DIFFUSION BEHAVIOR AND MICROSTRUCTURAL TRANSFORMATIONS IN PM STEELS CONTAINING SILICON

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INTRODUCTION

The effects of alloying iron and low-alloy steel powders with silicon, both alone and in combination with other elements, has been detailed by Schade et al.1 The authors described the effects of alloying with silicon on mechanical properties as a result of increases in ferrite hardness, alloy hardenability, and decreases in pearlite spacing. The current paper expands the original study by quantifying the effects of local chemical composition on hardenability in these silicon-containing alloys. It is shown that the diffusion of silicon from a master-alloy additive resulted in local variability in both silicon content and the resulting hardenability.

Individual alloying additives are introduced into the powder using different techniques. When molybdenum is used as an additive, it is usually prealloyed with the iron,2 while prealloyed powders rich in silicon, chromium, or manganese often contain relatively stable oxides when water atomized.3 Alloying with these elements is usually more effective when the additions are made to the powder mix as fine particulates manufactured using alternative techniques. However, as a mixture of individual particles, there are variations in alloy concentrations due to the distribution of the added particles throughout the mix; the locations containing higher concentrations of additive particles have the highest elemental concentration.

The distribution of the alloying particles added to the iron or low-alloy volume determines the starting points for alloy diffusion. The elements diffuse into the base iron or low-alloy particles and the local chemical composition changes, creating steep concentration gradients throughout the compact volume. At increased temperatures and/or for longer times at temperature, the depth of diffusion increases and the alloyed gradients become shallower. The
final local alloy hardenability is created at the end of residence time in the hot zone of the sintering furnace. Upon entering the furnace cooling zone, the cooling rate determines the transformation products that will form on a local basis in the microstructure.

To gain a better understanding of the silicon-containing alloys used in this study, experiments were undertaken to quantify the distribution of the alloying elements within the different systems after sintering. Techniques developed by Gungor and then DeHoff were used to describe the variability in chemical composition and the resulting differences in microstructure. These techniques use stereological methods to estimate nonuniformity in the structure and help develop a correlation with the local chemical composition and the resulting transformation products.

**EXPERIMENTAL PROCEDURES**

Mixtures of base powders and master alloys containing silicon, manganese, and chromium were used to prepare the compacts for hardenability testing, chemical analysis utilizing a scanning electron microscope (SEM) equipped with an energy dispersive spectrometer (EDS), and examination using light optical microscopy (LOM). The mean particle size (d$_{50}$) of the additives was 8–15 µm. Ancorsteel 1000B was used for the iron-base alloy systems and Ancorsteel 30HP (nominal molybdenum level of 0.30 w/o) was used for the iron-molybdenum prealloy. The d$_{50}$ of the ferrous-base powders was approximately 75–85 µm, with a small fraction 200 µm in diameter.

The powders were mixed with Acrawax C lubricant and graphite. Graphite additions were 0.70 w/o resulting in a sintered carbon of approximately 0.65 w/o. The test pieces were sintered in high-temperature Abbott continuous-belt furnace at 1,260°C (2,300°F) for 30 min in an atmosphere of 90 v/o nitrogen/10 v/o hydrogen.

The effect of silicon on quenched hardenability was studied using cylindrical compacts that were 25 mm (1 in.) dia x 25 mm high. These were pressed to a green density of 6.95 g/cm$^3$ at a nominal pressure of 690 MPa (50 tsi). After sintering, the samples were reheated to 900°C (1,650°F) and oil quenched. The quenched samples were sectioned at the diameter, with the exposed rectangular cross section mounted and prepared for hardness testing, microstructure evaluation, and chemical analysis. Microindentation hardness traverses were made at the middle of the sample height, from the edge to the center of the compacts (~12 mm).

LOM was used to estimate the proportions of the specific transformation products in the material volume at 1 mm increments from the quenched surface (edge) to the sample core. A manual point count using equally spaced points was used to generate these estimates. Multiple fields totaling an area of approximately 0.7 mm$^2$ were analyzed at each depth starting approximately 0.5 mm inside the surface edge to eliminate the effects of decarburization from heat treating.

Chemical composition estimates were performed using several EDS methods. These included examination of areas exhibiting differences in backscattered electron image (BEI) contrast, linescans consisting of multiple analysis points through specific transformation products, elemental maps displaying visual variations in alloy content, and point-count analyses on systematically chosen areas. In the point count analysis, a 6 x 5 equally spaced grid was superimposed on systematically chosen fields and chemical analysis performed at x/y intersections. The magnification used was 400x and the samples were in the unetched condition. Point spacing was 50 µm in both the x and y directions.

