Development of an Innovative Laser-Assisted Coating Process for Extending Lifetime of Metal Casting Dies

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1.0 EXECUTIVE SUMMARY

This is the final technical report submitted by Karta Technologies, Inc. 1892 Grandstand, San Antonio, Texas 78238 to the Department of Energy (DoE), Oakland Operations Office, 1301 Clay Street, Room 700N, Oakland, CA 94612-5208, under SBIR Grant Number:.DE-FG03 98 ER 82604. The period of this contract was from 9/2/1998 to 4/12/1999. The principal investigator was Dr. Madhav Rao Govindaraju.

Die casting dies used in the metal casting industry fail due to thermal fatigue cracking accompanied by the presence of residual tensile stresses, corrosion, erosion and wear of die surfaces. Failure of dies results in lost production time, reduction in quality of casting, and expensive replacement costs. Prevention of such failures to extend the lifetime of metal casting dies is critical to the industry.

Since most of the damage occurs at contact surfaces of the die with the molten metal, surface coatings could protect these dies. Current techniques used for coatings include ion implantation, plasma-spraying, pack cementation, and chemical and physical vapor deposition techniques. However, these conventional coating techniques are often unable to ensure adequate long-term protection to die surfaces. Coatings by these techniques have problems such as poor bonding, inadequate thickness and lack of thermochemical/thermomechanical compatibility with the substrate. Hence, there exists a need to develop novel surface coating technologies to improve the service life of die casting dies.

The primary objective of this Phase I program was to explore the feasibility of developing an innovative laser coating technology for improving die performance and to extend their life. The technique involved a laser coating process to deposit a protective coating followed by a laser shot peening step to eliminate the surface residual tensile stresses. The chemical, physical, surface properties, and performance of the coated dies were tested in simulated metal casting conditions.

During the Phase I study, Karta developed the processes of laser glazing, laser coating with TiC powders of three different sizes, viz., 30μm, 2μm, and 50 nanometers (nm) (~0.05μ), and laser shot peening of laser-coated samples. The study was done on H13 die material, which is a commonly used in the die casting industry. The processes of laser glazing and laser coating were developed using a CO_2 laser. Laser shot peening was performed using a pulsed Nd:YAG laser. The objective of the laser glazing process was to produce amorphous or rapidly solidified zones at the surface. The process of laser coatings with powders of TiC resulted in forming thick coatings. Coatings with finer powders produced thinner coatings, higher surface hardness, and the improved surface smoothness.

The coated samples were characterized by optical and scanning electron microscopy. The microhardness was determined by the Vickers hardness test method. The corrosion and erosion properties of coated samples in aggressive casting conditions were evaluated by testing the samples in molten A390 aluminum melt. The weight loss in samples due to corrosion and erosion was used to compare the performance of samples coated by different techniques.

The results indicate a general increase in surface hardness of the substrate with laser processing. The increase in hardness is more pronounced for the samples laser coated with fine powders of TiC. Laser glazed samples, showing a fine rapidly solidified microstructure in the surface layers showed an enhancement in hardness and corrosion resistance in aluminum A390 melt. Surface alloyed samples having a complex alloy phase consisting of TiC and other intermetallic compounds in the surface regions showed higher hardness, improved corrosion and erosion resistance. The improvement in corrosion resistance in molten aluminum is more remarkable for samples coated with nanocrystalline powders. The increase in corrosion resistance for samples coated with nanocrystalline powders is approximately 85% over uncoated samples. Samples coated with nanocrystalline powders also showed an enhanced erosion resistance. The enhancement in properties of samples with coatings having nanocrystalline powders can be attributed to the higher hardness, smoother surface finish, uniform and homogeneous coating microstructure. Laser shot peening of surface coated samples resulted in improved corrosion resistance. This improvement could be attributed to the presence of compressive stresses in the surface region.

The results of this research have demonstrated that laser coatings produced in Phase I investigation are beneficial in improving corrosion, erosion, and thermal fatigue resistance. The technology developed in this research can have a significant impact on the casting industry by saving the material costs involved in replacing dies, reducing downtime and improving the quality. The technology is versatile and can be extended to materials or components used in other industrial applications.

2.0 INTRODUCTION

The metal casting industry produces about 13 million tons of castings annually, valued in excess of $25 billion. Major users of these metal castings include the automotive industry, industrial machinery manufacturers, and aerospace industries. The industry employs nearly 217,000 people, and is dominated by small business [1]. In order to remain competitive, the industry is striving to improve productivity and reduce its production costs. One of the problem areas recognized by the casting industry is the die life.

Die life has a major impact on the production cost of die cast components, with the cost of die contributing an estimated 10% or more of the cost of a die casting. Most die casting dies used in the metal casting industry fail prematurely from thermal fatigue cracking. These thermal fatigue cracks are accompanied by the presence of residual tensile stresses, corrosion of die surface, or oxidation of the metal, and are accelerated by the high temperature of the die. Failures of die casting dies result in lost production due to downtime, die replacement and repair. The quality of the castings is also affected by poor casting surface finish and casting accidents due to broken die inserts. Prevention of such failures to extend the lifetime of die casting dies, which are very expensive, is very critical to the industry.

Since most of the damage occurs at contact surfaces of the die with the molten metal, surface coatings could protect these dies. Current techniques used for coatings include ion implantation, plasma-spraying, chemical and physical vapor deposition techniques. However, these conventional coating techniques are often unable to ensure adequate long-term protection to die surfaces. Coatings by these techniques have problems such poor bonding, inadequate thickness and lack of thermochemical compatibility with the substrate. Hence, there exists a need to develop novel surface coating technologies to improve the service life of die casting dies.

In this Phase I project, Karta proposed to develop an innovative coating technology using lasers for depositing protective coatings on die castings dies to improve their performance and extend their life. The primary goal of the proposed work was to develop a methodology for producing surface protecting coatings on die casting dies to improve the die performance. The produced coatings should be capable of withstanding the harsh environment of die casting, including repeated exposure to heating and cooling cycles, without cracking or spalling.

3.0 BACKGROUND

In this section, a brief description of common defects in die casting dies is provided. We will review currently used coating processes and delineate their shortcomings. The advantages of the laser surface modification processes are outlined. Karta's laser coating process to improve die performance is described.

3.1 Major Wear Mechanisms of die casting dies

In die casting, the metal is not poured into the mold (as is done in permanent molding or sand casting) but is injected under high pressures from 1000 to 100,000 psi. High production rates are made possible by using the die-casting process, from 100 to 500 cycles an hour and production commonly reaches 300,000 parts an hour. Die wear is a common problem in these dies due to the inherent multiple reuses of dies, high flow velocities of molten metal into the die cavity and rapid solidification of the molten metal leading to large thermal gradients. The major wear mechanisms in die casting dies are shown in figure 1. These mechanisms are (i) erosion, (ii) heat checking (thermal cracking), (iii) soldering and (iv) corrosion and oxidation [3].

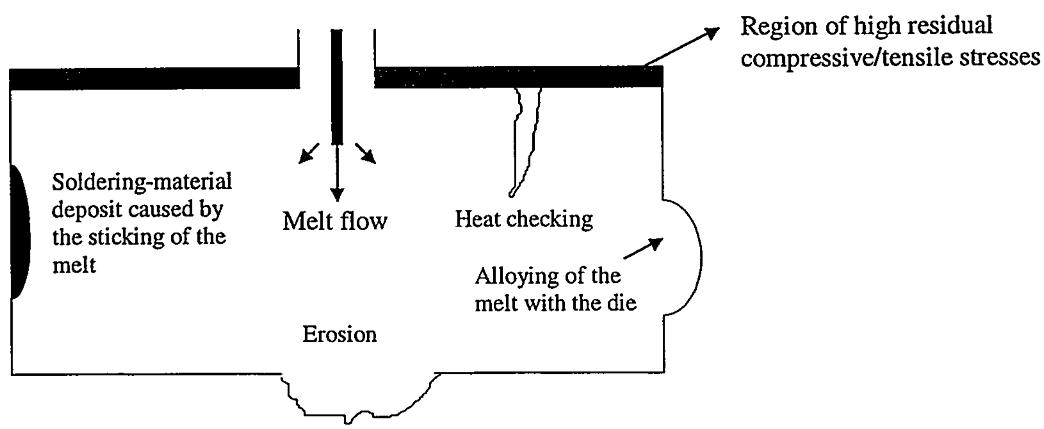


Figure 1. Schematic diagram of the different wear mechanisms in die casting dies

3.1.1 Erosion

Erosion in casting dies occurs as a result of the impact of the liquid metal. During the casting process the molten metal impinges the die cavity at high velocities causing erosion. Erosion reduces the ability to maintain close dimensional tolerances and affects the surface quality of the castings. The hardness of the component can have significant effect on the erosion behavior. Erosion generally accelerates with the increase in melt temperature and degree of melt turbulence.

3.1.2 Heat checking

Heat checking (also called thermal cracking) is caused by thermal fatigue. The surface regions of the die are under a state of high thermal fatigue due to alternate heating and cooling cycles associated with solidification of the melt. The die surface will be in compression during heating and tension during cooling of the die. These variations in surface stress condition results in formation of thermal cracks leading to eventual die failure.

3.1.3 Soldering

Soldering is the deposition of metal on the die surface caused by the sticking of the melt. This occurs as a result of the chemical interaction between the melt and the die surface during the solidification process.

3.2 Die Surface Protection Techniques

A variety of techniques are currently being used to extend die life, these include: surface coatings, shot peening of die surface to change the stress state, improving the heat treatment processes to impart higher toughness to die steels, improving the quality of lubricants used in the metal casting process, and changing the die geometry to reduce the intensity of wear. These techniques have been used independently or in combination with one another. However, the most commonly used strategy is surface protection coating. A comprehensive review of the coating methods and materials is given here.

3.2.1 Surface Coating Methods and Materials

In general, the requirements for an ideal coating for surface improvement are [4]:

- Excellent bonding between the coating and the substrate for longer life.
- Compatibility of thermophysical characteristics of coating and substrate.
- Adequate thickness to ensure long service life without delamination problems.
- Absence of any porosity to ensure high corrosion and oxidation resistance.
- Good mechanical properties (hardness, ductility, fatigue strength, shear strength and ultimate tensile strength).
- Good thermal and impact shock resistance.
- High thermal conductivity for quick dissipation of heat from the interface.
- Good dimensional stability.
- Low surface wear.

The surface coating methods can be categorized into three main categories: thick-film coatings by thermal spraying; thin-film coatings by physical and chemical vapor deposition (PVD and CVD); and ion-beam processing for ion implantation and ion-assisted coatings [5].

CVD relies on the dissociation of a mixture of precursor gases to deposit a thin layer of the coating material. Dissociation is induced by high temperature, or at low temperatures by rf or dc plasma. Examples of CVD coating are SiO_2 and TiB_2 for corrosion resistance; SiC, Si_3N_4 and TiN for wear resistance; and SiO_2 and Al_2O_3 for electrical resistance. CVD techniques are also employed to deposit high quality thin films of synthetic diamond.

PVD is a versatile process capable of depositing a wide range of coating materials. The PVD process produce surface layers that are the result of the deposition of individual atoms or molecules. The processes include vacuum evaporation, sputtering and ion plating [6]. These coatings can provide significant corrosion and erosion resistance to molten aluminum. Wang reports results of PVD coatings consisting of TiN, TiAlN, CrN on the die performance of H13 steels [7]. He reports that TiN coatings do not have long life because of low oxidation temperature and they provide poor heat checking resistance. It is likely that the influence of a coating on the heat checking resistance is determined by the substrate material and coating variables.

