized powder systems, and loose powder compacts were used to describe the mechanism of sintering, while the standard P/M grade powders, the compaction process, and the economic pressures to control sintering were rarely addressed. All of the required elements of part processing affect sintering and, in turn, the resultant appearance of the microstructure. Consequently, the effect of typical production conditions should be explored.

**Stereological Test Methods**

Stereology, or quantitative microscopy, is a collection of methods used to describe the three dimensional geometrical characteristics of the microstructure from two dimensional sections. The initial technique was developed in the mid-1800’s by a geologist named Delesse who demonstrated that, in a homogeneous material, the volume fraction of a constituent was equal to the area fraction shown on a random section through the material. Since that time, considerable development has taken place to further the use of stereology to include estimates of surface areas, distances, line lengths, curvatures, and many other parameters. Areas of extensive use include biology, medicine, geology, material science, as well as many others.

Stereological test methods overlay grids, lines, and points on images from many sources. In our case, the source of the images is the light optical microscope using reflected light to produce the images. The grids, lines, and points may be reticules within a microscope eyepiece, transparent overlays placed on a photomicrograph, or electronic overlays in an AIA system. Regardless of which type is used, the objective and effect are the same, to probe or take a sample of an image in a systematic manner and count ‘events’ or ‘hits’ where specific conditions are met. Examples include the crossing of a boundary with a line, a point within an array falling on a phase, or a feature being within a predetermined area. Events or hits are then used in expressions to form relationships that can be used to characterize specific geometric elements within the microstructure. The information generated using stereology is quantitative. The magnification of the image is controlled by an operator, and the lengths, spacing, and areas used in the overlays can be made to conform to individual requirements. Excellent references containing guidelines for developing test procedures are available in the literature.

The terminology used in stereology assigns designations for points, lines, areas and volumes, the sample probes representing the dimensions from 0 through 3, as the letters P, L, A, and V respectively. They are used in combination with each other to form meaningful relationships that describe the microstructure. For example, \( P_L \) is the notation for the number of points (or events) along a line. The large letter is quantified as the number of counts while the subscript reflects the
type of probe used to make the counts. \(P_L\) is usually described as “the number of points per unit line length.” In the evaluation of porosity, a line crossing a particle boundary produces one hit while the same line crossing a pore produces two hits, one on each side of the pore.\(^{18}\)

Table 1 describes some of the relationships that are accessible through direct counting and some that are determined through calculations. In many cases, the quantities seen along the top row are the desired values. The measurable values are found in \(R^0\) through \(R^2\) space and allow access to the \(R^3\) information.

Table 1. Parameters in local stereological systems\(^{19}\)

<table>
<thead>
<tr>
<th>Quantities not accessible through measurement in (R^3) space</th>
<th>Space</th>
<th>Volume fraction occupied</th>
<th>Specific surface</th>
<th>Mean surface integral per unit volume</th>
<th>Number of objects per unit volume</th>
</tr>
</thead>
<tbody>
<tr>
<td>(V_V)</td>
<td>(R^3)</td>
<td>(S_V)</td>
<td>(M_V)</td>
<td>(N_V)</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Measurable Quantities</th>
<th>(R^2)</th>
<th>Area fraction occupied</th>
<th>Specific perimeter</th>
<th>Connectivity number</th>
</tr>
</thead>
<tbody>
<tr>
<td>(A_A)</td>
<td>(L_A)</td>
<td>(N_A)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>(R^1)</th>
<th>Line fraction</th>
<th>Specific intercept number</th>
</tr>
</thead>
<tbody>
<tr>
<td>(L_L)</td>
<td>(N_L)</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>(R^0)</th>
<th>Point fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>(P_P)</td>
<td></td>
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</tbody>
</table>

| Stereological Relationships | \(V_V = A_A = L_L = P_P\) | \(S_V = 4/\pi L_A\) | \(S_V = 4 N_L\) | \(M_V = 2\pi N_A\) |

It is from combinations of events such as the ones cited in Table 1 that the properties used in this study were determined. The following list gives information on the individual relationships that were used and the formulae used in their calculations:

1. Volume fraction \((V_V)\): The total volume fraction of the phase of interest. In this case, the pore volume was the feature of interest. Calculation may be defined from the two component material by measuring either the pore area directly, or measuring the solid phase and determining the pore area by subtraction.
\[ A_A^S + A_A^P = V_V^S + V_V^P = 1 \]  \hspace{1cm} (1)

where the superscripts refer to either the pore or solid portions of the microstructure. Either area fraction can be measured directly. This equates to the volume fraction.