Estimation of the volume-related chemical compositions was sometimes complicated by the position of the analysis points and the locations of the pores. In some locations, the information generated by the electron beam was partially trapped within a pore and unable to reach the detector. When this was encountered, the point in question was eliminated from the data. It was also recognized that some pores contained an excessive amount of silicon, probably as an oxide from an additive particle. This data did not reflect diffusion of silicon into the base particles and had no effect on hardenability, therefore they were also omitted. The number of usable points included in this volume-fraction chemical-composition estimate exceeded 225 in all samples.

The relative accuracy of the silicon EDS analysis was improved through the use of standards made in the Hoeganaes Corporation Research & Development Laboratory. Compositions containing 0 to 3.2 w/o silicon in an iron matrix were melted, cast, and normalized after cooling to minimize alloy segregation. The silicon content was then measured using X-ray analysis and these results were compared with standards. They were then prepared using the same metallographic techniques required for the silicon-containing hardenability samples. EDS analysis was performed on multiple areas of each new standard and a linear-regression analysis performed. The R$^2$ value from this correlation was 0.99. All silicon concentrations reported here are the corrected values, as determined using the generated linear-regression expression.

**RESULTS AND DISCUSSION**

Four alloy composition groups were evaluated with their chemical compositions shown in Table I. The silicon, chromium, and manganese additions were made
with concentrated master-alloy powders. Selected results from the LOM and SEM testing of these silicon-containing mixtures were compared with similar tests on alloys without silicon to determine the contribution of silicon to diffusion and hardenability.

**Microindentation Hardness Profiles**

Figure 1 shows the microindentation hardness traverses from the sample edge to the cross-section core for the four composition groups. It should be emphasized that the locations for all hardness impressions were made blindly on unetched surfaces. In all cases, the hardness of the martensite ranges from approximately 700 to 800 HV0.05 and the non-martensite is in the 300 to 400 HV0.05 range.

In Figures 1(a), (c), and (d), there appears to be a

**TABLE I. NOMINAL BULK CHEMICAL COMPOSITIONS OF TEST SPECIMENS**

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Iron</th>
<th>Graphite (w/o)</th>
<th>Silicon (w/o)</th>
<th>Molybdenum (w/o)</th>
<th>Chromium (w/o)</th>
<th>Manganese (w/o)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>Bal</td>
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<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>Fe-Si</td>
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<td>0.90</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>Fe-Mo</td>
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<td>---</td>
<td>0.30</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>Fe-Mo-Si</td>
<td>Bal</td>
<td>0.70</td>
<td>0.60</td>
<td>0.30</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>Fe-Cr</td>
<td>Bal</td>
<td>0.70</td>
<td>---</td>
<td>---</td>
<td>0.35</td>
<td>---</td>
</tr>
<tr>
<td>Fe-Cr-Si</td>
<td>Bal</td>
<td>0.70</td>
<td>0.60</td>
<td>---</td>
<td>0.35</td>
<td>---</td>
</tr>
<tr>
<td>Fe-Mn</td>
<td>Bal</td>
<td>0.70</td>
<td>---</td>
<td>---</td>
<td>---</td>
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<tr>
<td>Fe-Mn-Si</td>
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<td>0.70</td>
<td>0.60</td>
<td>---</td>
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<td>1.0</td>
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</table>

**Figure 1.** Microindentation hardness traverses from the edge of the sample to the core. (a) Fe and Fe-Si, (b) Fe-Mo and Fe-Mo-Si, (c) Fe-Cr and Fe-Cr-Si, and (d) Fe-Mn and Fe-Mn-Si
clear separation of the martensitic and non-martensitic areas. In addition, most of the curves show consistency in transforming to either martensite or bainite/pearlite. The transformation behavior is exaggerated in the Fe-Si graph where the hardness appears to oscillate between the martensite and bainite/pearlite hardness ranges. The values indicate that the microstructure consists of large areas of martensite interspersed with large areas of bainite/pearlite. Only the molybdenum prealloy (Figure 1(b), Fe-Mo) shows a gradual decrease and increase in hardness. Examination of the Fe-Mn alloy shows two points where martensite appears to be present in areas of lower hardness transformation products. This mixed microstructure may be similar to that observed in the Fe-Si alloy. It is also obvious in all of the graphs that the addition of silicon provides a substantial increase in hardenability compared with the alloys without silicon.

**Alloy Distribution**

The Fe-Si sample was chosen for initial evaluation of alloying additive distribution due to the obvious variation in the transformation products along the hardness traverse. It is also the alloy with the lowest local hardenability throughout the compact, as indicated by the variability in hardness.

Figure 2 describes the variable silicon content in a completely martensitic area near the sample surface. Figure 2(a) is a secondary electron image (SEI) of the analyzed area. The more concentrated dot population in local areas of Figure 2(b) indicates a higher silicon content. This is quantified in Figure 2(c) where the relative positions along the dashed line in Figure 2(a) are the corresponding positions along the graph. Although a large portion of the composition in this area contains <0.5 w/o Si, the cooling rate was sufficient to transform the entire region to martensite.

