TiB_2-TiC-Al_2O_3 coating on Aluminium substrate by in-situ laser coating process using pulsed Nd: YAG laser

A Thesis Submitted in Partial Fulfillment of the Requirements for the Award of the Degree of

Master of Technology

in

Mechanical Engineering

(Production Engineering)

By

JAGESHWAR KUMAR SAHU

Roll no 212ME2300

Under the supervision of

Dr. Manoj Masanta

NATIONAL INSTITUTE OF TECHNOLOGY, ROURKELA

PIN-769008

ODISHA, INDIA

2014

DECLARATION

I the undersigned solemnly declare that the report of work entitled **"TiB_2-TiC-Al_2O_3 coating on Aluminium substrate by in-situ laser coating process using pulsed Nd: YAG laser"** is based on my own work carried out during the course of my study under the supervision of Dr. M. Masanta.

I assert that the statements made and conclusions drawn are an outcome of the project work. I further declare to the best of my knowledge and belief that the report does not contain any part of any work which has been already submitted for thesis evaluation in this University.

Name: Jageshwar Kumar Sahu

Roll no: 212me2300

National Institute of Technology Rourkela

Certificate

This is to certify that the report entitled"**TiB_2-TiC-Al_2O_3 coating on Aluminium substrate by in-situ laser coating process using pulsed Nd: YAG laser**"submitted by ***Mr. Jageshwar Kumar Sahu*** to National Institute of Technology Rourkela, is a record of bonafide research work carried out by him under my supervision and is worthy of consideration for thesis evaluation in Mechanical Engineering with specialization in **Production Engineering.** The embodiment of this report has not been submitted in any other University and/or Institute for the award of the any degree or diploma.

Date:

Dr. Manoj Masanta
Assistant Professor
Dept. of Mechanical Engineering
National Institute of Technology
Rourkela-769008

ACKNOWLEDGEMENT

Working on this project has been a great learning experience for me. There were moments of anxiety where I could not take even a step forward for quite a long time and sometimes it suddenly got solved. But I have enjoyed every bit of process and thankful to all those people associated with me during this period.

First, I offer my humble pranam on the lotus feet of Ma Saraswati for her subtle support in all difficulties throughout my life. It's my wish to express my gratitude towards my grandparents and parents for their eternal effort.

I would like to express my greatest appreciation to my supervisor Dr. Manoj Masanta for his encouragement and guidance, timely suggestions during the completion of the project. The discussions held with him during the research work, which helped me a lot in materializing this dissertation work and also to grow up my knowledge.

I would like to express my deep gratitude to respected H.O.D. Mechanical Engineering Department, Dr. K.P. Maity Sir, for his helpful solutions and comment enriched by experience, which improved my ideas for betterment of project.

My sincere thanks also to Prof. S.K.Sahoo who allowed working with laser coating machine. I would also like to thank Hem ram sir and Rajesh patnaik sir who helped for microhardness testing. I mention the help and support received from workshop assistants. The guidance and support received from all the members who contributed and who were part of this project, whose names could have not been mentioned here, are highly acknowledged.

It will be my pleasure to acknowledge, utmost co-operation and valuable suggestion from time to time given by staff members of Mechanical Engineering Department, to whom I owe my entire knowledge and also i would like to thank all those persons who have directly or indirectly helped me by providing books and computer peripherals and other necessary amenities which has helped in the development of this project.

Jageshwar Kumar Sahu

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Abstract

To improve the microhardness and wear resistance of mechanical components, laser coating has been applied to deposit in situ TiB_2-TiC-Al_2O_3 coating on Aluminium substrate using Titanium oxide, Boron carbide and Aluminium as the coating powder. The phase constituents and microstructure of the composite coating were investigated using field emission scanning electron micrograph (SEM) and X-ray diffraction (XRD). Vicker's Microhardness tester was used to measure the microhardness at the coating cross section. Results show that crack free composite coating with metallurgical bonding to the aluminium substrate obtained. Microstructure analysis confirms the formation of TiB_2, TiC and Al_2O_3 in the coating zone. The microhardness improved significantly in comparison to the as-received Aluminium substrate due to the presence of the hard reinforcement TiB_2 and TiC.

Keywords: Dilution, Laser Coating, Overlapping, Microhardness, Reinforcement

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List of abbreviations

Al : Aluminium
Al_2O_3 : Aluminium oxide
C : Carbon
CO_2 : Carbon dioxide
CNC : Computer numerical control
Co : Cobalt
Fe : Iron
f : Frequency of pulse
HV : Vickers pyramid number
LSE : Laser surface engineering
LSA : Laser surface alloying
MMC : Metal matrix composites
Mg : Magnesium
Mn : Manganese
Mo : Molybdenum
Nd-YAG : Neodymium-doped yttrium aluminium garnet
Ni : Nickel
p_o : pulse overlapping (%)
P : Phosphorus
P_{avg} : Average power
P_{peak} : Peak power
S : Sulphur
FESEM : Field emission scanning electron microscope
Si : Silicon
SiC : Silicon carbide

Ti	: Titanium
TiB_2	: Titanium boride
TiC	: Titanium carbide
T_{on}	: Time for which laser is on per pulse
U_x	: Velocity in x direction
VHN	: Vickers hardness number
WC	: Titanium carbide
XRD	: X-ray diffraction

Chapter 1
Introduction

- Laser coating
- Laser surface modification techniques
- Different methods of laser coating mechanism
- Process parameters for laser coating
- Advantages of laser coating
- Limitations of laser coating
- Applications of laser coating

1.1 Laser coating

Laser coating is a process in which surface properties of the various components are improved, with a material which has different metallurgical properties mainly higher hardness, wear resistance and corrosion resistance as compared to the base material. Laser coatings possess uniform composition and coating thickness and also exhibit superior metallurgical bonding to the base material [1]. In order to maintain the original properties of the coating materials there should be minimum dilution between the coating material and the substrate material. Laser coating is an advanced coating technology for producing extremely dense, crack-free and non-porous microstructures. Components coated with laser coating process produce surfaces with high resistance against corrosion, wear and high temperatures [2]. In addition to the new manufacturing process, laser coating process has shown its contribution to the maintenance industry also, resulting in component performances superior to those of uncoated ones. Fig. 1 shows a surface modification process by using Nd: YAG laser.