Ion implantation is another surface modification process used widely for improving the die life. Ion implantation is a low-temperature process, hence there is no thermal or dimensional changes in the samples. Ion implantation of steel and tungsten carbide tools with nitrogen can lead to an increase in resistance to abrasive wear [8]. Other surface coating processes currently being used are thermal diffusion [9], plasma spray process [10] and electrodeposition [11].

However, coatings produced by these conventional processes do not seem to have satisfied simultaneously all the listed requirements. For example, plasma-sprayed coated surfaces are prone to pitting due to weak bonding of the coating to the base metal. PVD coatings were shown to promote heat checking through the thermal fatigue crack initiation at the interface between the coating and substrate.

3.3 Laser surface Modification

Lasers are increasingly being used in diverse and broad applications ranging from eye surgery, to laser machining and laser guidance systems. Laser processing is a relatively new technique for modifying the near-surface region of materials. Typical laser processing techniques include transformation hardening, melting, cladding, alloying, coating, and smoothing. An excellent review of various laser processes and their applications in auto, aerospace and turbine industries is given by Singh [12].

Laser technology offers many advantages over other conventional processes for a number of reasons [13]:

1. Laser surface modification offers the possibility of tailoring the surface properties without changing bulk mechanical properties;
2. Production of novel surface alloys or structures that are unattainable by conventional processes;

3. Due to the nature of the process, scarce, expensive or critical materials can be conserved;
4. Production of near net shape processing with tailoring of material properties.

Lasers have been used in applications involving drilling, cutting, welding, surface hardening, shock hardening, surface alloying and cladding [14-20]. Laser surface alloying can produce different alloying composition and microstructural features on the surface of a substrate material, often resulting in improved wear, corrosion, and fatigue and impact resistance. It is often possible to obtain unusually fine microstructures, homogenization of microstructures, extension of solid solubility, and formation of nonequilibrium and amorphous phases [21, 22]. The high cost of a laser can be offset by using the same laser for many material processing applications through manipulating the laser process conditions. Laser parameters such as power density can be varied as a function of laser interaction time to obtain the required operating regions for various metal-processing operations.

3.4 Karta's Approach

As discussed in section 3.1, the metal casting dies fail mostly due to thermal fatigue cracking when the dies are exposed to reactive molten metals while operating under cyclic mechanical and thermal loading. These thermal fatigue cracks are accompanied by the presence of residual tensile stresses, corrosion of the die surface, or oxidation of the metal, and are accelerated by the high temperature of the dies.

Karta proposed an innovative approach to prevent die failures by a duplex process of depositing protective surface coatings by laser surface alloying followed by laser shot peening to eliminate the surface tensile stresses.

3.4.1 Step 1: Laser Surface Processing

The initial step of the proposed duplex process involves laser surface processing. The laser beam is focused onto the workpiece by an optical system and then scanned over the surface to be treated. During the short interaction time, this highly intensive energy source leads to a very local heating or melting of the material followed by a rapid cooling or solidification. The resulting surface properties depend basically on the chemical and microstructures formed at the surface layers during the processing.

Laser process can achieve a localized surface treatment limited to thin surface layers, typically 0.05-1 mm. This is mainly due to their very small and highly intensive heat source. In Phase I investigation, Karta has proposed to two different types of laser surface treatments. These are:

- Surface alloying of coating materials such as TiC with base metal, H13 die steel
- Surface glazing to produce rapidly solidified microstructure.

3.4.2 Laser surface coatings

The harsh environment of die casting process requires thicker coatings. These coatings will have improved corrosion, wear and thermal fatigue characteristics. In this technique, the alloying elements are applied as powders, either in loose powder form or pre-placed on the substrate as a thick slurry deposit.

The proposed process involves introduction of high melting carbides into the laser melt pool to form a complex surface coating. A schematic diagram of the process is shown in Figure 2. The complex coatings formed on the metal surface will provide the necessary erosion, corrosion and wear resistance properties. The process parameters must be selected according to the properties of the used components, and in particular the density of the carbides compared with the steel substrate, which determines the melt buoyancy.

Chemical composition of the carbides and/or metal powders, and the morphology of the powders significantly influences the physical, chemical and mechanical properties of the surface layer produced by this process. Hence, we proposed to investigate using two different types of TiC powders, which are commonly used as die coating materials. We compared commercially available powders of TiC with nanocrystalline TiC produced by the University of Idaho.

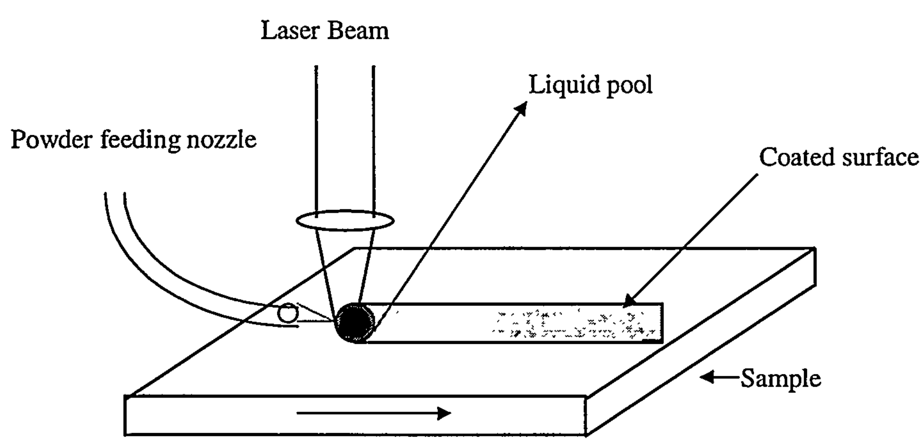


Figure 2. Schematic diagram of injection of alloy powders into a melt zone created by the high-power laser.

3.4.2.1. Nanocrystalline Powders of Titanium Carbides

Recent work at the University of Idaho has demonstrated the feasibility of synthesizing ultrafine carbides of metals and metalloids at ambient temperatures by mechanochemical processing [23]. The reaction:

$$\text{M-chloride} + CaC_2 \longrightarrow MC + CaCl_2 + C \qquad (1)$$

(where M is a transition metal or metalloid), is thermodynamically possible; but does not proceed in the forward direction, because of the unavailability of sufficient activation energy. Application of mechanical milling to the reactants *can* provide the necessary activation energy.

The general equation given above illustrates the basis for the synthesis of TiC. The typical equation for TiC is given below:

$$TiCl_4 + 2\,CaC_2 \longrightarrow TiC + 2CaCl_2 + 3C \qquad (2)$$

The reaction was induced and completed by mechanical milling of the reactants inside a Spex 8000 milling vial. Measurements of the vial temperature showed the start of the exothermic reaction after 12 minutes of milling. The reaction product consists of one mole of TiC and 3 moles of free carbon in a $CaCl_2$ matrix. The structural identity of carbon obtained from this reaction is still not clear. Some of the XRD peaks from carbon matched graphite while others cannot be matched with any of the carbon crystal structures. The by-product $CaCl_2$ is leached out sequentially by dilute formic acid and de-oxygenated water, with the aid of ultrasonic vibrator to enhance the dissolution of salt and a centrifuge to settle the leached fine powder in the leaching liquid.

This new powder produced by mechanochemical processing has many advantages over the conventional powders. These powders have barely detectable oxygen content thus imparting improved particle-wetting characteristics. The powders are much cheaper than the conventional powders. Because of their nanocrystalline nature, these powders are expected to demonstrate high mechanical properties.

3.4.3 Laser Glazing

In this process, our objective was to produce surface layers with a very fine microstructure, containing metastable and supersaturated phases. For certain alloys and high solidification speeds, it is even possible to obtain featureless crystalline or amorphous structures. The microcrystalline or amorphous structures have remarkable combination of properties as a result of their unusual atomic structure. Such properties include strength, hardness, ductility, toughness, and corrosion resistance.

Laser glazing process consists of melting a localized thin surface layer in intimate contact with a cold, solid substrate using a laser beam of high power density (10^5 - 10^8 W/cm^2) and short pulse time (10^{-5} - 10^{-8} sec). Laser glazing requires high incident power density of the order of that utilized welding, but with substantially shorter interaction times so that the heating effect is concentrated in a very thin region. Rapid surface melting occurs in a time during which little thermal energy penetrates into the base material. This leads to the development of extremely high thermal gradients, which promote rapid solidification of the melt. The pattern of solidification in laser glazed layers is that solidification starts at the melt layer/substrate interface and progresses towards the surface with continued cooling.

3.4.4 Step 2: Laser Shot Peening

It has been shown that heat checking or thermal cracking in the dies is mainly induced by residual tensile stresses caused by thermal cycling. The propensity to initiate cracks will be reduced if these stresses are reduced or relieved or changed from tensile to compressive in nature. This can be accomplished by shot peening process. Metalife, a commercial shot peening process has been successfully used for changing the die surface stress-state from tensile to compressive [2]. The penetration of compressive stresses was in the range of 0.25 to 0.38 mm.

Karta proposed laser shock processing as a part of the surface modification process, where a pulsed laser is used to irradiate the component to change the surface stress state from tensile to compressive. When a laser beam strikes the surface of the part, a high-stress shock wave is generated and propagates into the material. This shock wave produces a superficial plastic deformation in the surface. This surface deformation, which is similar to the mechanical effect induced by shot peening, work hardens the surface and creates residual compressive stresses extending 0.75 to 1.25 mm below the surface, which is several times the depth of conventional shot peening stresses. The advantages of this process over conventional shot peening include the absence of any surface roughness, or superficial particle inclusions and accessibility to process complex geometries. The deeper penetration of compressive stresses increases the material's resistance to fatigue, stress corrosion cracking and other surface-initiated failures. The improved surface texture will also provide better die wetting characteristics, thus improving die lubricity and metal flow.

4.0 TECHNICAL OBJECTIVES

The primary goal of the proposed work was to develop a methodology for producing surface protecting coatings on die casting dies. To meet this goal, several objectives were identified for the Phase I effort. These objectives were:

- Develop an innovative coating technology involving lasers for die casting dies. A duplex process will be developed involving laser shot peening and laser assisted coating process.
- Demonstrate the feasibility of using this methodology in providing the required surface protection for the die casting dies by testing and evaluating the chemical, physical and surface characteristics of the coatings.
- Examine and evaluate the advantages or disadvantages of using the duplex process in providing the required protection for the dies. This will be based on initial test results obtained on the coated and uncoated samples.
- Demonstrate the feasibility of using this methodology in providing the required surface protection for the die casting dies to withstand long exposures in the harsh environment of the die casting. This involves testing the coatings for erosion, corrosion, oxidation and heat checking.
- Select candidate coating materials and process for a comprehensive characterization and evaluation for Phase II.
- Develop strategic plan for developing and marketing the technology developed in Phase I (Phase II proposal).

5.0 OVERVIEW OF PHASE I WORKPLAN

The primary objective of this project was to develop surface protecting coatings for die casting dies. The following tasks were proposed originally to meet the project objectives.

5.1 Task 1 - Acquire specimens

We proposed to acquire die material commonly used in the casting industry. The material to be used in this project will be premium H-13 steel heat treated to North American Die Casting Association (NADCA) specifications. The composition of the H-13 steel is given in Table 1.