Figure 3 illustrates similar analyses, but in a region
halfway to the cross-section core. In contrast to Figure 2, this microstructure contains multiple transformation products, where the lighter gray areas are pearlite/bainite and the darker gray is martensite. Each transformation product has variable silicon contents as can be seen in the linescan graph. The combination of the alloy composition and sample cooling rate in this area of the compact was not sufficient to produce an all martensite microstructure.

As can be seen in Figures 2 and 3, a single transformation product is made of multiple chemical compositions. An example of the variety of compositions is seen in Figure 4, which shows a typical sample area from the Fe-Si sample at a slower cooling rate. The presence of two transformation products is seen as two distinct shades of gray in the BEI. The chemical compositions shown in Table II are not necessarily taken from this area, but represent analyses made of several areas in the same vicinity.

The above examples (Figures 2 through 4 and Table II) illustrate the variation of chemical compositions that define the individual transformation products and are present throughout the compact volume. The combination of martensite and bainite/pearlite is a product of both the local chemical composition and the cooling rate. At the surface, the cooling rate is sufficient to transform the austenite to martensite. As the location of examination is moved toward the center of the compact, the cooling rate is slower and more non-martensitic transformation products are formed. Nevertheless, the distribution of alloying elements is the same.

Figure 5 shows the difference in microstructure with LOM images taken at intervals from the cross-section surface. It is clear the change in cooling rate has a dramatic effect on the combination of transformation products that are formed. The first images are located at or near the surface, with the remaining at distances progressing farther toward the core.

Figure 3. Area containing a combination of transformation products halfway to the core of the Fe-Si cross section. (a) SEI, (b) an elemental-silicon map (Si Kα), and (c) a silicon-linescan profile of (Si Kα). In (b), the higher concentration of yellow dots indicates higher silicon content. The dashed line in (a) indicates the location of a 50-point silicon (Si Kα) linescan, with the contents shown in (c). Total image width is approximately 300 μm. Lightly etched with 2 v/o nital + 4 w/o picral.
Changes in the microstructure appear as a progression from all martensite (Figure 5(a)) to a small amount of bainite/pearlite (Figure 5(b)) with movement several mm from the edge. As the distance from the edge becomes greater, increasing amounts of the lower hardness transformation product are observed until

<table>
<thead>
<tr>
<th>Light Areas</th>
<th>Dark Areas</th>
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</thead>
<tbody>
<tr>
<td>1.00</td>
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</tr>
<tr>
<td>1.68</td>
<td>0.14</td>
</tr>
<tr>
<td>1.05</td>
<td>0.16</td>
</tr>
<tr>
<td>0.66</td>
<td>0.25</td>
</tr>
<tr>
<td>0.93</td>
<td>0.24</td>
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<tr>
<td>1.27</td>
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</tr>
<tr>
<td>1.86</td>
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<td>1.13</td>
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<tr>
<td>1.89</td>
<td>0.23</td>
</tr>
<tr>
<td>1.68</td>
<td>0.12</td>
</tr>
</tbody>
</table>

Figure 4. Representative area in the Fe-Si sample approximately half the distance to the center of the cross section. The variety of silicon levels shown in Table II are examples of what is found in the two transformation products (martensite—light gray, bainite/pearlite—darker gray). BEI unetched

Figure 5. Change in transformation products with movement toward the center of the compact. The light- and medium-tan phase is martensite and the darkest transformation product is bainite/pearlite. Movement from the surface progresses from (a) (edge), to (b), to (c), through to (d) (core). LOM etched with 2 v/o nital + 4 w/o picral
approximately half the microstructure is martensite near the compact center (Figure 5(d)).

The behavior of the other silicon-containing alloys is similar to that of the Fe-Si alloy, although with substantially more transformation to martensite in the core. Conversely, the alloys without the silicon addition contain much less martensite when examined away from the surface. In alloys where manganese and chromium are added without the silicon, they do not show substantial improvement in hardenability over iron alone. Figure 6 is an example of the chromium alloys both at the quenched surface and in the core of the cross section. Figure 7 illustrates the microstructure of the Fe-Mo-Si alloy, both at the surface and in the core. As can be seen in Figure 7 at a higher magnification, the formation of the non-martensitic transformation product is different in the prealloyed powder.

Correlation of the chemical composition with the transformation products was accomplished using both SEM and LOM. Light microscopy was used to estimate the proportion of the transformation products at various distances from the sample surface and SEM/EDS was used to estimate the distribution of the alloying additives through the compact volume. Each method gives volume-related information and provides data to help predict what transformation product will form with specific chemical composition–cooling rate combinations. In this part of the study, only the silicon-containing alloys were used for the estimates and predictions.