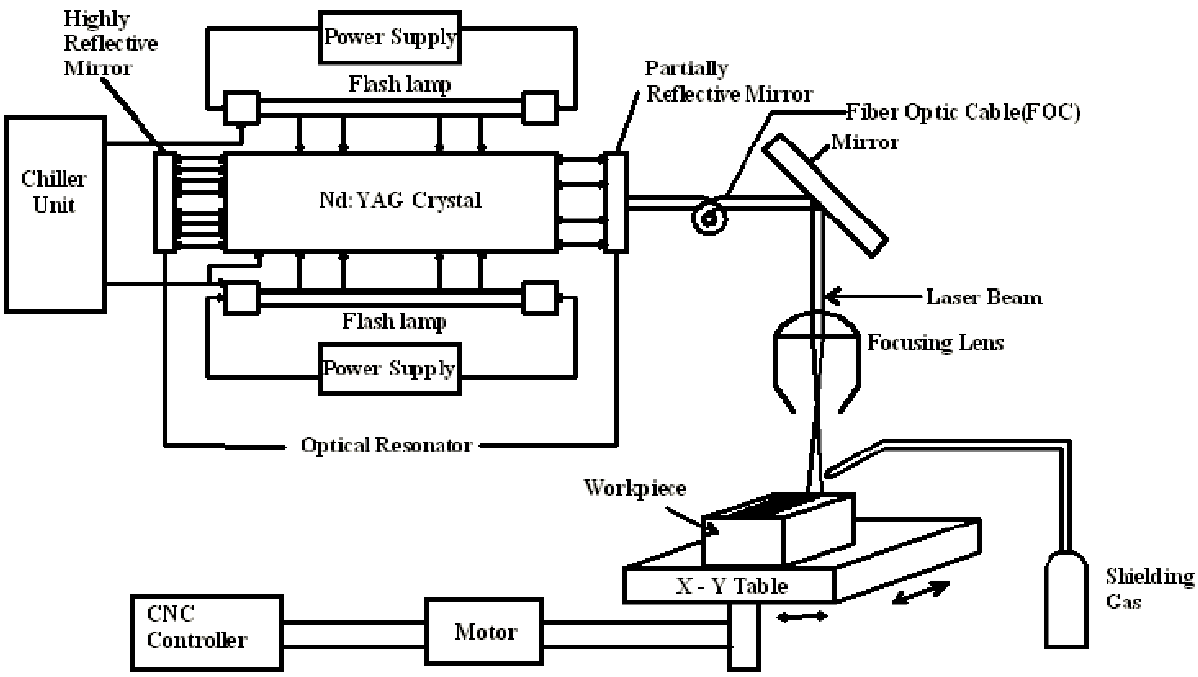


Fig. 1: Schematic sketch of Nd: YAG laser surface modification system [Ref. 3]

1.2 Laser surface modification techniques

Laser surface modification is a broad area of laser material processing basically used to change either microstructure or surface composition of a material to give it certain desired properties such as high hardness, wear resistance, corrosion resistance etc. Various laser surface treatment methods can be grouped as follows:

1. Laser treatment methods without the use of external material
    I. Laser surface heat treatment
    II. Laser surface melting
    III. Laser shock peening
2. Laser treatment methods with the use of external material
    I. Laser alloying
    II. Laser dispersing
    III. Laser cladding

1.2.1 Laser treatment methods without the use of external material

In this method of surface modification technique no external material is used for changing the surface properties. In laser surface heat treatment, no melting takes place, while in laser surface melting a thin surface layer of the workpiece is melted and due to the rapid quenching, form a new structure which is harder than the base metal. Laser shock peening generates shock waves which induce compressive residual stresses on the surface of the material.

I. Laser surface heat treatment

In laser surface heat treatment process the surface of the material is exposed to thermal cycle of rapid heating and cooling such that surface layers induce transformation. For example in the heat treatment of steels, they are first austenitized and then quenched, to induce martensitic transformation. The process does not involve melting, and the transformation occur in the solid state. Fig. 2 shows laser surface heat treatment process.

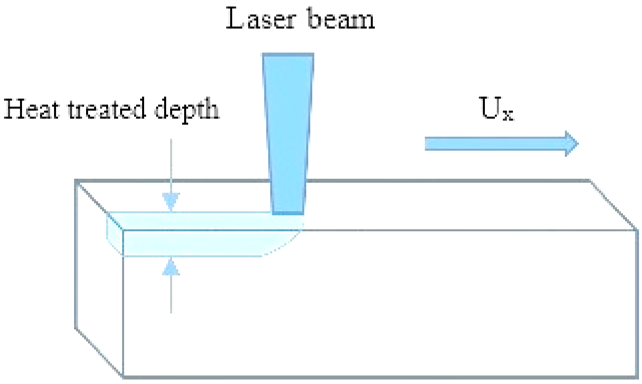


Fig. 2: Schematic of the laser surface heat treatment

II. Laser surface melting

Laser surface melting (also known as skin melting or glazing) involves melting of a thin surface layer of material which subsequently undergoes rapid solidification as a result of self-quenching, which results in alterations in the local microstructure. The microstructural changes may be accompanied by changes in properties such as hardness, corrosion resistance and wear resistance.

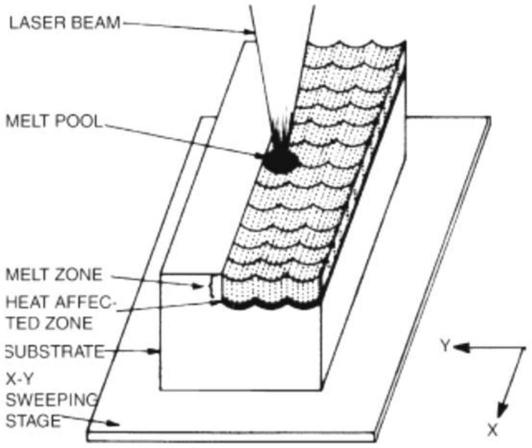


Fig. 3: Schematic of the laser surface melting [Ref. 4]

III. Laser shock peening

Laser shock peening is a process that imparts compressive stresses on the surface of a material. It is basically used for increasing fatigue life and improving resistance to cracking. One application of the process is making the leading edge of the turbine blades to resist the foreign object damage.