2. **Surface area** \((S_V)\): The unetched compact contains interfaces at pore/solid and solid/solid regions. From Table 1, it is shown that the \(S_V\) can be determined through two relationships. One uses the \(L_A\) and the other uses \(N_L\) of the interface regions. The \(L_A\) is equivalent to the pore perimeter and the \(N_L\) is the count of the line segments within the pores.

\[
S_V = 4/\pi L_A \hspace{1cm} (2)
\]

\[
S_V = 4 N_L \hspace{1cm} (3)
\]

It should be noted that equation 2 is well suited to AIA, while number 3 is suitable for manual or AIA techniques.

3. **Average Mean Surface Curvature** \((\bar{H})\): The curvature of a surface varies from point-to-point depending on how sharply the edges are curved. If the values vary as the surface is examined on a point-to-point basis, there must also be an average value. The average value is calculated from a determination of the total curvature and the specific surface area.

\[
(\bar{H}) = M_V / S_V \hspace{1cm} (4)
\]

where \(M_V\) is calculated as \(M_V = 2\pi N_A\).

All quantities shown in the four equations are accessible through the use of either an AIA system or well designed manual methods. In the case of this study, an automated system was used with some operator interaction.

As was stated previously, the manual stereological methods are designed to count events as they are noted. These can then be used in various expressions to obtain quantitative information about a microstructure. The process of obtaining quantitative information using the manual methods is indirect, although accurate. Another tool, the automated image analysis system, is capable of performing most of the manual counts, but in addition, various measurements can be taken directly from the prepared metallographic specimens. Size distributions, spacings, and determinations of various shape parameters are only a few of the many measurements available from an AIA system. Additionally, the possibility exists to have the operator interact with an automated system and have difficult to determine information counted.
Box-Counting Dimension (BCD)

The Box-Counting Dimension\textsuperscript{20-23} is a fractal-based method of evaluating shapes and structures. The test is similar to the more familiar fractal analysis techniques that use compass or ruler length measurements to evaluate roughness and irregularity of surfaces. In the study of sintering where the features being analyzed are pores, the edges of the individual pores become the subject of the test.

The test uses the pore edges in conjunction with a series of square grid overlays. The grids are placed over the image of the pore edges and the number of boxes that contain pore edges is counted. This process is repeated for each grid size and for the number of fields determined significant for the analysis. A plot is then made using the log of the total number of boxes at each size vs. the log of 1/size of the boxes. A linear regression analysis is performed on the plot and the slope of the line is the box-counting dimension.

Procedure

Test Bar Preparation

In the current study, a premix was made of iron powder (Ancorsteel 1000B), graphite (Asbury 3203), and lubricant (Acrawax C) to a F-0005 composition. The F-0005 was chosen for this portion of the study because of the simplicity of the C-Fe system and the lack of complications caused with the addition of other alloying additives. Dog bone tensile bars were then pressed using a hydraulic press at pressures of 400, 550, and 700 MPa (approximately 30, 40, and 50 tsi).

The tensile bars were sintered using a pusher furnace in order to control the residence time in the heating zone while retaining the ability to cool the bars for the required time to prevent oxidation. No presintering was used to remove the lubricant. The sintering trays were pushed directly into the hot zone, which had been preset to 1120 °C (2050 °F). Time in the hot zone was varied from 5 to 45 minutes in 5-minute intervals in a nitrogen-based atmosphere with the addition of 10 v/o hydrogen.

After sintering, tensile properties were determined for the 27 sets of the sintered bars. Cross-sections were cut from the ends of the tested bars and these were used for the metallographic examination. Unfortunately, the bars sintered for 5 total minutes exhibited excessive damage to the pore structure from the pressure exerted by the testing grips and could not be used in the evaluation.
Metallographic Sample Preparation

The cross-sections taken from the ends of the bars were mounted, ground, and polished. The polished surfaces were impregnated with epoxy, and the samples reground and repolished. The epoxy impregnation appeared to be mandatory with this soft material. In the absence of epoxy impregnation, smearing of the ferritic regions caused both a modification of the pore edges and completely closed some pores while obscuring some of the particle boundaries. Keeping in mind that the tests are based on an accurate reproduction of the pore edges, any distortion of these features will affect the results adversely.

