ABSTRACT

The design of ferrous powder metal compacts is currently limited by a limited understanding of how alloying elements diffuse from additives into the iron matrix. A number of factors, including heat treatment, compaction density, and particle morphology, affect this diffusion. In this study, scanning electron microscopy (SEM) and energy dispersive x-ray spectroscopy (EDS) were used to map the diffusion of various alloying elements from additive particles into a water atomized iron powder. The results of this work will yield a better understanding of the diffusion processes and allow for the optimization of sintering conditions.

INTRODUCTION

Chromium containing PM alloys are becoming more prominent in a move away from traditional alloying elements like Cu. Previous studies by Lindsley showed that sintering times and temperatures have a significant impact on the mechanical property performance of chromium containing PM steels [1]. Specifically increasing the sintering time from 8 minutes to 30 minutes at 1120 °C (2050 °F) increases the UTS from 700 MPa to > 900 MPa. Increasing the sintering temperature has a similar beneficial effect. A maximum strength of >1100 MPa was observed at 1260 °C (2300 °F) and 30 minutes at temperature. This increase in strength was attributed to greater alloy homogeneity and a corresponding increase in the amount of martensite transformation during sinter hardening.

Cu-containing mixes are easily sintered and upon melting, the Cu diffuses throughout the part. An understanding of the solid state diffusion characteristics of Cr into iron is necessary to the successful commercial utilization of Cr containing PM steels using chrome master alloy additions. The effect of Cr diffusing into the compact can be examined using secondary electron imaging of the changing microstructure with time and temperature. In addition, energy dispersive x-ray spectroscopy can be used to fingerprint and measure the diffusion of individual species through the Fe matrix under a variety of sintering conditions.
METHODS

This study utilized scanning electron microscopy (SEM) and energy dispersive x-ray spectroscopy (EDS) to map the diffusion of alloying elements. The powder used in this study was a binder treated premix containing Asbury 3203H graphite and 0.55 wt.% Acrawax C as a lubricant, and the composition is listed in Table I.

<table>
<thead>
<tr>
<th>Cr</th>
<th>Ni</th>
<th>Si</th>
<th>Mn</th>
<th>Mo</th>
<th>Cu</th>
<th>Gr</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>1.0</td>
<td>0.6</td>
<td>0.1</td>
<td>0.8</td>
<td>-</td>
<td>0.6</td>
<td>Bal.</td>
</tr>
</tbody>
</table>

Table I. Composition (in wt.%) of test alloy.

All samples were pressed to a density of 7.0 g/cm³. The samples were sintered in a 90% N₂ and 10% H₂ (vol.%) atmosphere. A test matrix, shown in Table II, was developed for sintering conditions at various times and temperatures to explore the effect of sintering conditions on diffusion. The average cooling rate from 650 to 315 °C (1200 to 600 °F) was 0.7 °C/sec (1.3 °F/sec). Following sintering, all samples were tempered at 205 °C (400 °F) for 1 hour.

Table II. Matrix of sintering conditions.

<table>
<thead>
<tr>
<th>Temperature (°C) (°F)</th>
<th>Time (minutes)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1120 (2050)</td>
<td>8</td>
</tr>
<tr>
<td>1150 (2100)</td>
<td>15</td>
</tr>
<tr>
<td>1180 (2155)</td>
<td>30</td>
</tr>
</tbody>
</table>

After sintering, all samples were prepared for scanning electron microscopy through bulk grinding and concluding with a 0.05 µm Alumina suspension polish. The samples were then etched with a 5% Nital solution for approximately 6 seconds. Each sample was mounted to a specimen stub with carbon tape and grounded to the stub with aluminum tape. Silver paint was also applied to the surface of the epoxy to further prevent electron charging and drift in the microscope. Data were collected at Drexel University’s Centralized Research Facility on a FEI XL30 scanning electron microscope. An EDAX Energy-Dispersive X-ray Microanalysis detector was used to perform elemental mapping and line scans on each sample. Secondary electron images and EDS maps were collected with the filament operating at 20 keV, a spot size of 4, and an aperture size of 100 µm. The EDS maps are composed of 32 consecutive frames, with a dwell time of 200 µs, at a resolution of 256x200 pixels. Line scans were taken with a dwell time of 200 ms, with each point sampling from an approximately 0.1 x 0.1 µm field.

RESULTS

Characterizing the diffusion of alloying elements into the Fe matrix is the primary goal of this study. EDS maps of Cr, Si, and Ni are shown in Figures 1, 2, and 3. Additive particles are visible in Figure 1 at
1120 °C (2050 °F) as enriched clusters of Cr and Si. The permutation of short sintering time (8 min) and 1120 °C sintering temperature results in minimal if any diffusion of the chrome and silicon from the master alloy into the iron matrix. At a sintering temperature of 1150 °C (2100 °F), Cr and Si diffusion improves dramatically, with the diffusion front entering the Fe matrix and inducing microstructural changes even at short sintering times. The enriched additive particles present at 8 minutes are no longer visible at this temperature.

