Utilization of a carbon-dioxide laser to form an amorphous metallic layer on gray cast iron with various amount of boron

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UTILIZATION OF A CARBON-DIOXIDE LASER
TO FORM AN AMORPHOUS METALLIC LAYER ON
GRAY CAST IRON WITH VARIOUS AMOUNTS OF BORON

An Abstract of a Dissertation
Submitted
In Partial Fulfillment
of the Requirement for the degree
Doctor of Industrial Technology

Approved:

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August 1986
ABSTRACT

The study of the amorphous metals is important because of their technological usefulness. One class of these materials, iron-based metallic glass, has shown great promise in application because of the superior chemical, mechanical, electrical, and magnetic properties of these materials.

This study was conducted to examine the capability of a medium-powered carbon-dioxide laser to form an amorphous metallic layer on the surface of a ferritic gray cast iron in order to improve the wear and corrosion resistance of engineered components. Boron was used as an alloying element for the retardation of nucleation and for the formation of the amorphous metallic layer. Homogenization heat treatment was followed by vacuum emission spectroscopy, which provided the quantitative information related to the chemical composition prior to the laser processing. The laser parameters were chosen and they were examined experimentally to identify the optimum conditions for the process.

The characteristics of the laser-formed layer on the surface of specimens were determined by chemical testing, x-ray diffraction techniques, scanning electron microscopy, and electron diffraction techniques to substantiate the formation of the metallic glass layer and examine its features. Micro-hardness examination was used to determine the hardness profile of the generated layer at the heat-affected zone. Metallographic examination provided such information as the surface condition, the depth of the fusion zone, and any defects caused by the process.
The test results led to the conclusion that the carbon-dioxide laser, with medium power output within a certain range of operation, is capable of forming metallic glass structures on the surface of gray cast iron, alloyed with boron. In such a process, the laser must operate at the pulse mode generating a pulse with short width and long dwell time. In addition, the boron content of the sample should be in the range of 3.8 (eutectic point) to 4.17 percent by weight.

The specimen with 8 percent boron content, after it was irradiated with the laser at the continuous mode, also produced an interlocking structure often seen in glassy structures. The identification and characterization of this structure was not within the scope of this investigation.

The hardness measurement of the untreated surface showed a notable increase in the hardness of the specimen containing two percent boron. The micro-hardness examination of the laser-treated area revealed that the treatment caused a further increase in the micro-hardness of the specimens.

Electron Diffraction Spectro-Analysis of the laser heat treated zones did not conform to the structures predicted by the iron-carbon-boron and iron-carbon-silicon ternary diagrams. The laser treated surfaces produced a super-saturated structure with a high hardness and good resistance to corrosion.
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A Dissertation
Submitted
In Partial Fulfillment
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Doctor of Industrial Technology

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Dedicated to My Parents

Mrs. Taherah Penahpoor Islamy
and Mr. Mohammad-Mehdi Torkzadeh Tabrizi

for without their support and encouragement this would have not been possible
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The completion of a degree gives a great sense of accomplishment to the student, as it is an end of a challenge for him, his family, the faculty members, and, as is the case for this investigation, the many industrial and research institutions which aided in the research. It is necessary to recognize these contributions, express appreciation, and give credit to those who aided in this work.

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CHAPTER I
Introduction

Surface hardening of ferrous metals and alloys is commonly carried out by induction or flame heating to produce a thin, hardened layer and, thus, improve resistance to wear, fatigue, and corrosion of engineered components. In the past several years, an alternative technology has emerged based on the use of laser surface treatment. In the early 1980's a new technique for surface treatment of ferrous alloys that utilizes high laser power densities accompanied by rapid quenching of the treated surface layer was in the research and development stages (Mazumder, 1983). This technique could yield an amorphous surface layer of high hardness and strength that was also tough, ductile, and high in corrosion and wear resistance (Pye, 1983).

The purpose of this investigation was to study the formation of amorphous structures on the laser-treated surface of various iron-boron alloys. Boron was used as an agent in the retardation of nucleation. A 1300-watt industrial carbon dioxide laser was used in heat treating the surface.

The secondary purpose of this study was to identify the relationship between the amount of boron present and the depth, character, and micro-hardness of the amorphous surface layer. These findings may provide insight into the application of such processes in industry to achieve higher quality, increased reliability, and reduced costs of gray cast iron engineered parts.
Statement of the Problem

What are the required procedures for development of an amorphous metallic layer on the surface of ferritic gray cast iron by application of industrial carbon dioxide laser radiation, and what is the effect of boron content on the formation, mechanical properties, and microstructure of such a metallic glass layer?

Research Questions

In conducting this study, answers to the following questions were sought:

1. What is the possibility of forming an amorphous metallic layer containing boron on the surface of ferritic gray cast iron by utilizing an industrial carbon dioxide laser?

2. What effect does adding boron have on the formation of a metallic glass layer?

3. What is the effect of boron content on the micro-hardness profile of the amorphous surface layer?

4. What is the effect of boron content on the depth of the amorphous surface layer?

5. What are the changes in the microstructural characteristics caused by variation in the boron content of the specimens?

Significance of the Problem

Cast irons are essentially alloys of carbon, silicon, and iron in which more carbon is present than can be retained in solid solution in austenite at the eutectic temperature (American Society for Metals,
Gray cast iron, among all of the cast irons, is the most common and the most widely used. It is the least expensive of all engineering materials (Clauser, 1975). Typical applications for gray cast irons include automotive engine blocks, machine tools, agricultural implements, and electric motor housings (Ross, 1980).

The worldwide annual production of gray cast iron exceeds 3 million tons, with a U.S. production exceeding 600,000 tons (Graham, 1984). The state of Iowa, where industries such as John Deere and Company and Viking Pump Inc. are located, has one of the highest cast iron production levels in the U.S. "Deere's foundries alone produce about 600 million pounds of cast iron per year, second only to U.S. Auto Industry foundries" (Graham, 1984, p. 74).

In such production, component failure from wear, fatigue, and corrosion is of major concern to the manufacturer. Engineers generally observe that wear, fatigue, and corrosion failure of engineered components are surface-oriented since the stress levels are often highest at the surface and the surface is subjected to environmental forces (Molian, 1984). Furthermore, the type and the uniformity of the microstructures contribute to the mechanical properties of the final products. After extensive tests of wear in gray cast iron, the American Society for Metals (ASM) Committee on Gray Iron (American Society for Metals, 1977) reported the following conclusions:

1. The wear characteristics are determined by microstructures.
2. The wear resistance is increased as the graphite flakes become finer.
3. The wear resistance increases, for a given type of graphite, as the matrix becomes more pearlitic and harder.

4. Pearlitic or tempered martensitic structures in the same hardness range are equal in wear resistance. (p. 359)

The experience of Deere and Company with gray cast iron indicates that "the flake shape of the graphite tends to focus loads in this type of iron, leading to stress concentration that can affect the life of parts made from such materials" (Graham, 1984, p. 75).

In principle, the engineering solutions to such problems are to alter the chemical composition and/or microstructure of the surface or to deposit on the surface appropriate materials different from those of the bulk material. Numerous processes including nitriding, chemical vapor deposition, cladding, and plating are commonly used to achieve this purpose (American Society for Metals, 1977). The development of high power laser radiation in recent years has provided an alternate technique for meeting this important engineering problem through laser heat treatment of the surface (Mazumder, 1983). The formation of an amorphous metallic layer on the surface of ferritic gray cast iron is expected to accomplish several objectives:

1. Improve the corrosion and wear resistance of ferritic gray cast iron engineered parts.

2. Reduce the cost of production by the elimination of processes such as ionizing, vapor deposition, and final finishing.

3. Provide opportunities for the production of new equipment and parts.
Limitations

A complete investigation of the formation and characterization of an amorphous metallic layer on the surface of ferritic gray cast iron by applying laser radiation with the addition of boron would require extensive and expensive experimentation over a long period of time, as well as specialized instrumentation. Limited financial resources, combined with limited access to the specialized instrumentation, limits this investigation to the examination of the microstructure and to the study of some mechanical characteristics of the gray cast iron material resulting from the laser treatments.

Since amorphous metallic glasses, particularly the iron base metal glasses, are relatively new materials, the information in this area is rather limited. Hence, the lack of prior research data in the literature was also a limitation.

Delimitations

The scope of this investigation will be delimited to the application of a 1300-watt continuous wave, pulsed laser as an energy source with the addition of boron to gray cast iron in increments of two percent by weight up to a total boron content of twelve percent. Furthermore, the investigation and the characterization of the amorphous layer will be delimited to the identification of the microstructure and to the results of micro-hardness testing procedures.
Assumptions

In this investigation, it is assumed that the thermal heat treatment process can provide a homogeneous structure throughout the specimens used in the investigation. Further, to prevent unduly complicating the subject, it is assumed that the heat gradient direction in the heat conduction process during the laser treatment is linear.

Definition of Terms

The following is a list of working definitions for the terms used in this dissertation:

BAINITE. "A metastable aggregate of ferrite and cementite resulting from the transformation of austenite at temperatures below the pearlite range but above $N_s$" (American Society for Metals, 1983, p. 7).

CEMENTITE. "A compound of iron and carbon, known chemically as iron carbide and having the approximate chemical formula $Fe_3C$. It is characterized by an orthorhombic crystal structure" (American Society for Metals, 1983, p. 13).

ENTHALPY. "A thermodynamic function of a system, equivalent to the internal energy plus the product of the pressure and the volume" (Gove, 1981, p. 757).

ENTROPY. "A measure of the capacity of a system to undergo spontaneous change, thermodynamically specified by the relationship $dS = dQ / T$, where $dS$ is an infinitesimal change in the measure for a system absorbing an infinitesimal quantity of heat $dQ$ at absolute temperature $T$" (Gove, 1981, p. 759).
FERRITE. "A solid solution of one or more elements in body-centered cubic iron. Unless otherwise designated, the solute is generally assumed to be carbon" (American Society for Metals, 1983, p. 30).

FERRITIC GRAY CAST IRON. A cast iron with essentially ferritic microstructure with a minimum amount of pearlite and no massive cementites.

GAUSSIAN DISTRIBUTION. "A theoretical frequency distribution used in statistics that is bell-shaped, symmetrical, and infinite in extent" (Gove, 1981, p. 941).

HOMOGENIZING. "Holding at high temperature to eliminate or decrease chemical segregation by diffusion" (American Society for Metals, 1983, p. 38).


INOCULATION. "The addition of a material to molten metal to form nuclei for crystallization" (American Society for Metals, 1983, p. 40).

MACROSTRUCTURE. "The structure of metals as revealed by examination of the etched surface of a polished specimen at a magnification not exceeding ten diameters" (American Society for Metals, 1977, p. 24).

MARTENSITE. "A metastable phase of steel, formed by a transformation of Austenite below the Ms temperature. It is an interstitial supersaturated solid solution of carbon in iron having a body-centered tetragonal lattice" (American Society for Metals, 1977, p. 24).
MATRIX. "The principal phase or aggregate in which another constituent is embedded" (American Society for Metals, 1977, p. 46).

METALLOIDS. "A relatively small number of elements, which have four electrons in their outer shells. These elements can exhibit valences that are either positive or negative" (Hurd, 1968, p. 13).

METASTABLE. "A state of pseudoequilibrium that has a higher free energy than the true equilibrium state" (American Society for Metals, 1983, p. 47).

MICROSTRUCTURE. "The structure of polished and etched metals as revealed by microscope at a magnification greater than ten diameters" (American Society for Metals, 1977, p. 25).

NUCLEATION. "The initiation of a phase transformation at discrete sites, the new phase growing on nuclei" (American Society for Metals, 1983, p. 50).

PEARLITE. "A metastable lamellar aggregate of ferrite and cementite resulting from the transformation of austenite at temperatures above the bainite range" (American Society for Metals, 1983, p. 52).

RARE EARTH METAL. "One of the group of 15 similar metals with atomic numbers 57 through 71" (Hurd, 1968, p. 13).

REFRACTORY. A material of very high melting point (Clauser, 1975).

SPUTTERING. A technique for the production of amorphous materials. This technique is based on an atom-by-atom constitution of the product and requires that the kinetic energy exceed the binding energy of the atoms in the substrate surface.
CHAPTER II
Review of Related Literature

Amorphous metals are new types of materials. They are produced by distorting the crystal structure of metallic materials. In the mid-1960's, Duwez, Willens, and Klement of the California Institute of Technology developed, for the first time, a splat cooling technique with a cooling rate of approximately $10^6$ deg k/s capable of producing thin layers of metallic glasses. Almost simultaneously, Miroshichenko and Salli of the USSR reported a very similar technique to produce amorphous alloys (cited in Davies, 1983).

In recent years, the unique properties of metallic glass layers have received increased attention throughout the world. The United States government has allocated nearly $170 million to rapid-solidification studies that will be funded through 1986. The USSR's main emphasis in developing amorphous metals has been for electric and electronic applications. The Japanese support research in this area and the United Kingdom has formed a special commission to assess the need for a demonstration melt spinning unit to produce rapidly solidified metal strips. (Pye, 1983, p. 37)

The worldwide interest in amorphous metals has been sustained to a great degree by the clear benefits of these materials in a number of applications (Raskin & Smith, 1983). Werner (cited in Raskin & Smith, 1983) estimated the following:

The full-scale substitution of ferromagnetic metallic glasses for conventional electrical steels would result in considerable savings. This includes a single saving of two-thirds of the more than $3 \times 10^6$ kwh of electrical energy annually wasted by conventional electrical cores [in electrical generators and transformers] in the United States alone. (p. 381)

Metallic glasses have much potential, and the demand for them will increase as the quality and reliability of production is improved.
Definition of the Amorphous Metals

Metallic glasses are defined as "metal alloys with no long-range atomic order" (Luborsky, 1983, p. 1). Metallic glasses are formed from molten alloys that are quenched rapidly. The rapid cooling produces "...atoms that are frozen in a melt structure which lacks three-dimensional atomic periodicity" (Chen, 1983, p. 169).

The above definitions seem too broad as they can be applied to crystalline materials with crystal imperfections and to supersaturated crystalline metals. There is another approach for defining amorphous metallic glasses. The term amorphous is synonymous with noncrystalline materials. Hence, "a definition of the crystalline state will automatically define the amorphous state" (Duwez, 1983, p. 12). The crystalline materials are defined as "a solid composed of atoms arranged in a pattern in three dimensions" (Cullity, 1967, p. 29) throughout the material. The definition of the crystals as given above is vague in the sense that it does not indicate the number of times a unit cell should be repeated before the structure can be called a crystal. This becomes more important as crystal imperfection is considered (Bak, 1983). It can be shown that the equilibrium concentration of vacancies increases exponentially with the temperature at which rapid solidification takes place (Porter & Easterling, 1981). Thus, the definition of a crystal cannot provide a conclusive description of amorphous metallic materials. Duwez (1983), the pioneer scientist in metallic glass, has stated that "the distinction between amorphous and micro-crystalline state ultimately
depends on the sensitivity of the experimental methods used for measuring the actual number of perfectly aligned unit cells in a given solid" (p. 12).

In this investigation, the definition of amorphous materials stated by Spaepen and Turnbull (1976) was used. They defined metallic glasses as "alloys which are distorted compositionally as well as topologically" (p. 205).

Rapid Solidification

Rapid solidification, which is synonymous with "quenching," is generally defined as "a process of rapid cooling from an elevated temperature by contact with liquids, gases, or solids" (Duwez, 1983, p. 3). The process has been practiced for centuries, and since the turn of the eighteenth century, its principle has been known to metallurgists. At that time, Robert Ransome accidentally discovered white or chilled cast iron when one of his molds split during casting (cited in Elliott, 1983). Since then, the quenching process has become an indispensable part of metallurgy and materials science.

Generally, the main purpose of quenching is "... to cool an alloy at a high enough rate so that phases stable at high temperatures are either partially retained, transformed into non-equilibrium phases, or both" (Duwez, 1983, p. 3). A secondary process, such as tempering, is then used to control the relative amounts as well as the microstructure of the desired phase and to achieve the optimum physical properties of the final product. In steel, for example, a change in the quenching rate alters or drastically changes the
microstructure from that of the equilibrium, resulting in changes in physical and mechanical properties. A Time-Temperature-Transformation (TTT) diagram such as the one shown in Figure 1 is commonly used to determine the cooling rate required to obtain a particular microstructure. The resulting microstructure for a known cooling rate can also be predicted from this diagram.

A metal, in solidifying from the molten state to the ambient temperature, undergoes a series of alterations. For example, during solidification, atoms become organized at the solid-liquid state. In allotropic materials, further reorganization takes place at the solid state. According to the kinetic theory of matter, in the solidification process "a temperature decrease results in decreasing atomic motion until at some point translational motion ceases and the atoms are restrained to the point of simple vibration about an average position" (Hurd, 1968, p. 33). This point is known as the solidus temperature.

In glass formation the main concern is to prevent the nucleation and crystallization of the metal by trapping the latent heat of fusion inside the atoms. Observation of changes in the volume as a function of temperature shows that the glass formation process follows a continuous path with a higher internal energy while the crystallization process is discontinued at the melting and vaporization temperatures. Figure 2 shows the changes in volume as a function of temperature.
Figure 1. Time-Temperature-Transformation diagram. From "Metallographic practice for ferrous heat treaters" by Buehler Ltd., 1983, Metal Digest, 22, p. 6. Copyright 1983 by Buehler Inc. Reprinted by permission.