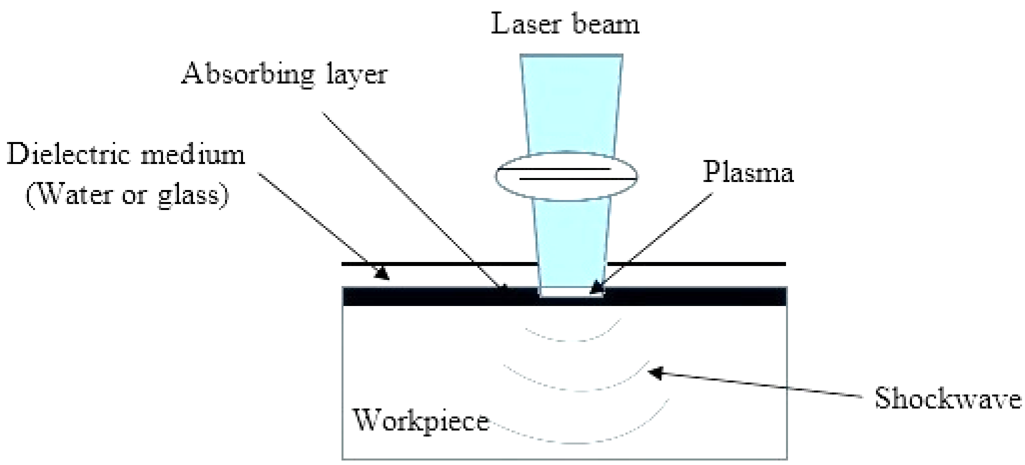


Fig. 4: Schematic of the laser shock peening process

1.2.2 Laser treatment methods with the use of external material

The three techniques, laser alloying, laser dispersing and laser cladding involve the formation of a melt pool of coating and substrate material. But they can be distinguished on the basis of degree of mixing between the coating material and the base or substrate material in the surface layer.

I. Laser alloying

In laser alloying process external elements completely mixed with base material in the surface region due to better reaction takes place between added elements and base material. In this process melting of very thin surface of a substrate material takes place using laser beam while adding one or more components. The molten substrate mixes with melted clad alloy to form a metallurgical bond between the substrate and the added elements.

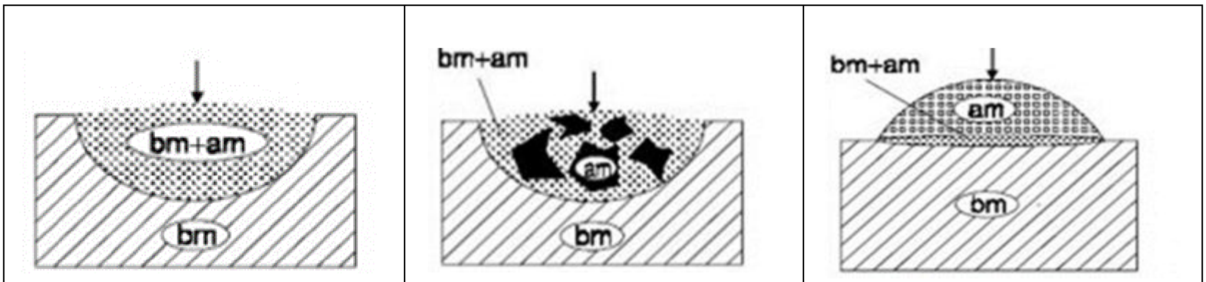
II. Laser dispersing

In laser dispersing process the additional material is dispersed non-homogeneity in the matrix of base and additional material. There is not complete mixing between the base material and the coating material.

III. Laser cladding

Laser cladding consists of covering the substrate surface with a coating of a different nature. The laser cladding process generates a surface layer which is bonded with the substrate through an interface layer which contains both clad and the substrate. When individual clads are partially overlapped to one another then a uniform layer is formed. Strong metallurgical bonding generates due to slight dilution of the cladding material into the substrate and makes it possible to obtain homogeneous microstructures. Hence the properties of the produced clad layer depends on the applied coating material and laser processing parameters.

Fig. 5 shows the degree of mixing of coating material and the substrate for laser alloying, dispersing and cladding process.



ALLOYING	DISPERSING	CLADDING

Fig. 5: Graphical representation of laser alloying, dispersing and cladding [Ref. 5]

From the Fig. 5 it is clear that, in case of laser alloying process homogeneous mixing of the additional material and base material takes place and laser treated surface so produce shows properties of both the coating and substrate material. In laser dispersing process the additional material is dispersed non-uniformly in the matrix of base and additional material. In case of laser cladding process layer of additional material at the top surface of the substrate material takes place with better surface property as compared to the base material.

In this work above three types of laser surface modification technique considered as laser coating process.

1.3 Different methods of laser coating mechanism

There are three common methods of metal delivery to the substrate in the laser coating process.

I. By pre-placed powder
II. By powder injection
III. By wire feeding

I. By preplaced powder

This is considered to be a two-stage laser coating procedure. In the first stage the substrate is covered with the pre-placed powder to be coated on substrate. In the second stage heat transfer takes place through the powder and partially melts the substrate and provides a metallurgical bond between the coating and the substrate surface. This method is not suitable for complex geometric shape and consuming more time than the powder blowing. In this method uniform covering of the coating material on substrate is achieved which results homogeneous and crack free coating with strong metallurgical bond to the base material.

