FINAL TECHNICAL REPORT

High Energy Density Coating of High Temperature Advanced Materials for Energy Efficient Performance

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Any findings, opinions, and conclusions or recommendations expressed in this report are those of the authors and do not necessarily reflect the views of the Department of Energy.
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2.0 EXECUTIVE SUMMARY

The project involved development of the technique and materials systems for coatings on ferrous (steel) and nonferrous (Al-alloy) structural alloys for high temperature wear and corrosion applications. Such coatings were ceramic-based (TiC, and TiB₂) and intermetallic (Fe-Al) materials systems. The laser-based and infrared plasma-based techniques were developed to deposit coatings on metal substrates. The use of laser, infrared plasma and combination allows coating of various surface geometries in selective manner with generation of novel and nontraditional microstructures within the coating and subsurface region. Due to control on processing parameters during both laser and infrared processing, various thermal conditions ranging from equilibrium to near- or non-equilibrium can be achieved to tailor the microstructure and both chemical and physical properties of the coatings.

Processing was investigated as a function of materials and processing parameters such as type of the material, energy density, mode of deposition of energy (pulse versus continuous), speed, etc. The microstructures within the modified surface and the interface (between the modified surface and the substrate) were characterized. Computational modeling based on thermodynamic calculations for evolution of phases during coating allowed prediction and design of microstructure as function of processing conditions. The functionality and effectiveness of coatings produced with experimental and theoretical approaches were evaluated through testing for dry sliding block-on-disc wear tests, high temperature furnace exposure oxidation tests, thermogravimetric (TGA) dynamic weigh change oxidation tests and potentiometric aqueous corrosion tests. These evaluations of coated materials indicated substantial improvements compared to the substrate in wear, oxidation, and corrosion performance. Such inexpensive substrate materials (steel and aluminum) coated with high performance material systems are highly economical for improved and efficient performance as structural materials in a broad range of applications such as hydro turbines, heat exchangers, die casting dies and inserts, continuous steel casting rolls, transfer rolls for flat glass, cutting and casting tools, combustion chambers in diesel engines, components for chemical processes, components for processing of pulp and paper, and auto engines, etc. The improved and longer lasting performance of these surface modified materials in a wide variety of applications hold tremendous potential in energy savings (up to $250 \times 10^{12}$ BTU/year) Although friendly commitments for industrial implementation of these materials systems and processing (engineering) techniques were obtained from industrial organization from various sectors, the time and lack of funding did not include the efforts on commercialization.

The specific observations of the present project included: 1) Plasma arc high density IR lamp can be used to coat Fe-Al alloys on 4340 steel. Process conditions and composition of precursor coating have to be carefully selected to retain iron aluminides on the surfaces of the samples. Under appropriate processing conditions, coatings free of porosity and cracks can be obtained using this technique. 2) Hardnesses of the coating and the heat-affected zone are a strong function of the processing parameters and hence can be tailor-made for an application. In the case of the samples processed with the IR plasma arc lamp, the hardness vary with the processing conditions. The processing conducted at lower energy density (2025 W/cm²) of IR lamp produced the harder (> 1.5 times) coating layer than those processed at higher energy density (2350 W/cm²). Similar trends for hardness of the coatings produced by laser based technique were observed. The hardness values within the coating were much larger (Knoop
hardness values >400) than that obtained for the base material (Knoop hardness values < 300). Also, the laser processing conducted at higher power (1750W) produced coatings of lower hardness compared to the coatings produced at lower power (1200W). Accordingly both IR and laser produced coatings at lower energies indicated higher wear resistance compared to the coatings produced at higher energies. Intermetallic compounds (stoichiometry) evolved in the coating was considered to be responsible for these changes. At higher energy of processing the coating stoichiometry was observed to be rich in Al compared that processed at lower energy thereby providing inferior hardness and wear properties. 3) Better corrosion resistance of laser coated iron-aluminide than the base steel may possibly be due to the superior oxide layer offered by mixed oxides. The aluminide in the composite coating was responsible to reduce corrosion and oxidation. The variation of corrosion current and oxidation resistance clearly indicates the influence of laser parameters in improving the corrosion resistance. It was observed that the Fe-Al coated samples exhibited significantly lower corrosion current (i_{corr}) in both sulfuric acid and sodium chloride solutions. The corrosion current roughly translates to corrosion rate. In other words, the laser coated samples are significantly corrosion resistant compared to the base materials. 4) Experiments involving oxidation in air, done in thermogravitometric analysis (TGA), indicated that laser processed samples were better oxidation resistant than substrate. All the time-weight gain/area relation followed either cubic (mostly) or parabolic. In other words, there is some extent of intrinsic oxidation resistance in coating as well as the substrate.

In light of the above mentioned specific observations and in relation to the project objectives several project accomplishments are achieved. Reliable, efficient and economic methods based on high energy laser and IR plasma lamp for coating ceramic and intermetallic materials on ferrous materials were developed. The development was conducted mostly proved for intermetallic coatings on structural steel (AISI 4340) they also proved their feasibility for coating ceramic systems such as TiC and TiB$_2$ on ferrous (steels) and nonferrous (Al) metals. The coating microstructures were thoroughly studied to understand their improved response to the chemical (corrosion, oxidation) and physical (hardness and wear) properties as function of processing parameters. The coating techniques (laser and IR plasma lamps) were configured to process the components of variety of sizes and shapes and are ready for processing industrial components in production environment. The following publication was based on the results obtained during the project: “Laser-Assisted Surface Modification of 4340 Steel with Iron Aluminum Alloys”, G. Muralidharan, P.G Engleman, C.A. Blue, V. K. Sikka, A.K Singh, A Khangar and Narendra B Dahotre, Proceedings of Materials Research Society (MRS) Symposium, Vol. 750, 2003.

Based on the experience of the present project the following recommendations are made. The work should be supported for development of Fe-Al/TiB$_2$ coatings on 4340 steel. Further development of Fe-Al coating on 4340 steel in for process conditions and alloy composition should be explored. Following the above efforts, dedicated efforts should be made for coating selected and important industrial components and should be field tested. These efforts should be done by identifying only one industrial sector and corresponding targeted components.
3.0 INTRODUCTION

In recent years, there has been a considerable increase in the potential and actual uses of certain ceramics and metals for structural, chemical, electrical and electronic applications in which strength; corrosion resistance; electrical conductivity and high temperature stability are basic requirements. Such major applications include hydro turbines, combustion chambers in diesel engines, die casting dies and inserts, continuous steel casting rolls, transfer rolls for flat glass, heat exchangers, cutting and casting tools, components for chemical processes, components for processing of pulp and paper, and auto engines, etc. In order to perform effectively and efficiently for these applications, different components must coexist and form the system as a whole. Also, integration of hybrid parts with ceramic-metal system into existing engineering designs can significantly enhance the performance of components. Additionally, the physical and economic limitations on production of large and complex shaped components out of one type of ceramic or metal alone often is expensive and unnecessary. Based on these requirements, surface modification technology is very critical for many structural applications.

Improved wear resistance and improved corrosion resistance. Both wear and corrosion resistances will extend the life of components used for various industries. For example, for each of the applications, the estimated improvement in life and corresponding tonnage of steel not required to be produced per year is listed in Table 1. In addition to extending the life of components, the industrial processing efficiency will also be enhanced by longer availability of equipment. The energy used for the total industrial sector in the United States is $25 \times 10^{15}$ BTU/year. Even an improvement of 1% in process efficiency will result in an energy savings of $250 \times 10^{12}$ BTU/year.

<table>
<thead>
<tr>
<th>Industry</th>
<th>Components</th>
<th>Estimated Improvement In Life</th>
<th>Savings (tons) Steel</th>
<th>Refractories</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydro power</td>
<td>Water turbines</td>
<td>4x</td>
<td>30,000</td>
<td>--</td>
</tr>
<tr>
<td>Chemical</td>
<td>Multiple components</td>
<td>2x</td>
<td>50,000</td>
<td>3,000</td>
</tr>
<tr>
<td>Pulp &amp; Paper</td>
<td>Multiple components</td>
<td>2x</td>
<td>20,000</td>
<td>5,000</td>
</tr>
<tr>
<td>Steel</td>
<td>Continuous caster rolls</td>
<td>3x</td>
<td>14,000</td>
<td>--</td>
</tr>
<tr>
<td>Glass</td>
<td>Transfer rolls</td>
<td>3x</td>
<td>6,000</td>
<td>10,000</td>
</tr>
<tr>
<td>Mining</td>
<td>equipment</td>
<td>4x</td>
<td>40,000</td>
<td>--</td>
</tr>
<tr>
<td>Aluminum</td>
<td>Die casting dies</td>
<td>2x</td>
<td>20,000</td>
<td>--</td>
</tr>
<tr>
<td>Automotive</td>
<td>Cylinder liners</td>
<td>1.5x</td>
<td>20,000</td>
<td>--</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td></td>
<td></td>
<td><strong>200,000</strong></td>
<td><strong>18,000</strong></td>
</tr>
</tbody>
</table>

Surface engineering consists of the design and modification of the surface and substrate to provide cost effective performance enhancement that is not possible using either component
individually. The modern manufacturing tools such as industrial lasers and infrared plasma that are available in domestic market have provided new possibilities to achieve this goal and remain competitive in the global market. Companies operating in the global economy are striving to extend the lives of old plants and systems by better engineering in the form of surface treatment of inexpensive materials to provide accurate, repeatable, and uniform properties. Thus the concept of extending component lifetime through service and repair is rapidly growing and becoming accepted practice. The high energy density processing tools such as lasers and infrared plasmas as technologically powerful and unique tools stand in the midst of these developments and offer tremendous potential for the purpose. In light of these needs for reduction of energy intensity for US manufacturing industry to remain competitive in world market and with potential of the proposed research to address these needs this project (DE-FC07-01ID14248) was awarded by DOE in 2001.