Note. $T_g$ = glass transition temperature

$T_l$ = fusion temperature

$T_b$ = vaporization temperature
Figure 2 shows that the change in volume is a function of temperature \( \frac{dV}{dT} \). However, at the fusion temperature, \( T_1 \), when crystallization takes place the temperature stays constant. In addition, the following conclusions can be made:

1. An amorphous metal is less stable than its corresponding crystalline metal.
2. An amorphous metal does not have a long-range crystal structure.
3. An amorphous metal has higher energy content than a crystalline metal.
4. An amorphous metal has higher volume and lower density than a crystalline metal.

The Effect of Alloying Elements in Glass Formation

The successful production of metallic glasses depends not only upon the cooling rate at which the solidification occurs but also on the alloy composition. According to the Hume-Rothery principle (cited in Hurd, 1968), the prime factors determining the solubility limits of alloying elements, and hence the mechanical properties of metals, are "the relative size factor [not less than 15%], the chemical affinity factor, the relative valence factor, and the lattice-type factor" (Guy & Hren, 1974, p. 268). Scott (1983) reported the same principle for binary and many ternary metal-metallic glass systems. According to Scott (1983) the most stable glasses are those in which the transition
metal constituents have these characteristics:

1. Different atomic size;
2. Strong interaction with the metalloid as measured by the heat of mixing;
3. Formed intermetallic compounds of different structures with the relevant metalloid. (p. 149)

The effect of adding solute atoms to a pure metal requires a significant diffusive rearrangement during the formation of the glass phase. This phenomenon becomes more obvious when the size and chemical character of the alloying elements differ considerably from that of the host element (Davies, 1983). Spaepen and Turnbull (1976) reported that in glasses of the types (Fe-M-B-Si) and (Ni-M-B-Si), where M is selected from a large number of metallic elements, the glass transition temperature, $T_g$, will change when the atomic size of M is not equal to iron or nickel.

Certain alloys, when restrained by quenching to remain compositionally disordered, become more stable in glass than in the crystalline form. Without such conditions, metallic glasses are thermodynamically less stable than the same crystallized state of the metallic alloy. This explains the fact that the glass transition temperature of the melt, $T_g$, has always been observed to lie well below the unconstrained liquid temperature, $T_1$ (Spaepen & Turnbull, 1976). Thus, glass formation requires that the melt be quenched at a temperature range from $T_1$ to $T_g$ rapidly enough to prevent crystallization. Under this condition, the metallic glass structure is metastable, so the atomic mobility needs to be kept low enough to prevent crystal growth.
As the concentration of alloying elements increases, $T_g$ generally increases, and $T_1$ closely approximates $T_g$ when measured dynamically under conditions of relatively rapid heating (Davies, 1983). The likelihood of quenching a metal to a glass will be greater when the components of the ratio of the glass transition temperature to liquidus temperature, $T_{RG}$, are close to equal. This ratio is sometimes called glass forming ability (GFA) (Spaepen & Turnbull, 1976). The alloy systems with the highest GFA are the following:

[Those that] manifest either one or more deep eutectics, or a steep and substantial decrease in $T_1$ with an increasing percentage of solute, to a 'plateau' over which $T_1$ is low in comparison with the melting point $T_m$ of the host metal. (Davies, 1983, p. 12)

Figure 3 is an iron boron equilibrium diagram which provides a graphic representation of the principles just stated.

**Heat Flow in Metallic Glass Formation**

The quenching rate is the fundamental information necessary to identify the glass forming ability of a process. In conventional heat treatment of ferrous metals, the workpiece is rapidly cooled from an elevated state of the austenitic region to a lower temperature below the critical temperature. Generally, in such processes, the entire body of a part is heated and stabilized at an elevated temperature; then the part is sunk into the quenching medium. In this process, convection is the main mechanism for removing the heat.

In laser surface heat treatment in general and in laser glass formation in particular, the quenching involves a complicated process.

Note. The solubility of boron in delta-iron is about 0.15 percent at temperature of $1381^\circ$. This is reduced to approximately 0.1 percent at $910^\circ$ for alpha-iron.
of convection, conduction, and radiation. In this process, a large amount of heat is removed from the heat-affected zone due to thermal gradients throughout the bulk metal. The development of an analytical equation for the laser quenching rate has been the subject of many investigations.

Mazumder (1983) developed an expression in three dimensions to determine the cooling rate for the quenching mechanism in laser processing. The equation is based upon a single pass criterion when the laser operates at the gaussian mode as:

\[
\frac{dT}{dt} = -V \left[ \left( \frac{x}{\alpha^2} \right) + \frac{V}{2\gamma} (1 + \frac{x}{\alpha}) \right] T
\]

where

\[
\alpha = (x^2 + y^2 + z^2)^{1/2}
\]

then

\[
\frac{dT}{dt} = -V \left[ \frac{x}{(x^2 + y^2 + z^2)} + \frac{V}{2} \left( 1 + \frac{x}{\alpha} \right) \right] T
\]

where

- \( \alpha \) = the thermal diffusivity of the material \( \text{cm}^2/\text{s} \)
- \( T \) = the temperature of the material at elevated state, \( C^0 \)
- \( t \) = the time in seconds
- \( V \) = the velocity of the laser in \( x \)-direction

This method of calculating the quenching rate is not adequate for two reasons: (a) The laser beam is falsely assumed to be a point source of energy, and (b) the processes of convection and radiation are not included in the equation.

Arata and Miyamoto (1972) presented an analytical expression for heat flow when the distribution of power in the laser beam is in the
gaussian or uniform mode. Their methods of calculation were based on the following assumptions:

1. The temperature in the fusion zone is steady.
2. The heat profile in the fusion zone is rectangular.
3. The latent heat of vaporization is negligible.

The above assumptions do not hold true for practical situations for three reasons:

1. The fusion zone has a dynamic temperature. For example, its temperature is decreased as a function of time.
2. The fusion zone has a gaussian rather than a rectangular shape.
3. The latent heat of fusion accounts for a large portion of the heat diffusion. Hence, it cannot be ignored.

Anthony and Cline's investigation (1978) of the surface treatment of stainless steel by laser melting led to the development of a quenching rate equation. In their findings, the quenching rate is expressed as a function of the laser velocity and the temperature gradient of thermal energy in the metal as below:

\[
\frac{dT}{dt} = V \times T
\]

where

\[
\frac{dT}{dt} = \text{the quenching rate}
\]

\[
T = \text{the temperature gradient in the material}
\]

\[
V = \text{the laser scanning velocity}
\]

In this investigation they studied the fusion zone in the melting phase, but they failed to include the heat of fusion, the diffusivity of the material, and the loss of heat as a result of the convection in
their calculations. The fusion zone in their study was assumed to have a semi-circular shape.

The presentation of an accurate model for the quenching process is very important in the development of an analytical quenching equation. However, "...to account for temperature-dependent thermophysical properties, numerical solutions are [also] needed" (Mazumder, 1983, p. 24). Such a numerical solution to the problem of rapid solidification was investigated by Mehrabian (1983). His investigation resulted in generating a curve for the total cooling rate as a function of the Biot number. The Biot number is described as midplane thermal internal resistance divided by surface film resistance. Its numerical value can be calculated as (Weast, 1979):

$$N_{B/h} = h \frac{L_m}{K}$$

where

- $N_{B/h}$ = Biot number for heat transfer
- $h$ = heat transfer coefficient
- $L_m$ = distance from midpoint to surface
- $K$ = thermal conductivity

Mehrabian's method of evaluating the quenching rate on the basis of computerized heat flow pattern is more accurate than the analytical methods. It further can generate an equation based upon the experimental results. The complexity of the process, however, limits the application of this process to research conducted in a very well equipped laboratory.

In the formation of glass by laser treatment, the solidification rate is controlled by the rate at which the latent heat of
solidification can be radiated, convected, and conducted away from the solid-liquid interface. The application of thermal energy to matter causes an increase in internal kinetic and potential energy. The internal kinetic energy is the energy of molecular motion and molecular velocity and is measurable in the form of temperature change (sensible heat). The internal potential energy (latent heat) is the energy of molecular separation or configuration and is the result of a change in relative molecular position (crystallization). The greater the degree of molecular separation, as in liquids or gasses, the greater is the internal potential energy (IPE). In other words, the internal potential energy is the latent heat of fusion and vaporization. The latent heat is stored in the form of the distance between the molecules. This principle is shown graphically in Figure 4.

The difference between the solid, the liquid, and the vapor or gaseous phases can be expressed in terms of the internal kinetic and potential energy. When the matter is in the solid phase, it has a relatively small amount of internal potential energy. The molecules are closely bonded together by their force of attraction and by the force of gravity. In solids, the position of the molecules within the material is fixed, and their motion is limited to vibration energy (Walton, 1976). Matter in the liquid phase has combined internal kinetic and potential energy. In the liquid phase the interatomic attractive and repulsive forces have the same magnitudes, causing the free movement of the molecules around one another, which destroys the
Figure 4. Temperature of a ferrous metal during solidification as a function of heat content.

Note. The illustration represents the iron containing 0.83% carbon, near eutectic point. The heat content of the specimen is approximated.
crystal arrangement. The following is an equation representing the relationship between the repulsive, attractive, and total forces as a function of the atomic distance between the atoms.

\[ r = -A/r^m + B/r^n \]

where

\[ A/r^m = \text{interatomic repulsion forces} \]
\[ B/r^n = \text{interatomic attraction forces} \]

The component \( B/r^n \) arises from interatomic repulsive forces; the component \(-A/r^m\) arises from interatomic attractive forces. The resultant interaction is shown as the total internal energy in Figure 5.

The laws of thermodynamics are applied to matter regardless of physical phases (Walton, 1976). Accordingly, thermal energy is not destroyed or used up in any process. Heat energy that leaves matter must be absorbed by another body with a lower temperature, and the rate of heat transfer is proportional to the differential temperature causing the flow of heat.

The analytical equations for the quenching rate and the geometrical shape of the fusion zone in laser processing presented by Mazumder (1983), in addition to the pattern of the heat presented by Mehrabian, Hsu, and Levi (1983) and Porter and Easterling (1981), were evaluated and presented earlier. Later in this investigation, an attempt will be made to identify a heat flow program compatible to laser processing and to generate an acceptable analytical equation for the quenching rate in this investigation.
Figure 5. Internal energy as a function of distance between atoms.

\[ \text{Repulsion energy} = B/r^n \]
\[ r_0 = \text{Atomic radius for minimum internal energy} \]
\[ E_0 = \text{Bonding energy} \]
\[ \text{Total internal energy, } r = -A/r^m + B/r^n \]
\[ \text{Attraction energy} = -A/r^m \]

**Note.** The total internal energy for a substance is the summation of the total attraction forces plus the total repulsion forces. The negative sign indicates the direction of the forces.
Classification of Alloying Elements

The right types of metals and alloying elements are essential to the formation of metallic glasses. Not all alloys can be made to solidify in the glassy form, regardless of how fast they are cooled from the melt (Ashbrook, 1983). Spaepan and Turnbull (1976) predicted, based upon theoretical calculations, that "... all pure monatomic materials, including metals, would form glasses if quenched rapidly enough" (p. 218). They asserted that the predicted quenching rate for the formation of such glasses may be operationally impossible to achieve. It has been proposed that "... in Fe-B alloys substitution of some of the iron by [a third element other than B with] larger atoms disturbs the close packing, thereby reducing the free volume and the diffusion coefficient. Furthermore, it is suggested that ternary glasses will be more resistant to crystallization than the constituent binaries" (Scott, 1983, p. 149). In some instances, the glass structure is so unstable that it is transformed into the crystalline structure at the ambient temperature in a matter of hours. Some materials that solidify as a glass are processed to convert them into microcrystalline materials to enhance their desired physical and mechanical properties (Ashbrook, 1983). The type of metal for metallic glass production, therefore, may be selected based upon the following criteria:

1. Its ability to form glass.
2. Its stability in the glass structure.
3. Its capability to enhance the desired mechanical, electrical, and other properties.
The classification of the composition of metals and alloys in the glass formation process has not yet progressed very far; however, a general classification was provided by Polk and Giessen (1983):

1. Metal-Metalloid systems (MT-M), with general chemical composition $T^2_{1-x} X^x$ where $T^2$ is Mn, Fe, Co, Ni, Pd, Au, or Pt and $X$ is B, C, Si, Ge, or P. The atomic weight of the metalloids may vary from 15 to 25 percent of the base metals by atomic weight.

2. Inter-Transition-Metal systems (I-TM) with the general chemical composition $T^1_{1-x} T^2_x$ where $T^1$ is a transition metal, such as Fe, Co, Ni, Rh, Pd, or Cu, and $T^2$ is included as stated above. The chemical weight of early transition metals may vary from 35 to 70 percent depending on the system.

3. Rare Earth-Transition metals (RE-TM) with the general chemical composition of $T^3_{1-x} T^2_x$.

4. Alloys of high valency elements such as gallium, tin, and lead with noble metals, Cu, Au, Ag, and other alloying elements at the deep eutectic temperature.

The first class, namely, transition metal-metalloid systems (MT-M), is the subject of this investigation. They are the most important alloying elements technologically. The iron-based amorphous materials particularly exhibited outstanding electric and magnetic properties (Davies, 1983; Gilman, 1983).

The emphasis on iron-based amorphous glasses "...began in 1972 when Ho-Sou Chen and Donald Polk drew out the first ductile glassy
ribbon of ferrous alloys" (Gilman, 1983, p. 346). Prior to 1972, the investigations of ferrous metallic glasses failed to show an industrial application for such amorphous materials. These studies, however, revealed the extraordinary mechanical (Davis, 1976), electrical, and magnetic properties (Tsuei, 1976) and the wear and corrosion resistance (Molian, 1984) of this new class of ferrous metals.

"Pratt and Whitney's attempts led to the development of a centrifugal atomization process, and successfully produced amorphous powder from several iron-rich Fe-Si-B alloys" (cited in Miller, 1983, p. 510). However, it is not known what size powder can be solidified in a fully amorphous state. The quenching rate of this process was calculated to be $10^5$-$10^6$ deg k/s. Liebermann's investigation (1983) in advanced melt spinning techniques has led to the successful production of amorphous metals with the chemical compositions of Fe$_{40}$Ni$_{40}$B$_{20}$ and Fe$_{81.5}$B$_{14.5}$Si$_{4.5}$ (p. 33).

"Researchers at the Minsk Power Metallurgy Institute have compacted amorphous fibers of Fe$_{48}$Ni$_{48}$B$_4$ and Fe$_{40}$Ni$_{40}$P$_{16}$B$_4$ into plates measuring 200 x 50 x 3 MM in size" (Miller, 1983, p. 515) by a modified melt extraction process. American Allied Corporation supplies ferrous metal metalloid ribbons under the trade name of "Metglas." Their production includes iron-nickel base alloys, cobalt base alloys, iron-(Ti-Be-Zr) base alloys, and iron-(Mn-Be-Zr) base alloys for high strength and improved strength to weight ratio (Pye, 1983).
Stempin and Wexell successfully produced amorphous sheets by placing the ribbon edge to edge in a heated die. "The pressure is raised up to 206 Mega-pascal (MPa), temperature is kept within 10 deg K of the glass transition temperature, and processing times were 25 minutes" (cited in Miller, 1983, p. 517). The composition and alloying elements used in this investigation were reported to be Fe$_{68}$-Li$_4$-Mo$_4$-Al$_6$-B$_6$, Fe$_{72}$-Ni$_6$-B$_6$-Mo$_2$, and Al$_{44}$-Cu$_{22}$-B$_4$-C$_4$-Li$_2$. Chien-Jung and Spaepen's investigation (1982) of iron boron systems revealed the formation of iron-based metallic glass with a boron content as low as five percent by weight (%/w). Previous research by Hasegawa and O'Handley (1976) indicated that in the splat-quenching technique, the iron-boron base metallic glass can be formed only over a limited composition range from 12-28 percent boron by atomic weight (approximately 2.5-7.5 percent by weight). Other researchers indicated that in the Fe-Si-B alloy system, the role of silicon and boron as agents for the formation of an amorphous structure is significant if Si + B is between 13 and 35 percent by atomic weight (approximately 2.5-9.5 percent by weight) (Davies, 1983).

In general, the objectives of the research in this area are:

1. to develop a technique leading to a new and meaningful mass production of metallic glasses, and
2. to investigate the effect of an alloying element such as boron, which is a metalloid, on the formation and characterization of this new class of materials.
Amorphous Metallic Production Process

Techniques for the production of a non-equilibrium structure may be divided into categories of quenching, molecular deposition, and external reaction (Jones, 1976). Quenching is the first and most promising process by which Duwez, Willens, and Klement of the U.S. and Miroshichenko and Salli of the U.S.S.R. achieved success in the formation of amorphous metals (Davies, 1983). In their method of production, "a liquid metal drop is propelled onto a cold surface where it spreads into a thin film and is thus rapidly solidified" (Luborsky, 1983, p. 3). This process generated a cooling rate greater than one million degrees centigrade per second. Such a cooling rate created a completely new metallurgy of a highly supersaturated solid solution, new metastable crystalline structures, and glassy alloys (Luborsky, 1983).