Stereological Testing

Testing was separated into three sub-programs. First, an AIA program was used to measure the amount of porosity in the cross-section from the tensile bar. The system employed for the analysis was equipped with a digital camera with a pixel array of 1280 x 960. Resolution of the array at the testing magnification was 0.232 \( \mu m \)/pixel. The procedure used to measure the amount of porosity was incorporated as a safeguard to ensure that the amount of pore area used to measure the stereological properties was approximately the same as the density of the overall bar. The area chosen was a stripe running from punch face to punch face, located near the center of the bar to take in consideration any density variations in the height of the bar. The density of the bar was calculated using 7.85 g/cm\(^3\) as the pore-free density. The calculated value was compared with immersion densities performed on selected samples at each compaction pressure. In general, the calculated densities were within ±0.05 g/cm\(^3\) of the immersion density values.

After determining the area to be used for the testing, a second program was utilized to generate the stereological counts. An array of ten, equally spaced horizontal lines was overlaid on each image. Determinations of the area percent porosity, the total number of line segments falling within pores, and the edge effect of the pores were made. In addition, a provision was added to the program to have the operator interact manually to count the number of prior particle boundary events along the array of lines. The manual aspect of the testing was found to be necessary due to the difficulty in performing automated detection of the faint particle boundaries (see Figure 1).

The third phase in the stereological testing used another program to count the number of pores within a given field area. A third program was used because it was felt that, at the same magnification, an accurate counting of the pores was difficult if not impossible due to the size and sometimes the shape of the pores. The magnification was halved to a resolution of 0.467 \( \mu m \)/pixel and an internal guard frame used to avoid the risk of eliminating pores or counting them more than once.
Figure 1. An example of the appearance of particle boundaries highlighted by the arrows in a sample pressed at 400 MPa and sintered for a total of 20 minutes.

To summarize the stereological testing; once the test area was selected, the $N_L$ of the pores and prior particle boundaries, $V_V$ of the porosity, and the number of pores within a test area were determined. These were the test values used in an attempt to calculate geometrical characteristics seen in the bars sintered for varying times in the heating zone and hopefully, discover some relevant differences.

**Box-Counting Dimension**

A separate AIA program was developed to have the BCD determined on multiple fields in a totally automated fashion. Again, the amount of porosity was checked at the resolution of 0.232 µm/pixel to ensure consistency in density. Once that was completed, a gray level image was determined and the pore perimeters extracted. A series of square grids was superimposed on the image of the perimeters and the number of boxes coinciding with the perimeters counted. A total of eight grids was used with the box size ranging from 24.5 µm to 1.75 µm.
Figure 2. Partial field image showing pores used for the box-count dimension. The area surrounded by the dashed line was used as an example to show the coverage of boxes containing the perimeter edges. In the figures below, the left column (a) shows the grid overlay and the right (b), darkened boxes containing portions of the perimeters. The box sizes are used as scale markers.

Figure 3, a and b. Grid #1, box size 24.5 µm.

Figure 4, a and b. Grid #3, box size 12.2 µm.

Figure 5, a and b. Grid #5, box size 5.9 µm.

Figure 6, a and b. Grid #7, box size 2.9 µm.
The test was repeated at a higher magnification. The box sizes of the eight grids for this test ranged from 9.75 µm to 0.65 µm. Figures 2 through 6 show images of a grayscale image, the grayscale image covered with square grids, and gray boxes from the square grids containing perimeter segments.

**Results**

Mostly, the results gave indications of the expected trends in reductions of the stereological test values. In particular, the specific surface area (S\(v\)) and average mean surface curvature (\(\bar{H}\)) were reduced as the sintering time was extended. The box-counting dimension also showed the expected behavior. The drawback in this initial phase of the study was that the magnitude of differences in the measured values between materials close in sintering time was not great enough to be seen. Apparently, the design of the test procedures lacked the sensitivity to detect the variations in the microstructure. The differences in microstructure and porosity were subtle, but unfortunately, the current methods were not able to differentiate between them. Each test technique will be discussed separately.