Table 1. Chemical composition of H-13 die steel

Element	C	Mn	Si	Cr	V	Mo
Wt%	0.4	0.4	1.1	5.0	1.1	1.0

5.2 Task 2- Development of Laser Processing Procedures

The laser processing part of this investigation was proposed to be conducted at Iowa State University (ISU). ISU has the required laser processing facilities needed for this project. PI was to design the experiments and use the ISU facilities for conducting and guiding the laser processing work.

In this task the experimental setup to develop a duplex laser process was to be configured. Table 2 gives the lasers to be used in this investigation. The first process involves developing the experimental plan for laser shot peening. The second process uses the laser coatings to modify the surface. Two types of laser surface modification processes were proposed to be investigated. These techniques are: laser surface alloying using powders of TiC and laser glazing to produce amorphous or microcrystalline regions in the surface layers of the die material. Based on the results of microscopical, mechanical and physical properties of the coated samples, we were to select one of these two laser surface modification processes for further experimentation.

Table 2. Specifications of Laser Systems to be used in the investigation

Laser type	Excimer	CO_2 (CW/Pulsed)
Wavelength, nm	193, 248, 308, 351	10600
Average Power, kW	0.05	1.5
Peak power, kW	20,000	5
Pulse repetition rate, Hz	1-100	1-100
Pulse time	nanoseconds	microseconds
Beam quality	Multimode	Gaussian

5.2.1 Step: 1-Laser Surface Coating Process

In this part of the Task 2, we proposed to evaluate two different types of laser surface modification processes. These processes are (1) Laser surface alloying (LSA), and (2) Laser glazing. The purpose of this step was to improve the surface characteristics of the die steels used in the casting industry. A CO_2 laser was to be used to conduct both the processes of laser surface alloying and laser glazing . CO_2 lasers are attractive because of their efficiency, better beam profile and small divergence.

5.2.2 Laser Surface Alloying

In this part of the task, we proposed to develop the laser processing methodology of depositing thick surface coatings consisting of TiC and other similar hard facing elements. Selection of these coating elements is important in this process.

The composition of the coating materials is very important in imparting the required surface protection for the die casting dies. Some of the requirements which needs to be considered for coating materials are:

- they should have a minimum mismatch in coefficient of thermal expansion (CTE)
- have low volatilization losses and be cost effective.
- chemical compatibility with each other coating materials and substrate

5.2.3 Step: 2-Laser Shot Peening

The laser shock surface treatment was proposed to be conducted using a nanosecond pulsed excimer laser. Use of excimer lasers have certain advantages for material processing applications. Excimer lasers emit in the ultraviolet region of the spectrum at six discrete wavelengths (157, 192, 222, 248, 308 and 351 nm). At these short wavelengths the absorptivity of most metals and ceramics is higher, thereby the reaction zone may be several microns deep. Ultraviolet rays can be focussed more tightly and produce higher structural resolution. The laser parameters that will be studied for obtaining satisfactory results are peak intensity, repetition rate, and number of scans of laser pulses.

5.2.4. Optimization of Laser Process Parameters

The surface characteristics and properties of the coatings produced depend on the chemical composition and laser process parameters such as power and dwell time. Variation in the laser wavelength, output power, beam diameter and traverse speed results in different power densities, interaction times and heating times which will in turn effect the laser/metal interaction and quality of the coatings.

In this task, we proposed to optimize the processing parameters to obtain reproducibly the coatings necessary for providing the necessary oxidation resistance at high temperatures.

The parameters which were to be studied include beam diameter, sample scan rate, powder feed rate and powder characteristics. The effect of these process variables on the physical, mechanical and structural properties of the coatings were to be evaluated.

During this process, we proposed to examine two different methods of adding the powder to the melt pool. The first method involves injecting the powders directly into the melt pool. The powders will be carried through a carrier gas such as Helium. The resulting vigorous reaction between melt pool and powders will result in a homogeneous mixture of particle and substrate giving rise to improved surface properties. The other method is preplacing nonadherent layers of powders on the substrate followed by laser scanning.

5.2.5 Laser Glazing

This part of the task involves determining the optimum laser parameters, which results in optimum coating properties. The laser parameters and melt depth were to be adjusted to produce cooling rates in the range of 10^6 to 10^9 K/sec. The percent of overlap as well as heat input in the subsequent passes will be controlled to prevent the devitrification of amorphous layers already formed.

5.3 *Task 3- Evaluation of Laser Processed Samples*

The physical, chemical and surface properties of laser processed samples were proposed to be determined using appropriate techniques. Following are the specific properties to be tested:

Optical microscopy to detect porosity, microcracks, and coating thickness
Scanning electron microscopy to evaluate interface between the coating and substrate, coating thickness

5.3.1 Evaluation of Coatings in Conditions Simulating Metal Casting Conditions

In order for the coatings to be successfully used in the industry, the coatings need to be tested for their resistance for erosion, corrosion and heat checking.

5.3.1.1 Corrosion/Erosion Test

For the Phase I, we proposed to evaluate only those samples, which have the optimum coating properties. To determine the corrosion and erosion resistance, the coated samples will be dipped in molten aluminum for periods of 1, 2, and 3 hours. The samples were to be completely immersed in the molten metal and rotated at 3 different speeds of 0, 50 and 100 rpm.

After each cycle of testing, the samples were to be characterized by optical microscopy, and scanning electron microscopy for the presence of microcracks, porosity and other surface defects. The weight loss in the coated and uncoated samples was to be determined. The data from samples which are placed in the melt without any rotation will give the corrosion resistance, whereas the data from the samples, which are rotating at different speeds will give the erosion resistance.

5.3.1.2 Thermal Fatigue Test

It is very important for the coatings to withstand repeated exposure to heating and cooling cycles, without cracking or spalling. It is known that the thermal fatigue conditions created in the coating due to these harsh environmental conditions will initiate thermal fatigue cracks also called heat checking. We proposed to evaluate thermal fatigue resistance of a limited number of coated samples. The test involves dipping coated samples in molten 384 aluminum and water alternatively with very little die lubricant. The cycle time typically is 30 seconds with 10 seconds of dipping time in aluminum. The samples were to be tested for about 10,000 number of cycles and will be evaluated for the presence of crack formation or spalling.

5.4 Task-4: Selection of Optimum Process Conditions

Based on the results of Tasks 5.3.1 and 5.3.2, we proposed to select optimum coating materials, optimum process parameters, which provide the required surface protection for the casting dies.

5.5 Task 5: Prepare Final Report and Phase II Proposal

During this task, the final report detailing the experiments conducted and the major results of the Phase I effort was to be prepared.

6.0 WORK ACCOMPLISHED - EXPERIMENTAL DETAILS

This section will summarize the experimental tasks completed during the Phase I study.

6.1 TASK 1: Sample Preparation

Orvar supreme hot rolled bars of H13 die steel were obtained from Uddeholm. Samples of 1.00 (wide) x 2.00 (length) x 0.5 (thickness) were machined. The edges of the samples were rounded off to remove or reduce the stress rising points. The chemical composition of the bars is given in Table 3. The samples were sent to Heat Treating, Inc., Round Rock, Texas, a commercial heat treating facility for heat treatment. The final hardness after heat treatment was 46 to 48 Rc.

Table 3. Chemical composition of H-13 steel

Element	C	Mn	Si	Cr	V	Mo
Wt.%	0.4	0.4	1.1	5.0	1.1	1.0

6.1.1 Types of Alloying Powders Used in the Investigation

We have used powders of TiC having three different particle sizes in the program. The general properties of TiC used in the program are given in Table 4. The particle sizes investigated in the study were 30μ, 2 μ, and 50 nm. Powders with particle size of 30μ were procured from Atlantic Equipment, New Jersey, and particles of 2 μ were ordered from ALFA AESAR (Johnson Matthey). Nanocrystalline powders with sizes of 50 nm were obtained from the University of Idaho. Characterization of the ultrafine TiC powder was carried out by performing x-ray diffraction (XRD) and transmission electron microscopy (TEM). The XRD pattern shown in Figure 3, shows multiple peaks corresponding to the presence of single phase TiC. Detailed examination of the fine crystals by TEM (shown as inset in Figure 3) revealed their size in the range of 20 to 100 nm.

Table 4. General physical properties of TiC

Melting Point, Degree C	3140
Boiling Point, Degree C	4820
Mohs Hardness	3200 Kg/mm^2
Density, g/cc	4.93
Crystal Structure	Cubic
Electrical Resistivity, Micro-Ohm-Cm	180-250

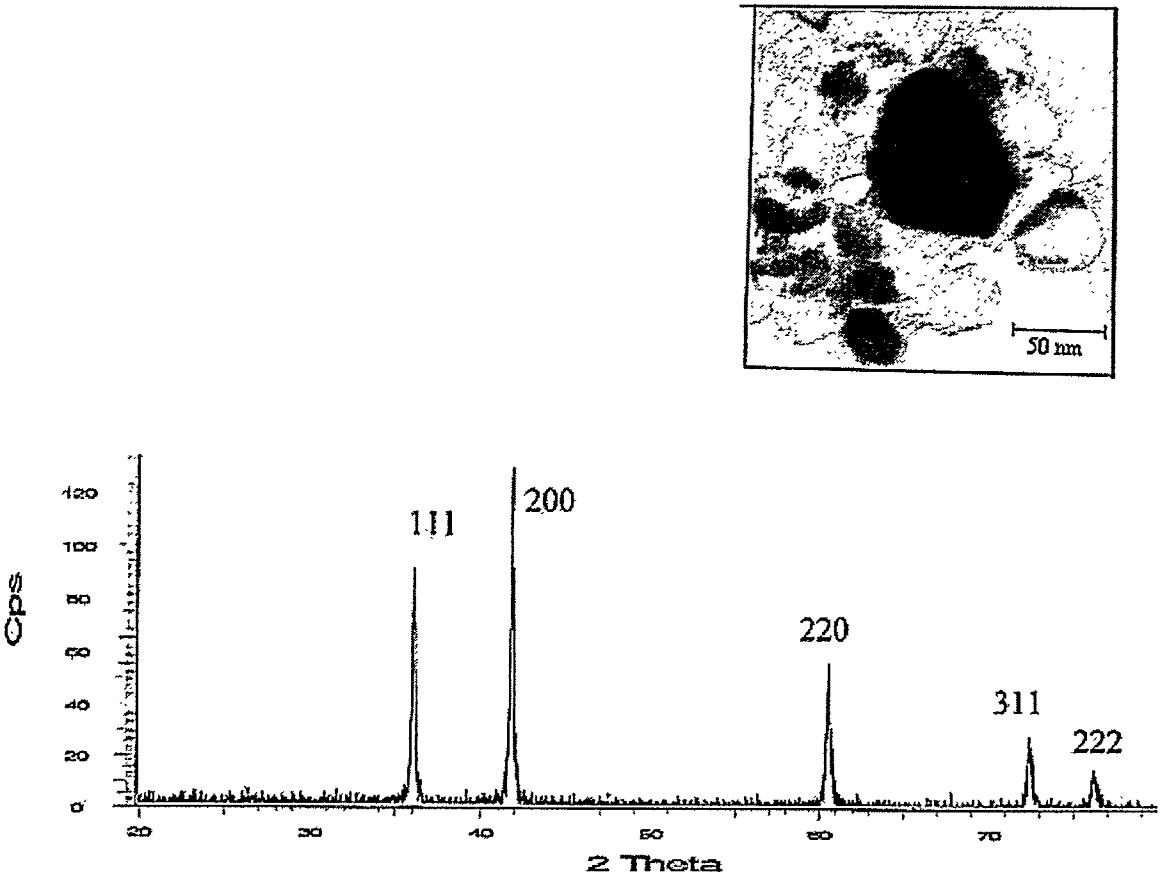


Figure 3. X-ray diffraction pattern of nanocrystalline powders of TiC, inset showing a TEM micrograph of TiC.