In general, two methods are presently used for metallic glass production (a) rapid solidification of liquids and (b) deposition of metallic vapors (Yeh, Samwer, & Johnson, 1983). The processes involved are splat cooling, thermal evaporation, sputtering, chemical deposition, electro-deposition (Scott & Maddin, 1976) and, more recently, laser glazing (Molian, 1984). The alloying element used as a glass forming agent in producing iron-based metal glasses commonly is boron in various amounts.

The ability of a continuous, high power CO₂ laser to generate power densities of up to $10^6$ watts/cm² makes it a useful instrument for a wide variety of material processing techniques (Duley, 1983). This vast controllable amount of energy, in conjunction with the rapid
self-quenching of ferritic gray cast iron, provides a new opportunity to generate an iron-based metallic glass layer on the surface of workpieces. In experimentation, pulsed lasers have been used to study rapid melting and resolidification of the surface layers of semiconductors and metals (Raskin & Smith, 1983).

Chien-Jung and Spaepen (1982) reported the formation of amorphous metals with the general chemical composition of Fe-B by utilizing Nd:YAG laser radiation. They demonstrated that the ultra-high cooling rate induced by picosecond Nd:YAG laser pulse irradiation can form glassy Fe-B alloys with boron content as low as five percent by weight (%/w). Snezhnoi, Zhukov, and Kokora (1980) investigated the formation of an amorphous surface by the application of Nd:Glass laser radiation to cast iron. The hardness of the amorphous surface was reported to be 1200 Vickers Hardness Number (VHN), which was significantly greater than the base iron hardness of 800-1000 VHN. Cullis, Webber, and Chew (1983) employed ruby laser radiation with a 2.5 nanosecond pulse in the production of amorphous alloys such as germanium, gallium phosphide, and gallium arsenide. The method consisted of polishing a single crystal sample in the crystalline orientations of (001) and (111). The samples were irradiated with a modified optical system assembled onto the laser system.

The United Technologies Research Center has developed a process, named "Laser Glaze," which is capable of producing rapid-chilled microstructures. The process was limited to selected materials and required a high cooling rate at thick sections. The limitation led to the development of a new form of laser processing, "Layer Glaze,"
"involving the introduction of wire or powder feedstock onto a moving substrate at the point of impingement of the continuous carbon dioxide laser beam" (Snow, Breinan, & Kear, 1983, p. 138). The cooling rate was believed to be approximately $10^4$ degrees centigrade per second. This process requires the application of high molybdenum-based or nickel-based superalloys which are both laser-weldable, phase stable, and mechanically strong at 760 degrees centigrade or higher (Snow, Breinan, & Kear, 1983). The Layer Glaze process is costly, complicated, and limited to those materials weldable to high molybdenum- or nickel-based superalloys.

Although the potential applications of the amorphous metals are well-known, the large scale production of this metallic glass is held back by the production process. The full production of metallic glass requires the development of a totally new technology (Pye, 1983).

The potential of the high power carbon dioxide laser to produce amorphous structures is based on the highly concentrated power densities of up to $10^3$ watt/cm$^2$, the extremely rapid self-quenching rate, and the rapid dissipation of heat through the bulk metal (Mazumder, 1983). Breinan, Kear, and Banas (1976) investigated the quenching process in laser processing. They reported the following:

Due to the steep temperature gradient established by the process, rapid solidification and subsequent solid-state cooling takes place following the passage of the laser beam. Average quench rates in excess of $10^6$ deg c/sec have been achieved in melt thicknesses in the 1-10 micron range. (p. 45)

Furthermore, the cooling rate can be increased by a secondary source, as will be explained in the laser processing section.
CHAPTER III
Procedures

Overall Methods

This investigation was a developmental type of research. The procedures were based on theoretical principles. Below is a schematic representation of the testing procedures, which is followed by a detailed description of each activity of the tests:

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Material and Preparation

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| Homogenization Heat Treatment |
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| Vacuum Emission Spectroscopy |
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| Laser Processing |
-----------------------------

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| Microstructural Analysis |
-----------------------------