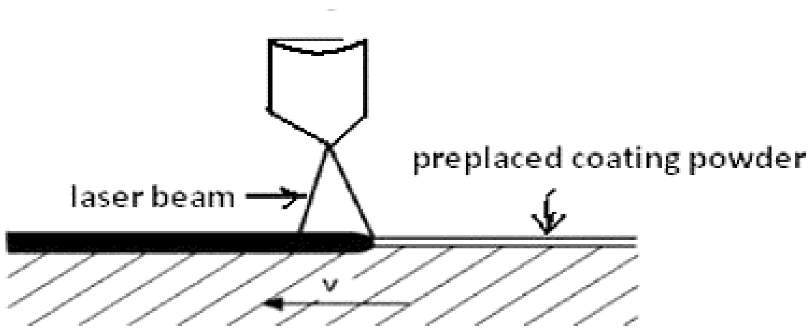


Fig. 6: laser coating by preplaced powder

II. By powder injection

In this method powder is injected into the path of laser beam. The powder is held through the tubing using an inert gas. The blown powder particles are partly melted by the laser beam. The laser creates a small melt pool on the substrate surface that fully melts the powder. The melt pool after solidification creates a clad layer. This results in a strong metallurgical bond between coating and substrate material with a minimal dilution.

There are two different methods of the powder delivery system. In first method powder particles are rendered to the substrate through a coaxial system where the laser beam and powder particles are feeding towards the substrate simultaneously.

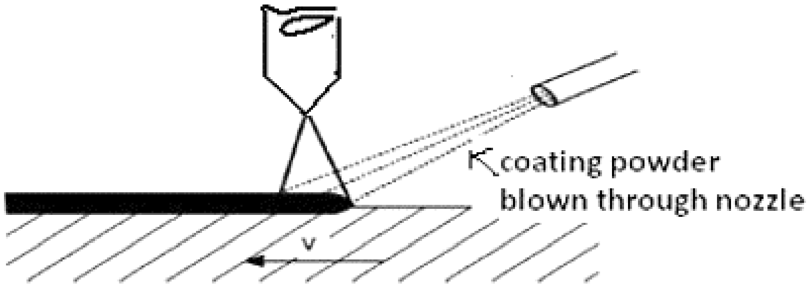


Fig.7: Laser coating by powder injection method

The second method is offline method or a lateral injection method where feed nozzle is positioned to the side of the laser. The location of the lateral feed nozzle affects the clad concentration. If the lateral feed nozzle is positioned in the direction in which the substrate moves, the cladding becomes more efficient because the powder is trapped between the substrate and melt pool.

III. By wire feeding

The third method of clad formation is through a wire feed. The wire is fed from a wire spool to the workpiece and laser interaction zone.

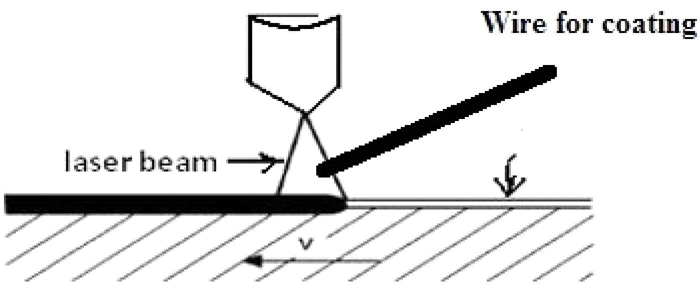


Fig. 8: Laser cladding by wire feeding system

Among all these process laser coating by preplace method has specific advantages i.e. homogeneous and crack free coating with strong metallurgical bond to the base material. Therefore for this work we have selected this method

1.4 Process parameters for laser coating

Laser coating with preplaced powder is having processing parameters like laser parameters, system processing parameters and powder properties.

A. Laser parameters

I. Type of laser
II. Peak Power or Average Power
III. Power density
IV. Beam size
V. Geometry and quality of beam
VI. Wavelength

B. System processing parameters

I. Laser scan velocity
II. Overlapping
III. Number of layers
IV. Surface pretreatment
V. Pre-heating and temperature during coating

C. Powder properties

I. Powder properties – composition, particle size and shape
II. Initial thickness of coating layer
III. Distribution

1.5 Advantages of laser coating process

Laser coating process has following advantages:

- Low dilution (min. 1-5 %) between the coating material and base material
- Excellent coating properties obtained with laser coating process
- Laser beam is a focusable, high intensity and controlled heat source
- Changes in the base material is minimum due to low heat load
- Controlled coating thickness is achieved
- Very narrow temperature field, ensuring the aimed microstructural changes
- Reasonable productivity and cost

1.6 Limitations of laser coatings process

Laser coating process has following limitations:

- Non-homogeneous energy distribution in the laser beam depending on the beam quality and geometry.
- The poor absorptivity of the laser beam in interacting with the metal surface reduces efficiency of the process.
- High cost of laser setup.
- Kinematics conditions of the workpiece and/or laser beam to different product shapes is difficult to adjust.

1.7 Applications of laser coating process

Industrial applications require components with good hardness, corrosion resistance and wear resistance properties. Laser coating is a process which can satisfy all these prerequisites. Laser coating can be used in the processes which require a high productivity combined with flexibility without compromising on quality of the product. Uniform quality with a low heat input makes this process suitable for a broad range of applications in which minimum distortion is needed.

Laser coating applications include spare part manufacturing, production of new components and maintenance and repairing of worn equipment and parts. Laser coatings are applied to produce surfaces resistant against adhesive, corrosive and abrasive wear, high temperature oxidation, wet corrosion etc. Typical applications of laser coating process are:

- Repairing of turbine parts, moulds, tools etc.
- Improved fatigue resistance of bearings, valves, axles, cutting instruments and other parts where working conditions are really dangerous
- Coating of valve components, sliding valves, discs, exhaust valves in engines
- Sealing joints and joint surfaces
- Building up complex 3D geometries.
- Coating of pump components
- Coating of cutting tools and blades to protect them from wear.

Chapter 2
Literature Review

- Laser Coating on pure Al substrate
- Laser coating on different Al alloys
- Laser coating with TiB_2, TiC, TiB_2+TiC on different substrate materials
- Laser coating using pulsed laser
- Problem identification and Objective of the work

2.1 Laser Coating on Pure Al substrate

Aluminium is a ductile, lightweight, relatively soft, malleable and durable metal. Structural elements made from Aluminium and its alloys are vital to the aerospace manufacturing and are also important as transportation and structural materials because of its low density and high durability to weight proportion. However a poor resistance to wear and erosion are serious concern for its prolonged use. Different methods of surface modification considered to improve the surface properties of Aluminum. Among these, laser surface modification was applied by various research groups for its specific advantages.