The existing limits of performance for the components can only be extended via surface enhancement technology, which presently appears to be the most suitable technical and economic approach as development of the bulk material is prohibitively time consuming and expensive. Furthermore, surface modification allows conversion of inexpensive substrate material for high performance applications without using very expensive bulk alloys. Thus there is a critical need to develop a more suitable and reliable surface modification technique(s). The proposed laser and plasma infrared-based techniques with operating parameters that can be precisely controlled for generating thermal conditions sufficient to synthesize/fabricate a product within the surface and subsurface region of the substrate material while producing both a minimum reaction zone and minimum impact on the microstructure within the substrate. The techniques through the control on and combination of the processing parameters can also be used to tailor the microstructure in and around the interface region between the modified surface and the substrate.

The proposed project was multi-organizational efforts that included academia (University of Tennessee) and federal research organization (Oak Ridge National Laboratory) Overall coordination of the project was conducted by the University of Tennessee (UT). Professor Dahotre served as the principal investigator and coordinated the technical activities. Dr. Vinod Sikka and Dr. Craig Blue of Oak Ridge National Laboratory (ORNL) were co-principal investigators. A laser based processing will be carried out at the Center for Laser Applications (CLA) of UT whereas infrared plasma lamp processing was conducted at the Infrared Processing Center (IPC) of ORNL. Center for Laser Applications is an accomplished center of excellence of the UT system. It has been in existence for the past 20 years and has been involved in numerous technologies related to lasers that have been conceived, developed and implemented in commercial/industrial environment. It is a leader in the development and application of laser related technologies. CLA’s association with the academic organization (UT) and its charter that includes applied research provide a unique opportunity to conduct the project both through fundamental understanding and industrial application point of view. Professor Dahotre has been involved in the past 20 years in developing applications of lasers for materials processing in auto, casting, electronic, manufacturing, etc. sectors. Infrared Processing Center of ORNL is the only center of its kind solely involved in developing materials and processing techniques for industrial applications related to wear and corrosion. Drs. Sikka and Blue are experts in materials processing and have been conducting several projects in cooperation with industry on infrared processing of materials.

This report presents the results of the work performed under this project. The report begins with the section on state-of-the-art of coating followed by the sections on project
objectives and approach to achieve them. The next major section is devoted to results and discussion that includes description on approach and methodology to produce coatings and microstructural, mechanical (hardness and wear), oxidation and corrosion properties characterization of the coatings. The report ends with the section on accomplishment, conclusions and recommendations. The corresponding references are also included at the end of the report.
4.0 BACKGROUND

4.1 State of the Art: Coating Technologies

Laser and plasma energy assisted surface modification procedures were employed in the present efforts to enhance metallic surfaces with thermal energy to create novel microstructures and surface chemistry modifications by external additives for coatings precursors (ceramics and metallic). The metal materials with enhanced surfaces for wear and corrosion resistance, have cross cutting applications in most of the industrial production sector in United States. Applications include: hydro turbines, combustion chambers in diesel engines, die casting dies and inserts, continuous steel casting rolls, transfer rolls for flat glass, heat exchangers, cutting and casting tools, components for chemical processes, components for processing of pulp and paper, and auto engines, etc. In these applications, however, these materials often experience extreme mechanical, thermal and chemical loading conditions and are expected to perform effectively beyond existing limits. The existing limits of performance for these materials can only be extended via surface enhancement technology, which presently appears to be the most suitable technical and economic approach. Also surface modification allows conversion of inexpensive substrate material for high performance applications without using very expensive bulk alloys. Thus there is a critical need to develop a more suitable and reliable surface modification technique(s) such as employed in the present project.

Many other existing surface modification techniques based on coating (physical vapor deposition, chemical vapor deposition, thermal spray, etc.) employed for this purpose are either prohibitively time consuming and expensive or produce coatings with physical and chemical nature that restrict their use for limited number of applications. When these methods are successful in producing reasonably sound coatings, they are seldom able to withstand the intended high service temperatures (> 500°C). On the contrary, the research conducted in this proposal promoted the synthesis of strong modified surfaces and significantly improved their performance for wear and corrosion applications. The laser and plasma infrared based techniques employed in the present work hold tremendous promise in competing with and possibly remaining a viable replacement for several existing surface modification techniques. The fact that laser and plasma infrared techniques can conducted in air without the need of any environmental chamber provides a flexibility of processing a component of any size and shape. Especially, delivery of laser beam via fiber optic provided additional flexibility of remote processing. These characteristics in supplement with precise control of operating parameters produce surface modification with a minimum impact on the microstructure, physical, and chemical properties of the substrate. The automation of the techniques has tremendous potential for reliability and repeatability in producing coatings.

4.2 Project Objectives

In view of above, following major objectives were set for the project:

- Develop a reliable, efficient and economic method of coating ceramic on metal using high energy density based technique. The development was conducted for ceramic systems such as TiC and TiB₂ on ferrous (steels) and nonferrous (Al) metals.
• Characterize the processed coating-substrate material systems for wear and corrosion properties under various conditions and establish a correlation between coating properties and process parameters.

• Develop an understanding the chemical, physical and microstructural transformations taking place in the selected representative systems during high-energy treatment. This knowledge about various transformations is believed to be necessary to subsequently develop highly efficient and cost-effective customized applications for the surface protection/modification.

4.3 Approach to Accomplish the Objectives

These objectives were accomplished by performing the following tasks.

4.3.1 Task 1: Enhanced Surfaces

This task was to create advanced materials through only enhancing the surfaces. At UT this task was carried out using lasers. However, at ORNL the surface enhancement was carried out using the high flux density plasma infrared source. The enhanced surfaces were created for ceramic-metal as the core material. The enhanced surfaces were created with the addition of coating precursor as external additive.

4.3.2 Task 2: Microstructural and Compositional Characterization

The physical appearance of the coating, coating depth and porosity were characterized using optical and scanning electron microscopes combined with digital image analysis. The microstructural characterization of the coating region, interface and heat affected zone were also performed by using optical and scanning electron microscopy. The distribution of solute elements in and adjacent to the interface region were analyzed using EDS and WDS techniques on the electron microprobe. Since the laser induced reaction coating technique with its large heating and cooling rates produces unconventional and nonequilibrium phases which control the mechanical and chemical properties of the coating and the interface, it was necessary to carry out a detailed phase analysis of the coated sample. Phases were be analyzed by using x-ray diffractometry and transmission electron microscopy. Computational modeling based on thermodynamic calculations for evolution of phases during coating was conducted for prediction and design of microstructure as function of processing conditions.

4.3.3 Task 3: Evaluation of Wear, Oxidation and Corrosion Behaviors

Wear behavior of the coated samples were studied by employing the block-on-disk tribometer under the dry sliding conditions at room temperature. The weight loss measurements were conducted under different sliding speeds and normal loads. Even though the tribometer is not equipped to provide high temperature and lubricating environments, these limited room temperature-dry sliding wear condition in supplement with high temperature corrosion results would provide substantial data to predict wear behavior of the coatings at elevated temperatures.
High temperature furnace exposure oxidation tests, thermogravimetric (TGA) dynamic weight change oxidation tests and potentiometric aqueous corrosion tests were conducted on coated samples.

4.3.4 Task 4: Assessment and Report Preparation

The assessment of the data and recommendation of directions for future efforts were done in the periodic meetings of the participating individuals either at ORNL or UTK. These meetings were conducted once in four months. These meetings also provided guidelines for quarterly reports to be prepared and submitted to DOE.

4.4 Relevant Qualifications and Past Experience of the Project Team Members

Dr. Narendra B. Dahotre is a Professor of Materials Science & Engineering at the University of Tennessee. He has been working in the area of laser materials processing for the past 20 years and has expertise in laser surface modification using industrial grade laser systems. Emphasis of his research has been study of structure-property relationship in laser-processed materials using analytical techniques such as electron microscopes, XRD, EMPA, etc. He has organized 12 symposia in the area of elevated temperature coatings and surface engineering. He has been editor/coeditor of 12 books in the area of elevated temperature coatings, ceramic-intermetallic coatings and lasers in surface engineering. He holds 15 US patents in the area of lasers and laser materials processing. He has authored or coauthored more than 100 scientific publications.

Dr. Vinod K. Sikka has 26 years of experience at ORNL in materials development, processing, and commercialization. His expertise includes understanding causes for heat-to-heat variability observed in stainless steels produced to ASTM Specifications, development and commercialization of high-strength Fe-Cr-Mo steels, and processing and properties of intermetallic alloys. Dr. Sikka has experience related to this project in research and management of compositional optimization, processing, production of large heats, properties, and commercialization. He has over 200 publications, 20 U.S. patents, and 6 R&D 100 Awards.

Dr. Craig A. Blue has initiated and developed the Infrared Processing Facility (IPF) at ORNL over the past six years. IPF is presently funded in excess of $1.5M/year that comes from an assortment of institutions including DARPA, NASA, Army, DOE and private companies. He has been actively involved in infrared plasma processing for ceramic coatings, surface heat treatment, joining and fabrication of advance materials. He has over 30 scientific publications and holds 3 US patents in the area of infrared radiation processing.
5.0 RESULTS AND DISCUSSION

5.1 Critical Review of Literature

In recent years, there has been a considerable increase in the potential and actual uses of certain ceramics and metals for structural, chemical, electrical and electronic applications in which strength, corrosion resistance, electrical conductivity and high temperature stability are basic requirements. Such major applications include hydro turbines, combustion chambers in diesel engines, die casting dies and inserts, continuous steel casting rolls, transfer rolls for flat glass, heat exchangers, cutting and casting tools, components for chemical processes, components for processing of pulp and paper, and auto engines, etc. In order to perform effectively and efficiently for these applications, different components must coexist and form the system as a whole. Also, integration of hybrid parts with ceramic-metal system into existing engineering designs can significantly enhance the performance of components. Additionally, the physical and economic limitations on production of large and complex shaped components out of one type of ceramic or metal alone often is expensive and unnecessary. Based on these requirements, surface modification technology is very critical for many structural applications.