6.2 TASK 2- Development of Laser Processing Procedures & Optimization of Process Variables

A schematic diagram of the laser experimental setup is shown in Figure 4. All the experiments were performed using a Model 820 Rofin-Sinar® continuous wave (CW) CO_2 laser, which has a rated power output of 1500 W. The beam was delivered to the sample through several mirrors and a focusing lens (127 mm in focal length and 28 mm in diameter. Laser experiments were conducted with the power varying from 500 W to 1500 W, and the traverse speeds of the samples in the range of 17 mm/s to 254 mm/s. The samples were mounted on the worktable. The focus position was adjusted from the surface to 10-mm below the surface to meet the specific experimental requirement. The assist gas was flown into the laser interaction zone at a pressure less than 1 psig. Both single and multiple scans of laser processing were performed using a computer numerically controlled (CNC) worktable. The overlap in multiple scans ranged from

10% to 30%. Figure 5 shows a schematic of the transverse profile of laser-glazed samples labeled with various dimensions. The penetration depth H was 0.65 mm (X value was 0.3 mm) for the optimum parameters. The bottom zone, represented by Y, did not contribute to the overlapping. The width Z was measured to be 0.366 mm, which provided an overlap of 30%. Overlapping is a percentage ratio of difference between width, Z, and distance of adjacent paths over the width, which can be expressed as:

Overlapping = [(width of a scanning pass-distance of adjacent passes)/width]*100%

6.2.1 Laser Glazing (LG)

This process uses a high-intensity CO_2 laser to melt the surface of a sample. The rapid solidification (cooling rates exceed 10^6 K/s) associated with " self quenching" produces fine and homogeneous microstructures. A number of combinations of laser parameters including power (500 W, 1000 W, and 1500 W), focus position (surface and below surface), and traverse speed from 17 mm/s to 254 mm/s were used to determine the optimum settings for producing smooth and crack-free layers. The optimum parameters for laser glazing are listed in Table 5.

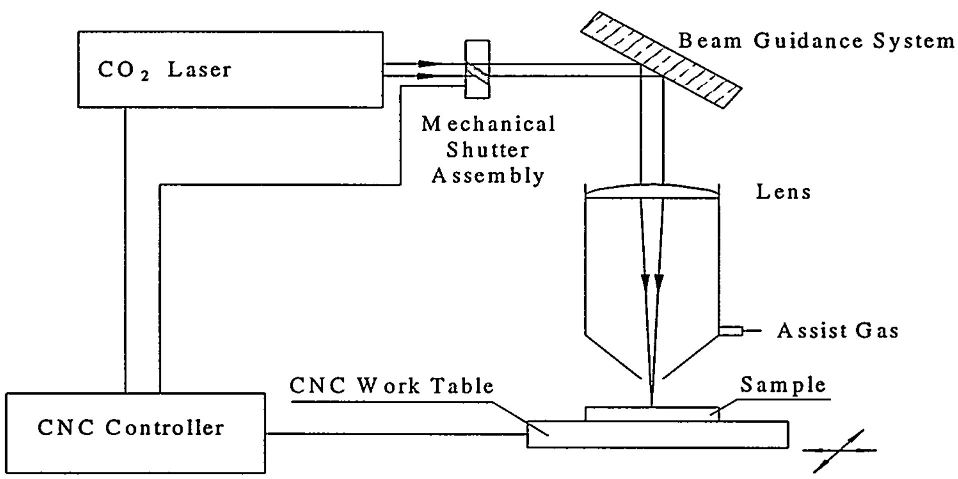


Figure 4. A schematic of laser setup for surface processing

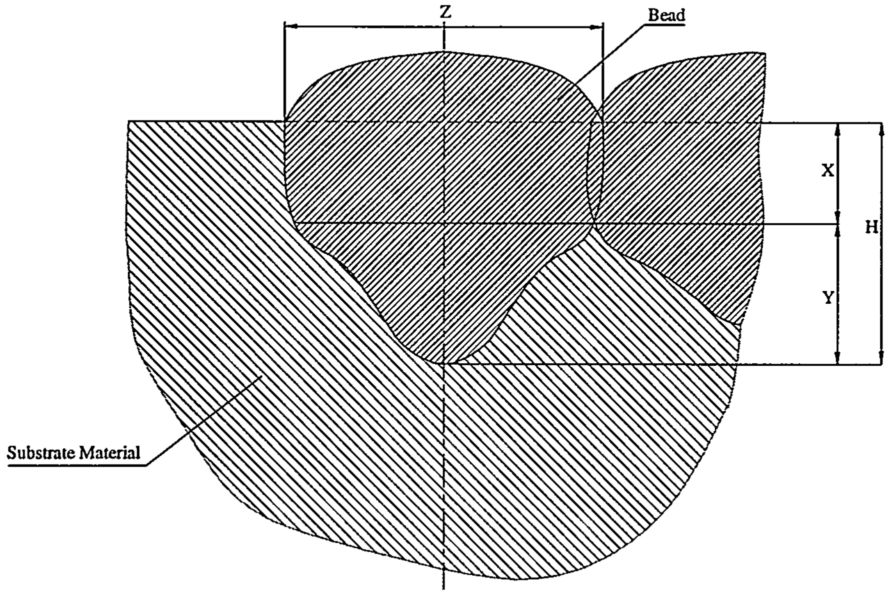


Figure 5. A schematic of the transverse section of laser glazed layers

When the laser power was kept constant, an increase in traverse speed produced more uniform and less defects (microcracks, porosity and etc.). When the traverse speed was made constant, lower laser power (500 W) produced better surface quality. Of all the parameter combinations, a laser power of 500 W and a traverse speed of 127 mm/s produced the best surface finish with minimal defects. The surface roughness was 4.2 µm (R_a) for laser-glazed samples and 0.7 µm (R_a) for as-received samples.

Table 5. Optimum parameters for laser glazing of H13 steel

Power, W	Focus	Traverse speed, mm/s	Overlap, Mm	Nozzle diameter, mm	Stand-off distance, mm	Assist gas
500	surface	127	0.25	2	3	Argon

6.2.2 Laser Surface Alloying (LSA)

LSA is a coating process that involves the changes in chemical composition and microstructure of the surface layers. In this process, the coating material is pre-placed (or added to the molten pool) on the substrate, and then the laser is used to melt the coating and a portion of the substrate to form an alloyed zone. In this work, the titanium carbide (TiC) powders of 30 µm, 2 µm and 0.3 µm (50 nm) in size were used as coating material. A powder slurry was prepared for 30 µm and 2 µm powders using a solution of agar and water as the bonding agent. First, 1.5 grams of agar was added to 1000 ml of distilled water and then heated to 85° C (accompanied by proper stirring), to obtain a homogeneous solution. Second, the powder was mixed with agar solution to form the slurry. For the 0.5μm (50 nm) powder, alcohol was used to form the slurry because the fine powder could be easily dissolved.

The slurry was applied on the surface of the substrate uniformly to a specific thickness and then dried using an electric heater. The thickness was built by adding more slurry. The powder was pre-placed to four thickness values: 0.01 mm, 0.02 mm, 0.1 mm and 0.4 mm. The thickness of the coating layer was measured using a weighing method. First the exact dimensions and initial weight of a sample were measured respectively using a dial caliper of 0.025 mm in accuracy and an electronic balance of 0.001 gram in accuracy. Second the coating was applied, dried and then weighed. By using the density of TiC carbide, the coating thickness was estimated.

LSA was performed using a range of laser parameters. The optimum parameters were selected based on the criteria of surface smoothness and defect free structure. The parameters are listed in Table 6.

Table 6. Optimum parameters for LSA of TiC powder on H13 steel

Power, W	Focus	Traverse speed, mm/s	Overlap, mm	Assist gas
500	10 mm below surface	42.3	0.25	Argon

The surface quality (surface smoothness, porosity, cracks, and etc.) of the laser-alloyed samples was significantly improved if a defocused beam rather than a focused beam was used. In addition, the alloyed zone thickness for the defocused beam was much smaller than that of the focused beam with the same parameters.

The effect of powder size on surface quality of laser-alloyed zone is shown in Table 7. The size of powder also degrades the surface quality of a pre-placed layer. Experiments indicate that 2 μm and 50 nm powders were capable of producing a smooth coating surface under the present conditions, since the fine powders are relatively easy to make into slurry.

Effect of traverse speed on the surface roughness is given in Table 8. The data indicate an increase in surface roughness with increase in sample traverse speed. The measured surface roughness at a traverse speed of 64 mm/sec is 16.5 μm. The increase in surface roughness could be attributed to lack of enough time for proper fusion of the slurry into the substrate and poor bonding to the substrate.

The dilution of the coating into the substrate depends on the volume of molten metal. Dilution is defined as the change in substrate composition of the surfaces by the diffusion of pre-placed coating. The dilution was evaluated approximately based on the measurement of the thickness of pre-placed powder layer and the penetration depth Dilution was calculated using the following equation:

Dilution = Area of melted substrate/(Area of coating layer + Area of melted substrate)

Increased amount of dilution is preferable for enhancing the properties of laser surface modified materials. In the present experiment, dilution ranged from 90% to 92% for both 2μm powders as well as the nanocrystalline powders of TiC from Idaho.

Table 7. Effect of powder size on surface quality

Powder Size, μm	Surface Quality
30	Surface smoothness, Ra, 15.6 μm; Some porosity and cracks.
2	Surface smoothness, Ra, 8.9 μm; Less porosity and fewer cracks.
0.05 (50 nm)	Surface smoothness, Ra, 12.2 μm; Less porosity and fewer cracks.

Table 8. Effect of traverse speed on surface roughness

(Laser power=500 W, powder size=2 μm, coating thickness=0.02 mm)

Traverse Speed, mm/s	21	42.3	64
Surface Roughness, μm	11.81	8.89	16.5

6.2.3 Laser Shot Peening (LSP)

Laser shot peening was performed using a pulsed Nd:YAG laser. The wavelength of the laser used was 1.06 μm. The pulse length was 15 ns. During each pulse energy of 200 mJ was delivered to the sample. The samples were coated with an absorptive black adhesive tape and immersed in distilled water (sample surface at about 2.5 mm from the water surface) for plasma confinement. The process parameters used for laser shot peening process are listed in Table 9. In the present experiment, only the samples coated with 2μ particles of TiC were shot peened. All the six sides of the samples were processed.

Table 9. Laser parameters using for shot peening experiment

Laser parameters	
Laser type	Q-switched Nd:YAG
Model	Quantel Y481
Pulse width	15 nsec
Pulse energy	200 mJ
Repetition Rate	10 Hz
Spot size	0.2 mm

6.3 Task 3- Evaluation of Laser Processed Samples

6.3.1 Characterization and Testing of Laser Processed Samples

6.3.1.1 Surface Roughness

A surface profilometer using 0.25 mm diamond probe was used to measure the surface roughness (arithmetic average, R_a) of laser-glazed and alloyed samples in both longitudinal and transverse directions. The differences in surface roughness between the two directions were marginal. The surface roughness of as-received samples was also measured.