Uenishi and Kobayashi [6] formed intermetallic compound Al_3Ti and its matrix composite layers on Al surface by laser cladding process. The powders used for laser cladding were pure Al, Ti, TiB_2, TiC and SiC. Continuous wave CO_2 laser with laser power of 2.5 kW, beam travelling speed of 1.67 mm/s was used for laser cladding process. During the process, TiB_2 melted by laser processing and then homogeneously precipitated as fine particles during the cooling stage. Al_3Ti inter metallic compound surface layer enhanced the wear property of Al substrate.

Dubourg et.al [7] investigated the influence of the microstructure and the composition of laser clad metal matrix composite (MMC) coatings on hardness and adhesive wear resistance of pure Al substrate. Si and TiC powder mixture was used for coating material. The laser beam of 1700 W with a spot diameter of 3 mm and scan speed ranges from 7 to 17 mm/s were used to develop the clad layer. The addition of Si and TiC reinforcement particles increases the hardness of the coating upto six to seven times than Al substrate and strongly influences the wear mechanism.

Dutta Majumdar et.al [8] studied the development of a hard SiC dispersed composite layer on Al substrate to improve its wear resistance property. Laser composite surfacing was carried out by using a continuous wave CO_2 laser with laser power of 3 kW, beam diameter of 3.5 mm, scan speed of 100 to 500 mm/min, overlapping ratio of 25% and Ar as the shrouding gas. The microhardness of the surface improved by two to three times and significant improvement in the wear resistance of the coated surface as compared to the Al substrate was achieved**.**

Dutta Majumdar et.al [9] developed a hard in situ titanium boride-dispersed Al matrix composite layer on Al substrate to improve wear resistance property. Laser coating is carried out by using a continuous wave CO_2 laser with a beam diameter of 3.5 mm, laser power of 1.2 to 1.5 kW, scan speed of 300 to 1100 mm/min, powder flow rate of 4 g/min and Ar as the shrouding gas. The microhardness of the composite surfaced Al improved up to three times as compared to Al substrate and a significant improvement in the wear resistance was observed.

Vreeling et.al [10] studied Al/SiC MMC layers prepared by laser processing using SiC particles onto the Al substrate. Al of 10 mm thickness was used as a substrate material. Single laser tracks with injected SiC particles (40–80 µm) were made with a 2 kW Nd: YAG laser. An interface reaction layer consisted of Al_4C_3 plates forming a good mechanical bonding between the SiC particles and Al matrix.

Vollertsen et.al [11] studied deep penetration method for dispersing of aluminum with TiB_2 using a fiber laser to enhance the absorptivity of aluminum. For laser processing power of 850 W, scan speed of 0.2 m/min, spot diameter of 3 mm and powder feed rates taken as 1.8-5.4 g/min. A higher penetration depth up to 2.7 mm was achieved compared to the conventional laser dispersing process.

Nath et.al [12] studied laser surface alloying of Aluminium with WC+Co+NiCr. Laser surface alloying was done by using continuous wave Nd: YAG laser operating in power range of 3 to 3.5 kW, beam diameter of 3 mm, scan speed ranges of 12 to 40 mm/s and precursor powder flow rate of 1×10^{-5} kg/s. The microhardness of the alloyed zone was significantly increased (200VHN to 650 VHN) as compared to the received aluminium substrate (22 VHN). The presence of the carbides in grain refined Aluminium contributed to the improvement in the wear resistance.

Senthil Selvan et.al [13] produced an electrodeposited nickel layer on Aluminium substrate by laser processing. A Continuous wave CO_2 laser was used to melt the electrodeposited nickel on Al. During laser alloying power and scan speed range were fixed at 1.1 to 1.5 kW and 0.3 to 1.1 m/min respectively with a constant beam diameter of 1 mm. A uniform coating was created on Al without cavitation and porosity. High hardness (600–950 HV) about 20 to 27 times of the hardness value of Al was obtained.

2.2 Laser coating on different Al alloys

Apart from pure Al, some work related to laser coating was done on different Al alloy.

Katipelli et.al [14] deposited hard and refractory composite coating on 6061 Al alloy by Laser Surface Engineering (LSE). The wear resistance of the coated surface was found to be high compared to the substrate. Microhardness measurements suggested high hardness values in the coating region and a strong bonding at the coating /substrate interface.

Kadolkar and Dahotre [15] investigated the laser surface engineering technique to deposit ceramic (TiC) coating on Aluminium alloy substrate. Considerably hard coatings of the order of 400 kg/mm^2 obtained which was approximately three times the hardness of the substrate material.

Man et.al [16] synthesized a 1.5 mm thick hard surface layer consisting of Ni–Al and Ti–Al intermetallic compounds to improve the wear resistance of Aluminium alloy AA 6061 by laser surface alloying technique. The surface hardness increased from 100 HV for untreated AA 6061 to more than 350 HV for the laser-treated sample. Accompanying the increase in hardness, the wear resistance of the modified layer reached about 5.5 times that of the substrate.

Man et.al [17] carried out laser surface alloying of SiC, Si_3N_4 on AA 6061 aluminum alloy. The cavitation erosion resistance and surface hardness of laser alloyed samples was increased by three times and seven times compared to the as-received AA 6061 alloy respectively.

Wong et.al [18] investigated the surface characteristics, microstructure and substructure of Aluminium-Si alloys with various Si contents by laser-melting treatment. Continuous wave CO_2 laser was used for laser treatment with power of 2 kW, power density of 62 to 208 W mm^{-2}, scan speed of 10 mm/s. Si content in the samples in (wt.%) ranges from 1.09 to 13.0%. The substructure in the laser surface melted zone changes greatly in the presence of Si content. The degree of hardening of the laser-melted surface increased with the silicon content of the Aluminium alloys.