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| Scanning Electron Microscopy |
| X-Ray Diffraction Analysis |
| Mechanical Prop. Examination |
```
Material and Preparation

Seven different types of specimens with the general composition of $\text{Fe}_x \text{B}_y \text{M}_{(100-x-y)}$, where $y$ ranged from 0 up to 10.10 percent by weight and $m$ included other alloying elements, were prepared. Ferritic gray cast iron was chosen as the base ferrous alloy primarily for these four reasons:

1. Ferrous alloys have good coefficients of absorption of carbon dioxide laser beams with a wavelength of 10.6 microns.

2. Ferritic gray cast irons have high coefficients of thermal conductivity, which should increase the quenching rate (Ross, 1980), hence leading to the formation of a metallic glass surface layer.

3. The alloying elements in the base alloys (Si, P) are among the glass-forming elements (Kumura & Masumoto, 1983).

4. They are extensively used by industries (Clauser, 1975).

5. Cast iron surface heat treatment is one of the present industrial problems (American Society for Metals, 1977). The industrial need for a new process of surface hardening is a major concern.

Boron was selected as an agent to improve the glass formability in several principle ways:

1. It retards the rate of nucleation of ferritic and pearlitic structure (Clauser, 1975).

2. It decreases the eutectic temperature while increasing the glass transition temperature (Scott, 1983).

3. It has an atomic size slightly larger than one third that of iron.
4. It has an important role in increasing yield strength of iron-based alloys (Kumura & Masumoto, 1983).

The role and the importance of boron as a glass-forming agent is well established, but the composition range in which this element can play its role in metallic alloys is not clear. Two major aspects of this study include (a) identification of the solubility limits of boron in the base alloy and (b) verification of the boron content range that leads to the formation of an amorphous metallic layer after laser heat treatment.

Viking Pump, Inc., of Cedar Falls, Iowa, supplied the ferritic gray cast iron, which was in the annealed condition with a ferritic matrix structure, a minimum amount of pearlite, no massive cementite, and no abnormal segregation. Table 1 shows the chemical composition of the cast iron supplied by Viking Pump, Inc. and Moly Corporation.

Table 1

<table>
<thead>
<tr>
<th>Elements by % weight</th>
<th>Cast iron</th>
<th>Ferro-boron</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alloys</td>
<td>Fe</td>
<td>C</td>
</tr>
<tr>
<td>Cast iron</td>
<td>93.28</td>
<td>3.25</td>
</tr>
<tr>
<td>Ferro-boron</td>
<td>70.00</td>
<td>0.50</td>
</tr>
</tbody>
</table>

Note. Information was supplied by Viking Pump and Moly Corporation.
Casting Procedure

Powder coating and spray coating are the two common methods of altering the chemical composition of workpieces to be subjected to laser processing (Duley, 1983). However, due to the need for an accurate and uniform chemical composition for this investigation, the casting process was chosen for the preparation of the specimens. Casting the specimens was to accomplish three goals:

1. To prepare the specimens within the chemical specification outlined for this investigation.
2. To prepare the specimens with uniform composition and microstructure.
3. To transform the chemical composition from iron-carbon equilibrium to iron-boron equilibrium.

Manual sand casting, described by LaRue (1981), was used to prepare the specimens. The molding materials were Olivine sand bonded with three percent Western and three percent Southern Bentonite. Ferro-boron was used as the principal alloy for the introduction of boron into the charge. Ferro-boron has a melting point of approximately 2079 degrees centigrade compared to 1535 degrees centigrade for the iron carbon alloy. This substantial difference in melting point required a drastic increase in the heat input when ferro-boron was added to the charge. The crucible was charged with 12.417 pounds of cast iron. When melted, the first specimen contained zero percent boron when poured. Then 10 pounds of ferro-boron in four separate 2.5-pound increments were added to the charge. When each 2.5 pounds of ferro-boron had melted, the next increment was added. The
resulting melt contained 12 percent boron and was poured to make a specimen. In the third charge, 2.683 pounds of cast iron were added to the remainder of the molten metal, and a specimen with 10 percent boron content was poured. This process was repeated to produce specimens with eight, six, four (two samples), and two percent boron content. Later each specimen was separated into five equal pieces, producing a total of 35 specimens. Table 2 provides the chemical compositions of the cast specimens.

The instrument used in the casting process to measure the carbon equivalent (CE) was a thermal analysis system manufactured by the Electro-Nite Co. operating on the basis of liquidus $T_1$ and solidus $T_3$ temperatures. The Quick Lab Thermal Analysis instrument was used in two different ways:

1. It provided information related to the carbon equivalent (CE). The carbon equivalent is a method used for evaluation of the effects of composition in unalloyed cast iron. The carbon equivalence (CE) is the summation of total carbon content in percentage (TC) plus one third the sum of the percent silicon and percentage phosphorus (American Society for Metals, 1983). The thermal analysis system provided further detailed information related to carbon equivalency, percentage carbon, and percentage silicon in the charge.

2. It confirmed the transformation of a molten alloy from an iron-carbon binary to an iron-boron binary equilibrium condition. This transformation was performed intentionally, and it was detected in three ways:
Table 2

Charge Composition of Cast Specimens

<table>
<thead>
<tr>
<th>Type of Melt</th>
<th>Alloying elements</th>
<th>Cast Pour in (lb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>#</td>
<td>metal</td>
<td>Fe</td>
</tr>
<tr>
<td>1</td>
<td>C.I.</td>
<td>11.50</td>
</tr>
<tr>
<td></td>
<td>Fe3B</td>
<td>-----</td>
</tr>
<tr>
<td></td>
<td>total</td>
<td>11.50</td>
</tr>
<tr>
<td></td>
<td>%</td>
<td>92.60</td>
</tr>
<tr>
<td>2</td>
<td>C.I.</td>
<td>7.33</td>
</tr>
<tr>
<td></td>
<td>Fe3B</td>
<td>7.00</td>
</tr>
<tr>
<td></td>
<td>total</td>
<td>14.33</td>
</tr>
<tr>
<td></td>
<td>%</td>
<td>80.00</td>
</tr>
<tr>
<td>3</td>
<td>Melt</td>
<td>10.73</td>
</tr>
<tr>
<td></td>
<td>C.I.</td>
<td>7.33</td>
</tr>
<tr>
<td></td>
<td>total</td>
<td>13.21</td>
</tr>
<tr>
<td></td>
<td>%</td>
<td>82.00</td>
</tr>
<tr>
<td>4</td>
<td>Melt</td>
<td>9.51</td>
</tr>
<tr>
<td></td>
<td>C.I.</td>
<td>2.69</td>
</tr>
<tr>
<td></td>
<td>total</td>
<td>12.20</td>
</tr>
<tr>
<td></td>
<td>%</td>
<td>84.14</td>
</tr>
<tr>
<td>5</td>
<td>Melt</td>
<td>8.41</td>
</tr>
<tr>
<td></td>
<td>C.I.</td>
<td>3.08</td>
</tr>
<tr>
<td></td>
<td>total</td>
<td>11.49</td>
</tr>
<tr>
<td></td>
<td>%</td>
<td>84.24</td>
</tr>
<tr>
<td>6</td>
<td>Melt</td>
<td>7.62</td>
</tr>
<tr>
<td></td>
<td>C.I.</td>
<td>4.09</td>
</tr>
<tr>
<td></td>
<td>total</td>
<td>11.71</td>
</tr>
<tr>
<td></td>
<td>%</td>
<td>88.38</td>
</tr>
<tr>
<td>6</td>
<td>Melt</td>
<td>7.73</td>
</tr>
<tr>
<td></td>
<td>C.I.</td>
<td>-----</td>
</tr>
<tr>
<td></td>
<td>total</td>
<td>7.73</td>
</tr>
<tr>
<td></td>
<td>%</td>
<td>88.38</td>
</tr>
<tr>
<td>7</td>
<td>Melt</td>
<td>3.76</td>
</tr>
<tr>
<td></td>
<td>C.I.</td>
<td>7.87</td>
</tr>
<tr>
<td></td>
<td>total</td>
<td>11.63</td>
</tr>
<tr>
<td></td>
<td>%</td>
<td>91.22</td>
</tr>
</tbody>
</table>

Note. The composition of cast iron was Fe29 C3 55 Si2 55 Mn 80 P 35

The weight of each mold was approximately 4.5 lbs.

Cast Iron is abbreviated as C.I.
1. By the error message from the thermal analysis system.

2. By the release of carbon in the form of graphite on the molten metals.

3. By the comparison of the microstructures of the cast specimens to iron-carbon and iron-boron microstructures.

The substitution of the element of boron for carbon was expected. Boron atoms, with an atomic number of five, are more active than carbon atoms, with an atomic number of six (Weast, 1979). Boron has a smaller number of electrons and a smaller atomic radius which can easily be diffused in the iron matrix, knocking out the carbon atoms. This process causes the substitution of boron for carbon and results in the transformation of an iron-carbon binary alloy to an iron-boron binary alloy. This process was later verified by emission spectroscopy, and the result is shown in Figure 6.

The molten metal could dissolve a certain amount of boron and carbon to reach the saturation point. The excess carbon was forced out of the molten metal as a powdery material on top of the crucible. If the molten metal had been cooled gradually, the saturation temperature would have decreased correspondingly and further addition of carbon would then have diffused out of the matrix. In sand casting, however, the reduction of temperature as the result of solidification is rapid enough to prevent the diffusion of the excess carbon, boron, and other elements outside of the matrix. Hence, it was expected that the cast sample would have a heterogeneous structure. The trapped alloying elements were shown as a totally distorted nodular shape in the matrix of iron-boron (Figure 7).
Figure 6. Substitution of boron for carbon and transformation of iron-carbon to iron-boron binary alloy.

Note. The illustration is drawn based on the result of the emission spectroscopy examination. The percentage weight of other alloying elements can be seen in Table 3.
Figure 7. Microphotograph of the sample with 4.17 percent boron content. The excess carbon diffused out of the matrix as distorted nodular graphite.

Note. A section of the base metal with 4.17 percent boron content was polished and etched with a solution of 30 percent $H_2O_2$, 22 percent $H_2O$, 48 percent HF. The white structures are alpha-iron, the dark structures are $Fe_2B$, and the segregated structure in black areas are graphite. Magnification 400X.
Homogenization Heat Treatment

The solidification of a homogeneous molten metal in the mold is often associated with a heterogeneous structure, coarse grains, internal porosity, shrinkage cavities, chilled casting, and general unsoundness of the casting. More important, when the molten mixture of iron-boron with its high solidification rate is poured into a cold mold, the mixture freezes by forming a solid skin of equiaxed grain in what is termed the chilled zone. "Following the initial thermal shock, the skin grows progressively inward with a relatively uniform advancing front until the entire casting is solid" (Allen, 1981, p. 572). Thus the solid specimens will possess a heterogeneous chemical composition and a dendritic microstructure across its cross-section. Figure 8 shows a dendritic structure formed after the casting process.

The elimination of chemical segregations caused by the remelting, alloying, and casting was done by the application of a homogenization heat treatment process. The homogenization heat treatment was applied for several purposes:

1. To transform the gamma-irons to alpha-irons.
2. To break up the clusters of impurities in the structure.
3. To relieve the internal stress generated by solidification of the mold.

Homogenization heat treatment consisted of heating the specimen into the austenitic region (1600 F⁰) and maintaining the temperature
Figure 8. A dendritic structure formed in the casting process.
Dendritic structures were most evident in cast metals with low boron content and with a slow cooling rate through the solidification range.

Note. Structure has treelike branching patterns with a preferential direction. The direction of the dendritic structure is co-axial with the direction of heat diffusion process.
for sixteen hours. This helped in eliminating pearlitic structures as well as in minimizing the segregation and abnormalities in the microstructure. The specimens were cooled at 55.5 degrees C (100°F) per hour to 200 degrees F. After that, the furnace was shut off, and the specimens continued to cool in the furnace. When the specimens reached the ambient temperature, the specimens were prepared for metallographic examinations. Figure 9 shows the heat treatment cycle.

Figure 9. Heat treatment cycle in the homogenization process.

Note. The homogenization heat treatment temperature was set at approximately 75 percent of the melting temperature at eutectic composition. Within the first few hours, the segregated carbon and boron can be dissolved in the matrix.
An accurate analytical chemistry procedure for the detection of the quality and quantity of boron and other elements present in various specimens was an important consideration in this investigation. Vacuum Emission Spectroscopy and Atomic Absorption Spectroscopy were used to provide an accurate measurement of the quality and the quantity of the alloying elements present in the specimens.

Quantitative analysis by emission spectroscopy permits the simultaneous and rapid detection of approximately seventy metallic and metalloid elements (Fritz & Schenk, 1966). A further advantage of this process is that a sample can be examined rapidly. A sample can be tested in just a matter of minutes.

Even though Atomic Absorption Spectrophotometry is more complicated than Emission Spectrometry, it has the advantage of identifying the quantity of elements by the process of elimination. Emission Spectroscopy was used to identify the chemical composition of all the alloying elements, based on the known boron content in the specimens.

The Atomic Absorption Spectrophotometry was performed at an independent laboratory in Chicago, and the Vacuum Emission Spectroscopy was performed at John Deere Foundry Waterloo. The results of these tests are tabulated in Table 3.
Table 3

Chemical Composition of the Specimens

<table>
<thead>
<tr>
<th>Designated group</th>
<th>Fe</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Al</th>
<th>Ni</th>
<th>Cr</th>
<th>Mo</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>93.28</td>
<td>3.25</td>
<td>2.70</td>
<td>0.41</td>
<td>0.19</td>
<td>0.09</td>
<td>0.006</td>
<td>0.034</td>
<td>0.037</td>
<td>0.003</td>
<td>0.00</td>
</tr>
<tr>
<td>2</td>
<td>91.80</td>
<td>2.58</td>
<td>2.41</td>
<td>0.44</td>
<td>0.16</td>
<td>0.06</td>
<td>0.006</td>
<td>0.255</td>
<td>0.158</td>
<td>0.112</td>
<td>0.02</td>
</tr>
<tr>
<td>4</td>
<td>88.68</td>
<td>1.95</td>
<td>3.51</td>
<td>0.71</td>
<td>0.05</td>
<td>0.01</td>
<td>0.140</td>
<td>0.307</td>
<td>0.318</td>
<td>0.156</td>
<td>0.17</td>
</tr>
<tr>
<td>6</td>
<td>86.70</td>
<td>1.68</td>
<td>4.38</td>
<td>0.58</td>
<td>0.15</td>
<td>0.22</td>
<td>0.016</td>
<td>0.303</td>
<td>0.236</td>
<td>0.166</td>
<td>0.57</td>
</tr>
<tr>
<td>8</td>
<td>86.47</td>
<td>1.45</td>
<td>3.41</td>
<td>0.59</td>
<td>0.10</td>
<td>0.02</td>
<td>0.240</td>
<td>0.313</td>
<td>0.260</td>
<td>0.141</td>
<td>0.01</td>
</tr>
<tr>
<td>10</td>
<td>85.36</td>
<td>1.15</td>
<td>3.18</td>
<td>0.75</td>
<td>0.05</td>
<td>0.01</td>
<td>0.060</td>
<td>0.283</td>
<td>0.325</td>
<td>0.136</td>
<td>0.70</td>
</tr>
<tr>
<td>12</td>
<td>82.58</td>
<td>0.90</td>
<td>3.77</td>
<td>0.73</td>
<td>0.04</td>
<td>0.01</td>
<td>1.010</td>
<td>0.327</td>
<td>0.375</td>
<td>0.154</td>
<td>1.10</td>
</tr>
</tbody>
</table>

Note. A more detailed table of chemical compositions is included as Appendix B.

Laser Processing

Laser glazing represents an improved, more reproducible technique for the production of rapidly cooled metals and alloys (Snow, Breinan, & Kear, 1983). "The ability of continuous, high-power lasers to generate power densities of up to $10^8$ watts/cm$^2$ makes them useful for a variety of materials-processing techniques" (Breinan, Kear, & Banas, 1976, p. 44). In such processes, the depth, geometry, and microstructural characteristics at the heat-affected zone (HAZ) are
functions of the laser process variables (Mazumder, 1983), laser beam characteristics, and quenching rate, which in turn are functions of laser parameters.

The laser parameters in a process such as glass formation can be divided into controllable and noncontrollable parameters. The controllable parameters are: (a) the pulse length and frequency, (b) the incident laser beam power, (c) the mode of the laser beam, (d) the transverse speed of the workpiece, (e) the type, velocity, and direction of the cover gas at the point of collision, and (f) the optical systems used. The noncontrollable parameters include the following: (a) the mode character in which the heat is distributed, (b) the polarization of the laser beam, (c) the ambient temperature, (d) the thermal lensing of the optical systems, and (e) the mode stability of the laser beam.

In the laser treatment process the following variables were used to produce a glassy layer:

1. The pulse duration;
2. The pulse number;
3. The power input;
4. The transverse speed of laser; and
5. The flow, pressure, and direction of the cover-gas.

The power transmitted to the workpieces was adjusted by changing the speed of the workpiece on an x-y table. The x-y table was driven by a computer numerically controlled machine. The input power also was varied by varying the electrical power input, the pulsing conditions, or the gas flow through the plasmatubes. Figure 10 shows the schematic of laser processing.
Figure 10. Schematic arrangement of laser processing.

- Laser beam
- Optical lens
- CNC table
- Axial nozzle
- 45° mirror

Direction of heat treating
The capability of the laser to emit pulses in addition to a continuous wave provided a greater option for processing. The 1300-watt carbon dioxide laser (Photon Sources, model V1003) used in this investigation had the capability of a continuous wave as well as a pulsing mode in the range of 0.1 microseconds to a full second. This capability proved to be important in controlling the quantity and pattern of heat dissipation, the quenching rate, and the formation of the amorphous layer. Hence, the implication of each mode in the heat pattern process was tested, and the most appropriate conditions were found. Then, these conditions were extended to the continuous mode.

The pulse duration and idle time between each pulse was chosen by the pulse-on and pulse-off dials. These dials can vary the pulse duration or idle time from zero microseconds to a full second. For example, choosing a pulse-on setting of ten and a pulse-off setting of ten generates a pulse mode with a 10-microsecond beam and a 10-microsecond interval before the next beam. If the pulse-on dial is set to any number and the pulse-off dial is set at zero, the laser operates in a continuous mode. Figure 11 is the graphic representation of this concept.

The maximum depth of penetration was obtained when the laser was operated at its full power of 1200 watts. The power output was measured by an internal power meter (calorimeter) in the laser. In such processing, the heat input also was increased with power input and decreased with the transverse speed of the workpiece. The transverse speed of the workpiece was kept constant, and the power was variable.
Figure 11. Schematic representation of laser pulses.

Pulsed mode:

\[
\begin{align*}
\text{pulse on} & = 1 \\
\text{pulse off} & = 5 \\
\text{pulse on} & = 5 \\
\text{pulse off} & = 5 \\
\text{pulse on} & = 10 \\
\text{pulse off} & = 5 \\
\text{pulse on} & = 20 \\
\text{pulse off} & = 5 \\
\text{pulse on} & = 25 \\
\text{pulse off} & = 5
\end{align*}
\]

Continuous mode:

\[
\begin{align*}
\text{pulse on} & = 5 \\
\text{pulse off} & = 0
\end{align*}
\]

Note. The pulse and continuous modes were the characters of the output beam used in this study. As illustrated, the pulse and the dwell duration were adjustable. In addition, the illustration shows the relation between the pulsed and the continuous mode.
Argon gas, the cover-gas used in this investigation, was directed through a 0.040" diameter nozzle coaxial with the laser beam. Its function was to eliminate oxidation and porosity and to increase the quenching rate by increasing the convection process. Argon was also directed through a 0.080" nozzle at an angle of 45 degrees to the table. The direction of flow was opposite to the direction of the CNC table movement. This arrangement further increased the convection of heat from the surface and increased the quenching rate. Cover gas pressure of 20 pounds per square inch (psi) was increased until gas pressure of 30 psi was found to produce optimum results.

The optimum parameters were found by experimenting with 180 different combinations of parameters on the surface of the sample with four percent boron content as shown in Figure 12. These parameters were studied on the basis of the melting condition and the depth of penetration. The parameters which produced unacceptable melting or shallow depth were identified and eliminated. The remainder of these parameters were used for heat treatment of the other specimens containing zero, two, six, eight, ten, and twelve percent boron.

The primary microscopic and metallographic inspections indicated the formation of glass at the place where the parameters were gas pressure 30 psi, power 600 W, and pulse duration 0.7-1.1 millisecond. For more details about the laser conditions, see Appendix C.

In the continuous mode, the relative velocity of the laser beam to the workpieces at the incident point was a function of the linear speed of the CNC table. In this process the linear speed was in the range of 10-400 inches per minute, calculated from the following equation.
Figure 12. Representation of pulse duration and power output in identifying laser parameters used for sample with 4.17 percent boron.

<table>
<thead>
<tr>
<th>Pulse duration</th>