Many problems exist, however, in synthesis/fabrication of ceramic-metal surface. In general, there is substantial difference between properties such as modulus of elasticity, coefficient of thermal expansion, and thermal diffusivity for ceramic-metal systems. Therefore, large thermally induced mechanical stresses are set up in the interface regions. In the past, this problem was circumvented with limited technical or commercial success using common techniques such as diffusion coating, functionally gradient coating and bond coatings via physical vapor deposition (pvd) [1-3], chemical vapor deposition (cvd) [4-7], thermal spraying [8-11], and weld overlay [12-13] techniques. Techniques such as diffusion coating have proven useful for producing coatings with good elevated temperature properties. However, because both pvd and cvd methods frequently require environmental chamber, their practicality is limited. Furthermore, they are also prohibitively time consuming and expensive because they rarely produce coatings of thickness >50 microns. In contrast, thermal spray technology does provide a coating of thickness up to 1000 microns, but it can have high porosity and a weak interface. The weld overlay technique is most economical to produce thick layers of thickness > 1 mm, however, it creates potentially critical conditions. The material at the interface is superheated for a long time resulting in accelerated reaction rates between different ceramics and substrates, and leads to extensive interdiffusion of species. This situation results in the formation of an entirely different microstructure with degraded mechanical and chemical properties. In addition, the relatively large heat source in these processes melts a large volume of the base materials, producing a coarse grain structure.

Thus, there remains a critical need to develop surface modification methods that can produce modified surfaces of thickness in the range of 100 microns – 1 mm are suitable for large components and field applications, and can produce structural modified surfaces/coatings for use at elevated temperature. Such methods will have tremendous potential for commercialization.

One approach to producing such modified surface/coating is high energy density laser [14-37] and plasma infrared [38-39] assisted surface modification. The recent advent of the multi-kilowatt laser with fiber optic beam delivery system and infrared lamps of various physical geometries mounted on a manipulator makes it possible to develop a versatile, and multipurpose
surface modification process. The most important advantage of LPIASM over other surface modification/coating techniques stems from the fact that LPIASM involve high cooling rates \(10^3\) to \(10^8\) K/s) and high energy densities (>3 kW/cm\(^2\)), which produce metastable phases by exceeding the solid solubility limit beyond equilibrium phase diagram prediction. This leads to development of wide variety of microstructures with novel properties, which cannot be produced by any conventional processing technique. Thus LPIASM holds a niche for producing modified surfaces of unique thickness range, material and microstructures.

However, with the exception of a few attempts a review of the technical literature uncovers very little about efforts to use integrated LPIASM for modifying surfaces for layer thickness >100 microns. Therefore, as long-term goals, this project will would develop the LPIASM technique to synthesize/fabricate novel material systems for reliable, repeatable and cost-effective performance in commercial environment.

### 5.2 Technical Approach and Hypothesis Guiding This Approach

The proposed approach involves synthesis and/or fabrication of the modified surface via chemical, microstructural and physical transformation in a controlled manner using external heating provided by high energy density laser beam and/or plasma infrared heat source. Localized heating of the precursor (elemental or alloy or molecular) deposited surface by the laser beam and/or plasma infrared heat source will initiate a chemical transformation, which will further be sustained to synthesize reaction products at the interface between the modified surface region and the substrate, resulting in chemical interaction and bonding. Such a technique can appropriately be described as a Laser and Plasma Infrared Assisted Surface Modification (LPIASM) process. The proposed research is designed to prove the feasibility of the technique for synthesis/fabrication of ceramic, composite and metal based modified surface layers on ferrous and nonferrous materials.

In LPIASM, unlike many other surface modification techniques, precise control over processing parameters allows creation of thermal conditions suitable to promote controlled reaction between the substrate material and precursor material to aid in increasing surface energy and wettability of substrates via formation of different products at the interface. Also in the proposed technique of LPIASM the action of powerful energy fluxes delivered by a laser and/or infrared source at a convenient location eliminates the need to heat a large volume of the material system by an external heat source thereby avoiding damage to the whole structure. This is particularly useful in critically thin sections or geometries that have complicated topographies. The rapid rates of heating and cooling in a narrow interaction region result in the formation of nonequilibrium and unconventional phases at the interface and prevent recrystallization of grains within both the substrate and the modified surface. This ensures that strengths are maintained. Through the appropriate selection and control of precursor mixtures and processing parameters (such as continuous wave mode, pulse tailoring technique, beam power, traverse speed, etc.), LPIASM can be tailored to synthesize/fabricate materials in the surface region which are physically and chemically compatible with a wide variety of ceramic or metal substrate systems.

Further insight into synthesis/fabrication of laser and plasma infrared modified surface can be obtained for reliability and repeatability in commercial environment by mathematical modeling
of the process. Such modeling will be based on chemical transformations and microstructures during LPIASM that will also take into account important laser process parameters.

The greatest challenges were more scientific than technological in nature, such as developing the fundamental basis for correlating microstructural, chemical and physical changes with process parameters and wear and corrosion properties. In light of this, the main targets included systematic evaluation of microstructural changes in relation to process parameters and wear/corrosion properties.

5.3 Experimental Methodology, Test Procedures and Characterization Methods

5.3.1 High Energy Density Processing: Infrared Plasma Arc Lamp and Laser

Infrared (IR) plasma arc processing was done at the Infrared Processing Center of ORNL. The center houses an infrared plasma processing facility that utilizes a unique technology to produce an extremely-high power density of 3.5 kW/cm² for a single lamp, the most powerful lamp in the world. Instead of utilizing a resistive element to produce infrared, controlled and contained plasma is utilized. The lamp consists of a 3.175-cm-diam-quartz tube, which can be 10, 20, or 35 cm long. The lamp is sealed at the ends where the cathode and anode are located. Deionized water mixed with argon or nitrogen gas enters at the cathode side via high-velocity jets impinging at a given angle. Due to the high velocities and pressure, the deionized water separates to the wall of the quartz and spirals down the length of the quartz in a uniform 2- to 3-mm film. This water film serves two purposes: (1) to cool the quartz wall and (2) to remove any tungsten particulate that may be expelled from the cathode. The gas moves in a spiral fashion down the center of the tube, and a plasma initiation device strikes the plasma. The plasma is stable and produces an infrared spectrum from 0.2 to 1.4 µm, similar to natural sunlight in energy distribution and color rendition. The color temperature of the lamp is in excess of 10,000 K. Powder coatings in this study are highly absorbing due to the open structures, and behave like small black bodies. The lamp has a typical life of approximately 1200 h and failure occurs in the anode or cathode, which are inexpensive and can be changed in approximately 15 minutes. Another key issue to point out is that the lamp has a consistent spectral output independent of lamp life and power level. Thus, the process coating will always be impinged upon with the identical infrared spectrum. The lamp is typically configured with a line focus or a uniform irradiance reflector.

Processing was performed with the sample placed in an environmentally controlled box with an IR-transparent quartz cover. In this work, the IR plasma arc lamp was used to synthesize coatings. The processing conditions used were: Trial #1: First scan at a power of 2025 W/cm² and a scan speed of 8 mm/sec, followed by an immediate second scan at 2350 W/cm² and a speed of 8 mm/sec., Trial #2: First scan at 2025 W/cm² and a scan speed of 6 mm/sec and the second at 2350 W/cm² and a speed of 8 mm/sec.

Hobart HLP 3000, 3.5 kW and Rofin Sinar R3000 3.2 kW Nd:YAG laser that generates an intense coherent monochromatic beam of 1.06 µm was employed in the present work. The
laser can operate in continuous and pulse modes. It equipped with 600 µm diameter 17-meter long fiber optic for beam delivery. The fiber is interfaced with an end effector that houses a set of spherical and cylindrical lenses. A combination of cylindrical and spherical lenses is put together to shape the laser beam output into a line configuration (6 mm x 600 µm) with dumbbell shaped energy distribution. In spatial mode, the high energy lobe at two ends of line beam compensates for rapid heat conduction (loss) to the surrounding material along the edges of the track and produces uniform thermal effects within the track. Such a line beam with unique energy distribution permit processing with minimum or no overlap between the successive passes. The laser is also equipped with 10-feet linear motion work station. The laser operation and beam and work piece motion are controlled with integrated PC based system. Such fiber optic based beam delivery provides an added capability of traversing the beam on the components of various shapes and sizes thereby making it suitable for industrial processing. In the present work several sets of processing parameters were employed that were optimized in accordance with earlier experience. One set of processing parameter included, laser beam power and traverse speed kept constant at 2kW and 100 cm/min where as other set included three different laser power settings of 1250 W (Low), 1500 W (Medium) and 1750 W (High) with the travel speed kept constant at 220 cm/min.

5.3.2 Materials

The selection of the coating composition depends upon the composition of the substrate to be coated and the method to be employed. In the present effort, several coating precursors were investigated.

Commercially available (99.5% pure) TiC and TiB₂ powders obtained from CERAC, Milwaukee, WI were used as precursor in some of the studies. The average particle size was 10 µm. The precursor in water-based organic vehicle (hydroxypropyl methyl cellulose) was sprayed on the substrate coupons using a manual spray gun. The average thickness of the pre-placed powder (precursor) was 150 ± 15 µm for 6061Al and 90 ± 15 µm for 4340 steel. Sprayed coupons were dried at 70°C for 1 hr prior to laser processing.

In addition, coatings of intermetallic materials were also synthesized. Argon gas-atomized FeAl alloy powder (Fe-41.7Al-0.18Mo-0.04Zr-1.1C-0.02B, in at.%), -100 mesh particle size, was mixed with pure Al powder resulting in an overall compositions of 75 mole % of Al in the FeAl-Al mixture. Another composition included 75 mole % of Al in the FeAl-Al mixture seeded with 15 vol% TiB₂. These mixtures were subsequently blended with water-based organic binder (hydroxypropyl methyl cellulose) and sprayed as a precursor coating onto coupons of 4340 steel (Nominal composition: Fe-1.8C-0.74Cr-0.7Mn-0.11Mo-1.7Ni-0.39Si, in at.%) using a manual spray gun.