Watkins et.al [19] studied the influence of the overlapped area on the corrosion behavior of laser treated 2014-T6 Aluminium alloy. Power density used was 3.2×10^5 W cm^{-2} with power of 1600 W and beam diameter of 0.8 mm and the scan speed was varied from 2 mm s^{-1} to 180 mm s^{-1}. The track overlap was 50%. Aluminium alloy substrates were precoated with different compositions of Cr, Al, W, Ni and Zr powder mixtures by plasma spraying. Pitting resistance of CO_2 laser melted alloys was increased compared with the as-received material.

Xu and Liu [20] formed an in situ synthesized TiB_2 particulate-reinforced metal matrix composite coating on 2024 Aluminium alloy by laser cladding with a powder mixture of Iron-coated Boron, Ti and Al. The laser cladding was carried out using a 3 kW continuous wave CO_2 laser. Laser parameters used were power of 1.7 kW, beam diameter of 3 mm and scan speed of 3 mm/s. The microstructure of cladding was composed of TiB_2, Al_3Ti, Al_3Fe, and α-Al. The surface hardness of cladding increased with the amount of added Fe-coated B and Ti powder. The wear resistance of laser cladding was increased with increasing TiB_2 and intermetallic compound.

Almeida et.al [21] investigated the microstructure and corrosion resistance of laser-alloyed Aluminium and ANSI 7175 Aluminium alloy with chromium. Laser surface alloying was carried by using laser power densities and interaction times in the ranges (1.1-2.6) x 10^5 Wcm^{-2} and 0.04-0.3 s respectively with a powder flow rate of 0.03 g s^{-1}, overlapping ratio of 50% and scan speed of 5 to 40 mm/s. Hardnesses as high as 155 HV and 300 HV were obtained on the alloyed Aluminium and 7175 Al alloy substrates, respectively which was greater than the hardness of initial substrates.

2.3 Laser coating with TiB_2, TiC, TiB_2+TiC on substrate materials

For laser coating process, as coating material different types of ceramic, alloy, intermetallic or composite of these were considered by various research group for specific application. Among these TiB_2 and TiC are ceramics those used as hard and wear resistance material in different component for their specific properties such as high hardness (TiB_2: 29.4 GPa, TiC: 28 GPa), high melting temperature (TiB_2: 3325ºC, TiC: 306 ºC), good wetting behavior and chemical stability. TiB_2– TiC composites are used as wear and high-temperature resistant structural components. Metal matrix composites (MMCs) and cermets reinforced by TiB_2–TiC exhibit improved mechanical properties. Various work related to laser coating of TiB_2-TiC was done so far.

Du et.al [22] deposited in-situ synthesized TiB_2 reinforced Fe based composite coating on AISI 1010 low carbon steel by laser cladding. Fe–Ti alloy, Fe–B alloy and iron powders were used as the precursor. Laser cladding was carried out with laser power of 2500 W, laser beam diameter of 3 mm and scan speed of 300 mm/min. A side jet of Argon with the gas flow rate of 20 L/min was used to prevent the sample from oxidation. The hardness and wear properties of the clad layer were greatly improved (about 25 times) due to the presence of uniformly distributed TiB_2 particles in comparison with the substrate material.

Du et.al [23] investigated the synthesis of TiB_2–TiC reinforced hard composite coating on AISI 1010 steel by laser surface engineering, using a powder mixture of Ni–Ti–B_4C. A continuous wave Nd: YAG laser with laser power of 1 kW power, 1 mm beam diameter and scan speed ranging from 30 to 90 mm/s were taken for laser processing. Argon was taken as shrouding gas. Composite coating improved micro-hardness 3–4 times of the steel substrate. The author further [**Du et.al [24]]** developed the TiB_2 and TiC reinforced Fe-based nano-composite coating on AISI 1010 steel by laser surface engineering using Ti, B_4C and Fe powder mixture as precursor with same process parameters as mentioned above. This coating offered the potential to increase the hardness and toughness simultaneously in developing wear resistance coatings.

Sun et.al [25] fabricated TiC–NiCrBSi composite coatings on Ti–6Al–4V substrate by laser cladding using a continuous wave CO_2 laser with constant laser power of 4 kW, beam diameter of 6 mm, scan speed of 8 mm/s and overlapping ratio as 50%. Laser clad TiC–NiCrBSi composite coatings exhibited excellent wear resistance. Hard particles such as TiC, $Cr_{23}C_6$, CrB and TiB_2 were dispersed in the matrix, which significantly enhanced the hardness of the clad layer and also enhanced the strength and toughness.

Emamian et.al [26] studied the effect of powder composition on formation of in-situ TiC within a Fe-based matrix coating on AISI 1030 medium carbon steel during laser cladding process. Fiber laser with average power of 1000 W, beam diameter of 2.5 mm, scan speed of 88.5-120 mm/s, overlapping ratio of 20%, and Argon (10L/min) as shrouding gas were taken for laser coating process. A higher volume fraction of TiC in the clad layer resulted in increase in clad hardness. Depending on powder composition and laser process parameters, the hardness can be increased up to 8 times than the substrate material.

Though different types of laser were used for surface modification, each type has specific advantages and limitations. Recent study shows that a pulsed laser is preferred to continuous laser for specific application because of the higher cooling rates with a reduced heat affected zone surrounding the melting region. Again short pulse width coupled with high-peak power, pulsed laser produces a sufficient melting depth. Number of work related to laser coating were done by using pulsed Nd: YAG laser.

2.4 Laser coating using pulsed laser

Das [27] studied the laser surface alloying with nickel of commercial pure Aluminium using an Nd: YAG pulsed laser. Parameters taken as power 120 W, pulse width 4 ms, pulse rate 10 s^{-1}, scan speed 2.1 mm/s, and overlapping ratio of 50%. Microstructural analysis of the laser surfaced aluminium with nickel showed non uniform distribution of the alloying element (nickel) irrespective of the depth of hardness. The alloyed layer microstructure was dependent on the composition and variation in the molten alloy pool during solidification under larger undercooling condition.