<th>Power</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 Dial Meas.</td>
<td></td>
</tr>
<tr>
<td>1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18</td>
<td></td>
</tr>
<tr>
<td>1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18</td>
<td>1000 1250</td>
</tr>
<tr>
<td>1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18</td>
<td>900 1050</td>
</tr>
<tr>
<td>1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18</td>
<td>800 925</td>
</tr>
<tr>
<td>1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18</td>
<td>700 780</td>
</tr>
<tr>
<td>1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18</td>
<td>600 620</td>
</tr>
<tr>
<td>1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18</td>
<td>500 500</td>
</tr>
<tr>
<td>1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18</td>
<td>400 400</td>
</tr>
<tr>
<td>1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18</td>
<td>300 300</td>
</tr>
<tr>
<td>1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18</td>
<td>200 200</td>
</tr>
<tr>
<td>1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18</td>
<td>100 100</td>
</tr>
</tbody>
</table>

Pulse duration in milliseconds x 10^{-1}

Note. * is the place that the metallic glasses were formed.
dial is the power output base on the dial adjustment.
meas. is the power measured with the calorimeter.
\[ S = \frac{d \text{(st.)}}{1275 \text{ (st/in)}} \]

where

- \( S \) = linear speed
- \( d \) = linear speed in steps
- \( \text{st} \) = steps

The optimum speed was determined based upon the following three requirements:

1. Temperature: The temperature at the fusion zone must be high enough to liquidize the surface of the specimen to the specified depth.

2. Energy transformation: The transformation of energy to the workpieces must be limited in order to allow the rapid dissipation of heat through the bulk mass of the specimens.

3. Cooling rate: There should be sufficient mass to satisfy the critical self-quenching rate requirements.

The incident laser beam diameter and characteristics were studied by profiling the raw beam in acrylate (polymethyl methacrylate). The resultant measurement was used to eliminate scatter and identify the characteristics of the beam. The adjusted beam was directed through an optical lens with a 5-inch focal length, and the size of the focused beam spot was calculated by using the following equation.

\[ D_0 \propto \frac{\lambda \times f}{d} \]

where

- \( D_0 \) = diameter of focused spot
- \( \lambda \) = wave length of the laser radiation
- \( f \) = focal length of the lens
- \( d \) = diameter of the raw beam
The laser's internal power meter monitored the power continuously. Hence, the power density of the process can be calculated using the equation below;

\[ P_0 = \frac{P}{A} \]

where

- \( P_0 \) = power density at the workpiece
- \( P \) = power at the workpiece
- \( A \) = area exposed to laser beam

The area of the workpiece exposed to the laser beam can be calculated using the equation below;

\[ A = \pi \times r^2 \]

where

- \( A \) = area exposed to laser beam
- \( r \) = radius of focused spot \((1/2 \text{ of } D_0)\)
- \( \pi = \frac{22}{7} \) constant

with an internal power of 620 watts and a 10% power loss due to three external optics, the power density is approximated with the following equations:

\[ P_0 = 620 \times 0.90 \text{ watts/} \quad 3.14 \times (0.005)^2 \text{ in}^2 \]

\[ P_0 = 7104677 \text{ watts/} \text{ in}^2 \]

**Verification of the Optimum Parameters**

In the primary optimization of the laser, the variables were included with the laser exposure time, pulse duration, and velocity of the pressurized cover-gas. The optimum laser condition was verified
by the formation of an amorphous surface. The formation of the laser amorphous surface was detected by use of the Debye back-reflection x-ray method. This method will be explained later in this study. In the primary investigation, the percentage of boron was kept constant. The sample with four percent boron content and minimum melting temperature was chosen as it had the highest glass formability $T_{rg}$ among the seven samples. Later, to extend the findings to all the specimens, the parameters were kept constant, and the boron content acted as a variable.

The purpose of quenching in the rapid solidification process is to cross the phase boundaries fast enough to prevent equilibrium reactions from taking place (Duwez, 1983). In other words, the character of amorphous metal is controlled by the rate at which the latent heat of fusion can be bypassed in the liquid-solid interface. This process, called an isothermal relaxation, happens in liquid quenched to a temperature below and near the glass transition temperature $T_g$. The development of a heat flow pattern for a rapid solidification process is based on the fact that the quenching can be accomplished by radiation, convection, conduction, or a combination of these, in the two different modes. The pulse mode provides a three-dimensional quenching rate exceeding five hundred thousand degrees per second. The heat pattern at the continuous mode follows a two-dimensional pattern with a quenching rate thousands of times less than that of the pulse mode. A heat flow pattern for pulse and continuous mode is shown in Figure 13.
Figure 13. Temperature distribution at the point of impingement in continuous and pulse modes.

Note. $T_1$ = liquid temperature  $T_m$ = liquidus temperature  
$T_s$ = solidus temperature  $T_a$ = ambient temperature
X-Ray Diffraction Examination

The heat-treated surfaces which had an indication of glassy structures were tested by an x-ray diffraction process. In order to eliminate excessive cost and time, the heat-treated surfaces were first subjected to metallographic examination. Those specimens which showed obvious crystal structures were temporarily set aside. Those specimens which could not be proved to have crystal structures were further subjected to a chemical examination that relies on the resistance of formed phases to acid attacks. The metallic glasses, like non-metallic glasses, have a good resistance to chemical corrosion. An application of a chemical solution (nital with 10% nitric acid), hence, can discriminate between the metallic and glassy structures.

In laser processing, however, the heat-treated surface may include equilibrium, saturated, and supersaturated structures as well as metallic glasses. The chemical resistance of these structures varies as the crystal structures change to saturated and supersaturated structures and ultimately to metallic glasses. There is a degree of variation in chemical resistivity in each of these categories, but there is not a well-defined line between each structure. Thus, the chemical examination cannot identify the glassy layer on the surface of the cast irons. The only advantage of using chemical tests was to identify the surfaces most likely to have glassy structures.

The heat-treated surfaces were classified in order of the least to highest reaction with the chemical solution. The laser-treated
surface with the least chemical reaction was examined by the Debye back-reflection x-ray radiation process. The x-ray examination of the specimen was continued until the test indicated the absence of the glassy structure and the existence of the crystal structure.

The preparation of a specimen for x-ray consisted of removing the distorted crystalline structure from the surface of the workpieces. The distortion of the crystals were caused by the grinding process. A chemical solution with a volumetric composition of 30 percent hydrogen peroxide ($\text{H}_2\text{O}_2$), 22 percent distilled water ($\text{H}_2\text{O}$), and 48 percent hydrogen fluoride (HF) was used to accomplish this. The important factor governing the results was the direction and the intensity of the reflected beam. When the specimen has a crystalline structure with relatively large grains, the reflected x-ray beam generates a pattern in a certain location on the photographic film.

The metallic glasses form when the atomic structures are distorted. The atoms in glasses occupy sites that do not belong to atomic lattice points of a crystal. "The position of these atoms do not change the direction, but [they] reduce the intensity of the diffracted beams" (Cullity, 1967, p. 140). Thus the intensity of the beam is not sufficient to generate a pattern on the photographic film. The x-ray method, hence, can indicate the presence or absence of crystalline structures. An x-ray diffraction of such a metallic glass layer is shown in Figure 14.

The x-ray examination in this investigation was performed at the Ames Department of Energy Laboratory in Ames, Iowa. The machine operated at a power of 40 kilowatts and 15 milliamperes. The exposure
time was 10 minutes. The x-ray machine was equipped with a Molybdenum tube appropriate for use in examination of ferrous metals. Analysis of the x-ray photographs indicated formation of the glassy structure in the surface of the specimen with four percent boron content under six different laser parameters as tabulated in Table 4 and illustrated in Figures 14 and 15.

Table 4

Optimum Laser Parameters for Glass Formation as Indicated by X-ray Diffraction Patterns

<table>
<thead>
<tr>
<th>Designated number</th>
<th>Pulse duration</th>
<th>Power</th>
<th>Cover-gas</th>
<th>Laser mode</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.7 Ms</td>
<td>600</td>
<td>620</td>
<td>30 pre.</td>
</tr>
<tr>
<td>2</td>
<td>0.8</td>
<td>600</td>
<td>620</td>
<td>30 pre.</td>
</tr>
<tr>
<td>3</td>
<td>0.9</td>
<td>600</td>
<td>620</td>
<td>30 pre.</td>
</tr>
<tr>
<td>4</td>
<td>0.10</td>
<td>600</td>
<td>620</td>
<td>30 pre.</td>
</tr>
<tr>
<td>5</td>
<td>0.11</td>
<td>600</td>
<td>620</td>
<td>30 pre.</td>
</tr>
<tr>
<td>6</td>
<td>0.9</td>
<td>500</td>
<td>500</td>
<td>30 pre.</td>
</tr>
</tbody>
</table>

1 = Measured 2 = Pressure 3 = Direction 4 = Continuous

Note. The parameters are those at which the metallic glass was formed. A more comprehensive list of the parameters that were tried is given in Figure 11.
Figure 14. X-ray diffraction pattern of the specimen with 4.17 percent boron content.

Note. The x-ray diffraction is a pattern from a location where the structure remained crystalline as evidenced by the presence of intense spots in the pattern. The nonuniform pattern of the Debye rings is due to preferred orientation in the specimen.
Figure 15. X-ray diffraction pattern of surface layer with distorted crystalline structure.

Note. This x-ray was taken of a specimen with the same parameters as in Figure 14 from a location where the metallic glass was formed due to pulsed laser treatment. The lack of the crystal pattern was indicated by the reduced intensity of the x-ray beam which resulted from the random location of the atoms.
Microstructural Examination

The microstructures of untreated samples were examined with a microscope. The purpose of this examination was to investigate the individual phases or microconstituents in the specimens. Clearly, the microstructure has a profound effect on the properties of castings. The microstructural examination included the detailed investigation of phase transformation, grain size, cracks, porosity, and segregation of alloying elements.

Even when the chemical composition of specimens are strictly controlled, variations, such as the solidification rate of the molten metal, may produce a wide variation in microstructures. The objective of the microstructural examination, therefore, was to observe the uniformity of the grain size and the presence or absence of inclusions and segregations in the untreated specimens.

The samples were ground, polished, and etched. The grinding was accomplished with a horizontal grinder, and the abrasives were silicone carbide grits of 120, 240, 320, 400, and 600, respectively. The polishing process was performed with 5-micron abrasive cloths. Two percent nital was the chemical solution used as the etchant. The selected microstructure of each specimen was recorded in photographs. These photographs were used for image analysis and characterization of the seven types of specimens used in this investigation.
Scanning Electron Microscopy

The limited resolution of the metallurgical microscope generated a need for an instrument with a capability of producing a higher magnification. The goal of utilizing Scanning Electron Microscopy (SEM), thus, was to obtain a highly magnified microphotograph of the specimen with the best possible resolution. Various techniques may be used to obtain enlarged images of the surface of a bulky, nontransparent sample with the help of electron beams (Heimendahl, 1980).

The SEM has a large depth of focus providing the possibility for observing uneven surfaces such as the microcracks and gas-pockets. Figure 16 is an SEM photograph of microcracks generated as the result of thermal stress on the heat-affected zone.

The SEM examination was performed by employing the Intelligent SEM S-570, developed by Hitachi, Ltd, of Japan. The instrument was operated by scanning the electron beam over the surface of the specimen. The resulting backscattered or secondary electrons form an image on a fluorescent screen (Figure 17).

The exposure time depended upon the condition of the specimens, and it was approximately one minute. The primary sources of the contrast were differences in the efficiency of emission of secondary electrons as a function of composition. Tilting the specimen with respect to the electron beam caused contrast by shadowing and permitted stereoscopic photography with a three-dimensional effect. Figure 18 shows these microphotographs under different magnifications.
Figure 16. Scanning Electron Micrograph of microcracks generated as the result of thermal stress on the heat-affected zone of the sample containing 4.17 percent boron.

Note. This shows the propagation of the microcracks on the base metal just outside the heat-affected zone. Magnification 1000X.
Figure 17. Scanning Electron Micrograph of the base metal for the sample containing 4.17 percent boron.

A.

B.

Note. A. is the secondary emission and B. is the back-scattered SEM microphotograph of the untreated area.
Figure 18. Scanning Electron Micrograph of the heat-treated zone for the sample containing 4.17 percent boron.

A. Low magnification.

B. High magnification.

Note. The laser parameters were pulse mode, power 600 watts, and pulse duration one millisecond. The cover-gas was argon at 30 psi. The structure is an austenitic structure.
**Hardness Examination**

The objectives of hardness testing are to measure the resistance of various microscopic points to penetration in order to generate hardness and micro-hardness profiles of the heat-affected zone of the various specimens. The examination included Rockwell and Vickers hardness of a selection from each group.

To obtain overall hardness for each group, a Rockwell hardness with C scale was used. A specimen representing each group was chosen randomly. The sample had the dimension of 0.5 x 1 x 3 inches to fulfill the requirement of the physical size.

Vickers hardness testing was chosen to measure the micro-hardness profile of the specimens. The indenter was a diamond pyramid with an angle of 136 degrees between opposite faces. The selection of the load was based upon the lower recommended range because such a low load increases the accuracy of the measurement and prevents the cracking and deformation of the indenter.

The hardness test was repeated at random locations five times for each sample, and the average of these was considered the micro-hardness value for that group. In this process, three types of hardness readings were taken:

1. The hardness reading of the base metal, which provides the relationship between the hardness and the boron content.

2. The micro-hardness profile of the specimen's surface in the plane perpendicular to the direction of laser heat treatment.
3. The micro-hardness profile of the depth at the center of the heat-affected zone, which was measured to generate the micro-hardness pattern as a function of the distance from the surface of the specimen.

The hardness and micro-hardness examination was performed at the Chamberlain Manufacturing Corporation, Waterloo Division, Waterloo, Iowa. The results are shown in Tables 5, 6, and 7.

Table 5

Hardness (Re) as a Function of Boron Content of the Untreated Specimens

<table>
<thead>
<tr>
<th>% boron in sample</th>
<th>Number of trial</th>
<th>Hardness</th>
<th>Ave.</th>
<th>Number R&lt;sub&gt;c&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1   2   3   4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>14  15  14  14</td>
<td>14.4</td>
<td>14.4</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>59  58  56  57</td>
<td>57.6</td>
<td>57.6</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>56  56  56  55</td>
<td>56.0</td>
<td>56.0</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>44  42  43  44</td>
<td>43.2</td>
<td>43.2</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>39  44  42  42</td>
<td>42.0</td>
<td>42.0</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>43  42  45  44</td>
<td>43.2</td>
<td>43.2</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>49  48  44  46</td>
<td>47.0</td>
<td>47.0</td>
<td></td>
</tr>
</tbody>
</table>

Note. The measurements are of selected samples from each group.
Table 6

Micro-hardness as a Function of the Distance from the Surface in the Heat-affected Zone for Various Laser-treated Groups

<table>
<thead>
<tr>
<th>% boron in sample</th>
<th>distance from the surface x .02 mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1098 935 1162 1162 1162 672 290 197</td>
</tr>
<tr>
<td>2</td>
<td>1231 1162 1231 1231 1162 889 347 241</td>
</tr>
<tr>
<td>4</td>
<td>1390 1162 1390 1307 1162 702 392 347</td>
</tr>
<tr>
<td>6</td>
<td>1489 1276 1347 1355 1581 1560 423 392</td>
</tr>
<tr>
<td>8</td>
<td>1952 1815 1815 1952 1815 1839 889 423</td>
</tr>
</tbody>
</table>

Note. The above table illustrates an increase in microhardness from 1098 for the sample without the element of boron to 1952 for the sample containing 7.1 percent boron. There is a sudden reduction between column five and seven. This sudden drop is due to the character of laser treatment and occurs at the bottom of the heat-affected zone. The measurements are of a sample from each group.
Table 7

Micro-hardness Profile of the Surface of Specimens Perpendicular to the Direction of Laser Heat-treatment

<table>
<thead>
<tr>
<th>% boron cont. of sample</th>
<th>5</th>
<th>4</th>
<th>3</th>
<th>2</th>
<th>1</th>
<th>0</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>197</td>
<td>658</td>
<td>1039</td>
<td>1162</td>
<td>1039</td>
<td>1098</td>
<td>1039</td>
<td>846</td>
<td>347</td>
<td>197</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>241</td>
<td>241</td>
<td>889</td>
<td>1162</td>
<td>1347</td>
<td>1162</td>
<td>1162</td>
<td>1231</td>
<td>889</td>
<td>247</td>
<td>247</td>
</tr>
<tr>
<td>4</td>
<td>347</td>
<td>889</td>
<td>1039</td>
<td>1059</td>
<td>1390</td>
<td>1347</td>
<td>1390</td>
<td>1307</td>
<td>1307</td>
<td>1231</td>
<td>347</td>
</tr>
<tr>
<td>6</td>
<td>392</td>
<td>889</td>
<td>1381</td>
<td>1390</td>
<td>1952</td>
<td>1581</td>
<td>1692</td>
<td>1692</td>
<td>1952</td>
<td>392</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>423</td>
<td>889</td>
<td>1452</td>
<td>1231</td>
<td>2105</td>
<td>1952</td>
<td>1952</td>
<td>1952</td>
<td>1552</td>
<td>423</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>332</td>
<td>1098</td>
<td>1098</td>
<td>1581</td>
<td>1307</td>
<td>1692</td>
<td>1581</td>
<td>1581</td>
<td>1039</td>
<td>1039</td>
<td>332</td>
</tr>
<tr>
<td>12</td>
<td>185</td>
<td>1162</td>
<td>1581</td>
<td>1307</td>
<td>1307</td>
<td>1581</td>
<td>1581</td>
<td>1581</td>
<td>1581</td>
<td>1581</td>
<td>185</td>
</tr>
</tbody>
</table>

Note. The column designated by zero is the hardness at the center of the heat-affected zone. The table shows an approximate symmetry between the hardness reading on the left and on the right side of the zero column. The table also shows a general increase in hardness number as a function of the boron content of the specimens. The measurement is for a sample selected randomly from each group.
CHAPTER IV
Analysis of the Results

Introduction and Implications

The purpose of the study was to investigate the possibility of forming an amorphous metallic layer on the surface of gray cast iron by utilizing industrial carbon dioxide laser radiation. The study was deemed significant because it investigated a new technique leading to the formation of ferrous-based metallic glass layers when the laser was operating at the pulse mode. It is hoped that this study will initiate an area of research that will lead to the utilization of such methods and materials in new production processes.

The Research Questions and Subquestions

The research questions which the study attempted to answer were as follows: What are the procedures required to develop an amorphous metallic layer on the surface of ferritic gray cast iron and iron boron alloys by the application of industrial carbon dioxide laser radiation, and what is the effect of boron content on the formation, mechanical properties, and microstructure of such metallic glass?

In an attempt to answer the research questions stated above, the following five subquestions were formulated. Answers to these subquestions led to answers to the research questions.

Subquestion One

What is the possibility of forming an amorphous metallic layer in the surface of ferritic gray cast iron containing boron by utilizing industrial carbon dioxide laser radiation?
Seven different types of specimens were subjected to chemical tests, x-ray back-diffraction examinations, mechanical properties evaluations, and Scanning Electron Microscopy analysis. Since metallic glasses exhibit a good resistance to chemical solutions, these could be used to distinguish between the crystal, supersaturated, and glassy surfaces of each specimen.