5.3.3 Test Procedures and Characterization Methods

Testing and analysis of coated samples included optical, scanning electron (SEM) and transmission electron (TEM) microscopies, electron probe micro analysis, x-ray diffractometry, micro hardness and wear testing, corrosion testing, oxidation evaluation. The details of these test and characterization methods are provided in the following sections.
5.3.3.1 Microscopy

Topographical and cross-sectional observations were made on the processed samples after etching with 2 vol. % Nital for steel and Kellings reagent for aluminum. Surface morphology was evaluated using a Hitachi-3500 scanning electron microscopy (SEM) (Hitachi, Tokyo, Japan). CAMBEX Electron Probe Micro Analyzer (EPMA) operated at 25kV was employed to analyze the cross-sectioned samples for the variation in composition as a function of position within the coating and the substrate.

Both mechanical and chemical performances of the coating are influenced by the interface between various phases within the coating as well as the substrate and coating. The microstructural evaluations of these interfaces can best be conducted by TEM analysis. TEM analysis was conducted using Hitachi 800 microscope operated at 200 kV. The coating thicknesses achieved are less than 500 microns. Also these coatings are relatively harder and brittle than the substrate material. Thus thickness and hardness pose complex problem in preparation of TEM samples from coating region using conventional techniques such as electropolishing and ion beam milling. Both techniques require mechanical cutting, grinding and polishing for preparation of submillimeter thick foil samples for further electropolishing or ion milling to achieve thin enough sample for TEM observations. The mechanical treatment in preparation of samples often lead to cleavage damage in harder samples and electropolishing and ion milling are extremely time consuming and unreliable in providing good samples. Also often they undergo differential ion/electrochemical thinning. In view of these shortcomings, newly developed Focused Ion Beam (FIB) milling and lift-out technique that utilizes a 30kV Ga \(^+\) ion beam to extract electron transparent specimens with nanometer scale precision was adopted in the present efforts. The FIB lift-out technique is especially very suitable to ceramic and iron-aluminide coatings as it allows sample extraction from extremely small volumes of unpolished material from a site at the sub-micrometer scale without introducing any artifacts of mechanical preparation. FIB milling was performed with an FEI Model 200 TEM FIB system at the University of Central Florida.

5.3.3.2 Phase Identification, Hardness and Wear Testing

A Philips Norelco X-ray diffractometer operated at 30 kV and 20 mA was used to characterize the starting coating precursor powders as well as the coatings with Cu K\(\alpha\) radiation. The diffraction range was from 20° to 100° with a step increment of 0.02° and a count time of 1 s. These observations were supplemented with microhardness tests (Knoop hardness, 100 gm normal load, 15 seconds loading time). X-ray diffraction measurements were carried out to identify phases present in the samples. The effect of processing on the wear resistance was studied using a block-on-disk tribometer under the dry sliding conditions. Coated coupons were tested for dry sliding wear against a hardened steel ring rotating at a linear speed of 4.6 m/s. Weight loss measurements were made after successive 2-minute intervals. Wear tests were conducted for a total of 10 min with a normal force of 50N

5.3.3.3 Oxidation Testing

The kinetics and mechanism of the oxidation were evaluated by exposing samples in a resistance furnace. These oxidation studies also helped estimate the long-term oxidation
response. The coupons were sectioned along the interface between the coating and the substrate on a slow-speed diamond laced wheel machine. This provided stress free sections of the coating (~ 500 microns thick) which were further cut into smaller samples of 5mm x 5mm. Similar dimension samples were also cut out from the substrate material (4340 steel) for performance comparison. These samples were exposed to air at constant temperature of 600°C inside an electric resistance box furnace. Initially it was decided that weight change measurements will be conducted for the time duration of 120, 240, 480 and 960 hours. However, due to very slow oxidation kinetics (high oxidation resistance) weight changes are reported only for time durations of 120 and 504 hours.

In order to conduct oxidation studies at various holding temperatures, thermo-gravimetric (TGA) studies were undertaken for the coating and the substrate. The coating alone cannot be directly heated in furnace, as the weight gain due to oxidation of substrate would shadow the coating. Hence, the substrates were carefully machined from the coating giving a thin layer of about 100 microns. The resulting samples were essentially the composite microstructure formed in laser processing. The TGA study was conducted at temperatures of 500°C, 700°C, and 900°C in air. The TGA furnace was heated at a rate 10°C/min with hold time of 3 hours followed by cooling at a rate of 10°C/min. The weight change as function of time was constantly recorded during the entire time of exposure.

5.3.3.4 Corrosion Testing

The aqueous corrosion performance of the coated sample was evaluated using potentiometric measurements. The Tafel calculations based on these measurements give access to the corrosion current regularly present at the surface of a metal which is in contact with a corroding solution [40-41]. The corrosion is expressed in loss of metal thickness per year. The Tafel method gives also access to other corrosion parameters such as the zero current potential (corrosion potential), the corrosion current and the polarization resistance of the sample under study. The Tafel calculation is a complete tool to study the corrosion process at a metal surface. Therefore, in the current study corrosion of laser processed samples were carried out to obtain Tafel calculation. The rectangular samples (10×10mm) were cut from the coated samples. These specimens were directly polished (without prior grinding on emery papers), using alumina slurry (0.05 µm) size suspension, on velvet cloth to remove oxidized layer, dirt and contamination from the specimen’s surface. Before polarizing, samples were ultrasonically cleaned with acetone solution. Anodic polarization and Tafel curves were recorded in the 1N sulfuric acid and 1% sodium chloride solutions. Solutions were prepared by adding AR grade sulfuric acid and NaCl crystal to distilled water. Anodic polarization curves were initiated from -300mV with respect to open circuit potential (OCP). However the Tafel plots were initiated from ±250 mV with respect to OCP. Both anodic polarization and Tafel plots were carried out at the scanning rate of 6V/h. The saturated calomel electrode (SCE) was used as the reference electrode and platinum as a counter electrode. The experiments were carried out at ambient temperature.

5.4 Presentation and Discussion of Results

Two widely used materials were used substrates: (1) a medium-carbon, ultrahigh-strength, low-alloy steel (AISI/SAE 4340), and a heat treatable aluminum alloy (6061-T651).
According to the ASM Metals Handbook, 4340 steel is considered the standard by which other ultrahigh-strength steels are measured. It combines deep hardenability with high ductility, toughness, and strength. Typical applications include fasteners; gears, shafts and crankshafts for engines; and critical structural members for aircraft. Aluminum alloy 6061 is used in applications where good strength, formability, weldability, and resistance to corrosion are required. Typical applications include bridge railings, marine applications, and transportation equipment.

5.4.1 IR Coating

The coatings on three 4340 steel samples were fused using the IR plasma lamp process at ORNL. The first alumina-coated sample was passed two times under the plasma-arc lamp under the following conditions: 900 Amp at a speed of 10 mm/s, followed by 900 A at 5 mm/s. The alumina in this sample melted as evidenced by a glassy surface, but the coating did not adhere to the steel, spalling off in large pieces upon cool-down. The second alumina-coated sample was passed under the plasma-arc lamp under the following conditions: 900 Amp at a speed of 10 mm/s, 900 Amp at a speed of 10 mm/s, followed by a third pass at 900 A at 5 mm/s. Although this coating appeared to have adhered it was only slightly more adherent than that on the previous sample. Examination using optical microscopy at magnifications up to 400 X showed that, as expected, the coating on this sample had undergone more melting due to the third heating pass. The third sample was comprised of a coating of TiB$_2$ powder on type 4340 steel. In this case the following parameters were used in the HDI process to fuse the coating: 900 Amp at 7 mm/s followed by 900 A at 5 mm/s. The TiB$_2$ appeared qualitatively to be tightly adherent to the steel but examination by optical microscopy and scanning electron microscopy indicated that the coating was not fully dense.

- Figure 1 shows a cross-sectional optical micrograph of the sample processed using condition 1, while Figure 2 shows the corresponding X-ray diffraction pattern. Analysis of the diffraction pattern shows the presence of FeAl. As in the laser-processed samples, an oxide layer is observed on the surface. Figure 3 shows a cross-sectional optical micrograph of the sample processed using condition 2, while Figure 4 shows the corresponding X-ray diffraction pattern. Peaks that would indicate the presence of intermetallic compounds were not observed in the diffraction pattern. It should be noted that the only difference between the two sets of parameters is that in the second set of processing parameters, the scan at the lamp power of 2025 W/cm$^2$ occurred at a speed of 6 mm/sec instead of the speed of 8 mm/sec used in set 1. The slower scan speed resulted in a larger heat input to the sample, thus causing increased dilution and the disappearance of the intermetallic compound.
Figure 1: A cross-sectional optical micrograph of a 4340 steel substrate with Fe-Al alloy coatings processed using the plasma arc lamp (Processing condition 1).

Figure 2: An X-ray diffraction pattern from the sample processed with the plasma arc lamp (Processing condition 1).
Figure 3: A cross-sectional optical micrograph of a 4340 steel substrate with Fe-Al alloy coatings processed using the plasma arc lamp (Processing condition 2).

Figure 4: An X-ray diffraction pattern from the sample processed with the plasma arc lamp (Processing condition 2).

Figures 5 shows the variation in Knoop hardness values as a function of position within the coating, the heat-affected zone, and the substrate for samples processed using the plasma arc
lamp. In the case of the samples processed with the plasma arc lamp, the hardesses vary with the processing conditions. The sample processed using parameter set 1 reveals hardness values within the coatings layer that are higher than those processed using set 1. Intermetallic compounds present in the sample processed using set 1 may be responsible for the higher hardness values. A significant feature in both samples processed using the plasma arc lamp is that a region with high hardness occurs at a distance of about 100 µm to 300 µm from the surface of the sample. Presence of a martensitic region, as observed in previous studies [22-25, 27] of laser processing of steel substrates, results in high hardness values. It should be noted that hardness values were measured at intervals of 50 µm only. Any variation over length scales smaller than this would not be observed.