6.3.1.2 Metallography

The laser-processed samples were analyzed using optical and scanning electron microscopy (SEM) for flaws including porosity and microcracks. The width of single-pass laser treated zone was measured and used to determine the overlap distance in multiple passes. Following that, the samples were sectioned using a cut-off wheel flooded with water to prevent tempering. The samples were then ground using a 80-grit sand paper and mounted in bakelite. The samples were polished sequentially in 240, 320, 400, and 600-grit emery papers, and then polished using 6 μm diamond paste. The samples were etched in a solution of 5% nitric acid in methanol. The etching time was about 1.5–2 minutes. SEM was then used to characterize the depth, profile, flaws, and microstructure.

6.3.1.3 Vickers Microhardness Test

The mounted samples were placed in a Tukon® microhardness testing machine, and were subjected to a load (P) of 1 kgf. A diamond pyramid indenter was used to generate square indentations. Vickers microhardness was calculated by measuring the diagonal length (d_l) of square indentations and using the formula:

$$VHN = \frac{1.854 * P}{d_1^2}$$

The Vickers hardness was measured along the depth of laser treated layers.

6.3.2 Evaluation of Coatings in Molten Aluminum – In Conditions Simulating Metal Casting conditions

6.3.2.1 Specifications of the molten metal

Corrosion/erosion and thermal fatigue tests were performed using aluminum alloy A390 with high silicon content. The A390 alloy is a hypereutectic aluminum silicon casting alloy. The advantages of A390 are high fluidity, high thermal conductivity, and superior wear resistance of the castings. The chemical composition of this alloy is 16 to 17% Si, 4 to 5% Cu, 0.6 to1.1% Fe. On a relative basis, the primary silicon particles in partially solidified A390 melt are hard, larger in size, and irregular in shapes with sharp corners. Consequently A390 results in higher wear to the sample surface than other aluminum melts.

6.3.2.2 Corrosion/Erosion Tests

An accelerated corrosion test was set up to evaluate the dissolution rate of coated and uncoated samples of H13 in both static and agitated melts. Figure 6 is a schematic diagram of the corrosion/erosion test setup. The setup shown in figure holds only one sample, but was later modified to hold up to four samples. Four samples were held symmetrically in the rotating arm, which is driven by an electric arm. The input voltage can control the speed of the rotating arm. The possible speeds of rotation are 50 and 100 RPM. The speed of the rotation enables us to study the effects of fluid flow on the sample erosion behavior. In Phase I, all the erosion experiments were performed at a speed of 50 rpm. The melt consists of A390, which was covered, with equal parts of potassium chloride and sodium chloride with 5-10% of additional sodium fluoride. The salt solution was used to reduce oxidation, prevent gas absorption, and metal loss. Samples were quenched in water after the desired corrosion/erosion time. The samples were cleaned with a 5% NaOH solution. The change in weight of the test samples was measured before and after each test.

Conducting the tests at 670 and 800 degrees C accelerated the corrosion/erosion rate during the tests. These temperatures are significantly higher than the temperature of 500-600 degrees C usually encountered in practice. Rotating the specimens in melt for much longer time than the actual contact time of 1 second which occurs during die casting process increases the severity of the test environment.

6.3.2.3 Thermal Fatigue Experiments

A laboratory test machine was designed and fabricated to simulate the die thermal fatigue failure through thermal cycling. The test set up is shown in Figure 7. The instrument is designed to dip the sample in molten aluminum, immerse it for a given preset time, rise it, swing it towards the water container, lower the sample slowly to dip in the water, keep it under water for a given preset time, and lift it. This completes one cycle of thermal fatigue experiment. The average time between dipping in melt and water can be varied between 10 –20 seconds. This cycle can be continued to the desired number of cycles. The tests involved cycling the samples between molten A390 and water with very little lubricant

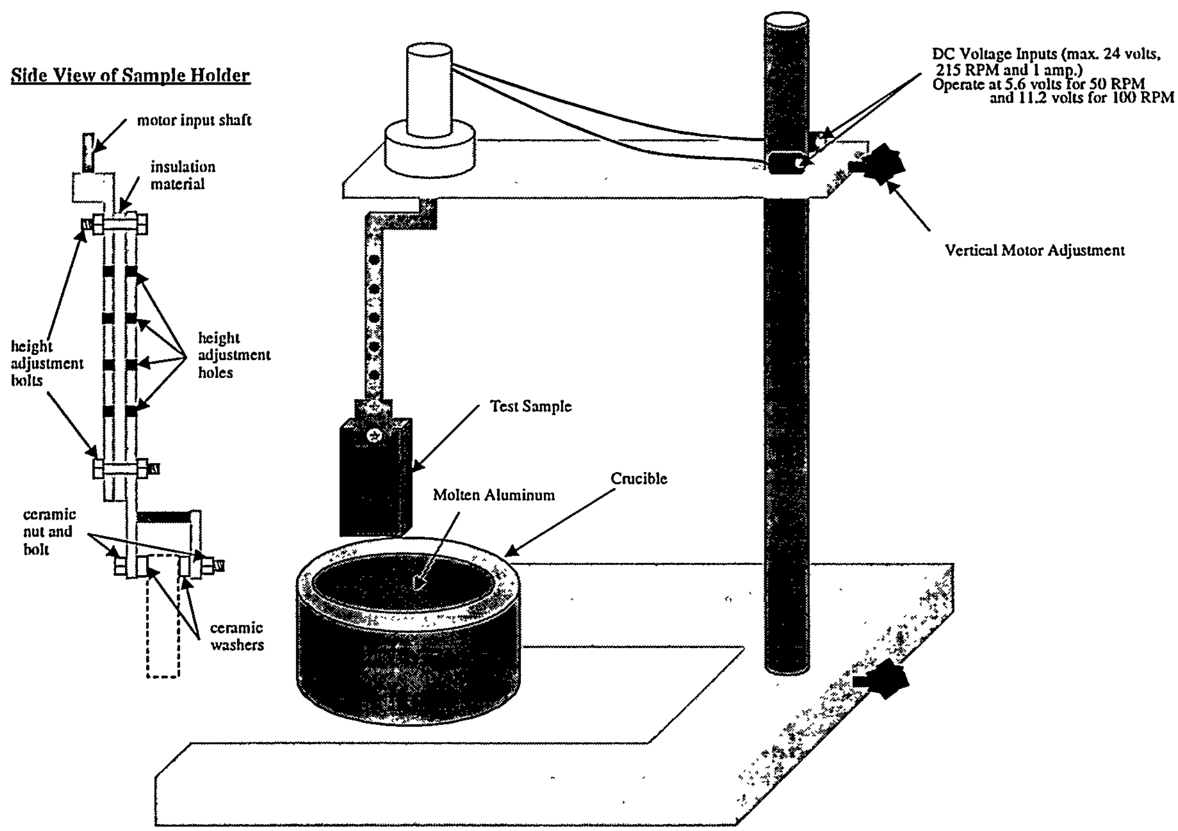


Figure 6. Schematic diagram of the experimental setup to evaluate the corrosion/erosion properties of laser processed and uncoated samples of H13 die steels.

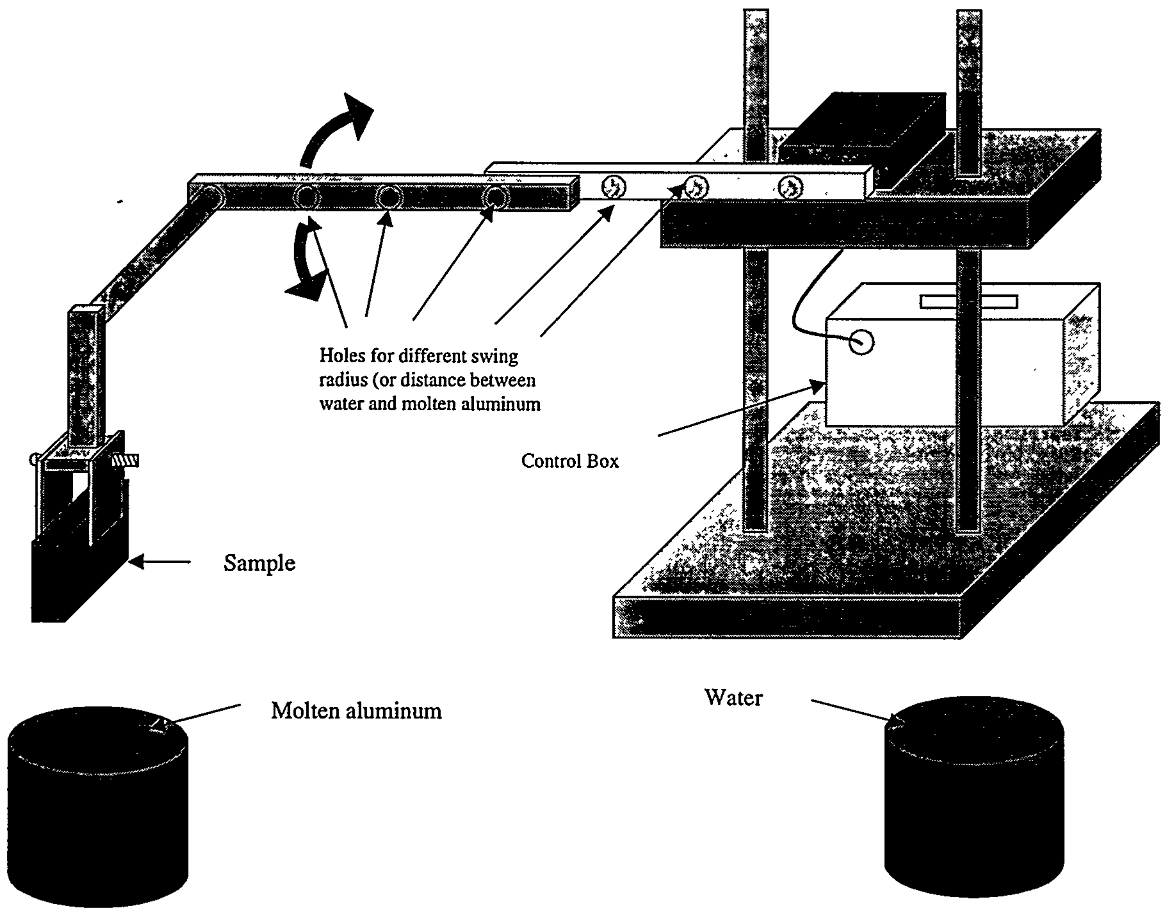


Figure 7. Schematic diagram of the experimental set up to evaluate the thermal fatigue properties of laser processed and uncoated samples of H13 die steel samples.

7.0 RESULTS AND DISCUSSION

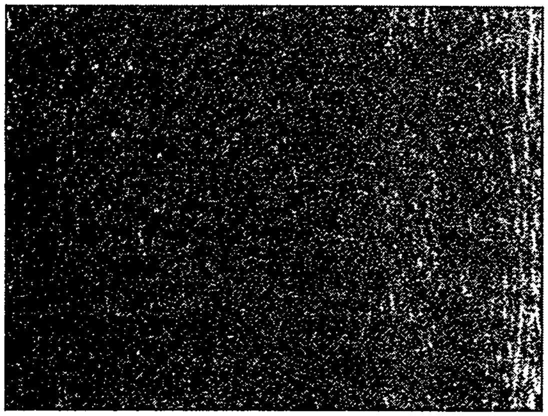
In the present investigation, Karta developed an innovative approach to prevent die failures by a duplex process consisting of an initial step of depositing protective surface coatings by laser surface alloying followed by laser shot peening to eliminate the surface tensile stresses. In the original proposal, the first step in the proposed duplex process was laser shot peening using excimer lasers. This step was designed to relieve the tensile stresses and introduce compressive stresses in the surface layers. However, a change in the process was implemented after a few preliminary experiments. The process of laser shot peening was performed using a Nd:YAG laser rather than an excimer laser as proposed. The decision was based on a few preliminary experiments and further literature search, which indicated the suitability of Nd:YAG laser for shock surface treatment of metals [24]. Excimer lasers, which were proposed earlier, are more suitable for the processing of nonmetallic materials. The process of laser shot peening was also carried out after the step of laser coating rather than before. It is intended to relieve the tensile stresses induced in the material during the coating process and introduce compressive stresses to improve the mechanical properties.