The pulsed laser heat-treated surfaces were subjected to a chemical solution of a highly concentrated nital. The test conditions were kept the same for all the heat-treated areas. Those which showed a high resistance to the chemical solution and had a distinctly rounded and bulby shape were irradiated with x-rays using the Debye back-deflection method.

In x-ray examination, the position of the atoms in the unit cell affects the intensity but not the direction of the diffracted beam, thus generating a more intense beam for the crystalline structure and a less intense beam for an amorphous layer. The x-ray patterns wereanalyzed by using the Stereographic projections technique. Those which showed a pattern caused by crystalline structures were disregarded. Those which showed clear indications of metallic glass structures and showed a lack of any pattern were identified, and their laser parameters were recorded. Those parameters are shown in Table 8. These are among the possible parameters: laser power ranges between 500 watts and full power, pulse duration ranges between six microseconds and a full second, and the cover-gas blown in the axial direction with gas pressure between 20 and 35 psi.
Table 8
Laser Parameters Under Which the Metallic Glass Was Formed

<table>
<thead>
<tr>
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<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>x</td>
<td>600</td>
<td>620</td>
<td>7 5</td>
<td>7</td>
<td></td>
<td></td>
<td></td>
<td>4</td>
<td>Ar</td>
<td>30</td>
<td>Axial</td>
<td>Ar</td>
<td>30</td>
</tr>
<tr>
<td>2</td>
<td>x</td>
<td>600</td>
<td>620</td>
<td>8 5</td>
<td>8</td>
<td></td>
<td></td>
<td></td>
<td>4</td>
<td>Ar</td>
<td>30</td>
<td>Axial</td>
<td>Ar</td>
<td>30</td>
</tr>
<tr>
<td>3</td>
<td>x</td>
<td>600</td>
<td>620</td>
<td>9 5</td>
<td>9</td>
<td></td>
<td></td>
<td></td>
<td>4</td>
<td>Ar</td>
<td>30</td>
<td>Axial</td>
<td>Ar</td>
<td>30</td>
</tr>
<tr>
<td>4</td>
<td>x</td>
<td>600</td>
<td>620</td>
<td>10 5</td>
<td>10</td>
<td></td>
<td></td>
<td></td>
<td>4</td>
<td>Ar</td>
<td>30</td>
<td>Axial</td>
<td>Ar</td>
<td>30</td>
</tr>
<tr>
<td>5</td>
<td>x</td>
<td>600</td>
<td>620</td>
<td>11 5</td>
<td>11</td>
<td></td>
<td></td>
<td></td>
<td>4</td>
<td>Ar</td>
<td>30</td>
<td>Axial</td>
<td>Ar</td>
<td>30</td>
</tr>
<tr>
<td>6</td>
<td>x</td>
<td>500</td>
<td>500</td>
<td>9 5</td>
<td>9</td>
<td></td>
<td></td>
<td></td>
<td>4</td>
<td>Ar</td>
<td>30</td>
<td>Axial</td>
<td>Ar</td>
<td>30</td>
</tr>
</tbody>
</table>

Note. Table 8 is the list of the parameters at which the metallic glass was formed. A detailed description of this process was given in Table 4.

The experimental results reinforced the theoretical principles: maximum glass formability of a metal is at the point where the ratio of the Glass Transition Temperature to the liquid temperature is closer to unity (Spaepen & Turnbull, 1976). The composition at the eutectic point has the lowest liquid temperature with the highest chance of glass formability. The specimen with boron content of 4.17 percent (close to the eutectic point 3.8 percent) had the most optimum conditions among the seven different types of specimens. At this point the glass forming-ability (GFA) was calculated to be:
GFA = \frac{T_{rg}}{T_1} \quad \text{or} \\
GFA = \frac{560}{2145} = 0.26

Even though the GFA was much less than one, the specimen had the highest glass formability ratio among the seven different samples. The addition or reduction of the boron content increased the liquid temperature, causing a reduction of the GFA of the metal. For the compositions with lower GFAs, a higher thermal energy transformation was required to remove the additional heat content of the specimens.

When the laser was operating in the continuous mode, the treated surface did not have an indication of a glassy layer. The lack of such structure can be attributed to two factors.

The first reason for the lack of the glassy layer was the reduced quenching rate. In laser production of metallic glasses, the heat is mainly dissipated by the conduction process through the bulk metal. The conduction of such thermal energy is directly related to the momentary surface area of the melted zone.

The observation of the laser heat-treated zone showed that with the pulsed mode the absorbed heat dissipated more rapidly than with the continuous mode. This can be attributed to the greater area of conduction in the pulse mode. The conductive area when the laser operates at the pulse mode can be approximated with the following function:

\[ f(x) = - \frac{C}{1 + x^2} \]

where

\[ C = \text{the equation constant} \]
\[ X = \text{the diameter at HAZ at the surface} \]
\[ f(x) = \text{the depth of penetration at the center of HAZ} \]
The value of X and Y are measurable and, for a constant power input, are functions of the thermal conductivity of the metal. The equation constant C is directly related to the power input, the pulse quality, the focusing point, and the optical system of the laser. For the specimen without boron content, X measured $22 \times 10^{-2}$ mm, Y measured $16 \times 10^{-2}$ mm, and the C was calculated at $17 \times 10^{-2}$. A graphic representation of the above function, when C is equal to one, two, and three is illustrated in Figure 19.

The equation was chosen on the basis of compatibility between the various patterns generated at the heat-affected zone and the graphic representation of the above equation.

The above equation is useful in calculating the surface area at the heat-affected zone when the laser operates in the pulse mode. An increase or decrease in such surface area directly affects the thermal conductivity of the process, leading to variation in the quenching rate. The numerical value can be shown in the following equation:

$$S_p = 4 \pi \int_x (c^2 x^2 + x)^{1/2} dx$$

where

$$\frac{dX}{dT} = \text{a function of time and the thermal diffusivity of the metal}$$

$$S_p = \text{the momentary surface area in the pulse mode}$$

The graphic illustration of such a surface area is shown in Figure 20. In laser processing under the continuous mode, the surface area is reduced to a two-dimensional surface area. As soon as the time
Figure 19. Graphic representation of the experimental equation adapted for the heat-treated pattern in laser surface treatment for three different parameters.

Note. This equation is applicable when the laser operates at the gaussian mode. The C constant is a function of the power input, the pulse quality, the focusing point, and the optical system of the laser.
Figure 20. The graph illustrates the conductive surface area on the base of the experimental equation when the laser operates at the pulse mode.

Note. The graph was drawn with C equaling two.
interval becomes close to zero \( (T \to 0) \), the surface area becomes close to the length of the curve between \(+X\) and \(-X\), hence leading to a smaller surface area and a reduction in the thermal conductivity of the process. The surface area under the continuous mode can be approximated in an equation:

\[
S_c = \int \frac{[(1 + x^2)^2 - 2CX]}{(1 + x^2)^2} \, dx \, dZ
\]

where

\[
dZ/dT = \text{The transverse speed of the laser beam}
\]

\[
S_c = \text{The surface area when the laser operates at continuous mode}
\]

The graphic representation of such a surface is illustrated in Figure 21.

The computerized solutions were developed on the basis of the experimental results. The parameters, such as \( C \) and \( N \), provide options for each trial. Appendix D contains the computer programs developed for the above areas. The substitution of numerical values for various parameters in the solution indicated a drastic reduction in quenching rate when the laser operated at the continuous mode. The quenching rate, consequently, became insufficient to form any glassy structures.

The second reason for the lack of a glassy layer when the laser was operating in the continuous mode was the secondary heat input which resulted from that mode. The glassy structures may be crystallized by a nucleation and growth process. The driving force is
Figure 21. Graphic representation of the conductive area when the laser operates at the continuous mode.

Note. The graph was drawn on the basis of the experimental equation when the laser operated at the continuous mode. The conductive area refers to the surface area between the liquid and solid specified by the heat-affected zone.
the difference in the activation energy between the glass and the appropriate crystalline phase. The free energy of a system can be expressed in the form of Gibbs Free Energy, denoted as follows:

\[ G = H - T.S \]

where

\( G \) = the Gibbs Free Energy of the system
\( H \) = enthalpy
\( S \) = entropy
\( T \) = the absolute temperature of the alloy

Figure 22 illustrates a hypothetical free energy configuration for glass and crystalline phases. In this figure the metallic glass is assumed to be in the metastable state compared to the more stable state of equilibrium of a metal. At equilibrium the rate of change of the Gibbs free energy (dG) is zero; more importantly, the energy content of the metal is in a lower state. At point 2 in the stable equilibrium configuration, the metal has minimum internal energy. Such a point is the most stable state at which the alloy has the crystalline structure at total equilibrium. At equilibrium conditions, application and removal of thermal energy produces, as in annealing, other crystalline structures with relatively the same structure. The change in internal energy content and Gibbs Free Energy is negligible if the new structure is the same as before.

The internal energy of the matter is drastically changed when a metastable structure is transformed into a crystalline structure. Point 1, which represents a metastable state (e.g., an amorphous metal), lies at a location where the rate of change in Gibbs Free
Figure 22. Hypothetical illustration of the Gibbs Free Energy diagram for a metal at the metastable state of metallic glass and at the stable state of the equilibrium condition.

Note. This hypothetical Gibbs Free Energy diagram illustrates the crystallization of a metallic glass. Point 1, which has free energy of $E_2$, is a metastable metallic glass. Point 2 represents the stable equilibrium state with free energy of $E_1$. The minimum energy required to transform a metastable structure (e.g., metallic glass) into a crystal structure is shown as $E_3 - E_2$. 
Energy is equal to zero. Such a point represents a metastable state because a relatively small amount of external energy \((E_3 - E_2)\) causes the transformation of the alloy into the crystalline structure.

Amorphous metallic structures can be formed with the laser on continuous mode. However, the transformation of the thermal energy from one pulse to the next is sufficient to cause nucleation and crystal growth, transforming the glass structures into crystalline structures. This statement agrees with the experimental observation showing the formation of the glassy structures when the laser was operating at pulse mode with a long dwell time. When there was sufficient distance between the two consecutive pulses, the quenching process was in a three-dimensional pattern, generating a high cooling rate. In addition, the transfer of heat from one pulse to the next was insufficient to transform the metastable metallic glasses into a crystalline state. When the dwell time decreased, as in the continuous mode, the pulses came closer together. Then, the transformation of heat from one pulse to the next was a driving force to transform any metallic glasses which had been formed into crystalline structures. In the latter case, the release of the stored internal energy of the metallic glasses and the heat buildup further reduced the glass formability of the metals.

Subquestion Two

What effect does adding boron have on the formation of a metallic glass layer?

As an alloying element, boron had significant effects on the formation of the amorphous metallic materials. The seven different
types of alloys prepared for this study had the general composition of $\text{Fe}_x \text{B}_y \text{M}_{100-(x+y)}$ with boron content ($y$) ranging between zero and 10.10 percent by weight. The iron content of the specimens ($x$) ranged from 93.28 to 82.58 percent by weight. M includes the alloying elements of C, Si, Mn, P, S, Al, Ni, Cr, and Mo. The experimental results indicated that a metallic glass layer formed on the surface of the specimen containing 4.17 percent boron. As the boron content increased, the glass formability of the specimens decreased. The visual examination of the specimens pointed to reduced crystal size as the result of the addition of boron. Such an examination, in addition to examination by SEM, revealed crack propagation on untreated and treated samples having higher boron contents.

Boron was chosen as an alloy to aid glass formation because it retards nucleation, decreasing the crystallization rate and increasing the possibility of glass formation on the treated surface. The alloys prepared were iron-boron with an eutectic point at 3.8 percent of the boron content at 2174°F. The specimens with boron content of 2.02 and 4.17 percent, which had higher glass forming ability (GFA) (the ratio of $T_{rg}$ to $T_1$ closer to one), were expected to form metallic glass more easily. The microstructural examination demonstrated partial dissolution of the boron content in the alpha phase of the iron-boron binary alloys. The additional boron precipitated out of the matrix as segregated structures in the form of the iron boron compounds FeB, Fe$_2$B, and FeB$_{19}$. Supersaturated iron-boron was formed as the result of rapid solidification of alloys in laser processing.
Subquestion Three

What is the effect of boron content on the hardness and micro-hardness profile of the amorphous surface layer?

The hardness profile of the heat-affected zone was carried out by Rockwell and Vickers micro-hardness testing. The untreated specimens showed a variation in the micro-hardness measurement from one point to another, depending upon the structure formed. The specimens were tested with a Rockwell tester, C scale. There was a direct linear relationship between the hardness and the percentage of boron content up to two percent. The hardness was found to decrease to a minimum with further addition of boron. This decrease can be attributed to the undissolved elements, such as carbon, or to newly formed compounds. This relationship is shown graphically in Figure 23.

The micro-hardness profile of the specimens also was measured on the surface in the direction perpendicular to the direction of heat treatment. The measurement showed a drastic increase in the hardness at the heat-affected zone. The hardness was relatively constant at the center of the fusion zone and decreased at the interface of the heat affected zone with the base metal. At the center, the graph showed a brief decrease in the micro-hardness values. This decrease is believed to be caused by the excessive heat and the limitation of the thermal conductivity of the base metal. Figure 24 is a graphic representation of the micro-hardness profile of the specimens. The micro-hardness values shown in Figure 24 are based on distances spaced
Figure 23. Hardness measurements as a function of boron content before laser treatment.

Note. The hardness measurement shows an increase in hardness for the sample with 2.02 percent boron containing Fe₂B and alpha-iron structures.
at $2 \times 10^{-2}$ mm intervals from the surface at the center of the heat-affected zone. The micro-hardness measurement of the specimens at the center of the heat-affected zone showed a relatively constant hardness with a slight reduction at approximately 0.02 mm from the surface. After another section of relatively constant hardness, there was a sharp reduction in the hardness numbers to the base of the HAZ. The reduction was due to the fact that the alloy near the center at the point of impingement was heated to a maximum temperature well above the melting temperature where the thermal conductivity of the metal was limited. The surface of the metal at a heat-affected zone is always subjected to loss of thermal energy by the processes of convection and radiation. The remaining heat must be conducted away through the bulk material. At the impingement point of the laser beam on the surface of the metal, the temperature is extremely high, and the surface area is small enough to prevent the rapid dissipation of the thermal energy, resulting in a reduction of the hardness of the metal. As the heat is conducted away from the impingement point, the thermal energy decreases, and the area of the conduction increases. This results in a relatively rapid quenching process and an increase in hardness. At the same time, as the distance from the point of impingement, which has a liquid-vapor interface, increases, the temperature of the metal decreases. At the bottom of the heat-affected zone, where the temperature just reaches the annealing range, the hardness number can be reduced even below the hardness of the base metal. This relationship is shown graphically in Figure 25.
Figure 24. Micro-hardness at the surface as a function of the distance from the center of the heat-affected zone. Samples indicated by percent of boron content.

Note. The direction of measurement was perpendicular to the direction of laser heat treatment. The graph shows a sudden reduction on the hardness. This sudden drop is due to the character of laser treatment and occurs at the bottom of the heat-affected zone.
Figure 25. Micro-hardness measurement as a function of depth of melt at the center of the heat-affected zone. Samples indicated by percent of boron content.

Note. The graph shows an increase in the hardness number as function of boron content. The specimens containing 8.70 and 10.10 percent boron were so brittle that they fractured when they were subjected to the hardness test.
**Subquestion Four**

What is the effect of the boron content on the depth of the treated surface layer?

The observation of the depth and the shape of the heat-affected zone of the laser-treated specimens revealed variation. The experimental investigation of the effect of boron on the depth at the heat-affected zone indicated an inverse relation between the boron content and the depth and uniformity of the microstructure in the heat affected zone. The addition of boron content generally affected the depth of the heat-affected zone in three ways:

1. Additional boron increased the emissivity of the specimen. The emissivity improved as the result of the segregated graphite structure and produced a dark appearance on the surface of the specimens.

2. Additional boron increased or decreased the depth of penetration depending upon the type of chemical compounds. In such a condition, a portion of the absorbed heat is used to break the bonding forces between the compounds.

3. Additional boron varied the thermal conductivity of the specimens. The absorbed energy must be conducted away through the base metal. When the base metal had a high thermal conductivity, the transformation of heat prevented heat buildup and reduced the depth of penetration. On the other hand, a decrease in the thermal conductivity of the metal caused heat buildup and increased the depth of penetration.
The effect of the boron on the melt depth was investigated by the measurement of the fusion thickness at the heat-affected zone for various specimens. For laser treatment, the surface of the specimens were polished and then coated with sprayed graphite to improve emissivity and produce a uniform melting zone. The laser parameters were adjusted to the maximum power with a constant speed of 400 inches per minute. Argon gas was used at 30 psi for all the specimens. The depths of penetration are shown in Figure 26. The result was a general reduction of the depth of penetration to just a trace in the specimen with boron content of about 10 percent. The change in melt depth within the seven different samples could be explained by the effect of the alloying elements on thermal conductivity and the heat content of each alloy. In addition, it was found that an increase of the boron content increased the thermal stress, leading to the generation of microcracks in the heat-affected zone. Such microcracks were observed to have a random orientation and to have initiated from the surface at the fusion zone.

The variation in the depth of penetration was also a function of changes in laser power or changes in speed of the moving table. To obtain data on the relationship between the depth of penetration and the laser power, the specimens were polished and coated with graphite. The transverse speed of the moving table was set at 400 inches per minute. This speed was chosen on the basis of the observation of the minimum surface liquidization and surface distortion of the metal.
Figure 26. Relationship between the boron content and the depth of penetration in the heat-affected zone.

Note. The laser operated at full power using argon at 30 psi as the cover-gas, and the transverse speed of the laser was 80 inches per minute. The graph shows a reduction of the depth of melt as a function of an increase on boron content.
The laser was at a maximum continuous output power of 1300 watts and a measured power rating of 1000 watts. The output power was reduced to 800, 600, 400, and 200 watts for each consecutive path. The results are shown as Figure 27. It should be mentioned that further increase in the power (by decreasing the transverse speed of the moving table) causes unacceptable surface melting and surface distortion. At the same time, decreasing the laser power to less than 200 watts reduces the depth of penetration to just a trace.