Fu et.al [28] studied laser alloying of AA 6061 aluminum alloy with Ni and Cr using a pulsed Nd-YAG laser with a spot diameter of 2 mm. Laser power of 100 to 300 W, traverse speed of 1 to 8 mm/s, overlapping ratio of 50 to 90%, pulse width of 4 ms and pulse rate of 10 Hz were used as processing parameters. The number and size of cracks and pores in the coatings increased with laser power and overlapping ratio. The hardness of the coating was 5 to 6 times that of the original substrate. Maximum hardness was found at a low laser power since higher powers lead to dilution of the hard phases by aluminum from the substrate.

Du et.al [29] carried out an experiment using pulsed Nd: YAG to modify the surface properties of AISI 1010 steel by laser synthesis with TiB_2 and Al powder. Average power of 400 W, pulse duration of 0.5–2 ms, repetition rate of 20 Hz, beam diameter of 500 µm, scan speed of 84.7 mm/s and 70% overlapping ratio were used to carry out the laser surface engineering. Coating achieved had hardness of (900 HV) and surface roughness of (Ra 6.1) possess minimum wear rate (0.113 mg/ (min cm^2)). Compared with the steel substrate, micro-hardness and wear resistance of the coating were improved significantly.

Wendt et.al [30] studied laser alloying of AlSi9 Aluminium alloy with Ti wire. For laser an Nd: YAG solid state laser (2 kW, pulsed) was used and scan speed taken as 300 and 500 mm/min. Ultra micro hardness measurements performed on the Ti-alloyed Al regions showed hardness values between 81 and 98 HV0, 0008 for the Al solid solution, and values of up to 1250 HV0, 0008 for the $TiAl_3$ dendrites resulted in high strength and hardness, connected with high wear resistance and low friction coefficients.

Gordani et.al [31] carried out laser surface alloying of electroless plated Ni–P coatings on Al-356 aluminium alloy using a 1-kW pulsed Nd: YAG laser (pulse duration: 200 ms and pulse frequency: 5–10MHz). Alloyed layer showing good metallurgical bonding with the substrate material. The hardness of the laser surface alloyed layer was found upto 940 HV due to formation of hard, fine intermetallic Ni–Al phases. The pitting resistance of the laser surface alloyed layer was significantly improved compared to the Al-356 alloy.

Vaziri et.al [32] investigated the influence of re-scanning on tribological behavior in laser surface alloying of Al with Ni using pulsed Nd: YAG laser. Laser power of 400 W, pulse frequency of 1–1000 Hz, pulse duration of 0.2–20 ms and pulse energy of 0–40 J were taken for alloying process. Though re-scanning of the laser-alloyed layers leads to the formation of pores and cracks but improve the hardness in the coating and lower the specific wear rate than a single alloyed layer.

Yan et.al [33] applied laser surface cladding technique to deposit (Ti, W) C reinforced composite coating on copper using pulsed Nd: YAG laser. During the process, laser power, pulse width, beam diameter, frequency and scanning speed were selected as 380W, 1.1ms, 1.5 mm, 60 Hz and 5 m/s, respectively. The reinforced MMC coating exhibited higher wear resistance and lower friction coefficient than that of copper substrate. Crack-free MMC coating with metallurgical bonding was produced with average microhardness almost 9 times that of the copper substrate.

Yan et.al [34] prepared Co-based alloy/TiC/CaF_2 self-lubricating composite coatings on a Cr-Zr-Cu alloy for continuous casting mold by Nd: YAG laser cladding. During the cladding process power, scanning speed and spot diameter were selected as 390 W, 5 mm/s and 1.5 mm respectively. Average hardness of the self-lubricating composite of unique microstructure coating was about twice than that of the pure Co-based alloy. The composite coating decreases friction coefficient and wear rate as the volume fraction of CaF_2 increases and TiC decreases.

2.5 Problem identification and Objective of the work

From the literature review it has been found that TiC, TiB_2 coating by laser surface engineering improves the surface properties like hardness, wear resistance of the materials. However, very less work related to the in situ formation of TiB_2+TiC+Al_2O_3 on Al substrate have been done to improve the surface property by using pulsed Nd: YAG laser. In the present work we have tried to achieve TiC and TiC-TiB_2-Al_2O_3 coating on Al substrate by pulsed Nd: YAG laser and to study the effect of various process parameters.

The objectives of the present work are as follows:

- Experimental setup design to develop laser coating using pulsed Nd: YAG laser in an inert gas (Ar) environment.
- To develop TiC coating on Al substrate to identify range of parameters for proper coating process.
- To develop TiC+TiB_2 coating on Al substrate by in situ reaction of TiO_2, B_4C and Al.
- To study the effect of Al content on the different mixtures taken for coating.
- To study the microhardness of laser coating cross section obtained by changing the laser processing parameters.
- To analyze the microstructure of the laser coated samples.

Chapter 3

Experimental Planning and Procedure

- Materials and equipments used in the experimentation
- Characterization of laser treated samples
- Experimental procedure for first phase of experiment
- Experimental procedure for second phase of experiment

3.1 Materials and equipment used in the experimentation

3.1.1 Substrate:

To perform the laser coating process for present work commercial Al was taken as coating material, the properties of which is shown in Table 1.

Table 1: Typical properties of Aluminium

Property	Value
Phase	Solid
Density	2.70 g/cm^3
Melting Point	660.32 °C
Boiling Point	2470 °C
Crystal structure	Face centered cubic
Thermal conductivity	237 W/m.K
Thermal Expansion	(25 °C) 23.1 µm·m^{-1}·K^{-1}
Modulus of Elasticity	70GPa
Hardness, Vickers (HV)	50

3.1.2 Laser system used for present experiments

Laser treatment is done by using a 200 W (maximum average power) pulsed Nd-YAG laser system [ALPHA LASER, GERMANY/ALT-200].

Detail specifications of the Nd-YAG laser system are as follows:

- Maximum average power = 200 W
- Pulse energy = 90 J
- Peak pulse power = 10 kW
- Pulse duration = 0.5-20 ms
- Frequency = 20Hz

The process parameters considered during the experiment were peak power P_{peak} (kW), the time for which substrate is exposed to laser per pulse or pulse duration T_{on} (ms), Frequency of laser F (Hz).