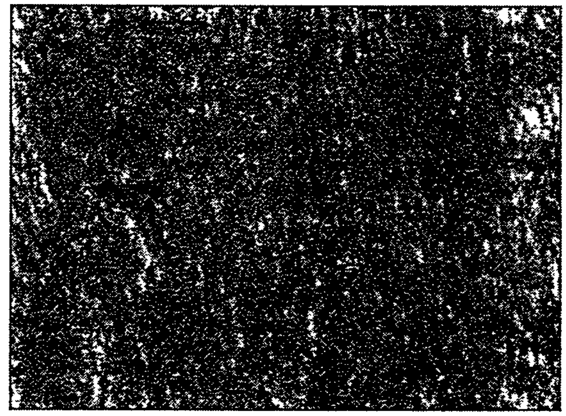
7.1 Microstructural Analysis of Laser Processed Samples

7.1.1 Laser glazed Samples

Scanning electron micrograph of the typical transverse section of a laser glazed sample is shown in Figure 8. Some inclusions are observed near the top surface. Figures 9a and 9b show the microstructures of the laser-glazed region and the substrate respectively. It can be seen that the microstructure in the glazed region is much finer and uniform than the microstructure in the substrate. The formation of the uniform and fine microstructure by laser glazing helps to improve the strength of the glazed zone.

Figure 8. SEM picture of laser scanning passes on laser glazed samples.





(a) (b)

Figure 9. SEM micrographs showing microstructures of H13 substrate at higher magnifications. (a) In the laser-glazed surface layers, 2000X, and (b) the substrate, 2000X. Note the fine microstructure in the laser glazed zone.

7.1.2 Laser Surface Alloyed Samples

Scanning electron micrographs of the transverse sections of LSA are shown for 2μm and 50 nm powders in Figures 10 and 11 respectively. As seen in the micrographs, the penetration depth for samples coated with 50 nm is about 2080 μm, which is approximately 13% larger than the penetration depth measured for samples coated with 2 μm. The larger penetration depth in samples coated with finer particles of TiC can be attributed to the improved absorption of laser energy. The alloyed zone is relatively free from defects in 50 nm sample. Figures 12 and 13 show the higher magnification images of the microstructures of the H13 steels laser surface alloyed with 2μm and 50 nm powders respectively. Once again, fine and uniform grain structures were observed. The differences between the microstructures are not discernible.

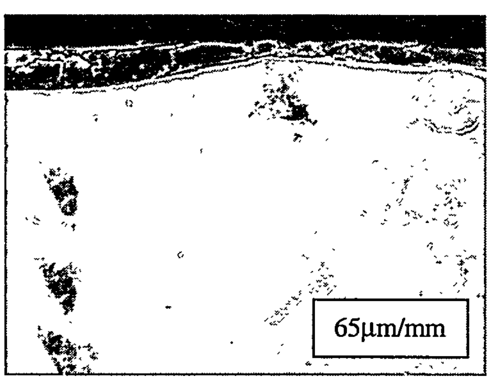


Figure 10. SEM picture of laser alloyed zone (2μm powders of TiC). Microhardness indentations can be seen in the micrograph.

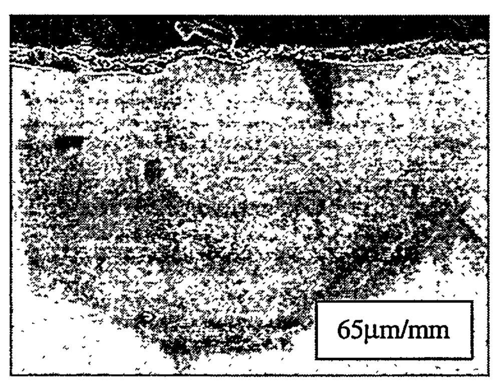


Figure 11. SEM picture of laser alloyed with 50 nm powders of TiC.

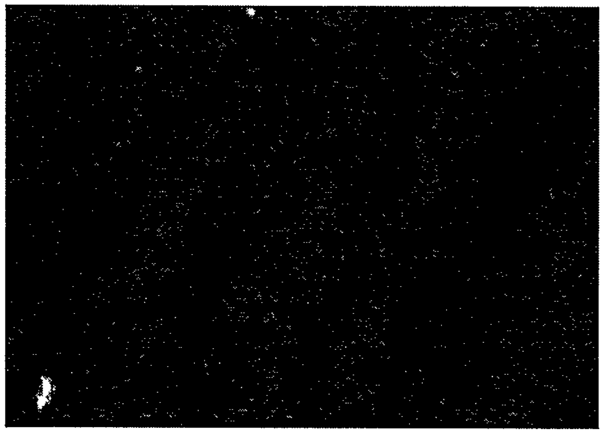


Figure 12. SEM micrograph at high magnification showing microstructure of laser alloyed zone for H13 die steels coated with 2 µm powder, 2000X.

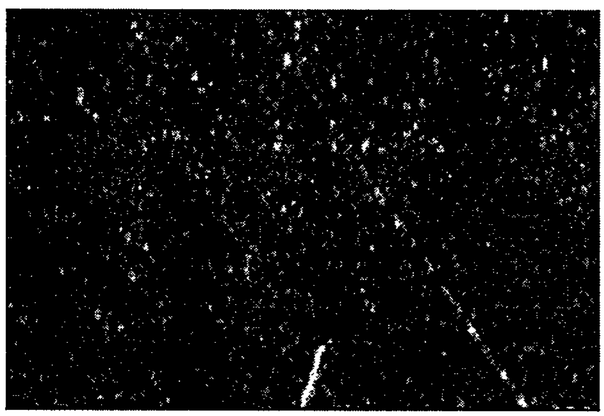


Figure 13. SEM showing a higher magnification microstructure of laser alloyed zone for H13 die steel sample coated with TiC powders with a particle size of 50 nm, 2000X.

7.2 Structural Analysis of Laser Processed Samples

X-ray diffraction analysis was performed to identify the phases formed during the laser processing. With the processing conditions employed in this experiment there was complete dissolution of the TiC in the melt which resolidified homogeneously into the surrounding molten steel matrix. Figure 14 shows the diffraction patterns for laser glazed, laser coated samples with TiC having particle sizes of 2µm and 50 nm. As can be expected, laser glazed sample did not show any evidence of TiC and indicated a relatively strong Fe peak. Laser glazed samples are expected to have an amorphous structure consisting primarily a complex phase of Fe. Samples having coatings of 2µm showed a strong presence of Fe and TiC. Even though the coatings of 50 nm or 0.5µm showed the presence Fe and TiC, the number of counts of TiC peak is less. These results indicate that the laser processing needs to the further optimized to increase the amount of TiC present in the surface layers of the laser coated samples. The low density of TiC is one of the probable causes of low amounts of TiC present in the surface layers. The density of TiC is 4.9 g/cm^3 compared with 7.9 g/cm^3 for steels. So it is possible that the particles simply float on the melt pool without mixing with the substrate. Further experiments can be performed in Phase II where the slurry consisting the nanosize particles of TiC can be injected at the beam-sample interface.

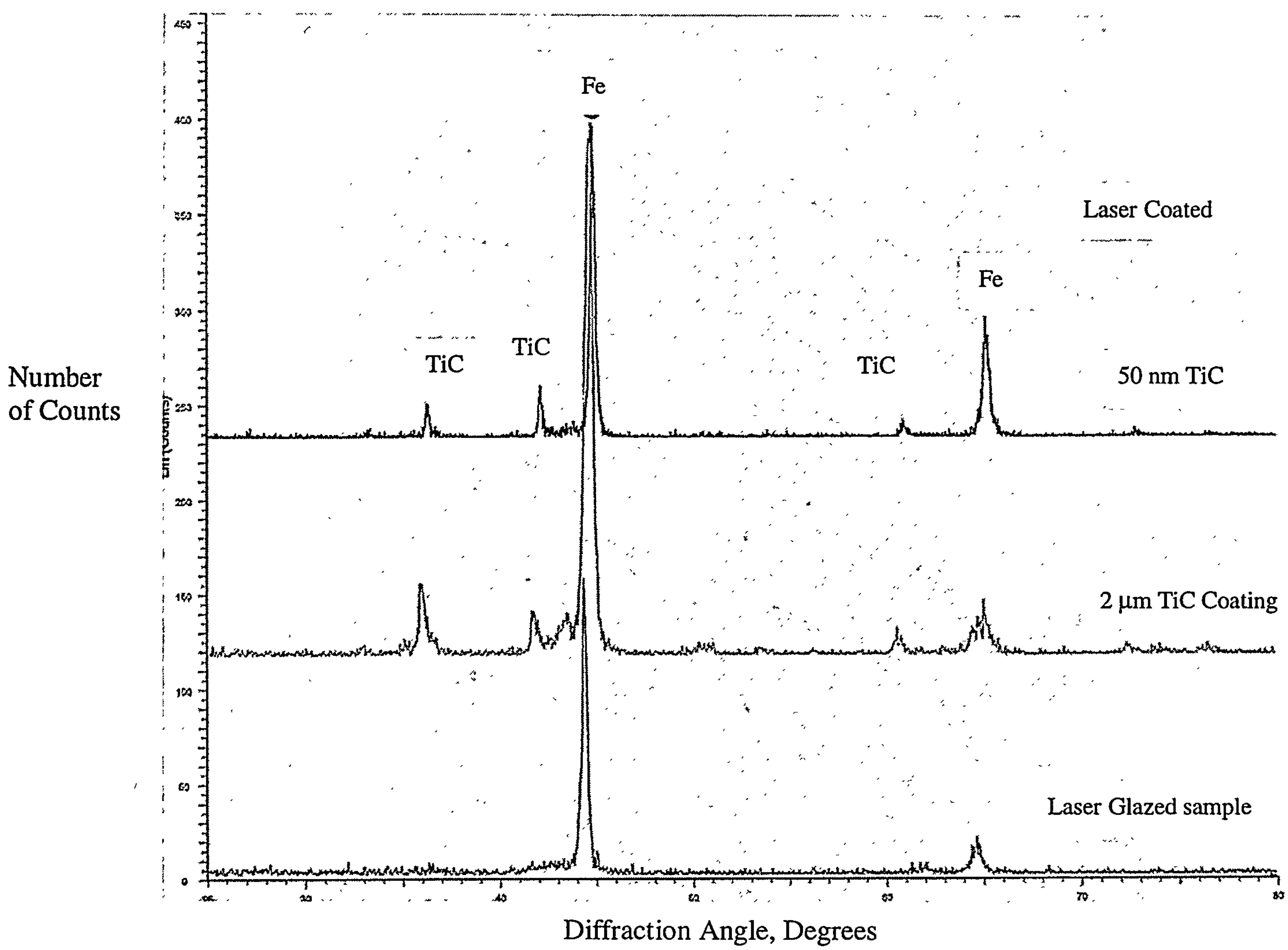


Figure 14. XRD patterns of laser processed samples.

