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Novel surface modification of steel using high-density infrared heating

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Novel surface modification of steel using high-density infrared heating

by

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A thesis submitted to the graduate faculty
in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

Major: Materials Science and Engineering

Program of Study Committee:
Brian Gleeson, Major Professor
Scott Chumbley
Palaniappa Molian

Iowa State University
Ames, Iowa
2007

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Abstract

High-density infrared heating is a surface heating technique capable of producing wear-resistant coatings over a considerably larger processing area than currently available techniques (e.g. lasers). High-density infrared heating from a plasma arc-lamp is typically used for thermal annealing of silicon wafers, but this project expands the use of the plasma arc-lamp to produce carbon-enriched wear-resistant coatings on steel substrates. The focus of this study was to establish plasma arc-lamp processing parameters for the production of such coatings on a 1018 steel. The phase transformations involved were found to be in accordance with what occur in a fast-cooled hypoeutectic Fe-C system. The resulting structures contained a significant amount of Fe$_3$C near the surface present as discrete plates and with the ledeburite (i.e., eutectic microconstituent). A large fraction of carbide and the fine scale of the structures resulted in high hardnesses, reaching 750 HV 0.1 and 980 HV 0.1 for the graphite-only and Fe-Mo-C surface-modified regions, respectively. The high hardness and carbide fraction resulted in a significant improvement in two-body sliding wear-resistance over a standard carburized-and-hardened microstructure.
1. Introduction

The goal of this project was to establish plasma arc-lamp processing routes for obtaining unique surface modification structures in steel, which in turn lead to exceptional properties. Steel is outstanding in its ability for use in applications requiring low cost, high strength, and good wear resistance. Steel also has the ability to be surface modified in order to improve its properties, and it is this aspect that was the focus of the current project.

There are many different reasons for surface modification, with imparting wear resistance being primary among them. Wear resistance can be improved through techniques such as hardening, carburizing, and nitriding. The result is a harder surface with greater ability to withstand wear conditions while keeping a ductile interior. A ductile interior is important because it allows for plastic deformation rather than brittle failure. This, in turn, allows for a lower hardness (and thus lower cost) steel to be used as the bulk alloy.

The aim of this project was improve the wear resistance of plain-carbon steel through the use of new processing equipment, a plasma arc-lamp, which is able to generate a large amount of thermal energy at the sample surface in a short time frame. The large amount of thermal energy over a sizeable area opens the possibility for an advanced surface modification route beyond current equipment capabilities.

With its ability to achieve wear resistance, steel was chosen as the base material for this project. Carbon and molybdenum were used as the surface-modifying elements. Carbon is currently employed as an alloying element to steel surfaces in smaller amounts with great success (e.g., carburizing). However, as shown by literature and this project, higher carbon amounts combined with iron have the ability to be more wear resistant than currently-employed processes that impart lower carbon amounts to the surface.
2. Basic Physical Metallurgy of Steel

Steel is based on the Fe-C binary system, the phase diagram of which shown in Figure 1. The Fe-C system has multiple forms, based on the whether the carbon exists as graphite or as a carbide. The stable state of carbon is graphite, but it is frequently observed (such as in steel) in association with iron as Fe₃C. Fe₃C is referred to as metastable with respect to graphite and in this form, is presented as the Fe-Fe₃C system. Both systems are shown in Figure 1. The basic phases and constituents of steel will be discussed, but first, it must be noted that steel is typically referred to as Fe-C with less than approximately 2.1 wt% C and minor alloying elements, while cast iron typically has 3-4.5 wt% C with larger amounts of alloying elements. The difference in classification is dependent mainly on the amount of carbon in the system.

Figure 1: Iron-Carbon phase diagram (solid lines represent Fe₃C equilibria, dashed for graphite).¹
2.1. Phases and Constituents of Steel

The structural forms of pure iron are α-Fe (ferrite), γ-Fe (austenite), and δ-Fe. In pure iron, ferrite is stable to 912 °C, while austenite is the stable phase between 912 °C and 1394 °C. Above 1394 °C, δ-Fe is stable up to 1538 °C, the melting temperature of pure iron. Large pressure changes are required for significant changes in the transition temperatures for these phases. A pressure-temperature phase diagram for pure iron is shown in Figure 2. All data in this thesis are given at a pressure of 1 atm (1.01325*10⁻⁴ GPa).

![Figure 2: Pressure-temperature diagram of pure Fe.](image)

Ferrite and δ-Fe are both body-centered cubic (BCC) in crystal structure, whereas austenite is face-centered cubic (FCC). Typically, when a metal undergoes a solid-state phase change on cooling, the new lattice structure is more compact, with a higher packing factor and thus, a higher density. Iron is an exception to that because the transition from austenite to ferrite upon cooling decreases the packing factor of the lattice structure (since FCC has a higher packing factor than BCC), thus increasing the volume. As follows by thermodynamics, BCC
ferrite is a lower energy state than FCC austenite at room temperature. According to Steinle-Neumann et al., the BCC crystal structure is stable mainly due to the presence of magnetism. BCC ferrite is ferromagnetic and magnetic effects are larger in larger volumes, favoring a more open lattice.

Ferrite has a Vickers hardness of 136 to 185 HV\(^4\) (HV = Vickers Hardness, Table 1) and only allows for a limited amount of carbon solubility (~0.022 wt% at the eutectoid temperature\(^5\)) before precipitating a carbide. Since the carbon atom is much smaller than the iron atom, the carbon can fit within the spaces between the iron atoms in the lattice structure. In ferrite and in δ-Fe, carbon is dissolved into the octahedral interstitial sites. However, the carbon atoms are too large for a perfect fit and introduce strain into the lattice. The interstitial sites in the BCC lattice are small when compared to the FCC lattice, especially in the smaller c-axis direction. Thus, ferrite and its BCC structure cannot absorb much carbon before the strain energy in the system is too large to be stable. Figures 3 and 4 show the octahedral and tetrahedral sites in BCC and FCC lattices, respectively.

Figure 3: Interstitial sites in the BCC structure.\(^6\)
Even a small amount of strain from the carbon interstitials adds significant strength to the lattice. For example, the tensile strength of 99.989% pure iron without carbon is 144 to 180 MPa. With the addition of 0.02 to 0.032 wt% C, the tensile strength approximately doubles to 298 MPa (similar levels of Mn, Si, S, and/or P were present in the samples). The increase in strength is due to the anisotropic strain field impeding dislocation motion. The anisotropic strain field within the iron is created due to an anisotropic distortion of the BCC lattice in ferrite. As mentioned above, the carbon is situated in the octahedral sites of the BCC lattice. Since these sites are smaller in the c-axis direction (Figure 3), the strain field is significantly larger in the c-axis direction, creating the anisotropic strain field.

As the temperature increases, ferrite becomes unstable and austenite (γ-Fe) becomes the stable phase (at 912 °C in pure iron). Austenite is slightly stronger than ferrite (240 HV, compared to 136 to 185 HV, Table 1) and can dissolve up to 2.11 wt% C at 1148 °C, significantly more than ferrite. In the both the FCC and the BCC lattices, carbon resides in the octahedral interstitials. In an FCC lattice, however, the size of the octahedral sites is larger than in the BCC lattice. With the larger sites, each additional carbon atom imparts less strain on the matrix. Thus, austenite can dissolve significantly more carbon before the lattice strain becomes too large and carbon precipitates.

Further temperature increases transform austenite into δ-Fe. δ-Fe is, like ferrite, BCC in structure. δ-Fe can dissolve only a small amount of carbon before the strain in its BCC lattice becomes too large for the lattice to be stable.
Table 1: Hardness of the different phases and constituents of Fe-C (*Note that some of the reported hardness values vary, so the hardness numbers reported here should only be used for rough comparison purposes. Reported values in Knoop, Vickers, and Rockwell C scales).

<table>
<thead>
<tr>
<th>Phase/Constituent</th>
<th>Hardness*</th>
<th>Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ferrite</td>
<td>150 to 200 HK (136 to 185 HV)&lt;sup&gt;4&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td>Pearlite</td>
<td>250 HK to 350 HK (237 HV to 345 HV)&lt;sup&gt;4&lt;/sup&gt;</td>
<td>Coarse/fine structure, respectively</td>
</tr>
<tr>
<td>Bainite</td>
<td>45 to 60 HRC (450 to 700 HV)&lt;sup&gt;4&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td>Cementite</td>
<td>≈800 to 1500 HV&lt;sup&gt;4,9&lt;/sup&gt;</td>
<td>Temperature and alloying element dependent</td>
</tr>
<tr>
<td>Martensite</td>
<td>Up to ≈65 HRC (840 HV)&lt;sup&gt;4&lt;/sup&gt;</td>
<td>Carbon content dependent</td>
</tr>
<tr>
<td>Ledeburite</td>
<td>Typically &gt; 700 HV&lt;sup&gt;1&lt;/sup&gt;, can reach ≈1500 HV&lt;sup&gt;10&lt;/sup&gt;, (virtually unmachinable&lt;sup&gt;8&lt;/sup&gt;)</td>
<td>Dependent on structure</td>
</tr>
<tr>
<td>Austenite</td>
<td>≈200 HB (240 HV)&lt;sup&gt;8&lt;/sup&gt;</td>
<td></td>
</tr>
</tbody>
</table>

The main reason that hardness is important in this project is that wear improvements can generally be correlated to an increase in hardness.<sup>11, 12</sup> Accordingly, a high hardness alloy is desired. As seen in Table 1, the hardest phases and constituents in the Fe-C phase diagram are martensite, cementite, and ledeburite. The goal is this project is to mix these microstructures to obtain a high hardness. Chapter 2 presents the phases and micro-constituents in the Fe-C system, while Chapters 3 and 4 present information on surface modification techniques and surface liquification, respectively.

2.1.1. The Fe-C System: Graphite and Cementite

Carbon occurs in many forms such as graphite, diamond, and fullerenes. Of these phases, graphite is the most stable thermodynamically. Diamond and fullerene crystal structures do not appear in the Fe-C system. As such, graphite is the only crystal structure of carbon discussed henceforth (carbon-containing compounds are still discussed).

In the Fe-C system, iron and carbon form an intermediate compound known as cementite, Fe<sub>3</sub>C. As mentioned earlier, cementite is a metastable phase in the Fe-C system, but it

<sup>1</sup> Referenced in Chapter 4, the ledeburite microstructure is observed and measured by various authors.
typically forms much quicker than graphite. Thus, the phase diagram for the Fe-C system is frequently represented on one plot with both the Fe-Fe$_3$C and the Fe-C (graphite) boundaries, as in Figure 1. Convention dictates that the composition axis is expressed in weight percent carbon, as opposed to weight percent Fe$_3$C for the Fe-Fe$_3$C system.

Cementite has an orthorhombic crystal structure and is a hard and brittle phase, with hardness ranging from ~800HV to 1500HV$^{4,9}$ (Table 1). Cementite is a line compound, with a fixed composition corresponding to Fe$_3$C. Cementite, like ferrite, is present in most steel and cast iron microstructures, either on its own or as a part of a micro-constituent. Figure 5 shows a microstructure of cementite on prior austenite grain boundaries, as well as within the pearlite.

Graphite is effectively a 2D hexagonal structure with weak van der Waals bonding between the layers. With the weak 3$^{\text{rd}}$ plane bonding, the effective strength of graphite is low. Thus, for high hardness, cementite outperforms graphite. However, graphite can be used as a lubricant, which can be useful for certain types of sliding wear.

2.1.2. The Fe-C System: Micro-constituents

One of the most common heat treatments for steel is to austenitize and cool. During austenitizing, the part is heated to a temperature at which only austenite is stable, held there for a certain time, and then cooled back to room temperature. As the steel is cooled, various phase changes can occur, depending on the cooling rate. Figure 6 shows a time-temperature-transformation (TTT) diagram for a Fe – 0.45 wt% C alloy (TTT curves are also known as isothermal transformation, or IT, diagrams). Two phases and three micro-constituents are shown on the diagram: austenite, ferrite, pearlite, bainite, and martensite, respectively. Austenite and ferrite have been discussed previously. Pearlite, bainite, and martensite are constituents of the Fe-C system. The other constituent of this system is ledeburite, which
comes from the eutectic (i.e., liquid $\rightarrow \gamma + \text{Fe}_3\text{C}$), rather than through the eutectoid (i.e., $\gamma \rightarrow \alpha + \text{Fe}_3\text{C}$) transformation on cooling.

Figure 6: Time-Temperature-Transformation Curve for a 0.45 wt% C iron-carbon alloy. A = austenite, B = Bainite, F = ferrite, M = martensite, and P = pearlite. 

Pearlite typically has a lamellar microstructure composed of alternating plates of ferrite and cementite. Pearlite forms upon cooling by the eutectoid reaction and is diffusion-controlled.

Figure 7: Pearlite schematic of carbon and iron redistribution and micrograph of pearlite lamellae.
Specifically, pearlite grows by a coupled growth mechanism, Figure 7, where excess iron in front of the cementite diffuses towards the ferrite plates. Similarly, the excess carbon in front of the ferrite diffuses towards the cementite plates. According to the Zener-Hillert analysis, the rate of pearlite growth \( G \) is:

\[
G = \frac{D^\gamma}{k} \cdot \frac{S^2}{\lambda^i} \cdot \frac{(C^\gamma - C^{\gamma+cm})}{(C^{cm} - C^\alpha)} \cdot \frac{1}{S} \left( 1 - \frac{S_c}{S} \right)
\]

(1)

Here, \( D \) is the diffusion coefficient, \( k \) is a geometrical factor (~0.72 in the Fe-C eutectoid), \( \lambda^i \) is the thicknesses of lamellae \( i \), \( C^\gamma \) is the carbon concentration in front of the lamellae in the austenite, \( C^\gamma \) is the carbon concentration in the lamellae, \( S \) is the interlamellar spacing, and \( S_c \) is the critical interlamellar spacing. The critical interlamellar spacing can be calculated by:

\[
S_c = \frac{2\gamma^{\alpha-cm}T_E}{\Delta H \Delta T}
\]

(2)

where \( \gamma^{\alpha-cm} \) is the interfacial energy, \( \Delta H \) is the enthalpy change, and \( \Delta T \) is the undercooling below the eutectoid temperature. For the relationship between the critical spacing and the observed spacing, Zener proposed a maximum growth rate at the spacing:

\[
S = 2S_c
\]

(3)

The Zener-Hillert equation assumed that the austenite and pearlite constituents were in local equilibrium at the reaction front and the rate-controlling step was volume diffusion of carbon in austenite. Puls and Kirkaldy agreed with Zener in a boundary diffusion model for isothermally formed pearlite, but modified the equation for a volume diffusion model based on a hypothesis of maximum rate of entropy production. They obtained a spacing of

\[
S = 3S_c
\]

(4)

Thus, either with the Zener assumption or the Puls and Kirkaldy assumption, it follows that the higher the undercooling, the lower the spacing that results, and vice versa.

Within pearlite, the lamellar spacing is important because the finer the spacing, the stronger the alloy. The Hall-Petch relationship is valid for both lamellar spacing and for grain size, as they can be interpreted as the same in this context. The Hall-Petch relationship states that

\[
\sigma = \sigma_0 + \frac{k}{\sqrt{d}}
\]

(5)

where \( \sigma \) is the yield stress, \( d \) is the grain size/lamellar spacing, and \( \sigma_0 \) and \( k \) are constants. The hardness measurements of pearlite correlate with the spacing to strength relationship, such that the hardness of pearlite ranges between 237 and 345 HV, the finer pearlite corresponding to the higher hardness.
Pearlite forms at higher temperatures in the TTT diagram; while at lower temperatures, bainite can form. However, the formation curves typically overlap (Figure 8) to a considerable extent, making microstructure interpretation difficult, such as in plain carbon steel.\(^6\) Kennon and Kaye\(^{18}\) found that both pearlite and upper bainite formed simultaneously and probably independently when isothermally transformed after austenitizing between 400 to 600 °C (steel with 0.80 wt% C, 0.77 wt% Mn). As for hardness, bainite is a harder structure than pearlite, with hardness values ranging from 450 to 700 HV.\(^4\)

Bainite is known to exist in two forms: upper bainite and lower bainite. Upper bainite forms at in the range of 350 to 550 °C; the lower end of the transition range is dependent upon carbon concentration. Below the transition temperature, lower bainite forms (TTT diagram shown in Figure 9). Microstructures of upper bainite and lower bainite are shown in Figures 10 and 11, respectively.

---

Figure 8: TTT diagram showing the start of the transformation to pearlite and bainite.\(^{18}\)

Figure 9: TTT diagram of bainite formation.\(^{19}\)

Figure 10: Upper bainite in 4360 steel, transformed at 495 °C, 750X.\(^{19}\)

Figure 11: Lower bainite in 0.66 wt% C – 3.3 wt% Cr steel, transformed at 350 °C, 1000X.\(^{19}\)
The microstructure of upper bainite typically consists of ferrite laths that nucleate at the austenite grain boundaries. The untransformed austenite near the lath edges becomes enriched with carbon and carbide particles precipitate between the ferrite laths. Lower bainite typically has plate morphology, as opposed to the lath morphology of upper bainite. The plates nucleate both on the grain boundaries and within the grains due to the high nucleation driving force, but remain thin due to the low diffusivity of carbon in iron at the lower bainite transformation temperatures.

In hypoeutectic and hypereutectic systems with high undercooling, a Widmanstätten structure can form. In hypoeutectic systems, a Widmanstätten ferrite structure forms, Figure 12 as a sawtooth formation from the grain boundaries, or as intersecting needles which form a regular, geometric pattern, Figure 13. In the hypereutectoid region, the Widmanstätten structure forms as cementite, instead of ferrite, Figure 14.

Figure 12: Widmanstätten ferrite in a isothermal transition. Fe-0.29C-0.76Mn (wt%), 725°C for 90sec.20

Figure 13: Widmanstätten ferrite slow cooled at 0.03°C/s from 850°C, Fe-0.53C-0.051Mn-0.006P-0.034S-0.205Si-0.046Cu (wt%).20
The Widmanstätten structure forms at high undercooling, as shown in Figure 15. The high undercooling drives the formation of the structure. Lower undercooling will cause the formation of ferrite and carbide on the grain boundaries, while pearlite and bainite will tend to form at compositions that are closer to the eutectoid composition.