**Stereology**

The concepts introduced and described in the Background and Procedure sections were used to find characteristics within the microstructure that could be used to separate materials sintered at different times. The volume fraction of porosity was measured and used as a control mechanism for choosing areas where further examination would be made. Fortunately, this parameter could be used at another time in calculating additional relationships such as feature separation.

The specific surfaces (S\(v\)) of the boundary regions, both pore-metal and particle-to-particle, were calculated. With the pore-metal regions, the trend existed where the lowest values were seen at the longest sintering times, but the amount of difference was less than could be used to safely separate marginally different materials.

The specific surface of the particle boundaries (S\(v\)) showed a larger difference. In Figure 7, a drop in specific surface area was clearly seen. This was especially true in the materials compacted at the highest pressure (700 MPa). The practical value of this finding is questionable because the sintering times used to produce the highest S\(v\) values were much shorter than what would be used in a manufacturing setting for the production of high quality P/M parts.
Figure 7. Specific surface area ($S_V$) of the prior particle boundaries.

The formula used to calculate the average mean surface curvature ($\bar{H}$) was given in Equation 4. This formula uses two stereological counts; the number of points per unit line length ($P_L$) and the number of features (pores) per unit area ($N_A$). The result from this relationship was also not as definitive as had been hoped. As stated previously, the $S_V$ of the pore-metal edges lacked a clear difference when comparing results of the various sintering times. A similar situation existed with the number of pores counted within a given test area. The average mean curvature was calculated using these two parameters, and consequently, also had the same lack of sensitivity. The trend was correct, but still not enough to separate marginally different materials.

**Box-Count Dimension**

Results from the use of this technique also resulted in a correct trend, but not enough difference to detect subtle changes in processing. Figure 8 shows the graphs from the higher magnification testing of the bars sintered for 10 and 45 minutes. As was seen in the stereological data, the direction of the results was correct, but the magnitude of the difference was not great enough to be of practical value.
Figure 8. Box-count dimension calculated on samples sintered for 10 and 45 minutes total time.

The box-count dimension is the slope of the linear trend line. In this example, the BCD for the 10 minute sinter was 1.034 while for the 45 minute sinter, it was 1.010. This resulted in a difference of 0.024. In this test, the fewer the number of boxes counted, the smoother the surface, and the better the sinter. Therefore, a sample with a better sinter will have a lower slope.

The two materials used in the example shown in Figure 8 were sintered for the extremes in time, 10 and 45 minutes in the heating zone, and their corresponding pore structures should have reflected their relative times at temperature. However, with the test in this design, the test was not able to distinguish one material from the other.

**Discussion and Conclusions**

In this initial stage of the study, standard test methods were used in an attempt to quantify changes in microstructural characteristics created by the sintering operation. The variation in sintering time was used to generate samples exhibiting a variety of mechanical properties and corresponding differences in microstructure. The results of the metallographic study were promising in that the trends appeared to be in the correct direction. However, the magnitude of
the differences did not appear large enough to differentiate between materials close in degree-of-sinter.

The slight variations in the appearance of the sintered structure created by varying the sintering time were not well detected using either the stereological methods or the box-count dimension. In the stereological testing, the standard techniques did not detect the slight, but important differences in pore structure. Visually, differences in pore structure were apparent, but the techniques used initially were inadequate for determining a statistical difference.

Obvious changes in the loss of particle boundaries were characterized and quantified well, but the smoothing of the pore edges with the resultant loss in specific surface area was not detected. In the future, the stereological techniques will be modified to take advantage of the features in the microstructure that exhibit changes as sintering takes place.

The BCD suffered from the same problem. In this case, the relative resolution of the test system is an area to be explored. Again, the loss of pore surface area was not well detected and, consequently, the changes in microstructure caused by the changes in sintering time were not seen. One aspect of the test method to be explored is resolution of the system. Changing the microscope magnification and/or the series of grid sizes may provide a more accurate reproduction of the pore structure and enable the microstructural differences to be seen.

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References