Figure 5: Variations in Knoop hardness values as a function of distance perpendicular to the surface and as a function of the process parameters in coatings processed using the plasma arc lamp.

In light of above mentioned observations, the following efforts were made on laser based coating. Exploratory test indicated the feasibility of laser for coating ceramics on ferrous and non-ferrous alloys. However, in line with IR lamp coating efforts, the focus was kept on Fe-Al based coating using laser. Intention was to identify Fe-Al as a suitable binder (matrix) system for TiB$_2$ to deposit TiB$_2$/FeAl composite coating on ferrous and nonferrous (Al-alloy) substrates with better process control and repeatability. Therefore, it was considered essential to first successfully deposit only coating of FeAl before attempting to coat FeAl with TiB$_2$ i.e. TiB$_2$/FeAl composite coating on ferrous and nonferrous substrates using laser based technique. Accordingly, the major efforts were focused on depositing only FeAl using lasers.
5.4.2 Laser Coating

Figure 6 shows an overview of the cross section of these laser processed samples. In both cases the coating is dense, adherent and defect-free (porosity and cracks). Coating is composite in nature with TiC particles in Al matrix and TiB\textsubscript{2} particles in steel matrix. The distribution of ceramic particles in both cases is uniform indicating better wettability within the selected ceramic-metal systems.

![Composite coatings produced using laser technique: (a) TiC/Al composite coating on 6061Al-alloy and (b) TiB\textsubscript{2}/steel composite coating on 4340 steel.](image)

X-ray diffraction analysis of TiC coated 6061Al surface indicated TiC and Al as the major constituents of the coating along with few other minor phases such as Al\textsubscript{2}O\textsubscript{3} and Al\textsubscript{3.21}Si\textsubscript{0.47}. Similarly, in TiB\textsubscript{2} coated steel surface TiB\textsubscript{2} is the major phase along with small peaks of metastable phases of type Fe\textsubscript{a}B\textsubscript{b} and Ti\textsubscript{m}B\textsubscript{n}. Formation of these additional phases in minor quantity in both coatings is attributed to high-energy input combined with high cooling rate by self-quenching during laser processing. Formation these phases can be controlled by controlling the processing parameters.

Hardness testing was performed using microhardness tester with Knoop indenter. Hardness values were recorded within the coating and the substrate and along the interface between the coating and the substrate. In all cases, the hardness was substantially higher (>3 times) in the coating compared to the substrate material. Also the indentation made along the interface did not show any cracking thereby indicating the coherent and strong interface. Further qualitative evaluation of the interface in various substrate/coating combinations was conducted by making series of indentation along the interface under subsequently increasing normal loads within the available range (50-1000 gm). None of the indentations within the range of normal load showed cracking at the interface. Such evaluation asserted the soundness and strength of the bonding (interface) between the coating and the substrate. As seen in the Figure 6, hardness indentations within various regions of the processed samples provide the relative nature of these regions. It is clearly seen that size of the hardness indentation within the coating is small compared to the indentation within the substrate indicating that the coating is substantially harder than the substrate. Also the lack of the cracking at the end of the indentation along the interface between the coating and substrate indicates that the interface is strong without any defects. Such strong interface and corresponding improved hardness in the coating is among other reasons to a
chemical bond formation through a reaction zone at the interface as shown in TEM micrographs in Figures 7 and 8. Thus these efforts to synthesize the coatings and post process analysis indicated that the coatings are sound and the process hold premise to produce a variety of ceramic coatings on different metallic substrates.

Figure 7. High resolution TEM images showing a nanosized reaction zone between the TiB₂ particle and Fe.

Figure 8. TEM image showing a reaction zone between the TiB₂ particle and the corresponding EDS spectrums.

Figure 8. TEM image showing a reaction zone between the TiB₂ particle and the corresponding EDS spectrums.
Figures 9 (a) – (c) show typical cross-sectional optical microscopy images of the samples coated with 25 mole % FeAl/75 mole % Al mixture using laser based processing technique with processing parameters mentioned earlier in experimental procedures (1250 W (Low), 1500 W (Medium) and 1750 W (High) with the travel speed kept constant at 220 cm/min). Note that there exists a near-surface band, which was not etched by the 2 vol. % Nital solution. The size of this band increases with increase in the power as is observable from the figures. Furthermore, as can be seen from the figures, the integrity of this layer is excellent and the interface between this layer and the heat-affected zone in the substrate is free of cracks and voids. Figure 10 shows the Fe and Al concentration as a function of position obtained using EPMA. From the figure it is clear that the power input has a significant influence on the maximum concentration of Al obtained at the surface and the distribution of Al as a function of depth. Maximum Al content of about 31 at. % is obtained at the surface for the lowest power input while the Al content drops to about 15.0 at. % for increased power levels. X-ray diffraction study shows the presence of an iron aluminide in the sample with the highest Al content at the surface and its absence when the Al content decreases to lower values. This is consistent with the known phase equilibria information which shows that the solid solubility of Al in Fe is about 18 at.% - 20.0 at.% at 200°C [42-43]. Furthermore, note that the depth to which Al is detected increases with increasing power input. At the lowest power input, Al can be detected to a depth of about 100 µm from the surface while at the highest power input, Al is observed up to about 275 µm. This clearly shows that intermixing, interdiffusion, and the dilution increase with increasing...
power inputs. A comparison of Figures 8 and 9 shows that the size of the unetched/lightly-etched regions is comparable to the distance to which there is detectable Al concentration.

Careful comparison of the Al concentration as a function of position for the different power inputs shows an additional trend. As the power input increases from low to medium, the maximum Al content at the surface decreases by about 45% while the depth to which Al is present increases by about 100%. However, as the power increases from medium to high levels, the maximum concentration of Al at the surface remains approximately the same, but Al is observable to a depth that is about 1.5 times greater than that observed for medium power levels. This would tend to indicate that more Al is retained within the sample at higher power levels.

Figures 11 (a) and (b) show the variation in Knoop hardness values as a function of position within the coating, the heat-affected zone, and the substrate. Indentations were made at an inclination to the normal to the surface (~20°) in order to maximize the number of readings that could be obtained within the coating. Note that the hardness values within the coating are much larger (Knoop hardness values >400) than that obtained for the base material (Knoop hardness values < 300). It is intriguing to note that the coating prepared with the lower Al content in the sprayed layer (Figure 11 (a)) exhibits on an average, larger hardness values in the surface layers than that obtained with the higher Al content precursor layer (Figure 11 (b)). Also, higher peak hardness values are observed in this sample as shown in Figure 11 (a).

![Graph](image1.png)

Figure 11. Variations in Knoop hardness values with laser power as a function of distance perpendicular to the surface in coatings prepared with (a) Precursor layer with 43.5 mole %Al, and (b) Precursor layer with 75 mole % Al.

Figure 12 (a) shows the results obtained from the block-on-disk wear tests. The cumulative weight loss obtained over a period of 10 minutes has been normalized with that obtained for the base material. A study of the wear rates shows that both processing conditions and the composition of the initial coating layer have a significant effect on the wear properties. The effect of the laser power can be observed by comparing the properties of the samples with the group that had the same initial composition of the sprayed coating. Note that the wear property is best when the laser power is low and worsens with increasing laser power.
The relationship between the wear properties shown in Figure 12 (a) and the average Knoop hardness values within the region 275 µm from the surface shown in Figure 12 (b), follow some interesting trends. The most prominent feature is that the average wear in the coatings prepared with the higher-Al content precursor layer is inferior to that prepared with the lower-Al content precursor layer. This is consistent with the trends in the average hardness values, as shown in Figure 12 (b). Note that for the same power levels, the average hardness in the samples prepared with the higher-Al content precursor is lower with corresponding larger wear rates.

The trends in the wear properties can be related to the microstructure of the coatings. As could be observed from Figure 10 and as argued earlier, there is evidence for the formation of iron aluminides on the surface only when the samples were processed with low laser power. In the samples processed with the higher laser power, dilution results in the formation of Fe-Al solid solution rather the iron aluminides. The effect of this microstructural change is dramatically reflected in the degradation of the wear properties. For example, if we consider the coatings prepared with the precursor containing 43.5 % Al (low Al), the change in wear properties between the low and medium power settings is drastic (about a factor of 3) while the average hardness decrease is only about 5%. The change in power setting from medium to high results in an increase in the average hardness by about 10% which results in an improvement in the wear properties by a comparable magnitude. These results, which show a significant influence of the phase constituents of the coating on the wear behavior, are consistent with previous measurements [44-46] conducted on the wear properties of bulk aluminides and Fe-Al solid solutions, which showed that the wear properties of the aluminides were much better than that of the solid solution. Our observations that show the wear properties of the coatings containing an iron aluminide are comparable to that of 4340 steel merit further study. Previous work on bulk materials shows that the wear properties of the iron aluminides are a strong function of the composition. For example, Fe$_3$Al with a composition of Fe$_{75}$Al$_{25}$ was found to be worse than 4340 in its wear properties, while Fe$_3$Al with a nominal composition of Fe$_{66}$Al$_{34}$ was found to better than 4340 with respect to its wear properties. On the other hand, FeAl with a nominal

![Figure 12. Variation in the (a) Normalized cumulative weight loss, and (b) Average Knoop hardness value over a 275 µm thick region at the surface, as a function of precursor Al-content and laser power.](image)
composition of Fe$_{64}$Al$_{36}$, showed wear properties comparable to that of 4340 steel. Alloying additions of Cr and Ti to FeAl was shown to improve the wear properties [47-52].

Although in general Fe-aluminides coatings are synthesized on steel substrate, it was noticed via x-ray diffraction analysis that the coating contains variation in stoichiometry of the composition. This is due to the effect of processing conditions on intermixing, interdiffusion, and the dilution of components of the coating precursor (Fe and Al). The coating has the highest Al content at the surface and it decreases to the level of absence depending upon the Al content in the precursor used to synthesize the coating along with the processing conditions. For example in earlier trials, maximum Al content of about 31 at. % is obtained at the surface for the lowest laser power input (1250 watts) while the Al content dropped to about 15.0 at. % for increased power levels (> 1500 watts) for 75 mol% Al in the precursor.