Both pearlite and bainite are diffusion-based transformations that occur when cooling steel from an austenitizing temperature. Martensite, on the other hand, is a diffusionless transformation. Martensite is different in that it is a body-centered tetragonal (BCT) constituent that is very hard and strong. Martensite forms when cooled from an austenitizing temperature at a sufficiently high rate to avoid the formation of other diffusion-based transformations. Specifically, due to the high cooling rate, diffusion does not have enough time to occur. However, FCC austenite is thermodynamically driven to transition to BCC ferrite. The distortion that results from the
austenite instability is the FCC-to-BCT transformation. This transformation is known as the Bain distortion and is shown in Figure 16. The Bain distortion can be shown by two FCC unit cells side-by-side, noting the center face atom of the shared sides. This middle atom of the FCC face can also be considered the center of the BCT crystal structure, but stuck in an FCC crystal structure. If this cell were removed from the FCC crystal structure and allowed to form the BCT dimensions of the martensite unit cell, Figure 17 would result. To obtain the correct unit cell dimensions, the removed FCC cell would contract 18% on the $x_3$-axis (c-axis) and expand 12% on both the $x_1$-axis and $x_2$-axis (a-axis and b-axis), giving the Bain distortion.

There are two microstructure variants of martensite in the Fe-C system. Steel that is low in carbon forms a microstructure known as lath martensite (Figure 18a), which is softer than the martensite that forms at high carbon concentrations. The martensite that forms at higher carbon concentrations is called plate martensite (Figure 18b). Lath martensite has long, fine, plate-like precipitates that grow in packets. Plate martensite has a more distinct structure of plates that form at angles to each other.

Martensite begins to nucleate at a critical temperature, regardless of the time elapsed during cooling (provided no other phase forms first, see Figure 6 for a TTT diagram). This temperature is known as the $M_s$ temperature. Similarly, the temperature at which the transformation to martensite is complete is called the $M_f$ temperature.
Most martensitic transitions are athermal. That is, the temperature, with respect to the $M_s$ and $M_f$ temperatures, governs the amount of material transformed to martensite; martensite formation is nearly independent of cooling rate, provided the rate is above a critical value. A few alloy systems are isothermal, e.g. Fe-Ni-Mn, Fe-Ni-Cr, and Fe-Ni.\(^6\)

The $M_s$ temperature is dependent upon the steel composition. An empirical relationship for the determination of the $M_s$ temperature was determined by Andrews,\(^23\) to be (wt\%, with modification by Kung and Rayment\(^24\)):

$$M_s(\degree C) = 539 - 423(\% C) - 30.4(\% Mn) - 17.7(\% Ni) - 12.1(\% Cr) - 7.5(\% Mo) + 10(\% Co) - 7.5(\% Si)$$

(6)

The $M_f$ temperature is affected similarly and a plot of the $M_s$ and $M_f$ temperatures as a function of carbon content is shown in Figure 19.

The hardness of various steel constituents is a function of the carbon content, Figure 20. As the carbon content increases, the hardness increases. In the case of martensite, however, there is a range of hardness values obtained at high carbon contents, as shown by the shaded region. The range of hardness values is due to retained austenite in the structure. Retained austenite is caused, in part, by high alloy content in the steel, which contributes to the

---

Figure 18: (a) Lath martensite in an Fe – 0.09 wt\% C as-quenched steel, 500X. (b) Plate martensite in an Fe – 22.5 wt\% Ni – 0.4 wt\% C alloy, 150X.\(^22\)

Figure 19: Ms and Mf temperature plot.\(^6\)
lowering of the $M_s$ and $M_f$ temperatures. The lower $M_s$ and $M_f$ temperatures delay the start/finish of martensite formation to temperatures as low or lower than room temperature. Other factors that influence the formation of retained austenite are completion of the prior austenite transformation, cooling rate, and stress.

The major strengthening mechanisms of plate martensite are interstitial solid-solution hardening and precipitation hardening, whereas in lath martensite, the major strengthening mechanisms are precipitation hardening and dislocation hardening. Minor contributions include grain size (via the Hall-Petch relationship), substitutional solid-solution hardening, interstitial solid-solution hardening (in lath martensite), and dislocation hardening (in plate martensite). The higher carbon content in plate martensite contributes to the lattice strain and the strengthening as a result. As for lath martensite, a large portion of the strength increase is due to the formation of dislocations. The dislocation density for a lath martensite structure can be large enough to be similar to a heavily deformed structure. The high dislocation density appears to be due to the presence of carbon out of solution. Experimental data suggest that most of the carbon is out of solution and segregates to dislocations and lath boundaries during quenching. The segregation is effective at increasing the dislocation density, and increasing the strength of the lath martensite structure. Thus, the net effect of adding carbon to the microstructure is an increase in the hardness, Figure 20.
The last of the constituents to be discussed is ledeburite. Ledeburite forms on cooling via the eutectic reaction, $L \rightarrow \gamma + \text{Fe}_3\text{C}$, and consists of a lamellar arrangement of austenite and cementite (while above the eutectoid temperature). Ledeburite is very hard and is said to be virtually unmachineable.\(^8\) The structure of ledeburite is shown in Figure 21. Similar to pearlite, the spacing of the ledeburite lamellae is dependent upon the rates of cooling and diffusion; the latter is generally fast since ledeburite is formed from liquid. The austenite present in ledeburite will generally decompose into pearlite and cementite upon further cooling, but the microstructure can retain some austenite or transform to martensite if it is cooled fast enough.

The details of the mechanism of metastable eutectic nucleation is still under some investigation,\(^{28,29}\) but the dominant overall theory for ledeburite formation comes from Hillert et al.\(^{30,31}\) The nucleation starts from Fe\(_3\)C plate shaped dendrites forming in a fanlike growth pattern, Figure 22, in both hypoeutectic and hypereutectic alloys. In hypoeutectic alloys, the first solid is austenite dendrites and the Fe\(_3\)C plate shaped dendrites nucleate on the austenite dendrites. The second stage for both hypoeutectic and hypereutectic alloys consists of the cooperative growth between the austenite and the cementite, as shown in Figure 23. The cooperative growth mode works in that cementite leads in the edgewise direction in a plate formation, with cooperative...
sidegrowth of cementite rods in austenite. The sidegrowth branches off from the initial edgewise growth.

The growth mechanism of the stable eutectic, however, is still being mildly debated, as some older research has tended to be forgotten. This is illustrated by a dialogue between Hillert and Rivera et al.\textsuperscript{32,33,34}

The basic mechanism proposed by Hillert and Rao\textsuperscript{31} and Rivera et al.\textsuperscript{32} in each of their papers is based on an initial formation of large austenite dendrites. Once the graphite nucleates, it will grow in cooperation with the austenite dendrites to form roughly spherical eutectic colonies, Figure 24. The graphite colonies do not correlate with the scale of the austenite dendrites, which are significantly larger than the gray eutectic colonies.\textsuperscript{32}
3. Surface Modification of Steel

As previously mentioned, surface modification is a technique used to improve the properties of steel, such as wear resistance and surface hardness. Since wear resistance typically increases with surface hardness, the focus for this project was on surface hardness, with minor wear testing to show the promise of the arc-lamp coatings.

Many different methods are practiced commercially that are able to increase the surface hardness of bulk steel. Surface modification is typically done in three broad categories – surface coatings, surface alloying, or surface hardening. Surface coating is when a coating or surface layer is applied to the steel, such as galvanizing. Surface alloying is when the composition of the steel is changed at the surface to create more desired microstructure/properties, such as carburizing. Surface hardening is when the metallurgy at the surface is changed to harden the metal, such as through thermal treatment. The main differences between the three are related to the specific capabilities of the techniques.

As a general rule, surface coatings allow for the most flexibility in design of the system because any type of coating can be applied to the surface, e.g. wear resistant, corrosion resistant, electrically conducting, etc. Coatings are also flexible in that they can be applied through a variety of different methods, e.g., thermal spray, plating, or vapor deposition. A benefit to coatings is that dissimilar materials can be used for the coating and the substrate, without being constrained by the phase diagram of the components. An example of this would be placing a hard, tungsten carbide and cobalt coating on a steel alloy. The ability to choose the coating allows for better matching between the coating, substrate, and application. One disadvantage to coatings is that the bonding layer between the coating and the base alloy is typically very thin, which can create stresses in the interface due to factors such as mechanical stress and thermal expansion mismatch during processing and service. The stresses generated at the interface can result in cracking and poor coating performance.

Surface alloying involves changing the composition of the steel at the surface to allow the properties of the steel to be more desirable. An example of this would be through carburizing. One advantage of alloying is that the transition between the case and the core is gradual, rather than a defined transition layer, as is typically the case with coatings. This project will be dealing mainly with surface alloying directly with the plasma arc-lamp.
Surface hardening is the simplest of the three since only the base metal is used, and subject to techniques such as thermal treatment. The simplicity serves as an advantage. In the broader category of surface metallurgy, other techniques, such as shot peening, are used to engineer for other properties, i.e. fatigue in this case. As for thermal treatment, a disadvantage to hardening is that it relies on the inherent ability of the material to become harder through phase transitions. Thus, only certain materials can be surface hardened through a heat and quench operation. As discussed above, steel undergoes a martensitic transformation that makes it harder, whereas other materials, e.g. aluminum, do not undergo a phase transformation upon rapid cooling and therefore, are not able to be hardened by a heat and quench operation alone. Other techniques, such as laser remelting, could be performed for grain refinement or for fine precipitate formation that would be applicable to a wide range of materials as well, but are not the focus of this project.

Beyond the general categories, the choice of surface modification method matters significantly and is dependent upon many factors, such as desired thickness of wear resistant layer, ability of component to take distortion, the operating environment, the contact loading, and cost.

Figure 25 compares the thicknesses of different surface engineering treatments. The thickness required is dependent largely upon the application. For example, highly loaded parts require thick cases since both the case and the core will be required to carry the load. The desired thickness for this project will be in the 0.1 to 1 mm range, as potential applications will likely be highly loaded and in high abrasive wear conditions.

Also of importance is the ability for the part to take distortion. Certain processes, such as carburizing, use heated environments, while others, such as thermal spray, ideally keep the interior of the substrate close to room temperature. Figure 26 shows an approximate temperature range for various surface treatments.
Figure 25: Approximate thickness of various surface treatments.  

Figure 26: Maximum expected surface temperatures for various surface engineering processes. The dashed vertical line is at 540°C, representing the temperature limit for distortion in ferrous alloys.
Other factors that influence the surface modification methods are the operating environment, the contact loading/geometry, and the cost. Operating environment can help determine if the coatings have any additional requirements, such as corrosion resistance or electrical insulation. Contact loading is another factor to be considered, because certain types of surface treatments are better in some loading conditions than others. For example, thermal sprayed coatings can fair poorly in point loading applications near the edges of the coatings. As for cost, it is always an issue. Figure 27 shows a schematic of approximate costs for each of the various techniques.

![Figure 27: Approximate cost of some surface treatments.](image)

The rest of this chapter presents details on hardening via heat treatment and carburizing, as these methods are the most applicable to this project. Heat treatment will be observed in this project as the steel is self-quenched after processing and carburizing will be observed through the surface alloying to be conducted in this project.
3.1. Hardening by Heat Treatment

One of the simpler methods of surface modification is hardening by heat treatment. Such hardening involves heating the surface of the part (perhaps the entire part as well) up to austenitizing temperature and then quenching to obtain a hard surface microstructure.

During heat treatment, the steel transforms to a solid solution of austenite. Then, the steel is quenched, forming martensite at the surface of the part and, if the entire part is heated and not too thin, pearlite and ferrite in the center (if the part is thin, martensite may be observed through the center of the part). Martensite is formed at the surface due to the high cooling rate there. In a part that is heated as a whole (such as in a furnace), pearlite and ferrite are often formed in the center because of the slower cooling rate in this region. The depth of the martensite is dependent upon the cooling rate and upon the thickness of the material present.

As for wear resistance, a thick layer of martensite is desired, which is frequently obtained by a very rapid cooling rate. While more martensite formation is good, there are a few caveats to a high cooling rate. High cooling rates have more potential to cause distortion in the part due to uneven cooling. Even with uniform cooling, thermal stresses can also develop within the part and cause cracking. Finally, a part that has been hardened completely through the center will be brittle, losing its previous ductility. Brittle parts may not be desired in the end application. Overall though, martensite formation is usually good for wear resistance.

Typically, hardening operations are followed by tempering. Tempering can be regarded as a lower temperature aging process. Through tempering, a wide range of strength, toughness, and ductility properties can be obtained, Figure 28. The microstructure changes across four general stages of tempering. The stages are dependent upon the temperature, since in industrial practice a couple hour of tempering time is common. The temperature ranges are approximate and vary depending upon the literature source.

In the aging reaction stage, up to ~100 °C, the carbon segregates to the dislocations and lath boundary regions and forms a precipitate, producing carbon depletion in the martensite lattice. In stage 1 tempering, $\alpha' \rightarrow \alpha'' + \varepsilon$-carbide ($\alpha''$ is low-carbon martensite and $\alpha'$ is supersaturated martensite), which occurs in the range of 100 to 250 °C. The $\varepsilon$-carbide appears as small ($\leq 2$ nm) diameter particles. The transition carbide, $\eta$, may also precipitate.
By tempering up to 200 °C, the $\varepsilon$-carbide particles develop into an array of needle-like morphology and create coherency strains across the planes, accounting for the increase in hardness observed in stage 1 tempering. In stage 1 tempering in steels with composition less than 0.2 wt% C, the changes are limited to the carbon segregation to the dislocations and boundaries, leaving no carbon left in solution to precipitate.

In stage 2 tempering, the retained austenite, $\gamma_R$, transforms: $\gamma_R \rightarrow \alpha + Fe_3C$ at higher temperatures, or $\gamma_R \rightarrow \alpha + \varepsilon$-carbide (or $\eta$-carbide) at lower temperatures. Stage 2 tempering occurs in the range of 200 to 300 °C and is associated with the reduction of retained austenite, Figure 29. In stage 3, from 250 to 400 °C, lath-like $Fe_3C$ precipitation occurs. At around 400 °C, the rodlike carbides dissolve and transform to spheroidal cementite. The third stage can also be marked by the formation of Hägg or Chi ($\chi$) carbides, and/or a monoclinic $M_5C_2$ structure (M is a combination of Fe and/or Mn atoms).

Figure 28: Selected property changes with tempering in an oil-quenched 4340 steel.

Figure 29: Transformation of retained austenite in stage 2 tempering in a Fe – 1.22 wt% C alloy.
From 350 to 550 °C, segregation of alloy and impurity elements can occur, resulting in various types of embrittlement. From 400 to 600 °C, dislocation recovery occurs, but keeps the grain size and shape of quenched martensite due to the structure being stabilized by the fine carbide precipitates. The fourth stage of tempering occurs from 500 to 700 °C, secondary hardening occurs by the precipitation of alloy carbides. Above 600 °C, coarsening of the carbides occurs, as well as recrystallization and grain growth.

3.1.1. Methods for Hardening

Hardening can be achieved by different methods; a few of the common methods in use are induction hardening, flame hardening, laser hardening, and electron beam hardening.

In induction hardening, an oscillating magnetic field is applied to a steel part, inducing eddy currents near the surface of the sample. The induced eddy currents then heat the surface. After a certain amount of time and temperature with the surface in the austenitic region, the part is quenched, resulting in the hardened surface without affecting the substrate. The main control method in induction hardening is changing the frequency to change the hardening depth. The case depth change is proportional to the square root of the inverse of the frequency.6

In flame hardening, a flame is used to rapidly heat the surface of the steel to an austenitizing temperature. Once the transformation to austenite is complete, the part is quickly quenched with an external quench medium to produce a martensitic structure.

Laser hardening and electron beam hardening are similar to flame hardening. Laser hardening is heating using a laser instead of a flame. With the amount of heat concentrated over a smaller area, the depth and width of the heat-treated zone can be smaller, as well as enabling the part to serve as an internal quenchant and cool the surface at a sufficiently high rate to obtain martensite. Electron beam hardening is conducted in vacuum and uses an electron beam to heat the sample. Similar to laser hardening, the electron beam method also has a very small heat-affected region, uses the rest of the samples as a quenchant (no external quenchant required) and can be used for selective hardening on a sample. Both of these techniques are much more precise and have smaller targets than the flame hardening method, an advantage to both of the techniques.
3.2. Carburizing

Carburizing is similar to thermal hardening, but adds an additional step of diffusing carbon into the surface to create a harder case through alloying. The additional carbon on the surface allows for a harder martensitic case to form (see Figure 20 in Chapter 2.1.2), while leaving the center as the more ductile and lower-cost carbon steel alloy. The result is a case that is more wear and fatigue-resistant.

In a typical commercial carburizing process, the part is heated above the austenitizing temperature and carbon is introduced to the surface of the austenitic matrix in a “boost” step. The part continues at a high temperature but without the further addition of carbon in a “diffuse” step. After sufficient time in the two steps (and possibly with two different temperatures), the part is quenched. The boost and diffuse steps in the carburizing process can be done either as one step or separately.

Carbon can be introduced to the surface of the part by a variety of means, as discussed in the next subsection. Once the carbon reaches the surface of the part, the carbon diffuses into the steel part to create a certain depth of carbon, known as the case depth, Figure 30. Once the part has been at an austenitizing temperature for the desired amount of time, the part is

![Figure 30: Microstructure of a carburized 0.15 wt% C steel pack carburized for (a) 1h, (b) 2h, and (c) 4h at 940 °C, respectively.](image-url)
quenched to from martensite at the surface; the surface is harder than it would have been through thermal hardening alone.

Typical amounts of carbon in the case are around 0.9 wt%, but can reach up to 1.2 wt%.\textsuperscript{6} Too much carbon in the case can potentially form free cementite and make the case more brittle than usual, while lower carbon contents do not reach the maximum hardness.

There is also a practical limit to adding carbon to austenite and still allowing the formation of martensite. Higher carbon contents in the martensite increase the driving force needed for martensite formation and lower the temperature which must be reached before martensite can form (i.e., the $M_s$ temperature). The lower $M_s$ and $M_f$ temperatures, with smaller contributions from the cooling rate and the residual stress from quenching, result in retained austenite in the microstructure after quenching. In cases where the $M_f$ temperature is above room temperature, the amount of retained austenite is small.\textsuperscript{6} A higher cooling rate (such as in water instead of oil) help to reduce retained austenite. Regions of high elastic stress, e.g. between the last martensite plates to transform, may also contribute to retained austenite.\textsuperscript{21}

The main benefit to carburizing for wear-resistance is the hardness and strength increases from the higher carbon martensite (for more information on martensite, see Section 2.1.2).