7.3 Microhardness of Laser Processed Samples

The Vickers microhardness indentations were taken on laser processed samples. Figure 15 shows the hardness indentations on laser glazed sample. It is clear that the size of indentation is larger in the substrate indicating the relatively low hardness of the substrate. The variation of the Vickers microhardness with the distance from the surface in laser glazed sample is shown in Figure 16. The surface layer exhibited a hardness as much as 30% higher than that of the hardness of the substrate. This is attributed to the homogeneous microstructure developed due to rapid solidification process. The decrease in hardness with the distance is believed to be the change in microstructures due to the lower cooling rates.

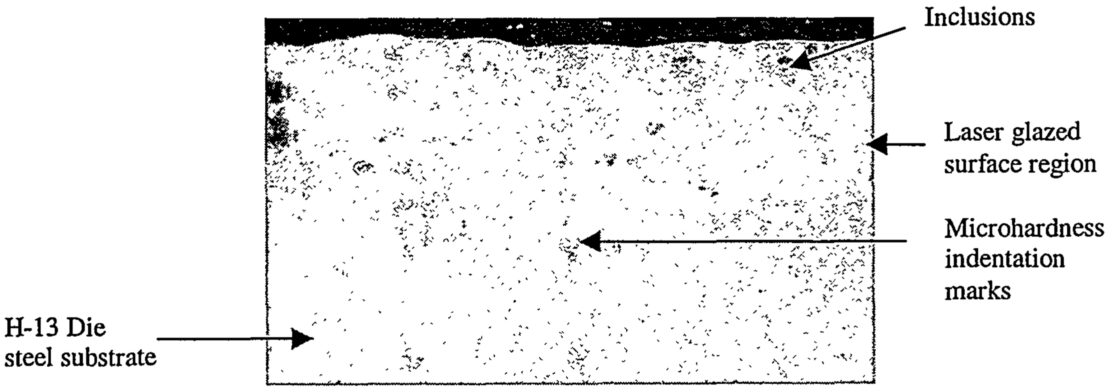


Figure 15. Microhardness indentations of a laser-glazed sample

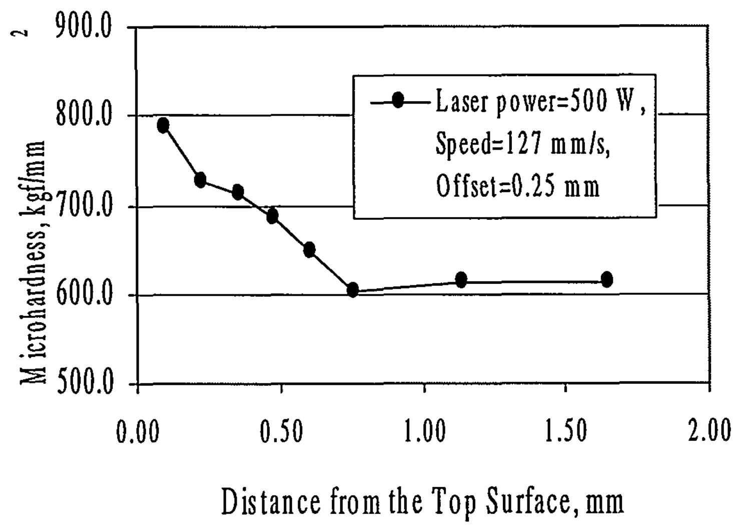


Figure 16. Variation in hardness profile as a function of depth for the laser glazed sample.

Figure 17 shows the Vicker microhardness profile from surface to bulk in H13 sample, laser coated with TiC powders of 2μm. The hardness in surface regions shows a 100% increase compared to the substrate. This increase in hardness can be attributed to the formation of a complex alloy phase consisting of TiC. The hardness levels achieved depend mainly on the amount of TiC dissolution. Typical values of microhardness obtained for various types of laser processed samples are reported in Table 10. In general, the hardness values for laser processed samples have shown an increase of 13 to 50% over the as-received or untreated samples.

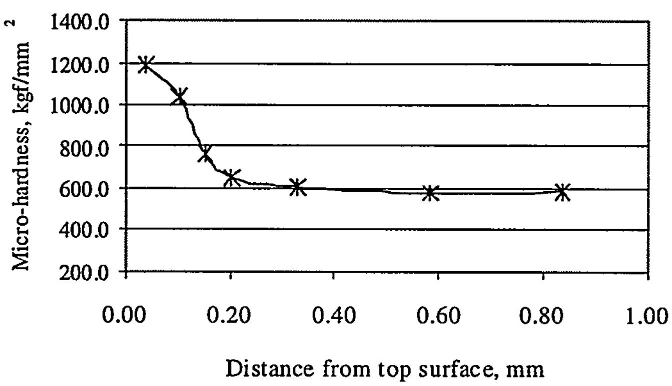


Figure 17. Variation in microhardness as a function of distance from the surface for laser alloyed samples with 2μ particles.

Table 10. Microhardness of H-13 and Laser Coated Samples

Process/ Material	Microhardness; Vicker's Hardness Number	Scatter in Measurement ± %
H13 Steel	514	4
Laser Glazed	579	7
2.0 μm TiC	658	32
2.0 μm TiC + Laser Shot Peened	860	8
50 nm TiC	250-1050	11

A comparison of the standard deviation values suggests that using finer sizes of TiC powders improved the quality and homogeneity of the coatings. However, a wide variation in the hardness levels is noticed for the samples coated with nanosize powders of TiC. The probable reason could be the presence of impurities due to leaching process in the powders. Another reason could be non-uniform distribution of TiC particles in the melt.

7.4 Evaluation of Coated Samples in Molten Aluminum Melt

The performance of laser processed samples of H13 steel in simulated metal casting condition was evaluated by performing corrosion/erosion resistance, thermal fatigue tests.

7.4.1 Corrosion Resistance in Static A390 Melt

Accelerated corrosion tests were conducted to evaluate the corrosion behavior of H13 steel samples in the static A390 melt at temperatures of 670 and 800°C. The samples were immersed in the melt for duration up to 20 hours. Effects of melt temperature and time of immersion results in the dissolution of sample. Yu et al., have discussed the corrosive effects of molten aluminum alloy on the H13 die steel [25]. They have attributed the rapid dissolution of H13 steels into the melt to the direct dissolution of substrate, and the formation and simultaneous dissociation of the intermetallic compounds such as τ_6 (Al_4FeSi). The solubility of iron in aluminum is limited by the differences in their crystal structures. For example the solubility of iron in aluminum at a temperature of 650°C is 1.8%.

In this study, we evaluated following types of samples:

- Laser glazed specimens
- Laser coated specimens with 2 µm size TiC.
- Laser coated specimens with 2 µm size TiC and laser shot peened.
- Laser coated specimens with 50 nm size TiC.

The results are shown in Figure 18, which show the weight loss per unit area as a function of time for all four different types of samples. The weight loss for an untreated sample of H13 steel is observed to be 3500 mg/cm^2, whereas the samples with surface protective coatings of TiC showed a weight loss of approximately 500 mg/cm^2. This decrease in weight loss corresponds to an increase in corrosion resistance of about 85% for the laser coated samples.

Figure 19 shows a SEM micrograph of the cross-section of corroded sample and x-ray elemental maps for aluminum, iron, and titanium. The micrograph shows the nature of corroded surface of the H13 substrate. The x-ray mapping of aluminum and other elements shows the nature of corrosion process. The presence of aluminum deep in the substrate (Fig 19b) indicates diffusion of aluminum into the substrate. Trace amounts of TiC can be seen in the surface layers, as shown in 19c.

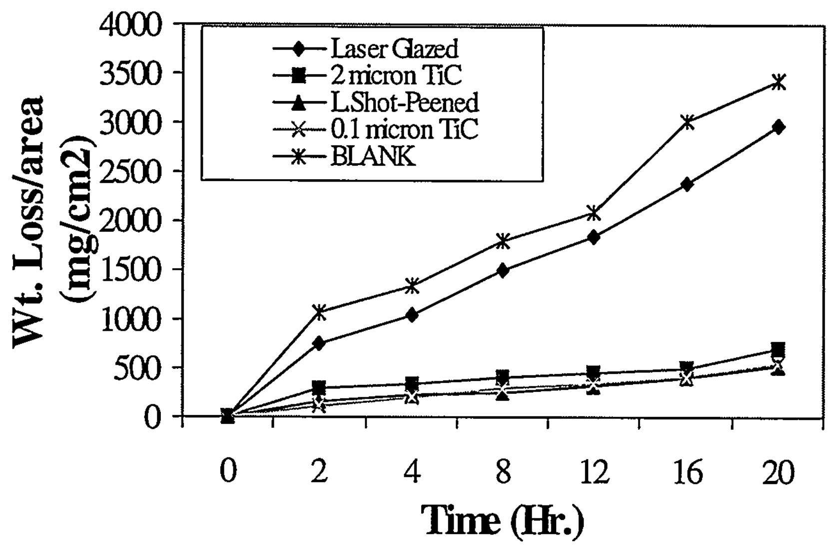


Figure 18. Plot of weight loss in samples of H-13 steel with immersion time in static A390 melt.

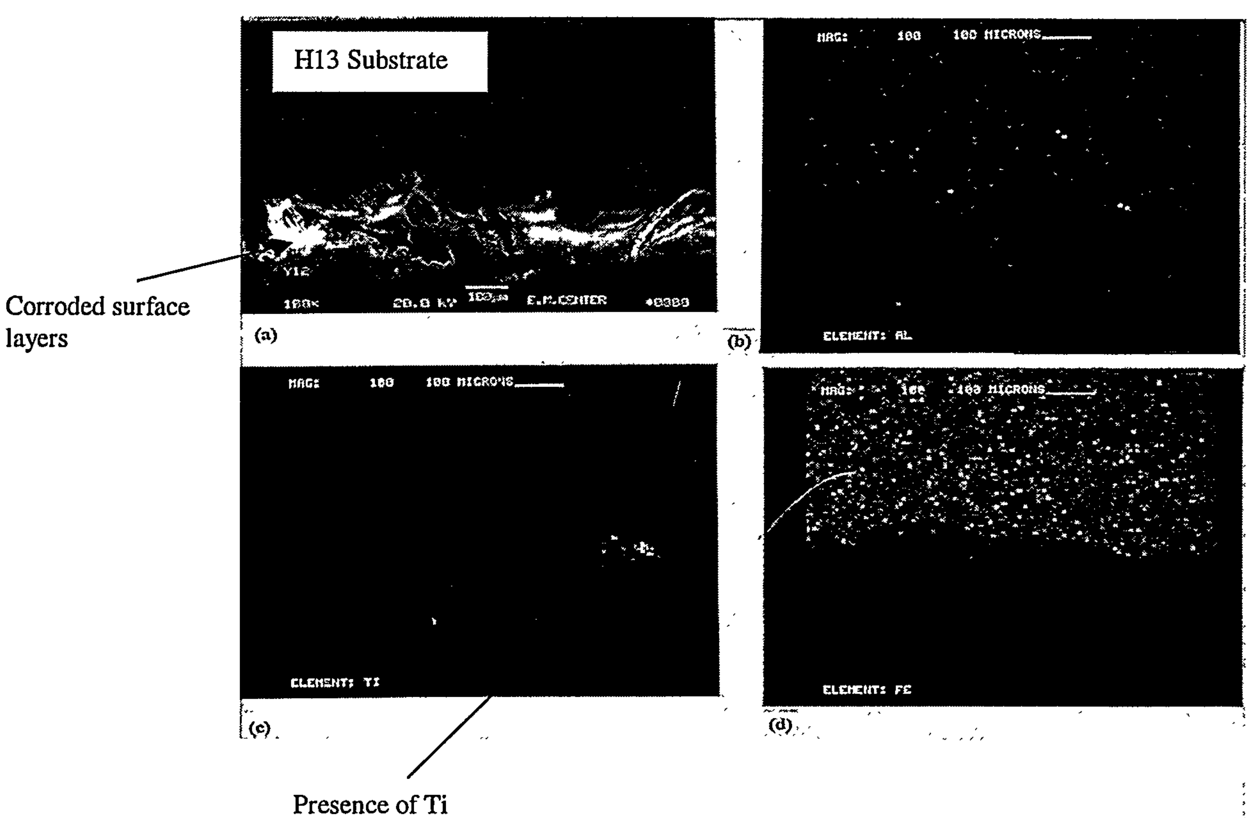


Figure 19. (a) A scanning electron micrograph of a cross section of a corroded H13 die steel sample coated with powders pf TiC. Corresponding x-ray elemental maps for aluminum, titanium, and iron are shown in figures (b), (c), and (d) respectively. The bright spots indicate the location and concentration of the respective elements.