The effect of the transverse speed of a laser beam on the depth of penetration for selected specimens was investigated (Figure 28). In this investigation, the speed ranged from 80 to 480 in/min. Three conclusions were reached:

1. There is a general reduction in the depth of penetration caused by an increase in the transverse speed of the moving table.

2. The specimens with lower boron content have a higher depth of penetration.

3. As the boron content of the specimens increases, the surface distortion and crack propagation increases.

**Subquestion Five**

What are the changes in the microstructural characteristics caused by varying the boron content of the specimens?

In light of the iron-boron binary phase diagram (Figure 29), it was possible to identify and characterize the constituents of the iron-boron binary alloys studied in this investigation. This image
Figure 27. Depth of penetration as a function of laser output power.

Note. Feed rate was kept constant at 400 in/min, and argon at 30 psi was the cover-gas.
Figure 28. Depth of melting at the heat-affected zone as a function of the transverse speed of the laser for selected specimens.

Note. The laser output power was kept constant at full power. Argon at 30 psi was used as the cover-gas.
analysis was later verified by Electron Diffracted Spectro-Analysis (EDS) and Electron-beam Microprobe.

Among seven different types of specimens only the first group with zero percentage boron was a conventional gray cast iron. Figure 30 shows the microstructures of the specimens without the element of boron, as received and also as processed. Figure 31 is a scanning electron micrograph and electron diffraction spectro-analysis of these specimens.

Delta-iron could dissolve approximately 0.15 percent boron at about 1381 degrees centigrade. The solubility limit of boron in gamma-iron was 0.10 percent and in alpha iron 0.15 percent at 915 degrees centigrade. The solubility was reduced as a function of the temperature. Hence, when there was a binary of iron with less than 0.1 percent boron, the solidification transformation process could be shown as the following diagram:

\[
\text{Liquid alloy} \rightarrow \Delta \text{-Iron} \\
\Delta \text{-Iron} \rightarrow \Gamma \text{-Iron} \\
\Gamma \text{-Iron} \rightarrow \alpha \text{-Iron}
\]

Such an alloy, therefore, was expected to have a basic ferritic structure.

The hypoeutectoid specimens containing more than 0.15 percent and less than the eutectic percentage of boron, 3.8 percent, are expected to have the structure of $\text{Fe}_2\text{B}$ distributed into the alpha-iron. The resulting structure was a ferritic structure with $\text{Fe}_2\text{B}$ as the iron-boron compound. The transformation of such alloying elements from liquid to solid could be formulated as shown:
Figure 29. Constituents of iron-boron binary alloys.

Percent boron content
Liquid alloy $\rightarrow$ Delta-Iron + Liquid

Delta-Iron + Liquid $\rightarrow$ Gamma-Iron + Liquid

Gamma-Iron + Liquid $\rightarrow$ Gamma-Iron + Fe$_2$B

Gamma-Iron + Fe$_2$B $\rightarrow$ Alpha-Iron + Fe$_2$B

The hypoeutectoid specimen containing 2.17 percent boron which was investigated in this study had additional alloying elements such as C, Si, Mn, P, S, and Cr. These elements formed microconstituents, resulting in three or more structures in the matrix of such alloys. Because the percentage weight of these alloying elements were relatively low, they generally appeared as segregated structures in the base matrix, or they precipitated in the grain boundary of the matrix, as can be seen in Figure 32.

The hypereutectoid iron, containing more than the eutectoid percentage and less than approximately 8 percent boron by weight, was expected to have a ferritic matrix with the iron-boron compound Fe$_2$B in the microstructure. The major difference between the hypereutectic and hypoeutectic structures was the relative percentage of Fe$_2$B structure compared to that in the base matrix of ferrite. The solidification transformation of this group of hypereutectoid irons was formulated as follows:

Liquid Alloy $\rightarrow$ Liquid + Fe$_2$B

Liquid + Fe$_2$B $\rightarrow$ Gamma-Iron + Fe$_2$B

Gamma-Iron + Fe$_2$B $\rightarrow$ Alpha-Iron + Fe$_2$B

The microphotographs of the hypereutectic structure of the iron boron binary alloys are shown in Figures 34, 35, 36, and 37.
Figure 30. Microstructure of the specimen without boron.

A. As Received

B. As Processed

Note. The microphotograph shows the graphite structures in the specimen without boron content. The photograph shows a partial transformation of type A graphite to type B graphite. Etched with two percent nital. Magnification \( 74 \mu \text{x} \).
Figure 31. Scanning Electron Micrograph and Electron Diffraction Spectro-Analysis of the sample without the element of boron.

Note. The structure consists of two microconstituents: (a) alpha-iron as a base structure and (b) dispersed graphite structure.
Figure 32. Microphotograph of the specimen containing 2.02 percent boron in the form of a dendritic structure with a preferential direction.

Note. The microphotograph shows the dendritic solidification structure of a specimen containing 2.02 percent boron. The black structure seen in the photograph is diffused carbon which resulted from the substitution of boron for carbon in the matrix of iron. Etched with two percent nital. Magnification 477X.
Figure 32. Microphotograph of the base metal for the specimen with 4.17 percent boron content.

Note. A hypereutectic structure of alpha-iron is the base structure. Etched with two percent nital. Magnification 744X.
Figure 34. Scanning Electron Micrograph and Electron Diffraction Spectro-Analysis for the specimen containing 4.17 percent boron.

Note. The base structure consists of three microconstituents: (a) FeB in the light areas, (b) Fe₂B in the dark areas, and (c) the black distorted graphite.
Figure 35. Microstructure of the specimen containing 5.57 percent boron prior to the laser heat treatment.

Note. The hypereutectic structure of the iron-boron specimen consists of alpha-iron (white) as a base structure and unetched retained carbide. Etched with two percent nital. Magnification 744X.
Figure 36. Scanning Electron Micrograph and Electron Diffraction Spectro-Analysis for the sample with 5.57 percent boron.

Note. The structure consists of three different microconstituents: (a) iron-boron and boron anhydride as a base structure, (b) alpha-iron, and (c) Fe-Si structures.
Figure 37. Microstructure at the heat-affected zone of the specimen with 7.1 percent boron content.

Note. This dendritic structure consists of alpha-iron (white) and gamma-iron (dark), disturbed by the carbide structure (black areas). Etched with two percent nital. Magnification 744X.
The photographs were taken of the specimens containing 4.17, 5.57, and 7.1 percent boron content. These samples were heated up to 1600 degrees F to dissolve the segregated structures and cooled slowly to allow the transformation of the austenitic structure into a ferritic structure. In general the specimens had a dendritic structure with a preferential direction. This was caused by the presence of the boron and by the cooling rate in the casting process.

Addition of boron exceeding approximately eight percent resulted in the formation of a new iron-boron phase. This new allotropic phase was an iron-boron compound, possibly FeB, which has an orthorhombic crystal structure. The FeB crystal structure exhibits two different crystalline parameters depending on the temperature of the samples.

Specimens with eight percent or more boron content, when cooled slowly, can include Fe₂B and FeB structures. The solidification transformation of these alloys could be formulated as follows:

\[
\text{Liquid alloy} \rightarrow \text{Liquid alloy} + \text{FeB}_{19}
\]
\[
\text{Liquid alloy} + \text{FeB}_{19} \rightarrow \text{FeB}_{19} + \text{Fe}_2\text{B}
\]
\[
\text{FeB}_{19} + \text{Fe}_2\text{B} \rightarrow \text{FeB}_{19} + \text{Fe}_2\text{B}
\]

The presence of both Fe₂B, which has a body-centered tetragonal (BCT) crystalline structure, and FeB, which has an orthorhombic (Ortho.) crystalline structure, caused internal stress and resulted in brittle parts. The internal stress led to the propagation of microcracks in the cast samples. In addition, the presence of these two compounds with different crystalline structures caused distortion in the crystal structure and sometimes the formation of a glassy structure. This could be seen in the sample containing eight percent
boron, in which the microstructure was in interlocking form. This type of microstructure is usually seen in material with glassy structure. Investigation of the microstructure of the sample containing 8.70 percent boron (Figure 38) revealed the presence of alpha-iron in the microstructure of the samples. The image analysis and the resulting microstructures from the solidification transformation process discussed above were used to analyze the samples at the equilibrium conditions where the cooling temperature was slow.

The laser heat-treated surface with a rapid quenching rate did not conform to the equilibrium iron-carbon or iron-boron constituent of binary alloys. The rapid solidification of the process did not allow the "reconstructive transformation" to take place. The high quenching rate allowed only a partial transformation of the constituents (displacive) and/or produced new microconstituents. The formation of these new structures were functions of three factors: (a) the temperature at which the quenching process took place, (b) the quenching rate, and (c) the chemical composition.

The laser treatment of the cast iron containing no boron did not allow sufficient time for diffusion of the excess carbon out of the matrix of the iron. This forced solidification process generated a structure with more alloying elements than could dissolve at that particular temperature. This supersaturated structure has higher internal stress, which caused higher hardness values. The matrix of the alloy, hence, had a uniform structure which lacked the microconstituents usually present. Figure 39 is the microphotograph of the laser-treated surface of the cast iron containing no boron,
Figure 38. Microstructure of the specimen containing 8.7 percent boron after the homogenization heat treatment.

Note. The structure is unretained gamma-iron (dark) with unetched carbide. Etched with two percent nital. Magnification 744X.
Figure 39. Scanning Electron Micrograph and Electron Diffraction Spectro-Analysis for the sample without element of boron.

Note. The Scanning Electron Micrograph revealed four distinguishable structures: (a) gamma-iron with the element of Si as a base structure, (b) gamma-iron with the elements of Al and Si as a directional structure, (c) Fe-Al-Si-Mn as spheroidal particles, and (d) S-Mn-Fe as particles with square structures dispersed in the matrix.
with analysis of each distinguishable structure by EDS. The heat-treated surface shows the dispersion of the segregated structures of Fe-Al-Si-Mn as spheroidal particles and of S-Mn-Fe as square particles in the matrix of supersaturated iron-carbide.

The addition of boron up to 2.02 percent by weight caused the retardation of nucleation and provided relatively more time for the alloying elements to partially diffuse out of the matrix, resulting in the formation of Fe₂B compound in the matrix of supersaturated gamma-iron (Figures 40, and 41). The specimen with 4.17 percent boron had basically the same structure as the 2.02 percent sample. The major difference was the formation of Fe₂B compound in the form of fine spheroidal structures were seen more often in the sample containing 5.57 percent boron (Figure 42).

The sample containing 7.01 percent boron had a diffused structure of Fe₂B in the matrix of gamma-iron (Figure 43). This structure had minimum segregation with maximum Fe₂B compound, which increased the micro-hardness measurement noticeably.

The structure of the sample containing 8.70 and 10.10 percent boron had an indication of Fe₂B compound in the form of spheroids and FeB compound in the form of a distorted structure with no particular pattern (Figure 44). Figure 45 is a comparison between the segregated micro-structures of the specimens with 2.02 and 7.01 percent boron content.
Figure 40. Microstructure of the specimen with 2.02 percent boron content after laser heat treatment.

Note. This is a hypereutectic structure of iron-boron with alpha-iron (white) and gamma-iron (dark). The boride is shown as a fine dispersion of small spheroidal particles in the matrix. Etched with two percent nital. Magnification 744X.
Figure 41. Scanning Electron Microphotograph and Electron Diffraction Spectro-Analysis of the sample with 4.17 percent boron after laser heat treatment.

Note. The structure consists of three distinguishable structures: (a) iron-boride with the element of Si as a base structure, (b) iron-boride with Si and P as a dark directional structure, and (c) iron-boride with the element of Si as a lighter directional structure for the samples containing 4.17 percent boron content.
Figure 42. Scanning Electron Micrograph and Electron Diffraction Spectro-Analysis of the sample containing 5.57 percent boron after the laser heat treatment.

Note. The structure consists of the following: (a) a fine dispersion of small spheroidal Fe-B-Si-Mn particles, (b) a directional Fe-B-Si structure, and (c) a base matrix of gamma-iron.
Figure 43. Scanning Electron Microphotograph and Electron Diffraction Spectro-Analysis of the sample containing 7.01 percent boron after the laser heat treatment.

Note. The microphotograph has identified two different structures: (a) iron-boride with the elements Al-Si as a base structure (light areas) and (b) Si as a directional structure (dark areas).
Figure 44. Microphotograph of the specimen with 8.70 percent boron content after laser processing.

Note. This is a supersaturated iron-boron structure in the heat-affected zone after the laser treatment. The structure contains FeB compound (dark area). The photograph also shows the cracks generated as the result of thermal stress. Etched with two percent nital. Magnification 744X.
The observation of the segregated graphite in specimens with four percent boron content or more indicated that the microcracks initiation form such structures and continued to other segregated structures. The scanning electron micrograph of such a microcracks is illustrated in Figure 46.

One of the general observations on the specimens containing boron was related to their dendritic structure. The size and the shape of such a structure was a function of the degree of undercooling at the onset of crystallization. This reaction was directly affected by the boron content, the method of casting, and the pouring temperature. The direction and the size of the dendritic structure was affected by the heat flow direction.

The structure of the metal at the heat-affected zone was also influenced by the boron content of the base metal. The microstructural observation of the heat-affected zone revealed the generation of a supersaturated structure of iron-boron-carbon alloy. This structure was formed when the liquid iron was accommodating the melted elements of carbon and boron and was frozen with a rate high enough to prevent complete diffusion and segregation of the carbon, boron, ferro-boron (FeB), and oxides of other elements from the matrix of iron. The trapped elements joined together as a compound or, as in the case of carbon, formed a distorted structure. The presence of such structure was related to their relative amounts as an element in the alloy. Further, the addition of boron reduced the presence of iron carbide in the structure. The structure of the samples containing 8.70 and 10.10 percent boron were predicted to have the
same structure as the sample containing 7.01 percent boron. The major difference was in the relative amount of each phase present in the structure.

One of the general observations on the specimens containing boron was related to their dendritic structure. The size and shape of such a structure was a function of the degree of undercooling at the onset of crystallization. This reaction was directly affected by the boron content, the method of casting, and the pouring temperature. The direction and size of the dendritic structure were affected by the heat flow direction.

The structure of the metal at the heat-affected zone was also influenced by the boron content of the base metal. The microstructural observation of the heat-affected zone revealed the generation of a supersaturated structure of iron-boron-carbon alloy. This structure was formed when the liquidized iron was accommodating the melted elements of carbon and boron and was frozen with a rate high enough to prevent complete diffusion and segregation of the carbon, boron, ferro-boron (FeB), and oxides of other elements from the iron matrix. The trapped elements joined together as a compound or, as in the case of carbon, formed a distorted structure. The presence of such structures was related to their relative amounts as an element in the alloy. Further, the addition of boron reduced the presence of iron carbide in the structure.
Figure 45. Microphotographs of the segregated structures of the specimen with (a) 2.02 percent boron content and (b) 7.01 percent boron content.

Note. The comparison of the photographs shows an increase in the segregated structures (shown as black area) as a function of the boron content. Etched with two percent nital. Magnification 744X.
Figure 46. Microphotograph of the microcracks generated from the segregated structure.

Note. The direction of the microcracks was random. As shown in the photograph, they always started from a segregated structure and continued to the next such structure. Etched with two percent nital. Magnification 744X.
CHAPTER V
Summary, Conclusions, and Recommendations

Summary

The exploration of techniques using laser processing to produce an amorphous metallic layer on the surface of ferritic gray cast iron, alloyed with boron, was the topic of this investigation. In this study, continuous and pulsed beams of an industrial carbon dioxide laser were utilized to form amorphous layers on the surface of ferritic gray cast iron alloyed with boron. It was believed that the highly concentrated laser beam and the consequent rapid solidification, in addition to the boron acting to retard nucleation, would provide the optimum conditions needed for the formation of amorphous metallic surfaces.

The experimental method used in this investigation was to cast specimens with various amounts of boron ranging from zero up to 10.10 percent by weight. The specimens were heat treated for several purposes: (a) to transform the gamma-iron to alpha-iron, (b) to break up the clusters of impurities in the structure, and (c) to relieve the internal stress which may be generated by rapid solidification of the mold. Emission spectroscopy was used to identify the exact chemical composition of the cast specimens. This examination provided information pertaining to the effective range of boron content in this process. This information also was used to identify the effect of the boron content on glass formability, mechanical properties, and the microstructural characteristics of the specimens.
The laser treatment was performed with various parameters, including laser power, transverse speed of the laser, depth of focus, and cover-gas flow. The optimum parameters were identified, recorded, and used for the treatment of the workpieces. The subsequent series of tests, including chemical examination, x-ray diffraction tests, scanning electron microscopy, and electron diffraction spectroscopy, revealed the formation of saturated and supersaturated structures at the laser heat-affected zone when the laser was operating at the continuous mode and the generation of amorphous structures when the laser was operating at the pulsed mode. The hardness and micro-hardness tests provided information related to the hardness profile of the specimens prior to and after laser processing.

Conclusions

The general conclusion drawn from the study is that the formation of metallic glasses is possible within the constraints of the quenching rates generated in the process. The dissipation of heat during the self quenching process always limits the depth of the metallic glass layer to less than a few thousandths of an inch.

The conclusions drawn from the results of the tests are listed below:

1. An industrial carbon dioxide laser with power output of up to 1300 watts and a wavelength of 10.6 microns is capable of producing an amorphous metallic layer on the surface of gray cast iron. Such
metallic glass can be formed when the lasers are operating at the pulse mode with output power of 600 watts and a short pulse \((7 \times 10^{-1} \text{ to } 11 \times 10^{-1} \text{ milliseconds})\) and long dwell time.

2. The laser processing under the pulse mode generated a heat-treated layer with non-uniform depth on the surface of the specimens. To improve the quality of the surface, the dwell time had to be reduced or the laser had to be operated at the continuous mode.

3. Laser processing with the continuous mode is a useful technique for the production of saturated and supersaturated structures by the method of rapid solidification of the treated metal surface.

4. The element of boron is a determining factor in the glass formability of cast iron. The most effective boron content was identified to be between 3.8 (eutectice composition) and 4.17 percent by weight.

5. Addition of boron to the cast iron caused internal stress leading to generation and propagation of micro-cracks throughout the specimens.