### 3.2.1. Common Methods for Carburizing

Common methods for carburizing steel include gas carburizing, pack carburizing, liquid carburizing, plasma carburizing, and vacuum carburizing. Gas carburizing is the most common method in use for large volume productions, and is becoming more common every year.\textsuperscript{6} Pack carburizing is another common method suitable to small runs. The other methods are used, but with less frequency. Gas carburizing and pack carburizing methods will be discussed in significantly more detail than the other methods, as those will be used in this project.

#### 3.2.1.1. Gas carburizing

Gas carburizing is conducted by heating the entire sample to an austenitizing temperature in a controlled-flow furnace atmosphere. The controlled atmosphere is a complex mixture of
carbon monoxide, carbon dioxide, hydrogen, nitrogen, water vapor, and an enriching gas, typically methane (natural gas), propane, or butane. The nitrogen is inert and serves as a diluent. In the reactions that follow, the input gas is assumed to be methane.

The input gas for the controlled atmosphere is called endothermic gas, and is typically produced in an endogas generator, separate from the furnace. The endothermic gas consists of the same elements that are in the controlled atmosphere, but is mainly carbon monoxide, hydrogen, and nitrogen. Endothermic gas, when produced by natural gas and with a natural gas-to-air ratio of 2.4, has a composition of:

\[
19.8\% \text{ CO} + 40.5\% \text{ H}_2 + 0.1\% \text{ CO}_2 + 0.5\% \text{ CH}_4 + 39.1\% \text{ N}_2
\]

Water vapor is not included in this formula, because the dew point is about 10°F (-12°C) at this ratio.

The endothermic gas provides the flowing atmosphere base for carburization, but as the carbon in the atmosphere is deposited into the steel, the carbon in the atmosphere must be replenished, while maintaining a low flow rate of endothermic gas (to maintain a constant carbon potential—the maximum carbon content the surface can reach—without replenishing the gas would require flow rates too large to be practical\(^{36}\)). This is done by adding the input gas (methane, propane, or butane) directly into the furnace. The carbon potential is held constant by adding methane to the atmosphere to form carbon monoxide and eliminating carbon dioxide and water vapor, via the slow reactions:

\[
\begin{align*}
\text{CH}_4(g) + \text{CO}_2(g) & \rightarrow 2\text{CO}(g) + 2\text{H}_2(g) \quad (7) \\
\text{CH}_4(g) + \text{H}_2\text{O}(g) & \rightarrow \text{CO}(g) + 3\text{H}_2(g) \quad (8)
\end{align*}
\]

Carbon monoxide serves as the main carburizing agent and needs to be replenished as the parts are carburized. As an example showing this need, a loss of 0.47 g C per cubic meter of endothermic gas at 925 °C will reduce the CO/CO\(_2\) ratio from 249 to 132, thus decreasing the carbon potential from 1.25 wt% to 0.8 wt%. As a baseline, 0.47 g C is roughly the same amount of carbon present in a part with 100 cm\(^2\) surface area, carburized to a 1 mm case depth\(^{36}\).

As previously mentioned, the main reaction controlling the carburization is via CO and is known as the Boudouard reaction:\(^{36}\)

\[
2\text{CO}(g) \leftrightarrow \text{CO}_2(g) + C(ss,\text{austenite})
\]
Equilibrium proceeds to further to the left as the temperature increases, as shown by the increase in the equilibrium partial pressure of CO against the total pressure of CO and CO\textsubscript{2}, Figure 31. The equilibrium constant for the Boudouard equation can be calculated by the partial pressures of CO and CO\textsubscript{2}, respectively, and the activity of carbon, i.e.,

\[ K_e = \frac{P_{CO}}{P_{CO}^2} a_C \quad (10) \]

The reaction constant, $K_e$, can be calculated from the free energies, such that

\[ \Delta G^o_{f(CO)} - 2 \Delta G^o_{f(CO)} = -RT \ln K_e \quad (11) \]

where $\Delta G^o_{f(CO)}$ and $\Delta G^o_{f(CO)}$ are the free energies of CO\textsubscript{2} and CO, respectively, R is the gas constant, and T is the absolute temperature. The free energies for CO and CO\textsubscript{2} formation are shown in Table 2.

The activity of carbon, $a_C$, is related to the carbon content in austenite, w (wt%), by:

\[ \ln a_C = -\ln \left( \frac{4.65w}{100 - w} \right) + \frac{9167 \left( \frac{4.65w}{100 - w} \right) + 5093}{T} - 1.867 \quad (12) \]

Table 2: Standard Thermodynamic Properties of Carbon Monoxide and Carbon Dioxide\textsuperscript{42}

<table>
<thead>
<tr>
<th></th>
<th>$\Delta H^o_f$, kJ/mol</th>
<th>$\Delta G^o_f$, kJ/mol</th>
<th>$S^o$, J/(mol*K)</th>
<th>$C_p$, J/(mol*K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td>-110.5</td>
<td>-137.2</td>
<td>197.7</td>
<td>29.1</td>
</tr>
<tr>
<td>CO\textsubscript{2}</td>
<td>-393.5</td>
<td>-394.4</td>
<td>213.8</td>
<td>37.1</td>
</tr>
</tbody>
</table>
Figure 32 shows the relationship between CO\textsubscript{2} content and carbon potential for endothermic gas from methane.

Besides the Boudouard reaction, carbon deposition can also come from interaction of carbon monoxide and hydrogen:

\[ CO(g) + H_2(g) \leftrightarrow H_2O(g) + C(\text{ss}, \text{austenite}) \]  

(13)

The net reaction of the process is the production of carbon and hydrogen:

\[ CH_4(g) \rightarrow C(\text{ss}, \text{austenite}) + 2H_2(g) \]  

(14)

As mentioned before, gas carburizing is the main method in use today for large-scale production. It has the advantage of being tightly controllable and shape independent, as well as being a less labor-intensive process for mass production. The disadvantages to the process are the safety hazards regarding the gases and the significant amount of time to start and shut down the process.

### 3.2.1.2. Pack carburizing

Pack carburizing is a method where a steel part is packed into a box and surrounded by a pack carburizing mixture. The box and mixture are sealed and heated to an austenitizing temperature of the steel, where the deposition of the carbon can occur.

The pack carburizing mixture consists of a carbon source (charcoal) and an energizer (a carbon dioxide source, such as Ba\textsubscript{2}CO\textsubscript{3}, Na\textsubscript{2}CO\textsubscript{3}, and CaCO\textsubscript{3}). The deposition works by creating carbon monoxide gas which is able to deposit carbon into the steel part. As in gas carburizing, the carbon monoxide deposits carbon according to the Boudouard reaction (for more information see Section 3.2.1.1):

\[ 2CO(g) \rightarrow CO_2(g) + C(\text{ss}, \text{austenite}) \]  

(15)

The carbon monoxide is created from the energizers and the charcoal (some is also created using the carbon dioxide present in the pack before it is sealed). Barium carbonate is the best known energizer and decomposes to its metallic oxide, according to:

\[ Ba_2CO_3(s) \rightarrow CO_2(g) + BaO(s) \]  

(16)
Carburizing compounds can also be made without barium, avoiding the hazards associated with barium, although decreasing the efficiency of the energizers.

The product of the energizer decomposition, carbon dioxide, combines with the carbon source, charcoal, to form more carbon monoxide:

\[ \text{CO}_2(g) + C(\text{charcoal}) \rightarrow 2\text{CO}(g) \quad (17) \]

As before, carbon monoxide serves as the deposition gas getting the carbon to the part.

There are many advantages to pack carburizing. First, this process is useful for complex parts and for achieving a deep case. The carburizing mixture also supports the part during the heat treatment, helping to reduce sagging. As for cooling, pack carburizing is a method that is adaptable to different cooling techniques, such as slow cooling within the pack, or quenching (to some extent) by opening the pack and quenching the part.

The disadvantages of pack carburizing include that it is a labor-intensive process when compared to gas carburizing, has poor case depth and carbon concentration control, and is not suited to shallow case depth deposition.

### 3.2.1.3. Other carburizing methods

Other carburizing methods include liquid carburizing, plasma carburizing, and vacuum carburizing. Liquid carburizing is a method that immerses a part in a molten salt bath, generally consisting of NaCN or KCN, sodium carbonate, and alkali metal chlorides. The advantages of liquid carburizing are the rapid heating due to the liquid atmosphere, close temperature control, more flexibility in obtaining different case depths, and good ability to obtain shallow cases. However, liquid carburizing is a labor-intensive process that has a significant amount of hazards associated with it regarding the poisonous salts and the cyanide wastes.

Vacuum carburizing is a four-step process where the conditions for each step (heating, carbon deposition, carbon diffusion, and quench) are separate and distinct. The heating step is carried out under vacuum initially to prevent oxidation. The carbon is then deposited with the furnace at temperature by introducing a partial pressure of a carburizing input gas (such as methane or propane). After a certain amount of time, the chamber is evacuated and held at temperature to allow for diffusion to occur. Finally, the part is quenched, often in a nitrogen
atmosphere. Plasma carburizing is similar to vacuum carburizing, except that the carbon deposition occurs quicker. Two electrodes are placed within the vacuum chamber and, while at temperature and under a partial pressure of either methane or propane, a few hundred volts are placed across the electrodes, creating plasma within the chamber gas. The plasma serves to ionize the gas quickly and allows for carbon deposition in shorter time frames.

### 3.2.2. Diffusion during Carburizing

The main consideration of the methods described previously is how to get the carbon to the surface of the metal in a controllable and safe manner. While this point is extremely important, one must also consider the subsequent diffusion of the carbon into the steel. Diffusion will control the case depth of the material and thus, the depth of the properties.

Diffusion is based on the activity and mobility of the elements involved. In a system not prone to atomic clustering, activity is proportional to the concentration of an element, so the preliminary discussion will be centered on the concentration. At the end of the chapter, uphill diffusion (diffusion against the concentration gradient) will be briefly discussed.

**Diffusion Mechanisms**

The two most common ways of atom movement are through vacancy diffusion (with a substitutional alloying element) and interstitial diffusion (with an interstitial alloying element such as carbon), Figure 33. Vacancy diffusion and interstitial diffusion occur when atoms jump into the adjacent vacant site (lattice site and interstitial site, respectively). Typically, interstitial atoms can be assumed to be surrounded by vacancies (in the interstitial sites), as the
concentration of interstitial atoms tend to stay relatively low when compared to the matrix atoms.

In the Fe-C system, the carbon atom is significantly smaller than the iron atom and occurs as an interstitial atom for that reason. Typically, interstitials have higher diffusion coefficients due to lower activation energy and fewer occupied (interstitial) sites surrounding the interstitial. In fact, Zheng and Zhang, in their research on laser carburized steel noted how the 300µm thick carburized layer (remelted) had an effectively uniform distribution of carbon due to the large diffusion coefficient of carbon.

Temperature Dependence of Diffusion
While Figure 33 is useful for explaining the basics behind the atomic movement in diffusion, the figure does not illustrate the deformation required to allow the diffusing atom to pass through (Figure 34). This deformation requires a higher energy for it to occur, called the activation energy. The additional energy most often comes from thermal sources. Thus, diffusion can be represented by an Arrhenius equation:

\[
D = D_0 \exp\left(-\frac{Q_D}{RT}\right)
\]

(18)

where \(D\) is the diffusion coefficient, \(D_0\) is a constant consisting of multiple temperature independent terms, \(Q_D\) is the activation energy for diffusion, \(R\) is the gas constant, and \(T\) is the temperature.

As can be seen from the Arrhenius equation, temperature is very important to diffusion, particularly for systems with large activation energies. In the Fe-C system, the activation energy is relatively low, only 80 kJ/mol for carbon diffusion in \(\alpha\)-Fe. Thus, the diffusion is significantly less dependent on temperature. Common activation energies are shown in Table 3. Overall, the higher the temperature, the more atoms that will have the required energy for diffusion, and the faster diffusion will occur.
Table 3: Common diffusion constants and activation energies.\textsuperscript{5}

<table>
<thead>
<tr>
<th>Species</th>
<th>$D_0$, m\textsuperscript{2}/s</th>
<th>$Q_D$, kJ/mol</th>
<th>Species</th>
<th>$D_0$, m\textsuperscript{2}/s</th>
<th>$Q_D$, kJ/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe in $\alpha$-Fe</td>
<td>$2.8 \times 10^{-4}$</td>
<td>251</td>
<td>Cu in Cu</td>
<td>$7.8 \times 10^{-5}$</td>
<td>211</td>
</tr>
<tr>
<td>Fe in $\gamma$-Fe</td>
<td>$5.0 \times 10^{-5}$</td>
<td>284</td>
<td>Zn in Cu</td>
<td>$2.4 \times 10^{-5}$</td>
<td>189</td>
</tr>
<tr>
<td>C in $\alpha$-Fe</td>
<td>$6.2 \times 10^{-7}$</td>
<td>80</td>
<td>Al in Al</td>
<td>$2.3 \times 10^{-4}$</td>
<td>144</td>
</tr>
<tr>
<td>C in $\gamma$-Fe</td>
<td>$2.3 \times 10^{-5}$</td>
<td>148</td>
<td>Cu in Al</td>
<td>$6.5 \times 10^{-5}$</td>
<td>136</td>
</tr>
<tr>
<td>Cu in Ni</td>
<td>$2.7 \times 10^{-5}$</td>
<td>256</td>
<td>Mg in Al</td>
<td>$1.2 \times 10^{-4}$</td>
<td>131</td>
</tr>
</tbody>
</table>

\textit{Fick’s First Law}

During carburization, the additional carbon at the surface creates a concentration gradient across the sample. When there is a steady-state concentration gradient (and the concentrations at the boundary are fixed, which is not necessarily true in carburizing), Fick’s first law phenomenologically states how the flux of the atoms will occur. According to Fick’s first law, the flux of atomic species B (in an A-B system) is equal to the diffusion coefficient of B multiplied by the concentration gradient of B with respect to distance, assuming steady state diffusion. Written out, that is:

$$J_B = -D_B \frac{\partial C_B}{\partial x}$$

(19)

where $J$ is the flux, $D$ is the diffusion coefficient, $C$ is the concentration, and $x$ is the distance. The negative sign indicates that the flux goes down the gradient, as opposed to up the gradient.

\textit{Fick’s Second Law}

While Fick’s first law is very useful in steady-state situations involving relatively thin samples, it is limited to certain practical situations. When the diffusion is time-dependent, as in carburizing, Fick’s second law applies:

$$\frac{\partial C_B}{\partial t} = D_B \frac{\partial^2 C_B}{\partial x^2}$$

(20)

where the variables are as in Fick’s first law, only with time, $t$, as an additional variable. Fick’s second law calculates how the composition versus distance profile changes with time (increasing or decreasing). When $\frac{\partial^2 C_B}{\partial x^2}$ is greater than zero, the concentrations increase with time. When it is negative, the concentrations decrease with time.
**Error Function Solution in Carburizing**

The typical quantitative solution for predicting the amount of carbon diffused as a function of depth, time, and temperature in steel is commonly known as the error function solution, Figure 35. The error function solution is derived based on Fick’s second law using the boundary conditions that the concentration at the stationary surface is constant ($C_s$) and the concentration in the bulk of the sample ($C_o$) is also constant. Thus, the sample must be large enough for this solution to be valid. The solution is:

$$C(x,t) = C_s - (C_s - C_o) \cdot \text{erf} \left( \frac{x}{2\sqrt{Dt}} \right)$$

(21)

where $x$ is the distance from the surface, $D$ is the diffusion coefficient, and $t$ is the time. The error function is a tabulated equation and can be calculated automatically by mathematical programs. Mathematically, the depth of the average between the surface and core concentrations can be estimated by $\sqrt{Dt}$. This is due to:

$$C(x,t) = \frac{C_s + C_o}{2} \quad \text{when} \quad \text{erf} \left( \frac{x}{2\sqrt{Dt}} \right) = \frac{1}{2}$$

(22)

By the tabulated values of the error function,

$$\text{erf} \left( \frac{x}{2\sqrt{Dt}} \right) \approx \frac{1}{2} \quad \text{when} \quad \frac{x}{2\sqrt{Dt}} \approx \frac{1}{2}$$

(23)

Thus, it can be roughly approximated that the half concentration difference will be at:

$$x \approx \sqrt{Dt}$$

(24)

**Uphill diffusion**

As mentioned previously, diffusion is dependent upon the activity of the elements. Under many conditions, concentration is proportional to the activity and diffusion proceeds down the concentration gradient. In certain cases, such as with silicon and carbon in iron, diffusion can occur up the concentration gradient, called uphill diffusion.

In the Fe-Si-C system, silicon raises the activity of the carbon in steel. Thus, carbon will diffuse away from the chapters with high carbon or high silicon (even if the high silicon area
has low carbon). As a result, areas with high silicon can end up with very low carbon contents when compared to the rest of the part. Overall, this process creates a non-typical concentration gradient and could present an issue in this project, although it is not expected to become particularly troublesome.
4. Surface Liquification Techniques

All of the aforementioned techniques of surface engineering are based on solid-state processes. Thus, the processes are constrained and simplified by the solid state of the steel. Certain equipment exists, such as the plasma arc lamp or the laser, which contain enough power density to rapidly liquefy the surface layer of the material without significantly affecting the base metal. This opens up surface modification to further flexibility in processing, potentially enabling the steel to have improved properties, such as hardness and wear resistance as desired in this project. Liquification will be used in this project and accordingly, the research previously completed is presented henceforth. Liquification has been examined using lasers and it is from that research that most of the background for this project comes.

Using lasers, related research has mainly been conducted regarding the surface remelting of cast iron, as well as with studies that have been conducted regarding carburizing through liquefication of steel. The cast iron research shows some of the possibilities within the surface layer without the additional step of alloying; it is discussed first, followed by the carburizing studies.

The phase identification in this chapter typically comes from (citations for examples) optical microscopy, electron microscopy (scanning electron microscopy, transmission electron microscopy), and x-ray diffraction, with additional techniques such as Auger electron microscopy and electron probe microanalysis for elemental distribution.

4.1. Laser Remelting of a Cast Iron Surface

Laser remelted cast iron surfaces have been produced in a variety of surface microstructures and corresponding to a range of hardness data. Tests were conducted on ductile cast irons/spheroidal graphite cast irons, gray cast iron, and eutectic composition cast iron.