Figure 8 is used to estimate the distributions of the additive diffused into the compact volume. From the randomly selected points where the silicon contents were measured, the values were arranged in rising order and cumulative number with silicon equal to or less than each value plotted. Since each point has the same volume measured then this is a cumulative volume expressed as a percentage of the total number of positions counted. These PM materials alloyed with particulate additives are confirmed to be heterogeneous in alloy distribution and, consequently, vary in the regions with sufficient hardenability to transform
to martensite upon cooling.

The proportion of transformation products is shown in Figure 9 for two alloys, Fe-Si and Fe-Mn-Si. The manganese–silicon alloy composition was included because the graph appears similar to the chromium–silicon and molybdenum–silicon alloys. This could be predicted by examining the microindentation hardness traverses where the three alloys are clearly in the martensite region. By quantifying area percent of the transformation products at a specific distance from the sample surface and estimating the alloy distribution throughout the compact volume, an approximate alloy content can be determined that will transform to martensite. This may apply in a through-hardening application or hardening to a particular depth below the surface.

Combining the Fe-Si data in Figures 8 and 9, the...
minimum silicon contents required to transform the compact to martensite at increments of 1 mm can be predicted. For example, the Fe-Si curves in Figure 9 show the proportion of martensite to non-martensite at the 6 mm distance is approximately 70:30 v/o. By examining the Fe-Si cumulative curve in Figure 8 and finding the 30 cum v/o on the y-axis (the non-martensite percentage), the silicon content needed to give the 70:30 ratio is approximately 0.37 w/o. These data combinations are shown in Figure 10, which is a predictor of the approximate silicon content needed to give a specific transformation product. Local silicon contents greater than these levels (any content above the curve) increase the hardenability sufficiently to transform to martensite and, conversely, any content below the curve will not.

The information gained from these volume-fraction estimates can also be used in alloy and process development. Quantities such as chemical-analysis distribution, local hardness, microstructure, density, etc., that show variability in the compact volume can be evaluated using these techniques. In alloy development, the effectiveness of complex or multiple additives with different base alloys can be investigated and correlated with the combination of transformation products in the microstructure and the resulting properties. Part-processing variables of sintering time, temperature, and cooling rate can be evaluated by looking at alloy distribution and/or microstructure. This information may also be relevant in part design, where part size and shape are strong considerations in how the microstructure is formed.

CONCLUSIONS
• Silicon has been shown to be effective in enhancing the hardenability of steels either as the sole alloying additive or combined with other elements such as molybdenum, chromium, and manganese.
• Metallographic techniques were used to estimate both the volume fraction of the transformation products and the chemical content distribution in a PM compact.
• These estimates were used to predict alloy compositions needed to through harden compacts of specific sizes.
• It may be possible to use these metallographic techniques in the evaluation of alloying methods such as binder treatments or diffusion alloying to assess the distribution and effectiveness of added alloying elements.
• PM materials, especially those alloyed with powder additives, are often heterogeneous in chemical composition and, consequently, microstructure. Metallographic techniques used to quantify alloy distribution clearly help in increasing our understanding of these materials.

ACKNOWLEDGEMENTS

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REFERENCES
The International Journal of Powder Metallurgy also recognizes the Excellence in Metallography “Awards of Merit” from the PM2014 World Congress:

The Effect of Copper Precipitation on Mechanical Properties at Operating Temperature of the Materials Used to Manufacture Powder-Forged Connecting Rods
Edmond Ilia, PMT, Metaldyne LLC, Plymouth, MI, USA

Characterization of the Interaction Between Copper and Nickel in Sintered Iron-Carbon Materials
Sarah Ropar, Amber Neilan, Bo Hu, Roland Warzel III, North American Höganäs, Inc., Hollsopple, PA, USA

Sintering Thermodynamics of Iron-Based Materials Containing the Solid Lubricant Molybdenum Disulfide
Kaline Pagnan Furlan, Thayna Andrea dos Santos, Cristiano Binder and Aloisio Nelmo Klein, Materials Laboratory (LabMat), Federal University of Santa Catarina (UFSC), Mechanical Engineering Department, Florianópolis, SC, Brazil

*Characterization of Ti-6Al-4V Powder In Electron Beam Melting Additive Manufacturing
Xibing Gong and Kevin Chou, The University of Alabama, Tuscaloosa, AL, USA
James Lydon and Kenneth Cooper, Marshall Space Flight Center, Huntsville, AL, USA

These papers were presented at the PM 2014 World Congress and published in Advances in Powder Metallurgy & Particulate Materials—2014, Proceedings of the PM2014 World Congress on Powder Metallurgy & Particulate Materials, and *on the AMPM Presentations CD, which are available from the Publications Department of MPIF (www.mpif.org).