Such variation in stoichiometry of Fe-aluminide is expected to greatly influence both mechanical and corrosion/oxidation properties of the coatings. It was found that the coating prepared with the lower Al content in the sprayed precursor layer exhibited on an average, larger hardness values in the surface layers than that obtained with the higher Al content precursor layer. Another very prominent feature noticed was that the average wear in the coatings prepared with the higher-Al content precursor layer was inferior to that prepared with the lower-Al content precursor layer which was consistent with the trends in the average hardness values. The trends in the wear properties can be related to the microstructure stoichiometry of the coatings. In the samples processed with the higher laser power, dilution resulted in the formation of Fe-Al solid solution rather the iron aluminides. A significant influence of the phase constituents of the coating on its wear behavior, is consistent with previous measurements conducted on the wear properties of bulk aluminides and Fe-Al solid solutions, which showed that the wear properties of the aluminides were much better than that of the solid solution. Thus it was considered very important to study relationship between microstructure and stoichiometry of these iron-aluminide coatings for further establishing their relationship with mechanical (wear/erosion) and chemical (corrosion/oxidation) properties for tailoring the properties of the coatings.

**5.4.3 Oxidation Response of Coating**

Oxidation response of the sample was evaluated on the basis of both long term and short term exposures of coated samples. Identification of the type and/or nature/mechanism along with the kinetics of the oxidation were part of the efforts. As the samples processed with laser based technique provided the best coatings of Fe-Al the oxidation studies were conducted on only these samples. These coupons were selected for oxidation from many other set of coupons processed under different materials and process parameters because initial x-ray diffraction analysis indicated that these coupons provide a wide and distinct range of iron-aluminide stoichiometry. The coupons were sectioned along the interface between the coating and the substrate on a slow-speed diamond laced wheel machine. This provided stress free sections of the coating (~ 500 microns thick) which were further cut into smaller samples of 5mm x 5mm. Similar dimension samples were also cut out from the substrate material (4340 steel) for performance comparison.

For long term exposure these samples were exposed to air at constant temperature of 600°C inside an electric resistance box furnace. Initially it was decided that weight change measurements will be conducted for the time duration of 120, 240, 480, 960, and 2464 hours.
However, due to very slow oxidation kinetics (high oxidation resistance) weight changes are reported only for time durations of 120, 504, and 2464 hours. Weight change in relation to time of exposure for various laser processing powers is presented numerically in Table 1 and graphically in Figure 13.

Table 1: Weight change as function of time during air oxidation of laser coated 4340 steel

<table>
<thead>
<tr>
<th>Sample Processed at</th>
<th>Substrate 4340 Steel</th>
<th>1200 Watts</th>
<th>1500 Watts</th>
<th>1750 Watts</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature of Exposure</td>
<td>600 °C</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Weight, mg</td>
<td>Time of Exposure</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0 hr</td>
<td>302.10</td>
<td>779.40</td>
<td>452.21</td>
</tr>
<tr>
<td></td>
<td>120 hr</td>
<td>303.17</td>
<td>781.03</td>
<td>453.17</td>
</tr>
<tr>
<td></td>
<td>0 hr</td>
<td>546.20</td>
<td>770.00</td>
<td>335.80</td>
</tr>
<tr>
<td></td>
<td>540 hr</td>
<td>555.00</td>
<td>776.56</td>
<td>338.50</td>
</tr>
<tr>
<td></td>
<td>0 hr</td>
<td>200.90</td>
<td>618.20</td>
<td>331.90</td>
</tr>
<tr>
<td></td>
<td>2764 hr</td>
<td>230.07</td>
<td>646.70</td>
<td>356.33</td>
</tr>
<tr>
<td>Weight Gain, %</td>
<td>Time of Exposure</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>120 hr</td>
<td>0.3542</td>
<td>0.2091</td>
<td>0.2367</td>
</tr>
<tr>
<td></td>
<td>540 hr</td>
<td>1.6111</td>
<td>0.8519</td>
<td>0.8040</td>
</tr>
<tr>
<td></td>
<td>2764 hr</td>
<td>14.8332</td>
<td>4.6102</td>
<td>7.3607</td>
</tr>
</tbody>
</table>

Figure 13: Relationship between %weight change and time of exposure for oxidized samples

The regression analysis of the experimental data provided a linear fit for weight change and time of exposure (oxidation) behavior in all coatings and the substrate sample (Figure 13). Such behavior is represented by the following equation where \( t \) is oxidation time (exposure time) and \( K \) and \( C \) represent oxidation kinetic constants.

\[
W = K t + C \tag{1}
\]

where \( W \) is % weight gain. Table 2 lists all the values of \( K \) and \( C \) for these samples.
Table 2: Oxidation kinetic constants for at constant temperature (600 °C).

<table>
<thead>
<tr>
<th>Sample Processed at</th>
<th>K (% hr⁻¹)</th>
<th>C (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1200 Watts</td>
<td>16.89 x 10⁻⁴</td>
<td>-1.5993</td>
</tr>
<tr>
<td>1500 Watts</td>
<td>29.48 x 10⁻⁴</td>
<td>-0.0606</td>
</tr>
<tr>
<td>1750 Watts</td>
<td>24.73 x 10⁻⁴</td>
<td>-0.7818</td>
</tr>
<tr>
<td>Substrate 4340</td>
<td>59.45 x 10⁻⁴</td>
<td>-0.4513</td>
</tr>
</tbody>
</table>

It is evident from Figure 13 that although for the initial period (up to 170 hr) the % weight gain for substrate 4340 steel is slightly lower than the % weight gain for samples processed at 1750 watts it is significantly higher (> 1.5 times) than all coated samples for rest of the range of exposure time. Among coated samples, % weight gain for the sample processed at 1750 watts is higher than those in samples processed at 1200 and 1500 watts. It appeared that both samples processed at 1200 and 1500 watts possess similar % weight gain without much variation throughout the exposure time. Similarly, lower values of oxidation rate constant K (Table 2) for all coated samples compared to substrate samples (< 0.5 times) is due to substantial improvement in the oxidation resistance of the coated samples. It is also indicative of the fact that kinetics of oxidation in all coated samples is significantly slower than the substrate sample. Furthermore, among coated samples, the oxidation rate constant K increases as the laser power used to process the sample increases. Such distinct behavior in oxidation response for uncoated versus coated and among the coated samples is due to Fe-Al coating and Fe-Al coating stoichiometry. Fe-Al (aluminide) is known to be oxidation resistant due to presence of Al in the composition. However, the degree of oxidation resistance (% weight gain and oxidation rate constant) appears to depend upon the content of Al in the Fe-Al coating composition. In the samples processed with the higher laser power, dilution resulted in the formation of Fe-Al solid solution rather the iron aluminides and therefore reduced oxidation resistance. A significant influence of the phase constituents of the coating on the oxidation behavior, are consistent with previous measurements conducted on the oxidation and wear properties of bulk aluminides and Fe-Al solid solutions, which showed that the oxidation and wear properties of the aluminides were much better than that of the solid solution.

Data in Table 2 and Figure 13 clearly show oxidation behavior of the coatings in comparison with the substrate. Even after such long exposure (2764 hours), all samples including substrate indicated linear oxidation rate at the constant temperature of exposure (600 °C). Although such linear oxidation behavior is an indication of ongoing oxidation process, it is clear that oxidation is much higher (% weight gain > 2 times) compared to coated samples. The weight change in coated samples, however, indicated very small (4-7%) spread in their values after 2764 hours of exposure. These observations are indicative of increased oxidation resistance in coated samples and possibly they would reach saturation oxidation behavior (very low weight change) with further (after 2764 hours) exposure time.

The coated samples and the substrate continued to display similar general oxidation behavior for long duration exposure (2764 hours) compared to the behavior observed initially for shorter time of exposure (540 hours). However, in contrast to earlier report for short duration exposure (540 hours), during long duration exposure (2764 hours) among coated samples, sample processed at 1200 watts showed the least % weight gain and both samples processed at 1500 watts and 1750 watts possessed similar % weight gain (6-7 % weight gain) without much variation throughout the exposure time. Similarly, continued lower values of oxidation rate
constant K (Table 2) for all coated samples compared to substrate samples (< 0.5 times) during longer exposure time (2764 hours) is due to substantial improvement in the oxidation resistance of the coated samples. It is also indicative of the fact that kinetics of oxidation in all coated samples is significantly slower (<40%) than the substrate sample.

A distinct higher oxidation resistance among Fe-Al coated samples compared to uncoated 4340 steel is due to presence of Al in the composition and stoichiometry of Fe-Al coating. The degree of oxidation resistance (% weight gain and oxidation rate constant) appears to depend upon the content of Al in the Fe-Al coating composition. In the samples processed with the higher laser power, dilution resulted in the formation of Fe-Al solid solution rather the iron aluminides and therefore reduced oxidation resistance. It was further noticed via x-ray diffraction analysis that the coating contains variation in stoichiometry of the composition (Figures 14-16). These analyses indicated the presence of phases such as AlFe, AlFe$_3$ (that are observed in equilibrium phase diagram for Fe-Al, (Figure 17) and Al-oxide and support the fact that Al exists in various stoichiometries.

Figure 14: X ray diffraction patterns obtained from Fe-Al alloy coatings prepared using the 75 mol% Al precursor and a laser power of 1250 W. For clarity only peak positions of selected phases are shown in the figure.
Figure 15: X-ray diffraction patterns obtained from Fe-Al alloy coatings prepared using the 75 mol% Al precursor and a laser power of 1500 W. For clarity only peak positions of selected phases are shown in the figure.