For the pearlitic ductile cast iron, Gadag and Srinivasan used a pulsed 500kW Nd:YAG laser and a 5kW continuous wave CO\textsubscript{2} laser (1-2 mm diameter beam) to transformation
harden and laser remelt a ductile cast iron. The initial microstructure of the steel was graphite spheroids surrounded by a ferrite region (due to carbon depletion), encased by a pearlitic matrix; the composition was not stated. For the CO₂ laser, the authors noted that low power levels of 500W to 1.1kW gave a microstructure of martensite, fine pearlite, or a mixture of these, with a hardness ranging from 400 to 500 HV 0.2 (HV x is Vickers Hardness tested at weight x in kg). For higher power levels of 1.2 to 2.5 kW and relatively longer interaction times, the resulting microstructure was ledeburite with some undissolved graphite spheres. The ledeburite microstructure showed a significant increase in the hardness, ranging from 700 to 900 HV 0.2. The CO₂ laser was able to produce a significantly harder microstructure of 60 HRC (Rockwell C Hardness, 698 HV), compared to the 45 HRC (448 HV) obtained by the Nd:YAG laser. The increase in hardness resulted in an improvement in sliding wear resistance by up to two orders of magnitude and noted that the wear resistance of the laser melted ductile iron was superior to the laser transformed ductile iron due to the higher hardness and homogeneity of ledeburite over martensite.

Molian and Baldwin⁴⁵ reported a dramatic increase in resistance to scuffing and sliding wear in a pin-on-disk test. The microstructure had a melt zone of dendritic ledeburite with smaller amounts of plate martensite and retained austenite present as well. The hardness obtained in the melt zone was 960 to 1000 HV with base metals of gray and ductile cast irons. These authors characterized the wear behavior, noting that the wear decreased with increasing surface hardness and with increasing case depth. Molian and Baldwin⁴⁶ also reported an increase in erosion resistance of laser-processed cast irons and related it back to microstructure. These authors stated that the erosion rate decreased with an increase in the surface hardness and the case depth; additionally stating that ledeburite decreased the erosion rate the most, followed by tempered martensite, and then pearlite. This was in contrast to the bulk alloy studies review by Molian and Baldwin, where there was no correlation between surface hardness and wear resistance, tending more towards some ductility being a requirement for erosion resistance, as opposed to hardness (due to harder surfaces tending to be more brittle).

Fouquet and Szmatula⁴⁷ obtained similar hardness values to those of Gadag and Srinivasan and a little lower than Molian and Baldwin, but for a pearlitic grey cast iron. Laser remelting (780 W CO₂ laser, 0.6 mm diameter spot, 1.6 mm/s velocity) yielded a microstructure of austenite dendrites with interdendritic ledeburite, Figure 36. The hardness of the melted zone was approximately 700 HV, increasing to 850-900 HV in the overlapping regions as some of
the austenite is converted to martensite. Other authors, such as Bamberger et al.,\textsuperscript{48} noted that the lower hardness values were obtained in the overlapping region due to the tempering of the martensite. The carbon content in the austenite was \(\approx 1.6\) wt\% C, while the martensite had a carbon content of \(\approx 1.2\) wt\% C, as determined from the X-ray diffraction measurements of the lattice parameter.

Bamberger et al.\textsuperscript{48} used a continuous wave CO\textsubscript{2} laser to remelt the surface of gray cast iron, pearlitic and ferritic nodular cast irons, and AISI 1045 steel, Figure 37. The laser settings were 700 W (1.2 kW laser), a 400 mm/s pass, with a 200 \(\mu\)m diameter and 50\% overlap between consecutive passes. The gray cast iron (Fe

Figure 36: The melt zone obtained by Fouquet and Szmatula after (a) laser processing and (b) tempering for 30 min at 425°C

Figure 37: Re-melted structures obtained by Bamberger et al.\textsuperscript{48}
– 3.4 C – 0.59 Mn – 1.8 Si – 0.18 Cr, wt%) was remelted to a region of austenite and fine ledeburite, with a hardness of 650 to 750 HV. The pearlitic cast iron (Fe – 3.5 C – 0.3 Mn – 2.4 Si, wt%) had a hardness of 450 to 550 HV, consisting of a mixture of austenite and martensite. The authors did not mention the presence of ledeburite; the absence of ledeburite and the presence of the austenite may partially account for the lower hardness than previously mentioned papers.

Continuing with the AISI 1045 steel (Fe – 0.47 C – 0.66 Mn – 0.31 Si, wt%), the remelted steel had a hardness of 500 to 800 HV with a martensitic microstructure; the lower hardness values were obtained in the tempered region where the laser passes overlap. The microstructure after remelting of the ferritic cast iron (Fe – 3.4 C – 0.3 Mn – 2.8 Si, wt%) was similar to that of pearlitic cast iron due to the similar compositions, despite differences in initial microstructure; accordingly, the hardness would be expected to be similar. The authors noted that the mean level of hardness can be correlated with the carbon content in the austenite due to solution hardening. The gray cast iron had 2.1 wt% C in austenite, while the pearlitic and ferritic nodular cast irons had 1.8 and 1.9 wt% C, respectively. For wear resistance, the laser remelted samples exhibited relatively low wear resistance in a block on cylinder test, Figure 38. The low wear resistance when compared to the D2 steel (Fe – 1.5 C – 12 Cr – 1 Mo – 1 V) was due to different wear mechanisms. The main mechanism in soft samples is ploughing or grooving of the surface, with chip removal upon further passes. For harder phases, the main wear mechanism occurs due to the creation of cracks near the graphite regions.

With a cast iron of eutectic composition (Fe – 4.2 to 4.4 C – 2.2 to 2.6 Si – 0.5 to 0.8 Mn, wt%) and remelting the surface with a CO₂ laser, Safanov measured a hardness of 950-1100 HV with mainly a ledeburitic microstructure, Figure 39b. Safanov also studied the remelting of a few ledeburitic steels and was able to reach a hardness of 1020 HV in the remelted zone of an R18 steel, with hardnesses of the other steels studied in the range of 500
to 700 HV; the composition of the steels studied is shown in Table 4. The R18 steel had a microstructure of dendrite cells 1-3 µm in diameter, Figure 39a, significantly smaller dendrites than the other steels, and were separated by 0.5 to 2 µm. The content of the ledeburite in the R18 steel was higher than the other steels. Safanov noted that an increase in the ledeburite in the microstructure increases the hardness and wear resistance in the ledeburitic class of steels as well as in cast irons.

Table 4: Composition of steels tested by Safanov.49

<table>
<thead>
<tr>
<th>Grade of alloy</th>
<th>C</th>
<th>Cr</th>
<th>Mo</th>
<th>V</th>
<th>Si</th>
<th>Other</th>
</tr>
</thead>
<tbody>
<tr>
<td>85Kh6NfT</td>
<td>0.8-0.9</td>
<td>5-6</td>
<td></td>
<td>0.3-0.5</td>
<td>0.15-0.35</td>
<td>0.09-1.3 Ni, 0.05-0.15 Ti</td>
</tr>
<tr>
<td>Kh12M</td>
<td>1.45-1.65</td>
<td>11-12.5</td>
<td>0.4-0.6</td>
<td>0.15-0.3</td>
<td>0.15-0.35</td>
<td></td>
</tr>
<tr>
<td>9Kh18</td>
<td>0.9</td>
<td>17-19</td>
<td></td>
<td></td>
<td></td>
<td>0.5-0.9</td>
</tr>
<tr>
<td>Kh18MF</td>
<td>1.17-1.25</td>
<td>17.5-19</td>
<td>0.5-0.8</td>
<td>0.1-0.2</td>
<td>0.5-0.9</td>
<td></td>
</tr>
<tr>
<td>R18</td>
<td>0.7-0.8</td>
<td>3.8-4.4</td>
<td>1</td>
<td>1.0-1.4</td>
<td></td>
<td>17-18.5 W</td>
</tr>
</tbody>
</table>

Safanov anticipated that an increase in cooling rate (from an increase in the scanning rate of the laser) should increase the hardness due to larger martensite content and closer spaced lamellae within the pearlite. However, Safanov observed that increasing cooling rate meant less interaction time with the laser and thus, less graphite dissolution and less ledeburite formation. The result was lower hardness and wear resistance as cooling rate increased. Thus, the residence time in the liquid state is important, which is a function of the scan rate.

On the lines of cooling rate, Chen et al.50 observed that for a ductile iron, high solidification rates (>5x10^4 K/s) yielded a structure of dendritic austenite with an
interdendritic cementite film, Figure 40a. Solidification rates less than $10^4$ K/s yielded a hard lamellar eutectic structure, Figure 40b,c. The hardness of the dendritic austenite and interdendritic cementite ranged from 400 to 650 HV with the lamellar eutectic structure increasing to 1000 to 1250 HV. Chen et al. accomplished this with a ductile cast iron, Table 5, and a CO$_2$ laser, set at a 1.0 mm diameter and a power density of approximately 500 kW/cm$^2$.

Table 5: Ductile Iron composition, Chen et al.$^{20}$

<table>
<thead>
<tr>
<th>Alloying Elements, wt% (&gt;0.05 wt%)</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>Cr</th>
<th>Ni</th>
<th>Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>3.56</td>
<td>2.75</td>
<td>0.51</td>
<td>0.052</td>
<td>0.090</td>
<td>0.39</td>
</tr>
</tbody>
</table>

The studies discussed thus far were focused on remelting a cast iron surface. Tsujikawa et al.$^{12}$ additionally alloyed the surface of spheroidal cast iron (Fe – 3.4 wt% C – 2.8 wt% Si). Their research showed that peak hardness up to 1300 HV (average hardness of 1150 HV) can be reached by alloying the surface with graphite and/or tungsten. These authors accomplished this with a 1.2 kW Nd:YAG laser at 800 W of power, a 2 mm beam diameter, and a 3 mm/s traverse. The corresponding energy density was 2.5x10$^8$ W/m$^2$. Four conditions of the cast iron remelt were tested: unalloyed, tungsten alloyed, graphite alloyed, and tungsten + graphite alloyed. The alloying constituents were applied with an acrylic rubber solution.

Figure 40: Microstructures obtained for ductile cast iron by Chen et al.$^{50}$
The hardness profiles obtained are shown in Figure 41. The fusion zone in all four samples shows a significant increase in hardness. The average hardness for each of the four cases was 820, 970, 1100, and 1150 HV 0.1, respectively. The increase in these hardness values resulted in a decrease in the wear rate of each of the remelted cast iron surfaces by up to two orders of magnitude, as tested in a pin on disk test.

The microstructure obtained by Tsujikawa et al.\textsuperscript{12} for the unalloyed sample was a hypoeutectic dendrite and ledeburite chill structure, with no graphite phase present. The microstructure in the tungsten-alloyed sample was similar to the unalloyed sample, but consisted of finer dendrites and more carbide formation. The graphite and tungsten plus graphite alloyed samples both consisted of hypereutectic microstructures with primary carbides and ledeburite. Some porosity was observed either due to the combustion of the graphite (despite N\textsubscript{2} protection) or vaporization of impurities. The hypereutectic samples did not completely dissolve the graphite from the initial microstructure, which was suspected to be occurring due to the decreased carbon concentration gradient in the hypereutectic alloys.

Overall, ledeburite is frequently referred to when discussing the remelted wear resistant structures; some authors have correlated the hardness to the amount of ledeburite in the structure,\textsuperscript{49} as well as with the carbon content in the austenite.\textsuperscript{48} Hardness values for fusion zones reached 1300 HV 0.1 (that sample had an average hardness of 1100 HV 0.1), in a graphite-alloyed cast iron surface with a hypereutectic microstructure.\textsuperscript{12}

![Figure 41: Hardness profiles for laser remelted spheroidal graphite cast iron.]()
4.2. Laser Carburizing of Steel

Multiple authors\textsuperscript{43,51-56,58} have tested laser carburizing of steel, with resulting carbon contents of near-eutectoid, to hypoeutectic, to hypereutectic. A summary of the different papers and the hardness values obtained is shown in Table 6. The authors listed henceforth obtained carburization by applying a graphite-powder slurry with a binder, such as amyl acetate,\textsuperscript{56} an organic binder,\textsuperscript{53} an inorganic binder,\textsuperscript{43} ethanol,\textsuperscript{58} or an acrylic rubber solution,\textsuperscript{12} followed by remelting the surface of the steel with a laser. Müller et al.\textsuperscript{51} used screen printing as their method of applying the graphite and Walker et al.\textsuperscript{52} obtained their carburized structures by alloying over repeated steps, up to 12, to obtain a structure with a maximum of 90 vol\% carbide, which corresponds to $\approx 6$ wt\% C.

Around the eutectoid composition, Müller et al.\textsuperscript{51} and Grünenwald et al.\textsuperscript{53} obtained martensitic surface structures. The microstructure and hardness profile obtained by Müller et al. is shown in Figure 42, and reaches a maximum hardness of $\approx 950$ HV 0.1. The same hardness was obtained by Grünenwald et al. with a carbon content of 0.7 wt\% C at the surface; the carbon content for Müller et al was not stated.

Increasing the carbon content, a microstructure of martensite and retained austenite was obtained by Müller et al., Figure 42, as well as a pearlite and secondary cementite structure. The hardness values obtained for these microstructures were 500 to 600 HV.

Other hypoeutectic microstructures obtained included primary austenitic dendrites with interdendritic eutectic.\textsuperscript{52,43,12,54} Walker et al.\textsuperscript{52} obtained a dendritic arm spacing of 2 and 3 $\mu$m for the iron and steel base metal experiments, respectively. This yielded a hardness of 650 HV, but required quenching in liquid nitrogen to achieve this. Samples quenched to room temperature had a lower hardness of 470 HV due to the presence of additional retained austenite. The composition of the base materials used by Walker et al. is shown in Table 6.

Zheng and Zhang\textsuperscript{43} obtained a much higher hardness, 1050 HV, than Walker et al. with the dendritic microstructure, Figure 43. These authors obtained a martensitic heat affected zone (550 HV) before the transition into the base metal. X-ray analysis by Zheng and Zhang detected ferrite, austenite, and multiple carbides of $\text{Fe}_x\text{C}$ (x=1, 2, or 3).
### Table 6: Laser carburizing data from various papers. (composition in wt%, γ = austenite (R for retained), α’ = martensite, HAZ = heat affected zone).

<table>
<thead>
<tr>
<th>Authors</th>
<th>Base Metal (Fe + elements &gt;0.05wt %)</th>
<th>Surface Conc.</th>
<th>Microstructure</th>
<th>Hardness, HV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Walker et al.</td>
<td>0.016C-0.12Mn-0.06P</td>
<td>Hypoeutectic</td>
<td>γ dendrites + interdendritic lamellar eutectic</td>
<td>650&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>Müller et al.</td>
<td>0.14C-0.15Si-1.02Mn</td>
<td>Not stated</td>
<td>α&lt;sup&gt;',&lt;/sup&gt;</td>
<td>950</td>
</tr>
<tr>
<td>Grünenwald et al.</td>
<td>0.16C-0.25Si-1.2Mn-1.0Cr</td>
<td>Hypoeutectic</td>
<td>α&lt;sup&gt;',&lt;/sup&gt; (dendritic growth)</td>
<td>950</td>
</tr>
<tr>
<td>Zheng and Zhang</td>
<td>#20 steel</td>
<td>Hypoeutectic</td>
<td>Fine dendritic γ</td>
<td>1050</td>
</tr>
<tr>
<td>Tsurikawa et al.</td>
<td>JIS SPC&lt;sup&gt;iii&lt;/sup&gt;</td>
<td>Hypoeutectic</td>
<td>γ dendrites &amp; ledeburite</td>
<td>1000</td>
</tr>
<tr>
<td>Tayal and Mukherjee</td>
<td>AISI 1018 steel</td>
<td>Hypoeutectic</td>
<td>γ dendrites or cellular</td>
<td>980</td>
</tr>
<tr>
<td>Katsamas and</td>
<td>0.15C-0.37Si-0.53Mn-1.65Cr-1.51Ni</td>
<td>Hypoeutectic</td>
<td>Primary dendrites (lath martensite room temperature) + interdendritic γ &amp; M&lt;sub&gt;3&lt;/sub&gt;C</td>
<td>550 to 770</td>
</tr>
<tr>
<td>Haidemenopoulos</td>
<td>0.10C &amp; ST22&lt;sup&gt;iv&lt;/sup&gt;</td>
<td>Hypereutectic</td>
<td>Primary carbide dendrites + eutectic matrix</td>
<td>700 to 900</td>
</tr>
<tr>
<td>Mordike et al.</td>
<td>0.10C &amp; ST22&lt;sup&gt;iv&lt;/sup&gt;</td>
<td>Hypereutectic</td>
<td>Primary carbide dendrites + eutectic matrix</td>
<td>700 to 900</td>
</tr>
</tbody>
</table>

<sup>a</sup> Required quenching to -196 °C. Room temperature quench hardness of 470 HV.

<sup>b</sup> A cold-rolled, low carbon steel. The composition was not stated.

<sup>c</sup> The authors state that at the surface, they obtained pure cementite solidification. Directly under that, supersaturated austenite dendrites formed. The process was gas carburizing. ST22 is low carbon steel, with UTS = 220 N/mm<sup>2</sup>. 
Tsujikawa et al.\textsuperscript{12} obtained a similar hardness and a similar microstructure of $\gamma$-dendrites and ledeburite to what was obtained by Zheng and Zhang. Both are still significantly higher than what other authors have obtained, such as Walker et al.\textsuperscript{52}

Figure 42: Laser carburizing of low carbon steel to different surface carbon concentrations (increasing C content from A to E).\textsuperscript{51}

Figure 43: Laser carburized structure of #20 steel. a) heat-affected zone, b) surface layer, 2000X.\textsuperscript{43}
Tayal and Mukherjee\textsuperscript{54} obtained both the dendritic structure and a cellular structure, Figure 44a,b. These authors varied the laser power from 1.06 kW/cm\textsuperscript{2} to 10.6 kW/cm\textsuperscript{2} and obtained these structures, as well as a eutectic structure and a hypereutectic structure, Figure 44c,d. The main difference in obtaining these structures was the melt depth. As such, the lower power scans had a smaller melt depth and the carbon was more concentrated, resulting in higher carbon concentrations.

The hypereutectic structure obtained by Tayal and Mukherjee,\textsuperscript{54} which stemmed from a high surface concentration of carbon (e.g. 5.5 or 5.6 wt\% C), consisted of primary carbides in an acicular morphology, Figure 45. With the hypereutectic structure, Tayal and Mukherjee were able to obtain hardness values up to 1050 HV. The authors did note that for this structure there was a light etching area between the hypereutectic structure molten zone and the martensitic HAZ that was mostly austenite, with a hardness of 600-620 HV. The

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{structures.png}
\caption{Structures observed by Tayal and Mukherjee.\textsuperscript{54} (a) Dendritic structure ($\gamma$ dendrites + ledeburite), (b) Cellular structure ($\gamma$ cells + ledeburite), (c) Eutectic structure, and (d) Hypereutectic structure (Carbide dendrites + lebedurite)}
\end{figure}
austenite is present due to its high carbon concentration, causing a depression of the $M_s$ temperature.