As expected, at 1180 °C (2155 °F), the diffusion front of Cr and Si reaches further into the matrix from the edge of a void. Additionally, void size decreases and pores become more rounded as the temperature increases and the sintering process continues.

Samples Sintered for 8 Minutes

![EDS maps of Cr, Si, and Ni](image)

*Figure 1.* EDS maps of Cr, Si, and Ni (columns left to right) of samples sintered at 1120 °C (2050 °F), 1150 °C (2100 °F), and 1180 °C (2155 °F) (rows top to bottom). The magnification factor is listed below each image.
Figure 2. EDS maps of Cr, Si, and Ni (columns left to right) of samples sintered at 1120 °C (2050 °F), 1150 °C (2100 °F), and 1180 °C (2155 °F) (rows top to bottom). The magnification factor is listed below each image.
Shorter sintering times are preferred for manufacturing applications. Figure 1 shows that at 8 minutes Cr diffusion is highly dependent on sintering temperature. Below 1150 °C (2100 °F), Cr diffusion is very slow and does not significantly penetrate the iron matrix. For these shorter sintering times, a higher temperature such as 1180 °C (2155 °F) will result in better intermixing and a more homogeneous microstructure. The diffusion behavior converges to a temperature-independent steady state at longer sintering times. Figures 2 and 3 do not show the same degree of change between sintering temperatures seen in Figure 1. Nickel diffusion is also affected by sintering time and temperature; however, the effect is less pronounced than that of the Cr or Si.
EDS line scans provide a higher resolution than maps for regions of interest such as the additive particle interface with the matrix. Figures 4 and 5 show examples of a line scan conducted across a region of interest. Below each graph is the corresponding secondary electron image after being cropped and straightened to properly align with the graph’s horizontal axis. These lines reinforce the microstructural changes corresponding to the concentrations of alloying elements and were used to calculate the position of the diffusion front with respect to the edge of a void for each sintering condition.

Figures 6, 7, and 8 plot the position of the diffusion front at a range of locations for each sintering condition. These values were calculated from line scans, taking the edge of a void as the starting position and measuring until the concentration of Cr dropped to the average value of the straight, stable part of the line. Across all times, samples sintered at 1150 °C (2100 °F) exhibit significantly greater diffusion than samples at 1120 °C (2050 °F). At 8 minutes, more thorough diffusion is achievable at 1180 °C (2155 °F), but at longer times this difference is less pronounced.

**Figure 4.** Example line scan. Sample sintered at 1150 °C for 8 minutes. Image at right represents the full area from where the scan was taken.
Figure 5. Example line scan. Sample sintered at 1150 °C for 8 minutes. Image at right represents the full area where the scan was taken.

Figure 6. Diffusion Front Position with respect to sintering temperature, at 8 minutes.
Figure 7. Diffusion Front Position with respect to sintering temperature, at 15 minutes.

Figure 8. Diffusion Front Position with respect to sintering temperature, at 30 minutes.
CONCLUSIONS AND FUTURE WORK

The techniques used in this study allow for the direct observation of diffusion behavior in a matrix of sintering conditions. Scanning electron microscopy and EDS mapping make it possible to correlate chemical composition with the observed Fe microstructure and ultimately the resulting mechanical properties. The Cr containing master alloy studied offers insight into the optimization of sintering conditions for these systems. While the desired diffusion is achievable at a sintering temperature of 1120 °C (2050 °F), longer sintering times are required that would limit production capability. For this Cr containing alloy, the most efficient diffusion requires higher sintering temperatures, in excess of 1150 °C (2100 °F).

The significance of the approach outlined in this study enables the development of lean high performance alloy systems through the use of master alloys. This alloying approach has the benefit of maintaining base powder compressibility with prudent use of alloying elements and amounts to produce PM steel components with the desired mechanical performance. Additionally, this approach offers greater flexibility for the powder producer and parts fabricator.

For the alloy system investigated, both Cr and Si are desirable alloying additions to Fe. Effecting sufficient diffusion from the master alloy into the Fe matrix is paramount. This study showed that effective diffusion can be done with either sintering temperature and sintering time. Longer times at temperature imply slower furnace belts speeds or longer hot zones in the furnace. Higher sintering temperatures may require new furnace design concepts.

Energy dispersive x-ray spectroscopy, the main analytical tool used in this study, has inherent limitations that make it unable to provide a complete picture of all the elements affecting material performance. While EDS is an excellent way to map alloying elements like Cr and Ni, its sensitivity to lighter elements such as O and P is quite poor. Auger electron spectroscopy (AES) is a high resolution technique capable of mapping these lighter elements and can provide more insight into the dynamics of sintering these alloys. In addition, the escape depth (< 5 nm) of Auger electrons makes this technique suitable for investigating surface phenomena, while a small electron probe size offers excellent in-plane spatial resolution.

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REFERENCES