Figure 16: X-ray diffraction patterns obtained from Fe-Al alloy coatings prepared using the 75 mol% Al precursor and a laser power of 1750 W. For clarity only peak positions of selected phases are shown in the figure.
Also, laser being a near non-equilibrium process, tends to produce many unconventional phases that often are not referenced in the standard database. This may be the reason that although there are many additional peaks that could be related to Al-base phases they remain unidentifiable (Figures 14-16). But, an in-depth analysis of the various phase fields, the stability of phases and effect of compositional variations could act as a guideline, which could be extended, to non-equilibrium conditions under certain assumptions. The Scheil module of the ThermoCal\textsuperscript{TM} software was used for computational calculations to predict the sequence of phase evolution from the liquid phase of Fe-Al (coating precursor composition). This module is based on the Scheil Gulliver model [53-54], which assumes that there is fast diffusion in the liquid and no diffusion in the solid phase. These assumptions can be extended to laser processing conditions. As during solidification of the melt pool, rapid rate of the process does not allow any diffusion in the solid phase during processing.

Calculation was started from a temperature of 1500 K (approx 50\textdegree higher than the temperature at which only liquid phase exists) and it was lowered in 1K steps. The calculation was repeated till no liquid was left. The results of the analysis are shown in Figure 18. The first phase to precipitate from the liquid is the BCC phase (\(\alpha\)-Fe). Further cooling indicated the sequence of phase appearance was \(\alpha\)-Fe (BCC) followed by FeAl (a complex defect hexagonal structure) and \(\gamma\)-Fe in the subsequent stages. The calculated terminal solidification temperature was 835K at which the mole fraction of the solid phases is equal to 1. Hence the solidification path can be summarized as following.

\[
\text{Liquid} \rightarrow \text{Liquid} + \alpha\text{-Fe (BCC)} \rightarrow \text{Liquid} + \alpha\text{-Fe (BCC)} + \text{FeAl (HCP)} \\
\rightarrow \text{Liquid} + \text{FeAl} \rightarrow \text{Liquid} + (\gamma\text{-Fe}) + \text{FeAl}
\]
These computational evaluations indicate that the dominant phase in the solidified coating should be FeAl along with austenitic iron. This also supported by XRD analysis (Figures 14-16). These both phases have been known to possess higher oxidation resistance. Although XRD (experimental) and Scheil (computational) analyses together reasonably well identify and verify the evolution of phases in the coating, the presence of additional phases in minor number and quantities may be due to the level of temperature and cooling rate generated at different laser processing powers. Dependable identification of phases in the coatings under present laser processing conditions and their correlation with wear and oxidation properties will allow to effectively employing computational technique to design phase formation and select corresponding laser processing conditions to tailor wear and oxidation properties of the coatings for various field applications.

The short duration accelerated exposure studies on laser Fe-Al coated samples was conducted using thermogravimetry analysis (TGA) technique. TGA allowed the study of oxidation response of the samples at multiple temperatures. Thermogravimetry, as the name indicates is measurement of weight gain as a function of temperature or time at constant temperature. As the temperature or time (at constant elevated temperature) increases, the metal get oxidized and in the process gains weight. The rate of weight-gain as a function time would
reveal how fast or how slow the material gets oxidized i.e. it helps in deducing the oxidation kinetics of the material.

The base AISI 4340 forms iron oxide layer. However, the iron oxide layer possesses numerous defects and, therefore, the oxidation continues. The mass diffusion of oxygen and/or metal ions through this porous layer is the only limiting factor. Coating and surface engineering can change this scenario and improve the oxidation resistance. In case of coating it is desired that once a layer of appreciable thickness is formed in oxidizing atmosphere, it remains intact. Also, the layer should be self-healing and non-porous. The coating will prevent further oxidation as lattice diffusion of oxidizing species and/or metallic species is usually very slow and rate limiting.

The weight gain due to oxidation under constant temperature as a function of time reveals the mechanism of oxidation and/or rate limiting step. Parabolic nature is best suited as once an oxidation layer is formed, it will slow down further oxidation. The rate of oxidation reaction is therefore inversely proportional to the scale thickness or the weight of oxide formed.

One of the primary goals of this project was to produce a coating that indicates significant improvement over the base substrate. Even though Cr, Ni and Mo present in AISI 4340 steel make it behave better than plain carbon steel, the amount of oxidation is quite significant. Therefore, thermogravimetric studies were undertaken for the coating and the substrate. The coating on substrate cannot be directly heated in furnace, as the weight gain due to oxidation of substrate would shadow the coating. Hence, the substrates were carefully machined from the coating giving a thin layer of about 100 microns. The resulting samples were essentially the composite microstructure formed in laser processing. It may be mentioned that even though the application temperature is about 450°C, the local variation, fatigue and thermal stress subject the surface materials to more severe conditions. Also, the phase transformation of the steel at about 850°C can significantly affect the oxidation behavior. Therefore, temperatures up to 900°C were investigated.

While the samples were heated (10°C/min), there was some amount of oxidation involved. However, the weight gain was not significant as the time spent during heating is less compared to the holding time. The initial weights of the samples were different; hence, for effective comparison, the weight was normalized with respect to initial weights. A typical time-percentage weight gain (normalized) at 900°C of the substrate and the coating samples laser processed at 3 different laser power (1250 W, 1500 W and 1750 W) are plotted in Figure 19. They are referred to as 1250 W, 1500 W and 1750 W samples respectively in this section.
Figure 19: Percentage weight change (normalized against initial weight) of the substrate and the laser processed samples.

The curve fitting with high correlation \( R^2 > 0.98 \), indicates power-law for the substrate and cubic for the sample laser processed at 1250 Watts with the oxidized layer having respective tendencies of continuously thickening and slowing down dramatically. The weight gains percentages are also extremely different. (30% vs. 3%). It may also be noted that the initial weight gains are not zero. This is due to some oxidation taking place during heating (at a rate of \( 10^\circ\)C/min) before the isothermal hold starts.

The approximate increase in the weight of the substrate was 30%. In comparison, weight gain observed for the 1250W sample was approximately 3%, which indicates superior high temperature oxidation resistance of the coating. Another key fact observed was that for the coating, the oxidation rate decreases with time (cubic behavior: polynomial 3). The curve became nearly horizontal with time, indicating the initial build up of the oxide layer prevents further oxidation after. In comparison, there is a steady increase in the amount of oxidation with time for the substrate (power law).

It is clear from Figure 19 and Table 3 that sample-1250 indicates the best oxidation resistance. The behavior of the substrate at 900\(^\circ\)C was best fitted with power-law. All other samples and substrate and 1250-sample at other temperatures exhibited polynomial of degree 2. In all cases the correlation factor was greater than 0.98. The isothermal oxidation weight gains for all the samples are reported in Table 3. The oxidation mechanism was further investigated by scanning electron microscopy. There is at least some thickness of oxide layer, which causes charging. Hence, to prevent charging, variable pressure mode was employed (20 Pa air).
Table 3: Normalized percentage weight-gain during isothermal oxidation of the substrate and the coatings. The values within brackets are the normalized percentage weight-gains at the start of isothermal holding (during heating).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Percentage Weight Gain (%age weight at start of hold)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>500°C</td>
</tr>
<tr>
<td><strong>Substrate 4340 Steel</strong></td>
<td>1.8 (0.7)</td>
</tr>
<tr>
<td><strong>1250 Watts</strong></td>
<td>1.2 (1.4)</td>
</tr>
<tr>
<td><strong>1500 Watts</strong></td>
<td>-1.2 (11.5)**</td>
</tr>
<tr>
<td><strong>1750 watts</strong></td>
<td>7.4 (4.8)</td>
</tr>
</tbody>
</table>

** Requires further investigation.

Figure 20 (a) represents the substrate sample oxidized at 900°C. The bright spot is oxide rich area formed possibly in progressive nucleation-and-growth mode. For comparison sample 143-1 oxidized at 900°C is presented in Figure 20 (b). It is clear from Figure 20 (b) that there is hardly any oxidation evident from the surface.

Figure 20: Scanning electron micrograph of: (a) AISI 4340 steel sample, (b) 1250 Watts sample, oxidized in air at 900°C for 180 minutes.
Metal oxidation processes are extensively used in industry for protection of materials against corrosion, oxidation and production of engineering ceramics and catalysts. The initial stages of oxidation (including oxygen adsorption and incorporation, oxide islands nucleation, and growth into a continuous film) have been actively studied and are now understood relatively well. It can be described, at least qualitatively, by the Wagner model of oxidation [55-56], in which diffusion across the oxide film is the rate limiting process. The kinetic equations in this region can not be integrated exactly, and only approximations for the oxide growth rate as a function of time can be obtained. This makes the experimental verification of theory based only on the measurements of the oxidation kinetics difficult. Oxidation rate provides information regarding the oxidation kinetics. The kinetics of the oxidation can be, at least qualitatively, determined from the time-weight gain relation. For prolonged performance of the component, it is desired the surface layer, once formed, prevent further growth of the oxidized layer. Typically this process is reflected by a parabolic or cubic relation. On the other hand, if the oxidized layer is unable to prevent further oxidation (for example, if the coating is not adherent and/or cracks), the time-weight gain curve will follow a linear relation indicating that oxidation is continuing and eventually the whole component will get oxidized causing failure. In case of mechanical failure or disintegration would be reflected by sudden change in the slope of the weight-time curve.

It was found that the oxidation rate follows cubic relation with time. The associated correlation factor ($R^2$) is very close to 1 indicating excellent curve fitting. Disturbance in the initial stage may be due to vaporization of volatile phase, migration of mobile atoms, and/or formation of the very thin film. Change in kinetic, if any, occurs at an early stage indicating good stability.