These results indicate a significant improvement in corrosion resistance for laser processed samples when compared with uncoated (blank) samples. The increase in corrosion resistance is marginal in case of the laser glazed samples. This could be due to the absence of any surface coatings having higher hardness. The increase in corrosion resistance was more significant for samples having laser coated with finer particles of TiC. Samples coated with nanocrystalline particles show the highest corrosion resistance. This could be due to the smooth surface morphology, low porosity of the coating achieved with the use of powders of nanocrystalline TiC.

The laser shot peened samples also have shown improved corrosion resistance, making them comparable with samples coated with nanocrystalline powders of TiC. These results on corrosion resistance of shot peened samples are in agreement with the published results of Khanna and Sridhar, who showed that laser shot peening increases the corrosion potential by nearly +100mV [26]. It is also well established that the process of laser shot peening is similar to conventional shot peening, the process in which compressive stresses are generated on the surface without increasing surface roughness [24]. The improved corrosion resistance of laser shot peened samples therefore can be attributed to the presence of compressive stresses in the surface regions of the materials. Further studies are, however, needed to confirm the stress-state of the laser shot peened materials.

7.4.2 Erosion Resistance in Agitated A390 Melt

The effect of melt flow on the die surface was investigated by mechanically rotating the test sample and evaluating the change in sample weight after a desired test time interval. Experiments were performed at temperatures of 670°C and 800°C at a rotation speed of 50 rpm. The samples were tested for 3 hours and the results are shown in Figure 20. This plot indicates that under identical working conditions, the coatings with nanosized particles exhibited improved erosion resistance.

It is known that erosion is a progressive loss of material from a solid surface due to the mechanical interaction between that surface and an impinging metal fluid stream [25]. Erosion results in washout of the die surface. Damage due to erosion could be limited by using materials with higher hardness. Experiments performed in this research have demonstrated that laser coatings with nanocrystalline powders can improve the erosion resistance. This can be attributed to the higher hardness, smooth surface, and low porosity of the laser processed samples. The improved erosion resistance of laser glazed samples can also be attributed to the surface smoothness. It may be noted that laser glazed samples showed poor corrosion resistance.

A comparison of the erosion rates at 670 and 800°C show and increase in erosion rate for all samples with rise in temperature. This can be attributed to the increase in melt flow velocity at higher temperatures leading to rapid dissolution of intermetallic layers into the turbulent melt. The higher temperature also enhances the diffusion rate of Al, Si and Fe, and the formation of intermetallic compounds, such as τ_6, τ_5, and τ_2.

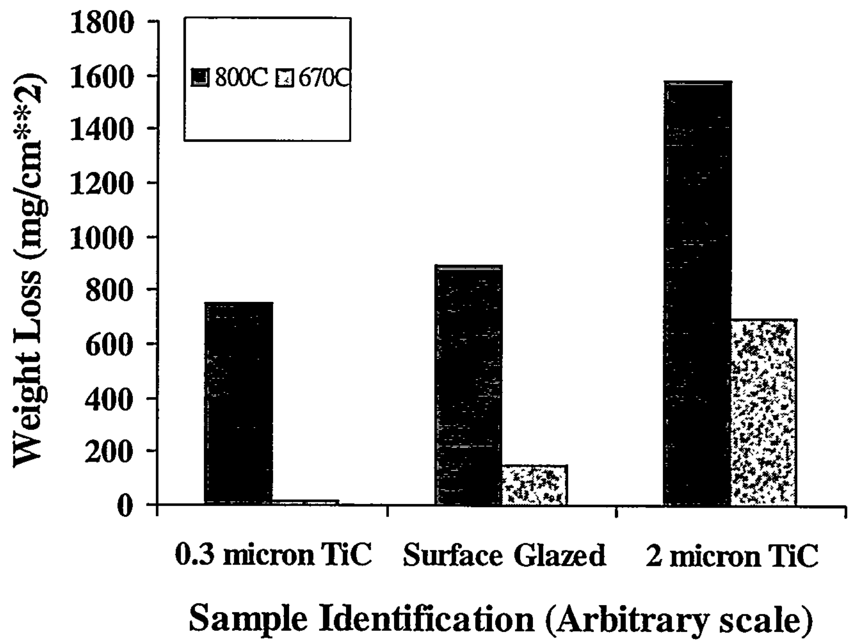


Figure 20. Plot of weight loss due to erosion of samples at two different temperatures.

7.4.3 Thermal Fatigue Resistance

Preliminary experiments for determination of thermal fatigue resistance or heat checking behavior of H13 steels were performed using molten A390. The experiment had to be discontinued due to experimental problems associated with metal splattering, broken crucibles. Hence, further experiments were carried out by thermal cycling in air. The experiments were performed using the experimental set up illustrated in Figure 7. The samples were lowered into the hot zone of the furnace, which was held at 850°C. The sample was pulled out after 15 seconds and air-cooled for 15 seconds to finish one thermal cycle. The samples were tested for 5000 cycles. It was seen that all the laser-processed samples performed the best with the least amount of weight pick up due to oxidation. The primary conclusion is that under cyclic thermal oxidation tests at 850°C, laser processed samples have demonstrated improved oxidation and thermal cracking resistance.

7.5 Summary of Results

Table 11 shows a summary of the results obtained in the present investigation. The results indicate an overall improvement in surface smoothness, hardness, corrosion, and erosion resistance by laser processing.

Table 11. Summary of Phase I Results

Process	Characteristic Features	Results
Laser glazing	Produces rapidly solidified microstructure in the surface regions	• Smooth surface, depth of surface modified layers is approximately 720 μm. • High hardness compared to substrate • High erosion resistance compared to untreated samples of H13.
Laser Surface alloying with powders of TiC	Process involved preparation of slurry, pre-deposition of the slurry on the substrate, laser irradiation using CO_2 laser under optimized laser process parameters.	• Produced thick coatings of the order of 2000 μm. • Produced complex alloy phases in the surface layers consisting of hard TiC
Particle size: 30 μm		• Rough surface
Particle size: 2 μm		• Smooth surface profile • High hardness compared to substrate • High erosion and corrosion resistance
Particle size: 0.05μm		• Improved surface smoothness • Varying hardness levels • High erosion and corrosion resistance
Laser surface alloying and laser shot peening	This duplex process involved laser shot peening of laser coated samples. Laser shot peening was performed using pulsed Nd:YAG laser. The process is expected to relieve tensile stresses produced during coating process and produce compressive residual stresses on the surface.	• High corrosion resistance. • Data on erosion resistance is not available.

8.0 CONCLUSIONS

The following conclusions can be drawn from the results of the study:

- It is feasible to form protective surface coatings of TiC using laser processing on H13 die casting die steels.
- The newly developed duplex process consisting of laser surface coatings followed by laser shot peening has improved the corrosion resistance of H13 steels.
- Laser glazed samples showed an improvement of 30% in microhardness compared to untreated samples.
- For surface alloying, the optimum laser parameters were dependent upon the thickness of the pre-placed powder and particle size of TiC powders. Surface coatings with good quality (smooth, pore-free) were obtained when finer sized powders were used. The penetration depth had a detrimental effect on the surface roughness. The optimum process parameters included using a laser power of 500 W, a defocused beam (10mm below the focal point), a traverse speed 42.3 mm/sec and a coating thickness of 0.02 mm. These parameters provided a penetration depth of about 0.2 mm.
- The laser processing, and mechanical test results on laser processed samples were reproducible.
- Particle size of TiC powders used for laser coatings affects surface morphology, corrosion, erosion behavior of laser coated samples.
- Laser coatings using nanocrystalline powders of TiC have demonstrated a pronounced improvement in surface finish, corrosion and erosion resistance.

9.0 MAJOR ACCOMPLISHMENTS OF PHASE I INVESTIGATION

- Developed a duplex process of laser coating methodology combined with laser shot peening process for die casting dies.
- Demonstrated the applicability of the newly developed laser assisted coating technology in improving the surface properties of H13 die casting die steels.
- Established the unique advantages of using nanocrystalline powders of titanium carbide in improving the performance of die casting die steels in the casting conditions.
- Designed and developed instrumentation to test the laser coated samples for corrosion, erosion, and thermal fatigue resistance in severe casting environment.
- Demonstrated an improvement of 85% in corrosion resistance for laser coated samples.
- Showed an improvement in erosion resistance for the laser coated samples compared to uncoated samples of H13 die steels.
- Established collaborative relationships with casting industries for further work in Phase II.

9.1 Advantages of Coatings Developed in Phase I

The inherent advantages of the new laser processing makes this approach very promising and have the capability to meet the needs of the casting industry. These advantages include:

- Formation of complex phase, flaw-free coatings having superior chemical, physical and thermal properties.
- Coatings produced by this process have low mismatch in coefficient of expansion with the substrate, have better bonding with the substrate and have low susceptibility for forming cracks.
- The process does not require vacuum or inert atmosphere.
- The process is well suited for automation and can increase the production rate due to the high-speed processing.
- Minimal adverse effects on the substrate are expected due to low heat input per unit volume.
- Post-processing operations are minimal.
- Material savings and conservation of strategic alloying elements can be achieved.

10.0 FUTURE WORK

Phase I work demonstrated that laser processing is a viable technique for depositing complex phase coatings consisting of powders of TiC. The results have indicated the advantages of using nanosize particles of TiC as coating materials. The research explored the application of laser shot peening process to induce compressive surface stresses on the die surfaces. However, for demonstrating the feasibility of the process, laser shot peening was performed only on a limited number of samples coated with 2μ particles of TiC. Due to the observed beneficial effects of the laser shot peening, it is proposed to extend the laser shot peening process to other types of coated and laser glazed samples also. Further, quantitative characterization using x-ray diffraction technique needs to be performed on laser shot peened samples. The changes in the stress state of the surface before and after shot peeening needs to be measured. X-ray diffraction results obtained on laser coated samples have indicated lower amounts of TiC in the surface layers for the samples coated with nanosize particles of TiC. It could be due to the density differences between steel and TiC. Due to the low density of TiC, it is possible that the particles were not able to mix homogeneously with the substrate. Hence, further experiments need to be performed to achieve uniform, homogenized surface coated layers. This could be achieved by injecting the slurry at the interaction zone of the laser beam and the sample surface.

In Phase I research, thermal fatigue experiments were performed involving repeated heating and cooling in air. For characterizing the performance of the coatings in realistic casting environment the experiments need to be performed in molten aluminum. Erosion experiments need to be performed at different speeds.

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