As with Tayal and Mukherjee, Walker et al. obtained a hypereutectic structure of primary carbides and eutectic, Figure 47. The hardness of this overall structure was reported by Walker et al. to be approximately 900 HV. The authors reported carbide contents as high as 90 vol% (6 wt% C), after successive alloying steps, as mentioned previously.

The eutectic and hypereutectic structures were also obtained by Müller et al., Figure 42. The hardness for the ledeburitic structure was between 700 and 800 HV, while the hypereutectic structure ranged from 800 to over 1100 HV.

In addition to laser carburizing, Zheng and Zhang alloyed surfaces with a boron-carbide/carbon powder mixture and Grünenwald et al. alloyed steel with a WC + 12 wt% Co mixture. Zheng and Zhang obtained a hardness of approximately 1280 HV, with a hardened depth of 300 µm in a microstructure of large blocky precipitates with ferro-carbides present in the matrix, Figure 46. X-ray analysis detected the presence of ferrite, austenite, Fe$_x$C ($x=1$, 2, or 3), and Fe$_y$B ($y=1$ or 2). The martensitic heat affected zone had a hardness of 600 HV.
Grünenwald et al.\textsuperscript{53} obtained a hardness reaching 1400 HV with a tungsten content of 45 wt\% in the surface layer. The microstructure consisted of fully melted particles. The hardness was found to be a function of the tungsten content – in general, the higher the tungsten content, the higher the hardness (the exception is when further alloying to an already fully martensitic structure). These authors, however, observed extensive porosity and cracking in the alloys having a tungsten content greater than 25 wt\%. They theorized that the porosity was from combustible components and larger amounts of dissolved gas from the higher flow rates used in the powder-application process, while the cracking was due to thermal stresses.

\textit{Gaseous alloying}  
Gaseous alloying in combination with laser heating has also been studied by Mordike et al.\textsuperscript{55} The authors tested laser heating of the surface of a 0.10 wt\% C steel and noted that, at austenitizing temperatures, CO\textsubscript{2} protective atmospheres produced a slightly higher hardness (not stated) than the maximum of 350 HV obtained in air, argon, or nitrogen atmospheres. When melted, the carbon pickup in the sample was significantly higher, also increasing the hardness. An intermediate hardness could be obtained through a gas discharge with a lower CO\textsubscript{2} flow rate and a high austenitizing temperature, avoiding the formation of δ-Fe.

For a stronger carburizing effect, the authors used acetylene and obtained a dendritic austenite structure at the base of the melted zone, proceeding to pure cementite solidification at the surface, Figure 48. The surface hardness in the cementite region was 1200 HV, and was separated from the austenite (600 HV) by a diffusion zone. The authors noted that should the high hardness not be desired (as in the case of embrittlement), the surface

\begin{figure}[h]  
\centering  
\includegraphics[width=\textwidth]{hypereutectic.png}  
\caption{Hypereutectic structure made with multiple carbon alloying steps by Walker et al.\textsuperscript{52}}  
\end{figure}
hardness can be lowered simply by decreasing the amount of interaction time between the laser and the sample.

**Cracking at the surface**

One potential issue associated with laser carburizing of steel is the cracking of the surface, as reported by multiple authors. Müller et al.\textsuperscript{51,52,56,58} minimized cracking by preheating the samples at temperatures of 400 to 500 °C. Tayal and Mukherjee\textsuperscript{56} studied the cracking of laser remelted surfaces alloyed with graphite powder and determined that the cracks frequently come from solidification stresses or thermal stresses. Solidification cracks commonly are observed as branched cracks that occur between the dendrites and are not filled in by interdendritic liquid; these cracks are typically seen in hypoeutectic alloys. Thermal stresses create straight cracks that are typically observed in hypereutectic alloys. The straight cracks form in hypereutectic alloys due to the low fracture strain in the structure with the cementite presence.

To minimize the cracking in hypoeutectic alloys (above 2.1 wt% C), increasing the amount of carbon would help as it would increase the fraction of liquid available to fill in the solidification cracks. To minimize the cracking in hypereutectic alloys, Tayal and Mukherjee suggested the possibility of preheating the sample. Other authors, such as Cooper and Slebodnick\textsuperscript{57} have had success at minimizing the thermal stresses in WC coatings on inconel by preheating the substrate to 300-450 °C to reduce the cooling rate. The preheating temperature used by Cooper and Slebodnick was dependent upon the width of the melt pool in the laser alloying. Tayal and Mukherjee concluded that the best microstructure that can produce a high hardness and be crack-free is a mixture of austenite dendrites and interdendritic ledeburite. The austenite dendrites provide the ductility necessary in the matrix to eliminate the cracking present in the material.
**Carbon Diffusion in Laser Remelting**

One other condition that needs to be examined is the diffusion of carbon in laser processing. Katsamas and Haidemenopoulouso,\(^5\) in their experimental work, obtained a surface hardness of 900 HV 0.2 through laser remelting the surface coated with a graphite slurry. The microstructure was hypereutectic with primary carbides in a eutectic matrix, Figure 49.

The authors also used a commercially available software package, DICTRA, to calculate the solid-state diffusion of carbon in the laser process. By assuming a constant carbon concentration at the surface (2 wt%, the solubility limit in austenite) and the temperature profile shown in Figure 50, the solid-state diffusion of the carbon was able to reach a depth of 15 µm in only 1.5 seconds, Figure 51. In the temperature profile, the austenitization is assumed to be completed in the \(A_1\) to \(A_3\) heating range and the carburization time the extent of the time above the \(A_3\) temperature.

Overall, the research regarding the surface alloying of steel indicates the resulting structures could have high hardness and good wear resistance, similar to the results obtained in cast iron. In both the steel and cast iron results, the eutectic structure appears to provide desired hardness potentially with some austenitic dendrites for crack resistance.

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**Figure 49:** Primary carbide dendrites in a eutectic matrix, over a super-saturated diffusion zone.

**Figure 50:** Surface temperature in the laser processing step.\(^5\)

**Figure 51:** Carbon diffusion during the cycle in Figure 50.\(^5\)
5. Plasma Arc Lamp

The equipment to be used in this project is a high-density infrared (HDI) emitter, known as a plasma arc lamp, and located at Caterpillar Inc. in Peoria. The lamp was originally designed for rapid thermal annealing of silicon wafers and is commercially available from Mattson Technology Inc. The lamp emits light by creating plasma between two electrodes, with the plasma surrounded by a shield of argon gas and a shield of water, all within a quartz tube, Figure 52. The plasma within the tube can reach 10,000 K and creates a wide spectral output ranging in wavelength from 0.2 to 1.4 µm, Figure 53, which is constant over all power levels. The constant spectral output is a big advantage of the plasma arc lamp because the spectral output of other IR techniques, such as tungsten filament heating, changes as the power increases, potentially changing the amount of power absorbed by the material.

The lamp located at Caterpillar is capable of producing a power density of 1.6 kW/cm², based on calculations at Mattson Technology and provided to Iowa State and Caterpillar. This power is produced over a 20 cm by 2.54 cm area (more concentrated over the center than the edges, see information on lamp reflectors below). A lamp of higher power density (but lower overall power output) at Oak Ridge National Laboratory (ORNL) in Oak Ridge, TN has been
said to produce a power density of $3.5 \text{ kW/cm}^2$ over a 10 cm by 3.175 cm area, heating the samples up to 3000 °C at rates greater than 1000 °C/s. No similar calculations have been conducted for the lamp at Caterpillar.

There are two types of reflectors commonly in use: the line reflector and the uniform reflector; schematics of these reflectors are shown in Figure 54. The lamp at Caterpillar is a line reflector. Lamp reflectors are available up to 35 cm wide, although some power density is lost due to the increased area.

Compared to other techniques the plasma arc lamp is not the most powerful in terms of power density, but is able to produce this power over a much larger area. Lasers and electron
beam heating are two techniques that can produce larger power densities, but both of these methods can only heat a very small area, rather than the large area that the plasma arc lamp can cover. For example, the laser spot sizes are often no more than a millimeter or two, while the electron beam sizes are even smaller. The larger area allows for processing large parts over a smaller time and the ability to have a large heat affected area, such as a large molten zone on top of steel.

Plasma arc lamp processing has many other advantages. For the processing capabilities, the lamp system is capable of very quick thermal input changes. The system responds very quickly to a power input change due to the low thermal mass of the system. In fact, the system can be shut off and turned back on within 1 millisecond.

The system also requires limited, if any, fixtures to attach the part. The set-up for the equipment, however, is a little more complicated. The lamp at Caterpillar has a fixed stage with a moveable lamp. With this setup, some scanning has been accomplished although the range of motion is limited.

As for the uses of the lamp, the plasma arc lamp system is a unidirectional heating technique. The depth of the heating depends on the lamp power and the time. Long heating times at low power can be used to heat the bulk of the sample, but typically most processes are for short heating times. Thus, the plasma arc lamp can be used to heat only the surface, while the bulk of the sample remains relatively cool. Benefits to a cool substrate include less energy used (little goes to the substrate), rapid cooling rates are possible, and the ability to not affect the substrate during processing. A main disadvantage to creating a large thermal gradient within the sample is the potential for thermal stresses and thermal shock to be present in the material. With the many microstructure features of iron that this project may encounter, this could be an issue for certain microstructure constituents, such as the hypereutectic microstructure. In Chapter 4, it was discussed how some authors\textsuperscript{51,52,56,58} observed thermal shock and cracking in the hypereutectic microstructure. With the slower cooling rates inherent to the plasma arc lamp compared to the laser, thermal shock was never observed in this project.
Within the capabilities of the system are many processes that normally take a large amount of processing, such as producing thin film materials. Examples of the processes that the plasma arc lamp has been shown to be capable of include sintering of alumina-zirconia-silica (AZS) ceramics, liquid phase sintering of TiAl thin sheet, selective heat treatment of aluminum and steel alloys, remelting of sprayed thermal coatings, and wear and corrosion resistant coatings. Rivard et al. have also been able to develop computer models that can predict the thermal history and the heat affected zone of the plasma arc lamp processed samples, as well as the melt pool depth.

Blue et al. have attempted three different coating application techniques: plasma spray and fuse, powder spray and fuse, and rapid infiltration. Plasma spray is a thermal spray technique which melts the coating particles in gas plasma and propels them to the substrate. The coating is built up over multiple passes of the spray gun, resulting in multiple splats of coating with oxides on their surface. The coating is then fused to the substrate using HDI to form a metallurgical bond, instead of a mechanical bond. Blue et al. tested this process on a hardfacing compound; the composition was not given. The microstructure before and after HDI processing are shown in Figure 55. The authors noted that they were able to achieve a hardness of 982 HV and drastically reduced the porosity in the structure.

The second method, powder spray and fuse, was accomplished by Blue et al. using a room temperature spraying technique. The technique involves using a powder/binder slurry and a high-volume, low-pressure paint gun. The slurry is sprayed and forms an even coating over the surface. After the spraying, the binder goes through a burnout process prior to HDI processing. The coating is then fused to the substrate using HDI.

Blue et al. have tested WC and Cr$_2$C$_3$ in ratios up to 70 vol% carbide in an alloy matrix; the matrix composition was not given.
The third method is rapid infiltration, where a carbide mat is applied to the surface and a metallic matrix is rapidly infiltrated into the mat and wetted to the substrate. With this method, Blue et al.\textsuperscript{59} placed a \( \text{Cr}_2\text{C}_3 \) coating on a steel pin used in die casting of aluminum. The coating seals the steel from the aluminum, to avoid forming a low temperature Fe-Al eutectic at 652 °C. The coating was reported to increase the lifetime of the pins by an order of magnitude.

Muralidharan et al.\textsuperscript{66} have coated 4340 steel with iron aluminide to create a surface that is resistant to oxidation and sulfidation in aggressive environments. This coating can also be reinforced with wear-resistant particles, such as TiB\(_2\) to add wear resistance to the coating properties as well (TiB\(_2\) particles have good wetting characteristics with FeAl\textsuperscript{68}). The coating was made by a two-pass heating with the plasma arc lamp, as well as heating with a Nd:YAG laser. The two-pass process consisted of a scan at 2025 W/cm\(^2\) and a second scan at 2350 W/cm\(^2\). Both scans were conducted at 8 mm/s. The resultant coating had a hardness of 400 to 500 HV, compared to < 300 HV for the bulk, although a small region of 700 to 800 HV values were obtained due to the formation of some martensite approximately 100 to 300 µm below the surface. The martensite formation was not observed in the laser-processed sample. A second set of scan properties was also tested with similar power levels, but the first pass of the scan was conducted at a slower scan speed, 6 mm/s. The result was
an increase in the loss of the intermetallic, thus potentially decreasing their performance in oxidation and sulfidation.

Two other things that Blue et al. have examined are the use of a transient liquid coating process to produce the tungsten carbide/nickel-chromium coating with a typical microhardness of 1000 HV, with compressive stress on the surface. This is comparable to the 1020 HV hardness of hard chrome plating and was achieved with a scan of 0.5 cm/s and a 1000 W/cm² power setting for the scan. The authors have also bonded a Ta-10W coating and a stellite coating to steel for corrosion resistance.

Two more tested wear resistance options were the application of a tungsten carbide coating with a nickel-phosphorous binder (60 wt% WC, 30 wt% Ni, 10 wt% P), and the application of an amorphous Fe-based alloy (Fe – 15 Cr – 14 Mo – 2 Y – 15 C – 6 B, wt%). The WC/Ni-P coating had a hardness of approximately 400 HV, compared to the 300 HV for the amorphous coating.

Overall, the plasma arc lamp has similar capabilities as the laser, but the power in the plasma arc lamp is not as concentrated and is distributed over a significantly larger area. As such, the ability to process large parts is beneficial, but significantly higher power densities can be obtained through focusing the laser to smaller areas. With the larger heated area and lower power density, the heating and cooling rates will be slower than with the laser. However, the large parts possess a large thermal mass, helping to increase the cooling rate. It is the large-scale potential of the parts involved in this project and the use of the plasma arc lamp as a processing tool for those large parts which make the study novel.

Beyond similarities to the laser, the plasma arc lamp also provides potential for the replacement of or supplement to conventional furnace surface chemical treatments, such as carburizing or nitriding. While these have not been investigated, they represent possibilities that the plasma arc lamp may be capable of.
6. Project Aims

As previously stated, the goal of this project was to establish plasma arc-lamp processing routes for obtaining unique steel-surface-modification structures that confer exceptional properties. There are many standard surface-modification techniques used today in industry to improve the properties of steel. While these techniques are effective, there exist pathways to obtaining harder structures, such as can be obtained by laser surface melting. The plasma arc-lamp provides similar capabilities to lasers, only over a larger area and thus increasing the benefit to industrial production.

The current project seeks to:

- Create a hard, wear-resistant surface microstructure through alloying primarily with graphite.
  - The graphite shall be applied through multiple methods to determine the effectiveness, including a slurry and a paste.
- Use the microconstituents ledeburite and cementite to form hard, wear-resistant surface-modified regions.
  - The further incorporation of martensite into the final structure will also be sought as a means to improve wear resistance.

This project will therefore use surface-melting via the plasma arc-lamp to increase the wear resistance of steel by creating a surface microstructure of ledeburite, cementite, and, possibly, martensite.
7. Experimental Procedures

Sample preparation either consisted of the arc-lamp treatment of a bulk, model-cast-iron, or the application of a graphite-containing coating on a cold-rolled steel substrate, followed by arc-lamp treatment. The model cast iron alloys were analyzed to determine a baseline for the surface-alloying treatment that was the focus of this project. 1018 steel was chosen as the primary substrate because it is a low carbon steel that contains low alloy content. As will be described in Section 7.2, the graphite-containing coatings were applied to the 1018 steel substrate by a spraying operation similar to painting, compressing of the coating, a bakeout, and finally, arc-lamp surface processing of the sample.

7.1. Model Cast Irons

Initial testing of the arc-lamp treatment was conducted on model cast iron samples of varying carbon content. Three different iron-carbon alloys were made at the Materials Preparation Center at Ames Laboratory from iron and graphite powders via induction heating and chill casting. The alloys were model systems, as they were nominally without any of the alloying elements present in cast irons. The alloy compositions were measured to be Fe – 2.98 wt% C, Fe – 4.10 wt% C, and Fe – 5.13 wt% C by combustion analysis (other impurities were less than 0.1wt%). Each of the three alloys was arc-lamp surface treated as a bulk sample to provide a baseline for comparison.

Prior to arc-lamp treatment, coupon samples of the Fe-C model cast iron compositions were prepared by grinding the surface to an 80-grit finish with abrasive paper. After grinding, the samples were blasted with a fine steel powder, less than 45 µm in size, to lower the surface reflectivity. The powder blast was conducted in a plasma-transferred arc (PTA) welder without striking an arc. The powder blast dulled the surface without the roughness typical of a large-grit blast operation.
7.2. 1018 Steel Substrate

The primary substrate for the coating development was 1018 cold-rolled steel. The measured composition range of the steel is shown in Table 7. A typical microstructure, Figure 56, is mainly ferrite with islands of pearlite, a standard cold-rolled steel microstructure nominally consisting of 23% pearlite.

| Table 7: Measured composition of 1018 steel used in this project, wt%.

<p>| | | | | | | | |</p>
<table>
<thead>
<tr>
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<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>C</td>
<td>Mn</td>
<td>P</td>
<td>S</td>
<td>Si</td>
<td>Cu</td>
<td>Cr</td>
</tr>
<tr>
<td>Bal</td>
<td>0.16-0.17</td>
<td>0.007-0.024</td>
<td>0.013-0.027</td>
<td>0.21-0.28</td>
<td>0.16-0.26</td>
<td>0.06-0.13</td>
<td>0.06-0.17</td>
</tr>
</tbody>
</table>

In preparation for coating application, the steel was ground with 80-grit abrasive paper to remove the mill-scale and create a flat surface. After grinding, the samples were preheated to 150°C and coated with a sprayed mixture of graphite-containing powder and binder; mixture information is shown in Table 8. The source powders used were natural graphite from Asbury Carbons and ferro-molybdenum from F.W. Winter Inc. and Co. The graphite powder was nominally sized at 5 µm, while the ferro-molybdenum was nominally 10 µm.