All the time-weight gain relation followed either cubic (mostly) or parabolic and none linear. As explained above, linear behavior is undesirable. Hence, it is good news that all the coatings’ time-weight gain relations follow cubic trend. The oxidation trend depends on the dynamic condition around the sample and the volume and the shape (surface area) of the sample. Therefore, the oxidation response observed earlier (Figure 13) is different than that observed in this latter efforts (Figure 19). There is some extent of intrinsic oxidation resistance in coating as well as the substrate. It is hypothesized that the substrate derive its oxidation resistance due to presence of Ni (reduces oxidation potential) and Cr (stabilized the oxide layer formed at the beginning). The oxidation resistance of the coating is due to the formation of a more tenacious, self-healing and adherent aluminum oxide layer in iron-aluminides, which has much higher oxidation resistance.

5.4.4 Corrosion Response of Coatings

The corrosion of metallic materials depends, to a great extent, on the formation of passive oxides. However the formation of passive oxides may be influenced by several factors such as chemical composition of material, processing parameters e.g. mechanical as well as thermal and surface treatments etc. Steels have iron oxide layer which is usually not passivated. However, iron-aluminide exhibits passivation due to a few atomic-layers thin, coherent and tenacious aluminum oxide film. In addition, alumina film in the aluminum containing alloys is responsible for high temperature oxidation resistance. In the current laser processed samples, the surface coating is a composite of several iron-aluminide phases and steel matrix. For passivation to occur
a monolithic coating of iron-aluminide is required since the 4340 steel matrix (not passivated) would destroy any passivation. Monolithic coating is mechanically inferior owing to inadequate adherence and non-coherence.

Better corrosion resistance of laser coated iron-aluminide than the base steel may possibly be due to the superior oxide layer offered by mixed oxides against further corrosion. Even though the coating was not monolithic, the aluminide in the composite coating was responsible for reducing corrosion and oxidation. The variation of corrosion current and oxidation resistance clearly indicates the influence of laser parameters in improving the coating resistance. It is interesting to note that the laser parameter (in this case power) responsible for providing best oxidation and corrosion resistance is same, possibly originating from the best structure that provides protection via passivation.

The laser treatment is known to produce non-equilibrium surfaces and graded microstructure which often reported to be useful for enhancing passive film properties and, therefore, the corrosion resistance of material. However, in case of in-situ synthesized aluminide coating, the phases present and their stoichiometry is very important. The stoichiometry and formation of phase is a strong function of thermal dynamics during laser coating. This is well reflected that the phase(s) and/or stoichiometry of the phase(s) formed at 1200 W laser power are most suitable for oxidation and corrosion resistance.

Another source of corrosion is sulfidation, which is the reaction of a metal or alloy with a sulfur-containing species to produce a sulfur compound that forms on or beneath the surface on the metal or alloy. It is known that sulfidation is one of the most severe modes of degradation of material in fossil combustion energy production application. It is known that iron-aluminide alloys possess good sulfidation resistance. However, its aqueous corrosion resistance is little known. The coating of Fe-aluminide is expected to enhance the corrosion resistance originating from moisture along with various other gases containing sulfur and chloride ions.

The Tafel calculation [40-41] is used to estimate the corrosion current regularly present at the surface of a metal which is in contact with a corroding solution. The corrosion is expressed in loss of metal thickness per year. The thermodynamic $\alpha_A$ and $\alpha_C$ parameters of the Butler Volmer equation (below) are also determined.

$$i = i_e \left[ \exp \left( \frac{\alpha_A nF}{RT} \eta \right) - \exp \left( \frac{\alpha_C nF}{RT} \eta \right) \right]$$

where $i_e =$ exchange current density  
$\eta =$ overpotential ($= R - F_i$)  
$n =$ number of electrons  
$\alpha_A =$ anodic transfer coefficient  
$\alpha_C =$ cathodic transfer co-efficient

- While the Butler-Volmer equation is valid over the full potential range, simpler approximate solutions can be obtained over more restricted ranges of potential. As overpotentials, either positive or negative, become larger than about 0.05 V, the second or the first term of equation becomes negligible, respectively. Hence, simple exponential relationships between current (i.e., rate) and overpotential are obtained, or the overpotential can be considered as logarithmically dependent on the current density. This theoretical result is in agreement with the experimental findings of the German physical chemist Julius Tafel [41], and the usual plots of
overpotential versus log current density are known as Tafel lines. The slope of a Tafel plot reveals the value of the transfer coefficient; for the given direction of the electrode reaction.

A voltametric curve \( i = f(V) \) having a zero current potential can be processed according to the Tafel method. The Tafel method gives also access to other corrosion parameters such as the zero current potential (corrosion potential), the corrosion current and the polarization resistance of the sample under study. The Tafel calculation is a complete tool to study the corrosion process at a metal surface. Therefore, in the current study corrosion of laser processed samples were carried out to obtain Tafel calculation.

Figure 21 illustrates the Tafel plots of laser Fe-Al coated 4340 steel including base material and Table 4 summarize the corrosion current data in H\(_2\)SO\(_4\) solution. Figure 22 shows the Tafel plots of similar specimens and Table 5 presents the corrosion current data.

![Figure 21: Tafel plots in 1N sulfuric acid solution](image)

**Table 4: Corrosion current in 1N H\(_2\)SO\(_4\) solution**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Corrosion current density (mA/cm(^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Substrate</td>
<td>2.2</td>
</tr>
<tr>
<td>Coating 1</td>
<td>0.35</td>
</tr>
<tr>
<td>Coating 2</td>
<td>0.19</td>
</tr>
<tr>
<td>Coating 3</td>
<td>0.72</td>
</tr>
</tbody>
</table>
It was observed that the Fe-Al coated samples exhibited significantly lower corrosion current ($I_{corr}$) in both sulfuric acid and sodium chloride solutions. The corrosion current roughly translates to corrosion rate. In other words, the laser coated samples are significantly corrosion resistant compared to the base materials. From the corrosion experiments, it was revealed that the coating synthesized with laser power of 1500 W showed better resistance than the coating processed at 1250 and 1750 in both sulfuric acid and sodium chloride. Neither the coating nor the base 4340 steel exhibited passivation tendency for the coating processed at 1250 and 1750 in both the media. These observations are similar to the observations made during several studies on aqueous corrosion of bulk Fe-Al type intermetallic compounds [57-62].

Table 5: Corrosion current in 1% NaCl solution

<table>
<thead>
<tr>
<th>Sample</th>
<th>Corrosion current density (mA/cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Substrate</td>
<td>0.036</td>
</tr>
<tr>
<td>1250 W</td>
<td>0.026</td>
</tr>
<tr>
<td>1500 W</td>
<td>0.023</td>
</tr>
<tr>
<td>1750 W</td>
<td>0.027</td>
</tr>
</tbody>
</table>

Figure 22: Tafel plots in 1N sulfuric acid solution
6.0 ACCOMPLISHMENTS

The project successfully accomplished all its objectives. It demonstrated technical feasibility and advantages of using high energy laser and IR plasma lamp methods for coating iron aluminide on a low alloy steel, to improve its wear, oxidation and corrosion resistance properties.

7.0 CONCLUSIONS

- Reliable, efficient and economic methods based on high energy laser and IR plasma lamp for coating ceramic and intermetallic materials on ferrous materials were developed. The development was conducted mostly proved for intermetallic coatings on structural steel (AISI 4340) they also proved their feasibility for coating ceramic systems such as TiC and TiB$_2$ on ferrous (steels) and nonferrous (Al) metals.

- The coating microstructures were thoroughly studied to understand their improved response to the chemical (corrosion, oxidation) and physical (hardness and wear) properties as function of processing parameters.

- The coating techniques (laser and IR plasma lamps) were configured to process the components of variety of sizes and shapes and are ready for processing industrial components in production environment.

- Process conditions and composition of precursor coating have to be carefully selected to retain iron aluminides on the surfaces of the samples.

- Under appropriate processing conditions, coatings free of porosity and cracks can be obtained using this technique.

- Hardnesses of the coatings and the heat-affected zones are a strong function of the processing parameters and hence can be tailor-made for the application. In the case of the samples processed with the IR plasma arc lamp, the hardness vary with the processing conditions. The processing conducted at lower energy density (2025 W/cm$^2$) of IR lamp produced the harder (> 1.5 times) coating layer than those processed at higher energy density (2350 W/cm$^2$). Similar trends for hardness of the coatings produced by laser based technique were observed. The hardness values within the coating were much larger (Knoop hardness values >400) than that obtained for the base material (Knoop hardness values < 300). Also, the laser processing conducted at higher power (1750W) produced coatings of lower hardness compared to the coatings produced at lower power (1200W), accordingly both IR and laser produced coatings at lower energies indicated higher wear resistance compared to the coatings produced at higher energies. Intermetallic compounds (stoichiometry) evolved in the coating was considered to be responsible for these changes. At higher energy of processing the coating stoichiometry was observed to be rich in Al compared that processed at lower energy thereby providing inferior hardness and wear properties.

- Better corrosion resistance of laser coated iron-aluminide than the base steel may possibly be due to the superior oxide layer offered by mixed oxides. The aluminate in the composite coating was responsible to reduce corrosion and oxidation. The variation of corrosion current and oxidation resistance clearly indicates the influence of laser parameters in improving resistance. It was observed that the Fe-Al coated samples exhibited significantly lower corrosion current ($I_{corr}$) in both sulfuric acid and sodium chloride solutions. The corrosion current roughly translates to corrosion rate. In other words, the laser coated samples are significantly corrosion resistant compared to the base materials.

- Experiments involving oxidation in air, done in thermogravitometric analysis (TGA), indicated that laser processed samples were better oxidation resistant than substrate. All the time-weight gain/area relation followed either cubic (mostly) or parabolic. In other words, there is some extent of intrinsic oxidation resistance in coating as well as the substrate.
8.0 RECOMMENDATIONS

Based on the experience of the present project the following recommendations are made.

- The work should be initiated for development of Fe-Al/TiB₂ coatings on 4340 steel.
- Further development of Fe-Al coating on 4340 steel should focus on optimization of process conditions and alloy composition.
- Following the above studies, dedicated efforts should be made for coating selected industrial components for field tests. These efforts should be focused on identifying one industrial sector and corresponding target components.
9.0 REFERENCES


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