6. The grain size of the structure is directly affected by the boron content of the specimens. Addition of boron tended to produce finer micro-structures.

7. Boron added to the molten metals tended to substitute for carbon, causing the diffusion of this element outside the matrix. This excess carbon can diffuse outside of the structure as a powdery material mixed with the oxide of other elements or may be trapped inside the structure as a segregated microstructure.
8. The image analysis of the seven different specimens showed that there is a direct relationship between the boron content and the presence of this segregated structure.

9. Hardness measurements were performed on the heat-affected zone of the seven types of specimens. The results indicated that the melted regions were much harder than the base metal, and the metal with the higher boron content showed the higher hardness measurement.

10. Even though the micro-hardness was increased as a function of boron content before laser treatment, the specimen with 2.02 percent boron has the highest hardness measurement.

11. Addition of more than 2.02 percent boron prior to laser treatment reduced the hardness of the specimens.

12. Micro-hardness measurement of seven different specimens indicated a Vikers hardness number (VHN) of 1098 for samples without boron. This hardness is approximately 5 times more than that of the base metal.

13. The maximum micro-hardness of 1952 VHN was measured at the heat affected zone of the sample containing 7.01 percent boron. This hardness number is more than twice the hardness number of common steels.

14. The depth of penetration of the specimens were affected by the boron content. An increase in boron content reduced the depth of penetration. The maximum depth of $13.8 \times 10^{-4}$ inches was measured on the specimens without boron. Under the same conditions, the specimens with 7.01 percent boron had a depth of $3.1 \times 10^{-4}$ inches.
15. The depth of melt at the heat-affected zone was a function of the transverse speed of the laser for various specimens. A speed of less than 80 inches per minute produced unacceptable melting while a speed exceeding 400 inches per minute produced unacceptably shallow depth (less than 0.001 in.).

16. The heat treatment of the specimen with high boron content caused thermal stress that led to microcracks in the specimen.

17. The laser produced a supersaturated structure different than that of the conventional heat-treatment process.

18. The addition of boron to the specimens proved to have a substantial effect on the glass formability of the specimens. However, the presence of boron in excess of five percent by weight generated microcracks in the specimen.

19. The addition of boron to the molten alloys caused the substitution of this element for the heavier, less reactive elements. These elements diffused outside of the matrix as slag or within the matrix as undesirable segregated structures.

20. The presence of boron as an alloying element increased the hardness and brittleness of the formed specimens.

21. The percent boron content of the specimens was a determining factor in the type of resulting micro-structure. Less than 0.015 percent boron can be accommodated in the matrix of iron, resulting in alpha-iron. Further addition of boron up to eight percent by weight produced alpha-iron and a new phase of the Fe$_2$B compound. The
specimens with a boron content exceeding 7.8 percent produced the iron boron compounds of $Fe_2B$ and $FeB_{19}$.

22. The electron diffraction spectro-analysis of the specimens without boron prior to laser treatment indicated two distinguishable microstructures, an iron-based structure and a graphite structure.

23. The scanning electron microscopy of the specimens containing 4.17 percent boron showed three microconstituents. They were believed to be (a) alpha-iron, (b) $Fe_2B$ compound, and (c) a distorted structure with undissolved elements including carbon, aluminum, silicon, and manganese in the form of oxide.

24. The effect of laser treatment in conjunction with boron content produced uniform supersaturated structures with high resistance to acidic solutions. These supersaturated structures did not conform to the microstructures predicted by the iron-boron-carbon ternary diagram.

25. The electron diffraction spectro-analysis of the specimen with 4.17 percent boron content revealed three distinguishable supersaturated structure of iron, boron with silicon, and phosphorus.

26. The addition of boron up to 7.1 percent by weight to the samples caused retardation of nucleation resulting in formation of two distinguishable structures of iron, boron, silicon, ternary alloys. These structures contradict the microstructure predicted by the iron-boron-carbon ternary diagram.

The findings of this investigation as related to the method of production can be outlined as follows:
1. The compound added to the charge must be free of elements in the form of an oxide. The addition of oxygen in any form to the charge causes the generation of boro-silicate glass as a gummy slag on top of the crucible, making it impossible to pour the desired specimens.

2. The sand casting used in this process had a quenching rate resulting in thermal stress within the specimens. Boron also can be a contributing factor in such thermal stress.

3. These excessive thermal stresses led to the initiation of cracks and their propagation within the cast specimens.

4. A secondary heat treatment for full annealing was required to eliminate such thermal stress.

5. The chemical analysis of the specimens indicated the presence of undesirable elements such as aluminum and lead in the structure. These undesirable elements were introduced into the structure by the addition of recycled gray cast iron and ferro-boron.

Recommendations

The study completed the first phase of research which may lead to the use of lasers in producing glassy layers on the surface of metals. There is much more work to be done to gather data and develop a reliable method for laser production of metallic glass layers.

Further research might be directed to the areas listed below:
1. The quenching rate is one of the major setbacks in the production of thick metallic glass. The design of a secondary instrument to improve thermal transformation could greatly advance the production of this type of material.

2. The appropriate technique for introducing boron in the structure of cast iron is a subject needing further investigation. A goal of this study was to identify the role of boron in the glass formability of the cast iron. The present data might provide insight into the development of a cost-effective process, such as physical vapor deposition, chemical vapor deposition, or sputtering deposition, to form a surface layer rich in boron. These processes presently are available and can be substituted for the casting process in future investigations. With these techniques it may be possible to deposit the appropriate amount of boron, or ferro-boron, to the depth required without causing the bulk metal to become brittle. At the present there is no data available related to such processes. The development of such data could greatly affect the quality and durability of the final product.

3. Transmission Electron Microscopy, further x-ray testing, and Electron-beam micro-probe can give further information in this area.

4. The metallic glasses are a non-equilibrium type of material. They have higher internal energy, which results in the tendency to transform into stable equilibrium state. The thermal stability of the metallic glasses is another area which needs further research.
5. The ferrous metallic glasses show promising electrical and thermal properties. Investigating these properties of the amorphous material might lead to the application of this method in electronic industries.

6. The rapid quenching process associated with the formation of metallic glasses has the potential for generation of thermal stress leading to propagation of microcracks on the formed surface. The development of a process for preventing these cracks or a heat treatment to relieve such residual stresses would greatly advance the industrial application of this method of production.

7. Instrumentation also needs research. The present industrial application of laser technology consists of cutting, welding, engraving, and heat treating. The instrumentation, hence, is developed to meet the requirements of such processes. Laser production of metallic glass requires a new instrumentation, such as optical thermometer, with specifications suitable for production of these types of materials.
References


### List of Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
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<tbody>
<tr>
<td>A</td>
<td>Area</td>
</tr>
<tr>
<td>ASM</td>
<td>American Society for Metals</td>
</tr>
<tr>
<td>ASTM</td>
<td>American Standards for Testing and Materials</td>
</tr>
<tr>
<td>A/r\text{m}</td>
<td>Attraction energy</td>
</tr>
<tr>
<td>B/r\text{r}</td>
<td>Repulsion energy</td>
</tr>
<tr>
<td>C</td>
<td>The equation constant</td>
</tr>
<tr>
<td>c</td>
<td>The speed of light</td>
</tr>
<tr>
<td>C_f</td>
<td>The conversion factor</td>
</tr>
<tr>
<td>CNC</td>
<td>Computer Numerically Controlled machine</td>
</tr>
<tr>
<td>E</td>
<td>Energy of photon</td>
</tr>
<tr>
<td>E_0</td>
<td>Bonding energy</td>
</tr>
<tr>
<td>D</td>
<td>Diameter of the disk</td>
</tr>
<tr>
<td>D_0</td>
<td>Diameter of the focused spot</td>
</tr>
<tr>
<td>d</td>
<td>Linear speed in steps</td>
</tr>
<tr>
<td>d_0</td>
<td>Diameter of the raw beam</td>
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<tr>
<td>E_r</td>
<td>Radiant energy in watts</td>
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<tr>
<td>f</td>
<td>Focal length of the lens</td>
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<tr>
<td>G</td>
<td>Gibbs Free Energy</td>
</tr>
<tr>
<td>H</td>
<td>Enthalpy</td>
</tr>
<tr>
<td>h</td>
<td>Coefficient of thermal conduction</td>
</tr>
<tr>
<td>h_c</td>
<td>The convection coefficient</td>
</tr>
<tr>
<td>HAZ</td>
<td>Heat-Affected Zone</td>
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HVN  Vickers Hardness Number
I-TM  Inter-transition-metal system
K  Conductivity of the cover-gas
k  Plank's constant
L  Distance contact
Lm  Distance from midpoint to surface
S  Entropy
s  Circular speed
Nb/h  Biot number for heat transfer
ro  Atomic radius for minimum internal energy
r1  Radius of the laser beam at the surface
r2  Radius of the fusion zone
RE-TM  Rare Earth-Transition metal alloys
SEM  Scanning Electron Microscopy
st  Steps
TEM  Transmission Electron Microscopy
TM-M  Transition Metal-Metalloid alloys
t  Time
T  Temperature of metal at fusion zone
Tb  Vaporization Temperature
g  Glass transition temperature
Tl  Fusion temperature
Tm  Temperature of the medium
Tp  Liquid transition temperature
\( T_{rg} \) The ratio of the glass to liquidus temperature

\( T_s \) Temperature of the surface

\( T_1 \) Temperature at the center of fusion zone

\( T_2 \) Temperature at substrate

\( \frac{dT}{dt} \) The quenching rate

\( u \) Viscosity of the cover-gas

\( V \) The laser scanning velocity

\( v \) Vibration

\( W \) Weight

\( \lambda \) Wave length of the laser radiation

\( \lambda_0 \) X-ray wave length
Appendix B

Chemical Analysis of

the Samples
### FOUnDRY PROCESS CONTROL CHEMICAL ANALYSIS REPORT

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>C</th>
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<th>P</th>
<th>S</th>
<th>Mn</th>
<th>Ni</th>
<th>Cr</th>
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<td>.014</td>
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<td>.001</td>
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<td>.022</td>
<td>.573</td>
<td>.303</td>
<td>.236</td>
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<td>.016</td>
<td>.025</td>
<td>.051</td>
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<td>.021</td>
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<td>.313</td>
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<td>.141</td>
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<td>.024</td>
<td>.024</td>
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<td>.015</td>
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<td>10%</td>
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<td>3.18</td>
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<td>.009</td>
<td>.752</td>
<td>.283</td>
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<td>.136</td>
<td>.205</td>
<td>.060</td>
<td>.023</td>
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<td>.013</td>
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<tr>
<td>12%</td>
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<td>.048</td>
<td>.011</td>
<td>.734</td>
<td>.327</td>
<td>.376</td>
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<td>.239</td>
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<td>.025</td>
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**Comments:**

**Analyst:** [Signature]

**Approved:** [Signature]
Appendix C

Laser Parameters
Laser and Equipment Parameters

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<thead>
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<th>Date</th>
<th>March 15 1985</th>
<th>By</th>
<th>Majid T. Tabrizi</th>
<th>ILT Order No.</th>
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<tbody>
<tr>
<td>Name</td>
<td>Research Project</td>
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<td></td>
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<tr>
<td>Part No.</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Material/Description</td>
<td>Gray cast iron and gray cast iron alloys with boron</td>
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<tr>
<td>Process</td>
<td>Laser treatment</td>
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Laser Mode: Ring Gaussian X Mode check

<table>
<thead>
<tr>
<th>Gas Panel: Open Cycle</th>
<th>Recirc</th>
<th>Previous settings</th>
<th>See</th>
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</thead>
<tbody>
<tr>
<td>Gas settings He, CO2</td>
<td>N.</td>
<td>Torr C Pot M.A.</td>
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<tr>
<td>Lens: f.l. 5</td>
<td>Type</td>
<td>No.</td>
<td></td>
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<tr>
<td>Gas Nozzle: Orifice 0.010</td>
<td>Type: Cyl.</td>
<td>Cone Nozzle clearance</td>
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<tr>
<td>Gas: Type</td>
<td>Pressure: PSI</td>
<td>CFM</td>
<td></td>
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<tr>
<td>Cover gas: Type Argon</td>
<td>Pressure: PSI</td>
<td>30PSI CFM</td>
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<td>Cover gas delivery:</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Lens head position: High Low x Tube above lens mount 5 inches</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Focus: On surface X Above surface Below surface</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dial indicator</td>
<td></td>
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<tr>
<td>Table plate or fixture:</td>
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<td></td>
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<tr>
<td>Handrel: RPM Motor RPM</td>
<td>FWD</td>
<td>REV. Motor ramp up</td>
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<td>Handrel position:</td>
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<td>Ramper: Up</td>
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<td>Burst count 90-99</td>
<td>Pulse on 1.0</td>
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<tr>
<td>Dwell</td>
<td>510</td>
<td>Interval 1</td>
<td>Pulse off .1</td>
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<tr>
<td>Down</td>
<td>100</td>
<td>1</td>
<td>Count</td>
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<tr>
<td>Power: Current Pot 600</td>
<td>Milliamps</td>
<td>Power Meter</td>
<td></td>
</tr>
<tr>
<td>OFF Delta Pot 620</td>
<td>Total Amps</td>
<td>Power Meter</td>
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<td>Computer Program: Special disk</td>
<td>Magtape No.</td>
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<tr>
<td>Feed Rate % (NFO) 10-100</td>
<td>Programed Speed P 1200</td>
<td>Actual Speed IPM 10-100</td>
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<tr>
<td>Notes:</td>
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</tbody>
</table>
Appendix D

The Computer Program for

Calculating the Quenching Parameters
PROGRAM HEATPATTERN(INPUT, OUTPUT);

(* THIS PROGRAM WILL CALCULATE AND LIST THE VALUES *)
(* OF THE X AND Y FOR EACH C CONSTANT. THE N IS *)
(* THE LEVEL OF PRECISION WHICH YOU MAY WISH TO HAVE*)

VAR
  C : INTEGER; (*LASER POWER FUNCTION*)
  I : INTEGER; (*PROGRAM CONSTANT *)
  N : INTEGER; (*DIFFRENCIAL CONSTANT*)
  X : REAL; (*DISTANCE IN X DIRECTION*)
  Y : REAL; (*DISTANCE IN Y DIRECTION*)
  TEMP : REAL;

BEGIN
  WRITELN ('WHAT IS THE VALUE OF N DIVISION');
  READLN (N);
  WRITELN ('WHAT IS THE VALUE OF C CONSTANT');
  READLN (C);
  x := 0.0;
  WRITELN ('THE VALUES ARE X Y');
  FOR I := 1 TO N DO
    BEGIN
      Y := -C / (SQRT(X) + 1);
      WRITELN(', X:17:5, Y:17:5');
      WRITELN('');
      X := X + C/N
    END
  END
PROGRAM AREACONT(INPUT, OUTPUT);

(* THIS PROGRAM CALCULATES THE AREAS *)
(* WHEN LASER OPERATES WITH THE *)
(* CONTINUOUS MODE *)

VAR

I: INTEGER; (* PROGRAM VARIABLE *)
C: INTEGER; (* FUNCTIONS OF POWER *)
N: INTEGER; (* THE NUMBER OF DIVISIONS *)
A : REAL; (* THE THERMAL DIFFUSIVITY *)
B : REAL; (* THE VELOCITY IN Z DIRECTION *)
D : REAL; (* THE DISTANCE IN X DIRECTION *)
X: REAL; (* THE DISTANCE IN Y DIRECTION *)
Y: REAL; (* THE DISTANCE IN Z DIRECTION *)
Z: REAL; (* THE DISTANCE IN Z DIRECTION *)
T: REAL; (* THE TIME IN SECOND *)
TH: REAL; (* THE ELEVATED TEMPERATURE *)
K : REAL; (* THE PROGRAM CONSTANT *)
L : REAL; (* THE PROGRAM CONSTANT *)
AREA: REAL; (* THE AREA UNDER THE CONDUCT. *)
TEMP: REAL; (* THE MAXIMUM TEMPERATURE *)
SPEED: REAL; (* LASER TRANS. SPEED *)
LENGTH: REAL; (* LENGTH TRAVELED *)
DIVLENGTH: REAL; (* THE ACCURACY CONST.*)
QUENCHRATE: REAL; (* QUENCHING RATE *)
TIMEINTERVAL: REAL; (* TIME INTERVAL *)

BEGIN

LENGTH := 0.0;
X := 0.0;

WRITELN('***********');
WRITELN('WHAT IS N DIVISION DO YOU LIKE?');
READLN(N);
WRITELN('THE N DIVISION IS. ', N);
WRITELN('WHAT IS C CONSTANT DO YOU CHOSE?');
READLN(C);
WRITELN('THE VALUE OF C CONSTANT IS. ', C);
WRITELN('WHAT IS LASER VELOCITY IN IN/MIN?');
READLN(V);
WRITELN('THE LASER SPEED IS. ', V);
WRITELN('WHAT IS TEMPERATURE AT FUSSION ZONE?');
READLN(T);
WRITELN('THE TEMPERATURE AT FUSION ZONE IS. ', T);
WRITELN('WHAT IS THE THERMAL DIFFUSIVITY. ', D);
READLN(D);
WRITELN(' THERMAL DIFFUSIVITY OF METAL IS. ', D);
WRITELN('***********');
AREA := LENGTH * SPEED * TIMEINTERVAL;
WRITELN ('THE SURFACE ARE UNDER THE CONT. MODE IS. ',
AREA := 20:15 )

END
PROGRAM AREACONT(INPUT, OUTPUT(LF\N=\l));

(* ***************************************************************)
(* THIS PROGRAM CALCULATES THE SURFACE AREA UNDER *)
(* CONDUCTION WHEN LASER OPERATES AT CONTINUOUS MODE *)
(* ***************************************************************)

VAR

I: INTEGER;
C: INTEGER;
N: INTEGER;

L: REAL;
X: REAL;
Y: REAL;
T: REAL;
K: REAL;
AREA: REAL;
TEMP: REAL;
SPEED: REAL;
LENGTH: REAL;
DIVLENGTH: REAL;
TIMEINTERVAL: REAL;

BEGIN

LENGTH := 0.0;
X := 0.0;

WRITELN ('WHAT IS THE N DIVISION DO YOU LIKE?');
READLN(N);
WRITELN ('THE N DIVISION IS. ', N);
WRITELN ('WHAT IS THE C CONSTANT DO YOU CHOSE?');
READLN(C);
WRITELN ('THE VALUE OF C CONSTANT IS. ', C);
WRITELN ('WHAT IS THE LASER SPEED IN IN/MIW?');
READLN (SPEED);
WRITELN ('THE LASER SPEED IS. ', SPEED);
WRITELN ('WHAT IS THE TIME INTERVAL IN SECOND?');
READLN (TIMEINTERVAL);
WRITELN ('THE TIME INTERVAL IS. ', TIMEINTERVAL);
BEGIN

FOR I:= 1 TO N DO
BEGIN

Y := -C / (SQR(X) + 1);
TEMP := Y;
T := TEMP - Y;
K := 'SPEED / 60.0';
L := C / N;
DIVLENGTH := (SQR(SQR(T)+SQR(K*L)))/1000;
LENGTH := LENGTH + DIVLENGTH;
X := X + L

END

END
BEGIN
FOR I := 1 TO 10 DO
BEGIN

Y := -C / (X * X + 1);
TEMP := Y;
A := TEMP - Y;
K := V / 60.0;
DIVLENGTH := (SORT(SQR(A) + SQR((K*C)/N))) / 1000;
LENGTH := LENGTH + DIVLENGTH;
X := X + (C / N);

WRITELN ('**********');
WRITELN ('VALUE OF X CALCULATED AS:', X);
WRITELN ('VALUE OF Y CALCULATED AS:', TEMP);
Z := V*1000/(60); (*VELOCITY IN/SEC*1000 *)
B := SORT(SQR(X) + SQR(TEMP) + SQR(Z));
QUENCHRATE := (-V)*(X/SQR(B)) + V/(2*D) *
(1 + (X/SQR(B))) * T;
WRITELN ('THE QUENCHING RATE ON THE BASE OF');
WRITELN ('MAZUMDER EQUATION IS', QUENCHRATE);

WRITELN ('**********');
END;
WRITELN ('**********');
AREA := LENGTH * V * T;
WRITELN ('THE SURFACE ARE UNDER THE CONT.');
WRITELN ('MODE IS.', AREA : 20:19);

END
END.
PROGRAM SURFACEATPULS(INPUT, OUTPUT);

CONST
  P = 3.141596;

VAR
  N : INTEGER;
  C : INTEGER;
  I : INTEGER;
  L : REAL;
  X : REAL;
  Y : REAL;
  T : REAL;
  K : REAL;
  TEMP : REAL;
  SPEED : REAL;
  AREAOFDISC : REAL;
  SURFACEAREA : REAL;
  LENGTHOFDISC : REAL;
  TIMEINTERVAL : REAL;

BEGIN
  WRITEln('WHAT IS THE N DIVISIONS?');
  READln(N);
  WRITEln('THE N DIVISION IS. ', N);
  WRITEln('WHAT IS THE C CONSTANT?');
  READln(C);
  WRITEln('THE C CONSTANT WAS. ', C);
  WRITEln('WHAT IS THE LASER SPEED, INCH PER MIN. ?');
  READ(SPEED);
  WRITEln('THE LASER SPEED IS. ', SPEED);
  WRITEln('WHAT IS THE TIME INTERVAL, IN SECOND ?');
  READ(TIMEINTERVAL);
  WRITEln('THE TIME INTERVAL IN SECOND WAS. ', TIMEINTERVAL);
  X := 0.0;
  SURFACEAREA := 0.0;
  L := C / N;
  FOR I := 1 TO N DO
    BEGIN
      Y := C / (((SGR(X) + 1) * 1000);
      LENGTHOFDISC := (2 * P * X) / (1000);
      AREAOFDISC := LENGTHOFDISC * Y;
      SURFACEAREA := SURFACEAREA + AREAOFDISC;
      X := X + L
    END;
  WRITEln('THE SURFACE AREA UNDER THE PULSE MODE WAS');
  WRITEln(' ', SURFACEAREA :20:15)
END.