The powders were mixed with a binder called Lisi 100i9 from Warren Paint and Color Company. Lisi 100i9 is a proprietary mixture consisting of a binder, a suspending agent, a corrosion inhibitor, and water. After surveying several binders, it was found that Lisi 100i9 created the desired suspension characteristics and green sample properties. The powders were mixed to a consistency similar to paint and sprayed using a Sharpe 998HVLP high-volume low pressure (HVLP) paint sprayer, available from McMaster-Carr. Pressure settings on the spray gun were similar to those used for paint: 36psi of line pressure and 1 psi.

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\(^v\) Other alloying elements not listed here have concentrations less than or equal to 0.02wt%.
in the cup. For spraying paint, the Sharpe 998HVLP spray gun commonly uses 3-6 psi in the cup and 40-45 psi of line pressure, with optimal paint-spraying operation at 7 cubic feet per minute of airflow; airflow was not measured for the parameters just stated. The lower pressures, especially in the cup, were used in the current procedure to reduce the amount of material consumed per unit of time, allowing more control for spraying thinner coatings.

The spray operation was conducted with a horizontally mounted substrate and vertically mounted nozzle to minimize running of the coating, Figure 57. The HVLP sprayer was mounted to a robot and was traversed across the sample 4 times at a speed of 50 mm/s, for a target coating thickness of 100 \( \mu \text{m} \).

<table>
<thead>
<tr>
<th></th>
<th>Nominal Coating Compositions, wt%</th>
<th>Powder to Binder Ratio (wt/wt)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphite only</td>
<td>Fe 0</td>
<td>Mo 0</td>
</tr>
<tr>
<td>Ferro-moly and graphite (20wt%Mo)</td>
<td>13</td>
<td>20</td>
</tr>
<tr>
<td>Ferro-moly and graphite (40wt%Mo)</td>
<td>27</td>
<td>40</td>
</tr>
</tbody>
</table>

After spraying, the coatings were pressed in a hand-operated hydraulic press (Carver Lab Press, Model #3393) in order to increase their density. The samples were then heated in a flowing nitrogen atmosphere at 350ºC to bakeout the binder and the water from the Lisi 100i9. After the bakeout, the samples were ready for arc-lamp treatment.
7.3. Additional techniques

Other sample preparation methods that were tested included a grit-blast with 24-grit steel. At the thin coating thicknesses that were initially being produced, the ground finish gave a more uniform structure. It is possible that a grit blast with finer-grit steel could be used in place of the 24-grit, but that is outside the scope of this thesis. Steel grit was chosen to match the grit to the substrate, such that any embedded grit will be melted during arc-lamp processing.

Additional application methods were also examined, such as applying the coating by spreading a slurry or a graphite cement paste. Both the slurry and the graphite-cement paste had the advantage of being significantly quicker to apply than by the spray method. The slurry, however, was difficult to uniformly apply at a thickness of 100 µm, while the graphite-cement paste tended to be extremely porous and did not have the flexibility of adding additional alloying elements. Thus, the spray method was chosen for its ability to make a thin, uniform coating over the sample, taking into account surface imperfections (such as a minor slope) and for its flexibility to be used with any coating material.

7.4. Surface Modified Structure Characterization Techniques

The resulting surface-modified structures were characterized using optical and scanning electron microscopy for visual phase identification. Chemistry was obtained using electron probe micro-analysis (EPMA).

Phase identification was conducted using x-ray diffraction (XRD) on the surface of the sample after a cleaning operation. Not all of the graphite-containing coating was able to be removed, causing a residual graphite peak to appear in the XRD scan without being present in the surface-modified region. The thin nature of the surface-modified region prevented large scale material removal to eliminate the residual graphite peak. Electron backscatter pattern (EBSP) or orientation imaging microscopy (OIM) was also attempted on one sample to determine the crystal structure of one phase.

To gauge potential wear resistance, microhardness measurements were taken of each surface-modified region to determine an average hardness. The Vickers scale at a 100 g load was chosen to enable correlation with literature data testing of similar coatings. After further
development on coating quality was completed, a ball-on-flat wear test was conducted to show the promise of these coatings. The wear test was conducted in a high-frequency-reciprocating rig (HFRR) from Cameron Plint. The initial expected application of these coatings would be mainly involved in two-body or three-body sliding wear, and as such, a two-body wear test was chosen. The test apparatus was a high-frequency reciprocating rig with a 52100 hardened steel ball (58-66 HRC) oscillating linearly at 10 Hz under 150N load over the coated steel. The test was conducted at 125 °C and under lubricated conditions, test conditions that are used frequently at Caterpillar.

### 7.5. Arc-lamp treatment

All samples were processed under the arc lamp under a flowing nitrogen atmosphere. The sample was held in a stationary position while the arc-lamp was capable of movement. Samples were processed in three physical conditions, Table 9, at varying speeds and times, and at the same power level. Initial testing started with a stationary lamp varying the processing time and proceeded to a scanned lamp, where the speed of the arc-lamp traverse was varied. Multiple-pass traverses were also conducted where the lamp would pass over the sample four times.

**Table 9: Sample and arc-lamp parameters during processing.**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Physical state</th>
<th>Number of passes over sample</th>
<th>Typical preheat parameters (not always used)$^{\text{vi}}$</th>
<th>Typical pulse parameters$^{\text{vi}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stationary</td>
<td>Stationary</td>
<td>N/A</td>
<td>150 A for 2 min</td>
<td>1000 A for 2 – 6 sec</td>
</tr>
<tr>
<td>Stationary</td>
<td>Single Traverse</td>
<td>1</td>
<td>Not used</td>
<td>1000 A at 4 – 8 mm/s</td>
</tr>
<tr>
<td>Stationary</td>
<td>Multiple Traverses</td>
<td>4</td>
<td>Not used</td>
<td>1000 A at 24 – 32 mm/s</td>
</tr>
</tbody>
</table>

$^{\text{vi}}$ As shown in Figure 60, the power corresponding to 150 A current is 32 kW and 396 kW for 1000 A.
The typical arc-lamp process can consist of two different steps: a preheat and a pulse. A preheat followed by a pulse was used to create a slow-cooled microstructure, while a pulse alone was used to create a fast-cooled microstructure.

The power-control variable for the arc lamp is the current into the system, but the voltage varies as well. The output power is slightly parabolic and is largely due to the excess current that the arc-lamp applies to sustain a higher idle.

### 7.5.1. Arc-lamp cooling rate

Cooling rate measurements for the plasma arc-lamp were conducted on 1018 steel samples that were grit blasted with 16-grit alumina oxide, brushed with a steel-bristle brush, cleaned with acetone, and then arc-lamp processed in air at 1000 A with speeds of 4 mm/s, 6 mm/s, and 32 mm/s for 4 passes, as well as for 6 seconds stationary on a large sample. For the 1000 A, 6 mm/s run, a Mikron 7604 Pro IR Thermal Imaging Camera measured a maximum temperature over 1800 °C, with a cooling rate over 1500 °C/sec. The size of the sample was a 1” x 1” x 1” (H x W x D).

The cooling rate reached over 3000 °C/sec for a 3” x 3” x 1” sample that was arc-lamp treated at 1000 A stationary for 6 seconds, as well as for a 1000 A pass on a 1” x 1” x 1” sample that was processed in a 4-pass traverse at 32 mm/s.

The cooling rate for a 1” x 1” x 1” sample that was arc-lamp treated with 1000 A at 4 mm/s was not able to be measured because the maximum temperature of the camera (approximately 1900 °C) was exceeded.

Very high cooling rates were achieved through the solidification temperature range of steel, and decreased to a few hundred °C/sec through the eutectic temperature. The coatings, however, did not form martensite without additional alloying elements because the cooling
rate from the eutectoid temperature was less than 20 °C/sec, significantly less when calculating the cooling rate down to room temperature.

Figure 61: Temperature profile for a 1018 steel sample, arc-lamp treated with 1000 A at either 6 mm/s, 32 mm/s for 4 passes, and 6 seconds stationary, data points every 0.1 sec. The 6 second run was a large sample, 3” x 3” x 1”.
8. Cast Iron Surface Treatment

The cast iron, arc-lamp treated work presented below forms the background for the graphite alloying work which was the focus of this project.

8.1. Effect of Arc-Lamp Parameters

Single scanned traverses were conducted on the model cast iron samples at speeds of 4 and 6 mm/s with a power of 1000 A, Figure 62. The amount of liquid formation for all 3 alloys at the 4 mm/s traverse rate was significantly greater than for the 6mm/s alloys. The microstructures, however, were similar in the 2.98 wt% C and 4.10 wt% C alloys, while a change was observed in the 5.13 wt% C alloy, as will be discussed in the following.

8.2. Microstructure

The as-cast microstructures of the cast-iron samples are shown with corresponding arc-lamp processed structures in Figure 63 (optical) and in Figure 64 (SEM). As predicted by the phase diagram and verified visually, the as-cast microstructure in the 2.98 wt% C alloy consisted of dendrites surrounded by a eutectic matrix. The dendrites were initially austenite that decomposed to pearlite upon cooling; the matrix was ledeburite, Figure 63a. The as-cast microstructure of the 4.10 wt% C alloy was similar, Figure 63c, while the as-cast 5.13 wt% C alloy consisted of graphite flakes surrounded by ledeburite, Figure 63e.

Overall, the arc-lamp surface treatment did not significantly alter the as-cast microstructures, although there was an increase in the fineness of the microstructure. The 2.98 wt% C alloy had significantly finer dendrites after arc-lamp processing (b) than the as-cast structure (a); the dendrites are surrounded by a ledeburite matrix.
Figure 63: Model cast iron microstructures. Alloys were arc-lamp processed at 1000 A with a traverse rate of 6 mm/s.
Figure 64: SEM of model cast iron alloys. Alloys were arc-lamp processed at 1000 A with a traverse rate of 6 mm/s.
The 4.10 wt% C as-cast alloy initially had a dendritic structure surrounded by a ledeburite matrix (c). After arc-lamp processing, the dendrites became increasingly finer (d), similar to the 2.98 wt% C alloy.

The 5.13 wt% C as-cast alloy had graphite flakes (e), which disappeared after arc-lamp treatment in favor of proeutectic carbide formation (f). The 5.13 wt% C alloy did, however, exhibit a structural change between the two different traverse speeds tested: 4mm/s (Figure 65) and 6mm/s (Figure 63f). At the slower rate, nodular graphite formed at the surface of the alloy, replacing the flake graphite in the as-cast alloy, as verified by energy dispersive spectroscopy (EDS).

8.2.1. Chemistry and X-Ray Diffraction

As previously mentioned, bulk chemical analysis was conducted on the model cast iron alloys by combustion spectroscopy. The bulk alloys were measured at 2.98, 4.10, and 5.13 wt% C, respectively.

To determine the phases present in the microstructure, XRD was conducted. XRD detected the presence of ferrite, iron carbide, iron oxides (both Fe$_2$O$_3$ and Fe$_3$O$_4$), and graphite in some of the alloys, Figure 66. The 2.98 wt% C alloy (a) contained ferrite and iron carbide, with a minor amount of graphite. No graphite was observed in the microstructure, however, and the graphite was possibly a contamination issue from other samples, but no evidence for that was observed. After arc-lamp processing, XRD analysis of the 2.98 wt% C alloy detected both ferrite and iron carbide again, along with Fe$_2$O$_3$ and Fe$_3$O$_4$ (b). No graphite was detected after processing.

The 4.10 wt% C alloy was found to contain ferrite and iron carbide (c), which agrees with the visual interpretation of the microstructure. After processing (d), iron oxides were detected (Fe$_2$O$_3$ and Fe$_3$O$_4$), but there were also two large peaks that correspond to the expected
intensities. One of the two peaks (the third-largest in the spectrum, at 39.8°), corresponded to a similar peak from Fe₃C, but the documented Fe₃C spectrum had a significantly smaller intensity. The other peak (the largest peak in the spectrum, at 43.8°), either corresponded to a peak of Fe₃C or of martensite. No martensite was observed in the microstructure, so both of these peaks are expected to be from iron carbide, but the peaks may also represent unanticipated phases that were not a part of the analysis.

The 5.13 wt% C alloy was observed to have ferrite and iron carbide in the as-cast condition (e) and graphite, ferrite, Fe₃C, Fe₂O₃, and Fe₃O₄ after processing (f). The absence of a graphite peak in the as-cast condition was notable because of the significant visual presence of graphite in the as-cast microstructure, Figure 63e.

The XRD analysis of the model cast irons provided a spectrum with significant deviations in peak intensities from the documented powder diffraction samples, as well as the absence of some small peaks. The differences likely can be attributed to the solid-state nature and directionality of the phases from the way the transformations occurred. As is visible in the microstructures, Figure 63, there is a significant orientation relationship in all of the alloys that provides a texturing effect to the x-ray diffraction patterns that likely contributed to the differences in the intensities from the standards.
(a) Fe – 2.98 wt% C As-cast.

(b) Fe – 2.98 wt% C As Processed.

(c) Fe – 4.10 wt% C As-cast.

(d) Fe – 4.10 wt% C As Processed.

(e) Fe – 5.13 wt% C As-cast.

(f) Fe – 5.13 wt% C As Processed.

Figure 66: XRD of model cast iron alloys. Alloys were either as-cast or arc-lamp processed at 1000 A with a traverse rate of 6 mm/s.
8.3. Hardness and Wear Properties

With the finer microstructure in the 2.98 wt% C and the 4.10 wt% C alloys, it follows that there was a slight increase in hardness, Table 10. The 5.13 wt% C alloy, on the other hand, showed a slight decrease in hardness. The hardness results show that the arc-lamp traverse rate did not significantly affect the hardness. The decrease in the hardness of the 5.13 wt% C alloy is within experimental variation. A hardness trace for each alloy is shown in Figure 67.

Table 10: Microhardness of the cast iron alloys before and after arc lamp treatment

<table>
<thead>
<tr>
<th>Alloy</th>
<th>As-Cast (HV 0.1)</th>
<th>4 mm/s (HV 0.1)</th>
<th>6 mm/s (HV 0.1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.98 wt% C</td>
<td>510 ± 30</td>
<td>570 ± 30</td>
<td>560 ± 40</td>
</tr>
<tr>
<td>4.10 wt% C</td>
<td>660 ± 70</td>
<td>720 ± 30</td>
<td>720 ± 20</td>
</tr>
<tr>
<td>5.13 wt% C</td>
<td>750 ± 40</td>
<td>720 ± 50</td>
<td>740 ± 60</td>
</tr>
</tbody>
</table>

Figure 67: Hardness traces for each of the three model cast iron alloys

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vii Error bars are ± 1 standard deviation.

viii Calculated as a weighted average between the phases. The Fe – 4.10 wt% C alloy was fine enough as-cast that a weighted average calculation was not beneficial.
9. Graphite Surface Alloying

The focus of this project was graphite alloying a steel surface using the plasma arc-lamp. The process has the potential to produce a variety of microstructures, with corresponding benefits and also potential problems associated with them.

9.1. Effect of Arc Lamp Parameters

One of the main issues affecting the arc-lamp processing capability is the issue of power control. Ideally for the graphite-alloyed coatings, maximum power is used (given coating considerations and lamp capabilities) without creating too much liquid that would consolidate into a ball. Too little power creates a situation where the steel surface does not melt, therefore not creating any surface-modified region whatsoever. Figure 68a shows a coating that was alloyed primarily with graphite and a minor addition of ferro-molybdenum powder. This sample has a relatively uniform surface-modified region, typically about 100 to 200 µm thick. There is a minor amount of green coating left on the surface that did not alloy with the molten layer. This residual green coating was deemed important because once it disappears, macrostructures similar to Figure 68b result, in which surface tension effects take over and the liquid consolidates into a balled-up region on the surface. A bubbling was observed with these coatings significantly affecting the uniformity. More information is provided in Chapter 11.

![Fe-Mo-Graphite sample after arc lamp processing. The coating will be relatively uniform after the unalloyed coating is removed.](a)

![Graphite alloyed sample, showing the balling up of the liquid region and complete alloying of the coating with the substrate.](b)

Figure 68: Typical coating surfaces after arc lamp processing.
9.2. Microstructures

The resultant microstructures ranged from pearlite to hypoeutectic, depending on the arc-lamp processing parameters. The processing parameters that result in more heat input (described in Section 7.5.1) into the sample result in more carbon-diluted structures. The hypoeutectic microstructure, Figure 69, is formed when the coatings are arc-lamp processed at a power level of 1000 A at traverse speeds of 6 mm/s or greater. These were the fastest traverse rates, resulting in the highest cooling rate. At a traverse rate of 4 mm/s, a pearlitic microstructure with Widmanstätten (or acicular) carbide is formed due to dilution of the carbon-content, Figure 70. When the cooling rate is slowed down even further by the addition of a preheat, a pearlitic structure can be observed, Figure 71. Further discussion on each of these microstructures is provided in the following sections.

(a) Large sample, 2% nital.
(b) Interface of sample in (a), Stead’s reagent.

Figure 69: Typical hypoeutectic structure, most commonly observed when the sample just barely melts. Microstructure that occurs when the coating is the most uniform.

(a) Large sample, 4mm/s.
(b) SEM picture of sample similar to (a).

Figure 70: Pearlite with Widmanstätten carbide in from a sample that had the liquid ball up. Structure most commonly observed when the liquid starts to ball and within most dendrites.
The hypoeutectic structure was what was most commonly observed in a quality graphite alloyed coating, i.e., relatively uniform with high hardness. It formed through the rapid solidification of a liquid-surface layer that had absorbed some of the graphite from the coating. A schematic of the different phases and constituents present in the hypoeutectic coating is shown in Figure 72; each phase will be discussed in more detail later. As will be shown, the microstructure includes austenitic dendrites at high temperature. It is the presence of these dendrites that allows the inference that the coating composition is hypoeutectic.

Figure 71: Pearlitic structure. Preheat of 150A for 2 minutes plus a pulse of 1000A for 6 seconds.

9.2.1. The Hypoeutectic Structure

The hypoeutectic structure was what was most commonly observed in a quality graphite alloyed coating, i.e., relatively uniform with high hardness. It formed through the rapid solidification of a liquid-surface layer that had absorbed some of the graphite from the coating. A schematic of the different phases and constituents present in the hypoeutectic coating is shown in Figure 72; each phase will be discussed in more detail later. As will be shown, the microstructure includes austenitic dendrites at high temperature. It is the presence of these dendrites that allows the inference that the coating composition is hypoeutectic.

Figure 72: Schematic of structures found in the hypoeutectic coatings.
Upon arc-lamp heating, a thin layer of liquid forms beginning at the interface between the steel and the carbon coating. The initial melting is facilitated by the high thermal conductivity of the graphite and corresponding ability to transfer heat to the steel substrate very quickly. This is evidenced by the formation of this coating leaving an amount of unalloyed coating at the sample surface after processing, as indicated by the arrow in Figure 73.

A predicted temperature profile is shown in Figure 74. This was calculated based on 1018 steel (composition in Section 7.2) being solely in the solid state and using room temperature properties that are summarized in Table 11. An assumed surface temperature of 1550 °C is shown in Figure 74 because it provides a depth of the molten zone similar to the thickness of the hypoeutectic structure visible in many microstructures. It was assumed that the lamp was stationary, instantaneously reached the surface temperature, and sustained the surface temperature long enough to set-up the thermal gradient. The assumptions used are significant simplifications, but the calculation serves to provide a basis for the thermal profile in the sample and the structures that forms because of it. The calculation was based solely on thermal conduction (i.e., convective mixing was not considered):

\[
\frac{\partial^2 T}{\partial x^2} = \frac{k}{\rho \cdot C_p} \frac{\partial T}{\partial t} \tag{25}
\]

Which was used in its differential form (i is the subscript for the distance, j for the time):

\[
\Delta T_{i,j+1} = \frac{\left(\Delta T_{i+1,j} - 2 * \Delta T_{i,j} + \Delta T_{i-1,j}\right)}{(\Delta x)^2} \frac{k}{\rho \cdot C_p} \Delta t + \Delta T_{i,j} \tag{26}
\]

Constants used in the calculation are shown in Table 11 and the conduction was assumed to occur for 4 seconds (a typical arc-lamp processing time, albeit with a traversing lamp).

The high temperature region, shown in Figure 74b, shows a near-linear thermal gradient with the equilibrium phases shown. Note, however, that no thermal effects for the phase transitions were accounted for in the calculation and the carbon content is only 0.18 wt% C, significantly lower than the carbon content in the coating.
Table 11: Steel constants.

<table>
<thead>
<tr>
<th>Constant</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermal Conductivity, k</td>
<td>51.9 W/(m*K)</td>
</tr>
<tr>
<td>Density, ρ</td>
<td>7.8 g/cm³</td>
</tr>
<tr>
<td>Specific Heat, Cₚ</td>
<td>0.486 J/(g*°C)</td>
</tr>
</tbody>
</table>

(a) Overall profile

(b) High temperature region.

Figure 74: Calculated temperature profile.

A similar calculation based on a heat flux of 800 W/cm² was completed internally at Caterpillar by Adrian Catalina which showed that, after 4 seconds, the temperature reached 1540 °C at a depth of 5 μm below the surface. The calculation accounted for carbon diffusion upon heating and the thermal transitions present for the steel, assuming a solid carbon source. The carbon content reached 5.2 wt% C at the end of the 4 second thermal treatment. Melting began at 2.3 seconds into the thermal cycle with a carbon content of 2.1 wt% C. The model by Adrian Catalina showed that the calculation in Figure 74 significantly overestimates the heat input into the sample.

9.2.1.1. Coating Formation

For the carbon contents being considered, the first solid to form is a proeutectic phase and will form austenite, cementite, or graphite, as predicted by the phase diagram. If cementite or graphite were the proeutectic phase, either would form as long, straight plates.
Since neither of these phases was observed in significant quantities growing from either the liquid-atmosphere surface or the solid-liquid interface, it follows that the dendrites were initially austenite. This was verified, as described later, by SEM showing pearlite inside the dendrites, which formed as a decomposition product of the austenite upon cooling.

Solidification occurred from both the solid-liquid interface and from the liquid-atmosphere surface. The presence of dendrites growing towards the surface, as in Figure 75, would indicate that solidification began at the solid-liquid interface. However, some dendrites are observed to grow from the surface, as in Figure 76. Thus, solidification may apparently proceed from both interfaces.

Since the carbon content in the dendrites was significantly higher than 0.48 wt% C (the peritectic composition),\textsuperscript{ix} it is assumed that enough carbon diffusion occurred upon heating such that the BCC phase did not form at high temperature. As such, it follows that the first solid to form is austenitic dendrites, which will grow from a FCC + liquid region. The model by Adrian Catalina\textsuperscript{73} showed that the carbon diffusion is fast enough for this to be true.

\textsuperscript{ix} Composition calculated from Thermo-Calc based on composition of 1018 steel.
With the formation of austenite dendrites, carbon is rejected back into the liquid, enriching it in carbon to the ledeburite eutectic composition, 4.30 wt% C, as predicted by the iron-iron carbide phase diagram, Figure 1. Ledeburite, Figure 77, is formed over the graphite eutectic in the presence of a higher undercooling and, once nucleated, quickly grows throughout the microstructure.\textsuperscript{31,74}

The enriched interdendritic region can even form a hypereutectic structure, as indicated by the arrow in Figure 78. The region is considered hypereutectic because it consists of cementite plates that form as the proeutectic phase in a hypereutectic white cast iron. A similar microstructure was observed by Hillert and Steinhäuser in a bulk hypoeutectic alloy, Figure 79.\textsuperscript{30} In the hypoeutectic alloy, the proeutectic phase is the austenitic dendrites and with the enrichment of the liquid in carbon, sufficient driving force exists for cementite plates to also nucleate. This cementite forms much as a proeutectic phase and no cooperatively with the austenite, which would represent eutectic/ledeburite growth.

Upon cooling, austenite decomposes to pearlite, Figure 80, or pearlite with Widmanstätten carbides, Figure 70b, depending upon the cooling rate and the local composition. Martensite was also observed in the Fe – Mo – C coatings that are discussed in Chapter 10.

In Figure 81, formation of the Widmanstätten carbide can be shown by the growth of the Widmanstätten needles out of the interdendritic carbide, similar to the structure shown in Figure 14.
As previously stated, Widmanstätten or acicular carbides formed inside the austenite from the dendrites (the hypoeutectic region in Figure 72). These carbides require a high undercooling to form, as described in Section 2.1.2 (otherwise, carbide precipitation would occur as grain-boundary allotriomorphs). The presence of a high undercooling is evident from the formation of ledeburite surrounding the austenite dendrites, which requires a high undercooling. The presence of the Widmanstätten or acicular carbide may also be helped by the faster velocity of the incoherent interface growth versus the slower precipitation of the carbon onto the grain boundaries.

Underneath the dendrites, there was occasionally a region that Katsamas and Haidemenopoulos observed, Figure 49, and called a super-saturated diffusion zone (one of the two possible morphologies of transition zone #1 in Figure 72). Tayal and Mukherjee mention a similar region and called it retained austenite. In the arc-lamp process, this region appears white under the base of the dendrites, Figure 71. The super-saturated zone is hypereutectic, as determined by EPMA (further discussion is provided in Section 9.2.4), and no OIM pattern was able to be discerned from the region, despite careful electropolishing. Additionally, despite etching with nital, ammonium persulfate, and Stead’s reagent, very little structure was
discernable in the region, even in the SEM, Figure 82. The region was suspected to be retained austenite.

The other possible microstructure in transition zone #1 is an extension of the pearlite with Widmanstätten carbide region, as indicated by the top arrow in Figure 83.

The final two regions that occurred in all of the graphite alloyed samples is a pearlitic region followed by a region of Widmanstätten ferrite (transition zones #2 and #3 in Figure 72). These transition zones appear optically as in Figure 83 (the bottom arrow points to a Widmanstätten ferrite structure), with SEM images of the pearlite and associated regions are shown in Figure 84a and b, respectively.

The start of the transition zones (top of the 3 transition zones in Figure 72) could either be a gradual interface or a sharp interface, Figure 85. The sharp interface tended to occur when the samples were melted at faster rates, either through a faster rate in the single scan (≥8 mm/s), or through a quadruple speed pass that crosses the surface four times (4X at ≥24 mm/s). Further analysis of this topic is provided in the discussion section.
9.2.2. Pearlite and Pearlite with Widmanstätten Carbides

The pearlite samples with Widmanstätten carbides, Figure 70, were observed throughout the structure when the samples were heated at slower traverse rates and within the dendrites as previously mentioned. The main factor involved is the dilution of the carbon, with respect to the amount of liquid formation.

This structure was observed in samples where the carbon coating was completely dissolved and the liquid started to ball up, Figure 86. Based on the EPMA measurements, which will be discussed in Section 9.2.4, the carbon composition was diluted to below the maximum carbon solubility point in austenite (2.1 wt% C at 1148 °C in Figure 1). Thus, the equilibrium solidification path would take the alloy through the entirely single-phase $\gamma$ region and then to the two phase region that is austenite and carbide. With the undercooling present in the system (as shown by the presence of ledeburite and previously discussed with the formation of this structure inside the dendrites hypoeutectic coatings, in Section 9.2.1), the carbides form as Widmanstätten carbides. Upon further cooling, the remaining austenite transforms to pearlite.
The formation of the pearlite with Widmanstätten carbides was aided by the slower traverse rates. At the slower traverse rates, there is a larger amount of heat input into the sample itself, which slows down the cooling rate. More information on the cooling rate was discussed in Section 7.5.1. There is often a significant amount of melting in the substrate (primarily on the edges) when this structure is observed through the sample. The greater amount of heat in the sample produces more liquid, which serves to dilute the carbon content.

The fully pearlitic structure, Figure 71, was typical in samples that were preheated by the arc-lamp. These samples lost much of the ability to serve as a self-quenchant and as such, returned to room temperature via slow air cooling. The slow cooling allowed significant time for solid-state diffusion to occur, deepening the carbon-enriched area and allowing significant time for pearlite to form.

### 9.2.3. Multiple alloying steps

The creation of a hypereutectic surface structure was attempted using multiple alloying steps. Unfortunately, this did not provide any benefits to noticeably increasing the carbon content and therefore changing the structure entirely into a eutectic or hypereutectic structure. Multiple alloying steps even hurt the overall coating (1000 A, 4 pass, 32 mm/s sample) by slightly reducing the thickness of the carbon-enriched layer, Figure 87 (a, b). The microstructures were effectively the same as a single-step process, Figure 87, and the depth did not change much. The main benefit was the conversion of one of the coatings into a coating with more ledeburite (e, f). The reason for the conversion was an absence of macroscopic balling of the liquid. However, the reason for the absence of the balling is unknown, but could be affected by more uniform melting with the presence of carbon already in the system or a thicker coating of graphite placed on the sample.
Figure 87: Microstructures of multiple alloyed samples after initial alloying and after 3 cycles of alloying and arc lamp. Lamp parameters were 1000 A with 4 arc lamp passes at varying speeds.
9.2.4. Chemistry and X-ray Diffraction of the Microstructures

EPMA was conducted to determine the phase compositions within the different microstructures. Starting from the substrate, two compositional traces were measured on the sample in Figure 88. The sample had a microstructure that is mainly pearlitic with Widmanstätten carbides and contains a thin hypoeutectic region on the surface. As indicated in Figure 89, the average carbon content increased slightly from the coating base to the surface, at which point the carbon composition increased to over 5 wt%, indicating the presence of a local hypereutectic region. The carbon content reaches 1.85wt%C in the pearlitic region with Widmanstätten carbides, still under the maximum solubility of carbon in austenite as indicated by the phase diagram, but well over the eutectoid composition. The carbon content measured in the eutectic region is significantly higher, but is subject to more variation due to the fineness of the structure. A trace through the hypoeutectic structure of the same sample yielded an average of 5.8 wt% C in the ledeburite region, with a carbon content of 2.0wt%C in the dendritic regions, for an overall carbon content of 3.7wt%C.

![Figure 88: Sample arc lamp processed at 1000 A with a traverse speed of 4 mm/s.](image)
The white hard-to-etch region has an average carbon content of 5.27 wt% C, well above the eutectic composition. An EPMA trace through this region at a constant depth in the coating is shown in Figure 90. As described in earlier, the region also has no discernable microstructure when etched, nor does it show a crystal structure under OIM (e.g. the iron
carbide structure). Katsamas and Haidemenopoulos observed a similar structure and called it a super-saturated diffusion zone, while Tayal and Mukherjee mentioned a retained austenite region. Therefore, the region was suspected to be retained austenite.

XRD detected the presence of iron carbide, ferrite, and graphite in the hypoeutectic microstructure, Figure 91, as well as a little bit of Fe$_3$O$_4$. The detected phases allow the determination of the microstructural description stated previously. Fe$_2$O$_3$ was detected on other spectra as well, but FeO was not detected. Similar results were obtained for coatings that were pearlitic with Widmanstätten carbide.

Figure 90: Carbon content in the super-saturated diffusion zone. EPMA trace, constant depth in coating.
9.3. Hardness and Wear Properties

The biggest advantage to the hypoeutectic microstructure is its ability to achieve a high hardness and be crack-free, as concluded by Tayal and Mukherjee. The average hardness values for each of the three main phases in the surface-modified structures analyzed are shown in Table 12. The hardness for ledeburite matches the highest hardness in the arc-lamp treated model cast iron alloys that contained ledeburite. The Widmanstätten carbide strengthens the pearlite to create an intermediate hardness between ledeburite and pearlite; the pearlite is significantly harder than cited by literature in Table 1. This is likely attributed to the extremely fine scale of the pearlite and the super-saturation of carbon. Ledeburite is within the range cited in Table 1, and slightly lower than that achievable by martensite. The high hardness is beneficial, as high hardness is frequently correlated with better wear resistance.
Table 12: Hardness for each phase, graphite alloyed samples.\textsuperscript{x}

<table>
<thead>
<tr>
<th>Microstructure</th>
<th>Hardness, HV 0.1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ledeburite</td>
<td>750 ± 100</td>
</tr>
<tr>
<td>Pearlite with Widmanstätten carbide</td>
<td>520 ± 40</td>
</tr>
<tr>
<td>Pearlite</td>
<td>430 ± 40</td>
</tr>
</tbody>
</table>

---

To further characterize the mechanical properties of the hypoeutectic coating, a wear test was conducted, as described in Chapter 7. The wear-test results are only a small sampling of data to show the real-life applicability of the coating. The coatings were compared to a baseline of carburized 1018 steel with a 1 mm case depth in a quench and temper operation with parameters commonly used at Caterpillar.

These coatings showed a greater than 2X wear volume improvement over the baseline 1018 carburized and hardened sample in a 16 hour test. Improvements ranged up to 4X as good in the 1 and 4 hour tests. The improvement is likely due to the high carbide fraction present at the surface of the graphite-alloyed samples.

The typical surface hardness for the 1018 carburized and hardened microstructure was 830 HV 0.1, as shown by a traverse in Figure 94. The hardness is surprisingly higher than the

\textsuperscript{x} Error bars are ± 1 standard deviation.
ledeburite hardness, which indicates that carbides must be more wear-resistant than tempered martensite, despite the slightly higher hardness of the tempered martensite.

Figure 93: 16 hour ball-on-flat wear tests with their 3D profiles and a corresponding 2D cutout.

Figure 94: Hardness traverse of the 1018 carburized and hardened sample.
9.4. Laser Alloying

For a simple comparison to the literature results, a number of samples were prepared using the same spray methodology as applied to the arc-lamp samples, described in Section 7.2. The laser samples were processed using a 10 mm x 10 mm square beam from a Nd:YAG laser with a 2400 W output. The sample traverse speed was varied to show the range of different microstructures possible, Figure 95.

The 200 mm/min sample, Figure 95a, has a carburized structure. As the traverse rate decreases to 150 mm/min (Figure 95b) and 100 mm/min (Figure 95c), the resulting microstructure shows a super-saturated diffusion zone similar to the zone occasionally seen in the graphite samples with large substrates. The 100 mm/min sample also includes a eutectic zone at the surface and shows a large super-saturated diffusion zone, when compared to the thickness of the eutectic region. Cracking was observed between the eutectic region and the diffusion zone, presumably due to thermal stresses. The 50 mm/min sample, Figure 95d, formed a dense dendritic structure very similar to the dense dendritic structure in arc-lamp processed samples were the liquid has just begun to ball up, Figure 96. The alloying zone in the 50 mm/min laser-processed sample was up to 780 µm thick, significantly deeper than any of the arc-lamp samples that did not ball-up, and achieved an average hardness of 690 HV 0.1. A hardness trace through the 50 mm/min sample is shown in Figure 97. The coating regions for the other samples were too thin to obtain accurate microhardness measurements.
Figure 95: Laser carburized microstructures. Coating preparation is the same as prior the preparation prior to arc-lamp treatment.

Figure 96: Arc-lamp processed sample where the liquid has just begun to ball up.
The observed laser-processed structures are similar to those observed in literature, such as the eutectic structure observed by Tayal and Mukherjee$^{54}$ in Figure 44c and the super-saturated diffusion zone observed by Katsamas and Haidemenopoulos$^{58}$ in Figure 49.

![Figure 97: Hardness trace for the 50 mm/min laser carburized sample.](image)
10. Ferro-molybdenum and Graphite Alloying

The next surface-modification route investigated involved alloying the graphite coating with ferro-molybdenum. Molybdenum was chosen as the alloying element addition to increase the hardenability of the surface-modified region and to potentially introduce new carbides. Ferro-molybdenum was chosen to provide a cost-effective route for adding molybdenum.

Two different coating compositions were tested: Fe – 40 wt% Mo – 33 wt% C and Fe – 20 wt% Mo – 67 wt% C. The coatings were applied in the same way as those that were alloyed with only graphite, as described in Section 7.2. The Fe – 20 wt% Mo – 67 wt% C coating increased the hardness in the ledeburite to 980 HV 0.1 from 750 HV 0.1 in the graphite-only coatings, and also increased the quality of the arc-lamped surface modifications. More hardness data will be shown in Section 10.3 and further discussion on the quality of the arc-lamp coatings follows in Chapter 11. The Fe – 40 wt% Mo – 33 wt% C coatings were more difficult to work with in the spraying process and tended to ball-up very easily during arc-lamp processing. As such, only initial testing was completed on these coatings.

10.1. Effect of Arc Lamp Parameters

The arc-lamp parameters tested for the Fe – 20 wt% Mo – 67 wt% C coating were 1000 A and 4 to 8 mm/s for the single pass samples or 24 to 32 mm/s for the multiple pass samples. Based on the knowledge built in the graphite-alloyed samples, no preheat tests were conducted, with the goal of obtaining a hypoeutectic structure.

The coatings acted similarly to the graphite coatings, with the added benefit of improving the uniformity of the coating by the reduction of the gas bubbling. Further discussion on the coating uniformity is provided in Section 11.1.

10.2. Microstructure

The microstructures resulting from the Fe – 20 wt% Mo – 67 wt% C coating were either martensitic or hypoeutectic, Figure 98, depending on the speed of the arc-lamp traverse.
Martensite was observed with an arc-lamp power of 1000 A at a speed of 4 mm/s, while the hypoeutectic microstructure was observed with speeds ≥6 mm/s.

As with the graphite-alloyed samples, the microstructure of the Fe – 20 wt% Mo – 67 wt% C coating consists of initially austenitic dendrites surrounded by the ledeburite eutectic. Further information on the formation of the hypoeutectic structure can be found in Section 9.2.1, regarding the graphite-alloyed structure.

The main benefit that the molybdenum addition provides is the increased hardenability of the coating, allowing the system to form martensite easier, both within the dendrites of the hypoeutectic coating, Figure 99, and in some cases, uniformly, Figure 100. The martensite within the dendrites is similar to the plate martensite structure shown in Figure 18b. Verification of the martensite was completed visually. However, there is the possibility that martensite, as referred to in this project was actually bainite.

![Images of the coating at different speeds and reagents](image-url)

Figure 98: Fe-Mo-graphite coating, applied as Fe – 20 wt% Mo – 67 wt% C.
10.2.1. Chemistry and X-Ray Diffraction

Higher concentrations of molybdenum were found in the eutectic regions of the sample (being rejected into the liquid during solidification). The eutectic regions were found by EPMA to contain 1.4 wt% Mo and 7.0 wt% C, while the dendrites had significantly lower Mo and C contents, at 0.4 and 3.8 wt%, respectively. An EPMA trace for the samples in Figure 101 is shown in Figure 102.

As seen in Figure 101, the top of the transition region (zone numbers 1-3 in Figure 72) is a sharp transition. The EPMA trace shows that a small amount of molybdenum, up to 0.5
wt%, was absorbed into the transition region. The molybdenum was assumed to come from solid diffusion because of the sharp increase in molybdenum content at the beginning of the hypoeutectic region. The carbon content, however, is too high for the region to be originally only austenite. The region may be a combination of pearlite and a super-saturated diffusion zone, appearing similar to the transition zone in Figure 98c.

![Alloy Content](image)

Figure 102: Carbon content as a function of distance, starting at the base of the coating and ending in the hypoeutectic region.
Additionally, the carbon content in the hypoeutectic region was greater than the carbon content in iron carbide, 6.7 wt% C, which indicates the potential presence of other carbides that were not detected in the XRD analysis.

XRD detected the presence of iron carbide, martensite, and graphite, Figure 103. The peak at 50.6° (2θ) cannot be explained at this time, and could be due to texturing effects. The microstructure is highly textured. The excess peak, however, may also represent an unknown phase. Two oxides, Fe$_2$O$_3$ and Fe$_3$O$_4$, were detected on other spectra as well. FeO, however, was not detected.

Figure 103: XRD Spectrum for a sample of Fe – 20wt% Mo – 67wt% C that was arc lamped at 1000 A at a speed of 8 mm/s. Graphite is from a residue left over from the coating process and is not a part of the coating structure.

10.3. **Hardness and Wear Properties**

The Fe-Mo-C alloys also had a higher hardness than the graphite-alloyed samples, as seen in Table 13. The increase in hardness is largely due to the formation of martensite from the austenite decomposition in both the dendrites and the ledeburite.
Table 13: Hardness for each phase, Fe-Mo-C and graphite alloyed samples.$^{\text{xii}}$

<table>
<thead>
<tr>
<th>Microstructure (Fe-Mo-C)</th>
<th>Hardness, HV 0.1 (Fe-Mo-C)</th>
<th>Microstructure (Graphite)</th>
<th>Hardness, HV 0.1 (Graphite)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lедебурит</td>
<td>980 ± 90</td>
<td>Ледебурит</td>
<td>750 ± 100</td>
</tr>
<tr>
<td>Мартенсит</td>
<td>630 ± 100</td>
<td>Пирит с карбидами Видманнштетта</td>
<td>520 ± 40</td>
</tr>
<tr>
<td>Пирит</td>
<td>520 ± 30</td>
<td>Пирит</td>
<td>430 ± 40</td>
</tr>
</tbody>
</table>

The increase in hardness translates into an increase in the wear resistance of these coatings, over both the 1018 carburized samples, as well as the graphite-alloyed coatings. The 16 hour wear test showed a reduction an over 5X reduction in wear volume, when compared to the baseline 1018 carburized sample. The shorter 1 hour and 4 hour tests also showed similar improvements. The ledeburite region in the Fe-Mo-C coatings was harder than the tempered martensite of the 1018 carburized and hardened baseline. As such, it is expected that the wear of the Fe-Mo-C coatings would be a significant improvement over the baseline, especially when considering that the graphite-alloyed coatings showed an improvement in the wear rate over the baseline, despite the lower hardness.

The wear volume calculation for the Fe-Mo-C coatings is difficult because of the non-uniformity in the surface. The wear scar is not significantly large enough to uniformly degrade the surface to where the initial surface non-uniformities have been completely replaced by wear scars, as is evident in Figure 104e. The overall wear volume improvement is significant and largely due to the increase in hardness from the transition of the pearlite within the dendrites to martensite. To better characterize the wear, especially on the Fe-Mo-C coatings, longer and/or harsher wear testing is required.

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$^{\text{xii}}$ Graphite alloyed sample microhardness measurements are also reported in Table 12. Error bars are ± 1 standard deviation.
Figure 104: 16 hour ball-on-flat wear tests with their 3D profiles and a corresponding 2D cutout.
11. Discussion

In simple terms, the graphite surface-alloying process resulted in a white cast iron coating on top of a steel substrate. The resultant product has a hard, wear-resistant coating without severely affecting the substrate. The ability to put a wear-resistant coating on a softer steel substrate allows for easier and cheaper manufacturing of the part, when compared to adding alloying content for hardenability. Research on lasers has been shown to produce similar structures, but the benefit to the arc-lamp process is that it could easily be scaled to produce large parts very quickly.

The system in general behaved in a manner that was consistent with the traits of a fast-cooled hypoeutectic Fe-C alloy, where the undercooling present contributed greatly to the microstructure in the formation of both ledeburite and Widmanstätten carbides over the graphite eutectic and grain boundary carbides, respectively. If slow-cooling, equilibrium conditions existed, the microstructures would have been as outlined schematically in Figure 105, with a presence of both graphite and cementite (the stable and metastable systems). The stable Fe-C system would be visible in the hypoeutectic coating, while the metastable Fe-Fe₃C system would be present from the transition zone into the substrate.

For the schematics in Figure 105, the same hypoeutectic carbon content is assumed. At the beginning of solidification, proeutectic austenite dendrites would form as was found in the current study. Below the austenitic dendrites would be a region of heat affected zone that
would be entirely austenitic (the transition zone in Figure 105a) to a certain depth. As equilibrium solidification would continue, the graphite eutectic would form (in the hypoeutectic region) as graphite colonies, shown schematically by Hillert and Subba Rao in Figure 24. The eutectic could include some directionality to the microstructure. The austenite dendrites would be present, but they would not be visible distinct, as is the case in the current study. The austenite dendrites in gray cast iron are significantly larger than the graphite eutectic colonies. So on a fine scale, the microstructure would appear as entirely graphite colonies in an austenitic matrix, as observed by Rivera et al., Figure 106. Rivera et al. also observed that the graphite colonies tend to cross the austenite dendrite boundaries, so the austenite dendrites would not be evident without special metallographic techniques.

Upon further equilibrium cooling to room temperature (in the hypoeutectic region), the austenite in the graphite colonies would transform to ferrite, with the excess carbon causing growth of the graphite. In the transition zone, however, the metastable system would be present. The transition zone would be initially austenite to a certain depth. The austenite would decompose to pearlite, while the excess carbon would form as grain boundary carbides. The difference here is that the pearlite would form as was currently observed, but instead of the Widmanstätten or acicular carbides, grain boundary carbides would form due to the slow-cooled state of the sample.

Instead of the graphite eutectic in equilibrium, however, the ledeburite eutectic forms in a metastable equilibrium. The graphite eutectic typically would form at a lower undercooling, but once the ledeburite eutectic is nucleated, it grows very quickly throughout the microstructure. In this system, with relatively rapid self-quenching, achieving the required undercooling for the nucleation of cementite is not difficult, as can be observed microstructurally from the frequent observation of ledeburite without observing the graphite eutectic. As for the structure within the dendrites (pearlite with Widmanstätten carbides), equilibrium would dictate pearlite formation with the excess carbide precipitating at the grain boundaries. However, the high undercooling present in the system drives the formation of
the Widmanstätten carbides. The cooling rate is fast enough to form martensite in the alloy system, but not with the graphite-only alloying addition. The cooling rate is still fast enough to create the necessary undercooling to form the Widmanstätten carbides.

The system also has relatively fast diffusion in the liquid, as the main diffusing element is carbon. Only a slight amount of segregation was observed in the alloy content of the coating with respect to depth. The variation with respect to depth may be due to either incomplete mixing or to segregation of the alloying elements during solidification. The amount of variation with depth in the alloy content, however, is small enough that for practical purposes, the mixing can be assumed to be complete.

### 11.1. Process Results

The development of this coating still needs some work, as certain processing issues have yet to be solved, such as a bubbling of the coatings, Figure 107. The bubbling was frequently observed in the graphite-only coatings, but only occasionally in the Fe-Mo-C coatings. This is postulated to be due either to a hydrophobic interaction between the graphite and the Lisi 100i9 binder or the formation of gas bubbles inside the coatings, likely CO and CO$_2$. No tests have been conducted to determine the validity of these hypotheses. Fortunately, the ferro-molybdenum and graphite coatings reduced bubble formation for unknown reasons and significantly more uniform coatings were able to be produced. As such, there has not been a critical need to determine the cause of the bubble formation in the graphite coating, as it is possible to engineer around the issue and produce a harder and more wear-resistant coating in the process.

Overall, the arc-lamp process is very good for putting high-melting-temperature coatings on a lower-melting-temperature substrate (the high-melting-temperature coating is the initial coating, graphite in this case). The graphite coating is very high melting, which ensures that the substrate will receive enough heat for melting to occur. In fact, the melting in this system
begins at the interface between the coating and the substrate. The graphite layer never reaches temperatures high enough to cause melting or significant sublimation. Once the liquid layer melts, it dissolves the graphite above it and swelling towards the surface, Figure 108.

Surface tension also plays a significant role in the coating process, as surface tension will cause the liquid to ball-up. The surface tension therefore either needs to be overcome by a mechanical bond to the substrate, ensuring that the substrate gets plenty of heat, or through starting the melting at the interface with a solid coating still on top of the system. This project used the third option as a way of overcoming the surface tension that is inherent to a process of this type. Systems that require both the coating and the substrate to be melted, therefore, can be harder to process using the arc lamp, especially in the case where the coating forms liquid at a lower temperature than the substrate.

Based on the work completed in this study, greater coating thicknesses may be possible but may require more complicated arc-lamp processes, such as pulses of the lamp during the scan to sustain the desired surface temperature.

### 11.2. Microstructure and Thermal Model

The interface between the hypoeutectic region and the pearlitic transition into the substrate was either a sharp interface or a gradual interface structure. As discussed in Section 9.2.1, the interface tended to be sharp at faster traverse rates, including the samples where the traverse rate was quadrupled and the sample was scanned four times. The presence of such a distinct interface suggests a very steep thermal gradient, one that effectively eliminates a mushy zone. The only other way this can be accomplished is by having the composition at the eutectic. The samples studied here appear to have both of these factors contributing to the sharp interface, as the samples with the sharp interfaces appear to have further spaced dendrites and more volume fraction of the eutectic. The higher fraction of the eutectic would
correspond to a higher overall carbon content, one that is closer to the eutectic composition, therefore decreasing the temperature range of the mushy zone.

The higher speed traverses create a steeper thermal gradient in the samples because of the lack of time for the thermal diffusion to occur. The depth of the thermal gradient is susceptible to changes in the traverse rates based on how much time the heat has to diffuse into the sample. Thus, both of these factors appear to figure in the sharpness of the interface.

These interface observations tend to show that the thermal model presented in Section 9.2.1 allows for significantly more thermal diffusion than the actual arc-lamp process. The model assumed a stationary heat source and temperature at the surface. The temperature aspect of that assumption is believed to be a decent approximation for a high-speed traverse. However, for a stationary sample, there is expected to be a significant heat-up time (with reference to the total run time) and a rising temperature throughout the run. The multiple pass samples also have a lower temperature gain during each pass of the arc lamp, making it easier to maintain a constant surface temperature during the pass.

Additionally, with a traverse, the time when the peak power is actually over a given sample location is quite limited. The model does not account for the thermal diffusion through the coating, which is not expected to be significant for these coatings due to the amount of graphite present, but the thermal energy required for melting the steel substrate would be significant. Overall, the thermal gradient is expected to be significantly steeper than is indicated in the calculated temperature profile from Section 9.2.1.

It is also worth noting that compressing the graphite-containing coating was very useful in reducing the density of the dendrites and therefore increasing the carbon content of the alloyed layer. The compressing of the coating increased the density of the graphite that was absorbed by the liquid during melting, as well as likely aiding heat transfer to the substrate. Compressing the coating may be difficult to achieve in a production process or with parts that are to be coated over more than a flat surface.

As shown, based on the direction of the dendrites in the graphite-alloyed hypoeutectic coating, solidification proceeded from both directions. However, visual observation revealed that the dendrite density was higher at the bottom of the coating, indicating that the solidification direction was primarily from the substrate. Nucleation was apparently
determined by the local conditions for solidification, as it often began from the coating surface, either from the liquid-atmosphere interface or, from the (typical) case of excess undissolved graphite, the liquid-graphite interface. The excess graphite, therefore, was shown to serve as a nucleation site for the austenitic dendrites. The dual-directional solidification served to illustrate the point that nucleation is heterogeneous.

The surface-modified structures that were formed with 1018 substrates and applied coatings had relatively randomly oriented structures, due to the heterogeneous nucleation occurring in multiple locations both at the solid-liquid interface and the liquid-graphite interface. The relatively random orientation was supported visually, as well as with XRD patterns that closely resembled powder diffraction spectra and thus, can be considered random. The relatively random orientation is in opposition to the model cast iron alloys, which visually show a definitive orientation dependence growing out from the substrate. The orientation dependence from the model cast iron alloys was not surprising, as the substrate already contained the basic phases that were present in the near-surface region. With the prior orientation already established, the creation of an orientation dependent structure is not surprising. The XRD patterns for the model cast irons did not match the intensities of the documented powder diffraction samples, which was surmised to be from the orientation dependence of the model cast irons.

The microstructural examination presented herein was conducted on the basis of the characteristic features present in typical steel and cast iron microstructures. As such, there is the possibility that the phase referred to as martensite in the Fe-Mo-C surface-modified regions was actually bainite. Detailed micro-chemical examination of each phase was not conducted and is outside the scope of this thesis.

11.3. Hardness and Wear Results

The overall hardness results were lower than some of the values obtained in literature, such as those obtained by Tsujikawa et al.\textsuperscript{12}, but were within the ranges specified in Table 1. The hardness values for ledeburite were on the lower end, only 750 HV 0.1, compared to the literature values that were greater than 700 HV 0.1. The values found for pearlite and pearlite with Widmanstätten carbide were higher than expected for pearlite by itself, and may
likely be attributed to the fine scale of the pearlite, the presence of other carbides, and the supersaturation of components in the structure.

The wear results, while promising, must be used cautiously. First, only limited tests were conducted to determine the broad-based potential for these coatings in wear applications. With the choice of 1018 steel as a base metal, the substrate has very little inherent wear resistance. As such, if this coating were to be used as is described in this process, as soon as the coating was worn out, the substrate would have very limit ability to limit the wear. A higher carbon or higher alloyed steel may make a better substrate choice for wear applications for that reason.

The wear improvements shown by this coating are based largely on the carbide fraction at the surface, when compared to the tempered martensite structure that carburized 1018 steel is based on. The hardness of the carbide phase is significantly higher than the hardness of martensite, Table 1, especially after it is tempered. The expected hard phases and constituents in the iron-iron carbide system are ledeburite, cementite, and martensite. The Fe–Mo–C coatings utilize all three of the microconstituents to create the hard, wear resistance surface. As mentioned previously the hardness of the ledeburite in the graphite-alloyed coatings is lower than the hardness of the 1018 carburized and hardened microstructure, which would result in an expectation that the carburized and hardened microstructure should have a lower wear volume than the graphite-alloyed samples. Thus, the inherent wear resistance of the tempered martensite must be lower than ledeburite, at least for the compositions studied.

The wear tests that were conducted were early-hour tests, where the fraction of carbide in the microstructure was high. The wear rates in these coatings will likely increase as the coating gets thinner due to the amount of carbide in the sample. The carbide fraction tends to decrease as the depth into the coating increases. As more carbide is worn away, the volume fraction of the softer, pearlite constituent (with Widmanstätten carbide) increases, which is expected to increase the wear rate. The carbide removal will be of significance in a production mode should a finish operation after arc-lamp treatment be required.
11.4. Future Work and Conclusions

Overall, the surface-modified regions were well-behaved with respect to the metastable phase diagram, given the large undercooling, and consistent with literature formation mechanisms of white cast iron. The surface-modified regions had a significant amount of carbide formation near the surface, from the ledeburite and the cementite, as well as very fine structures throughout the system. The large fraction of carbide and the fine scale of the structures result in a high hardness, a hardness that reached 750 HV 0.1 and 980 HV 0.1 for the graphite-only and Fe-Mo-C surface-modified regions, respectively.

Future work on this project should include testing different methods of controlling the melt zone to achieve a thicker coating, trying other coating compositions and alloying elements that may provide additional hardness and wear resistance, as well as continuing to improve the production focus through the use of larger samples that are actual Caterpillar parts. Additional alloying elements that may be worth examining are other carbide forming elements, such as chromium and tungsten. The thickness of the coating is extremely important because the thicker the coating that can be processed, the more coating will be useful for performance in the wear-resistant applications.

This project has shown that high-density infrared processing allows the ability to highly alloy steel for wear-resistance through surface liquification on a significantly larger scale than currently available technologies. The wear-resistant surface microstructure was achieved using the phases of ledeburite and cementite to create the wear-resistance. The presence of austenite may have helped to reduce or eliminate any cracking found in the samples, as cracking was not an issue during the process. The resultant coating has shown significant potential for wear-resistance improvement over the standard carburized microstructures.
References


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