The average power (P_{avg}) can be calculated considering the three parameters (P_{peak}, T_{on} and F) as:

$$P_{avg} = P_{peak} \times T_{on} \times F \quad (1)$$

Fig. 9: Pulsed Nd: YAG laser setup

3.2 Characterization of laser treated samples

3.2.1 FESEM

FESEM or Field Emission Scanning Electron Microscope was used to visualize very small topographic details for microstructure analysis of the surface or cross section of the samples. Energy-dispersive X-ray spectroscopy (EDS) analysis was done to identify different elements present and their distribution inside the developed coating.

3.2.2 X-Ray diffraction

X-ray diffraction (XRD) technique was applied to identify the different compounds present in the coating as crystalline material. Copper was selected as target material. The scanning range was $20^{\circ}$to 80°. The step size under each study was taken as 2°/min.

3.2.3 Vickers microhardness tester

Microhardness testing is a method for measuring the hardness of a material on a microscopic scale. A precision diamond indenter is impressed into the material at loads from a few grams to 1 kg. The impression length measured microscopically and the test load is used to calculate a hardness value. The hardness values obtained are useful indicators of a material's properties and expected service behaviour.

Experimental planning

Experiment was conducted in two phases. The first phase was the initial experiment where TiC coating was done on Al substrate using pre placed TiC powder and the second phase was the final experiment done with in situ reaction of TiO_2+B_4C+Al to form a composite of TiB_2-TiC with some other compounds. Aluminium was chosen as substrate material.

3.3 Experimental procedure for first phase of experiment

Initially to determine the range of peak power, frequency and scan speed that has to be considered during the laser coating process, first phase of experiment was performed.

3.3.1 Sample preparation

For first phase of experiment Aluminium plates of size 30×50×3 mm^3 was used as substrate material. Aluminium plates were polished with 220 SiC emery paper to remove the oxide layer. Then the samples were cleaned and degreased with ethyl alcohol and acetone respectively.

3.3.2 Pre –deposition of Powder or powder mixture

TiC powder of 44 µm average size was used for deposition material. Coating powders mixed with acetone and organic binder then dispersed over the substrate surface and dried in room temperature. Initial coating thickness of 150 ± 10 microns was taken for first phase of experiment.

3.3.3 Laser processing

After preparing the samples coating was done by using an Nd: YAG pulsed laser (ALT-200) with process parameters as listed in Table 2. Pre placed samples were placed within inert gas chamber on three-axis CNC controlled table. By adjusting the height of the table laser beam was focused on the sample surface and diameter of the beam was fixed as 1.5 mm for both of the experiments. Laser beam of Gaussian shape temporal distribution was used to scan over the specimen by moving CNC table to get a particular ratio of pulse overlapping.

Relation between laser scan velocity (v), beam diameter (d) and pulse to pulse overlapping (p_o) has been calculated by eq. (2) as described by Samant and Dahotre (2010).

$$v = f \times d \times (1 - p_o/100) \quad (2)$$

Where v = Velocity of specimen (mm/s)

f = Frequency (Hz)

d = Beam diameter (mm)

p_o = pulse overlapping (%)

Argon gas was used as protective atmosphere to avoid oxidation of substrate layer during laser processing of samples. Figure 10 shows schematic diagram of TiC coated samples. During the experiment the laser treatment was done by taking different range of peak powers (1-3 kW), frequencies (5-18 Hz), pulse duration (6-12 ms) and scan speed (2.5-10 mm/s) which are tabulated in table 2. The spot diameter was kept constant as 1.5 mm.

Table: 2 Experimental parameters to develop TiC coating on Aluminium

Sl. NO.	P_{peak} (kW)	F (Hz)	T_{on} (ms)	P_{avg} (W)	Speed (mm/s)	Percentage of overlapping
1	1	14	12	168.00	8	60
2	1	14	12	168.00	6	70
3	1	14	12	168.00	4	80
4	1.5	8	14	168.00	4	60
5	1.5	8	14	168.00	3	70
6	1.5	8	14	168.00	2	80
7	2	8	10	160.00	4	60
8	2	8	10	160.00	3	70
9	2	8	10	160.00	2	80
10	2	6	14	168.00	3	60
11	2	6	14	168.00	2.25	70
12	2	6	14	168.00	1.5	80
13	2	7	12	168.00	3.5	60
14	2	7	12	168.00	3	70
15	2	7	12	168.00	2	80
16	2.5	8	8	160.00	4	60
17	2.5	8	8	160.00	3	70
18	2.5	8	8	160.00	2	80
19	3	6	9	162.00	3	60
20	3	6	9	162.00	2.25	70
21	3	6	9	162.00	1.5	80

3.3.4 Preparation of laser coated samples for various analysis

To measure the microhardness and microstructural analysis laser coated samples were polished with 220, 600, 1200 grade SiC polishing paper at the cross section. Final polishing was done with diamond paste suspended polishing cloth.

3.3.5 Analysis of prepared samples by XRD, FESEM, Micro-hardness tester

After preparation of the coated samples Optical microscopy and FESEM analysis were done for microstructure study. XRD analysis was done for identification of coating material. The microhardness was taken on LECO microhardness tester (LM248AT) at the cross-section of the coating layer and near surface region of the samples with 50 gf load and 10 s dwell time.

3.4 Experimental procedure for second phase of experiment

On the basis of results obtained from first phase of experiment, which is discussed in results and discussion chapter, process parameters for second phase of experiment was selected which is tabulated in Table 3.

3.4.1 Sample preparation

For second phase of experiment Aluminium plates of size 30×50×8 mm^3 were used as substrate material. In second phase of experiment the thickness of the substrate is more than the initial one to avoid bending of the substrate during laser coating that has occurred during initial phase of experiment. Then Aluminium plates were prepared same as the first phase of experiment.

3.4.2 Pre –deposition of powder or powder mixture

Powder mixture of TiO_2, B_4C and Al with different composition was used for deposition material. Coating powders mixed with acetone and organic binder then dispersed over the substrate surface and dried in room temperature. Initial coating thickness of 250 ± 50 microns was taken for second phase of experiment.

3.4.3 Laser processing

After preparing the samples coating was done by using an Nd: YAG pulsed laser (ALT-200) with process parameters as listed in Table 3. Here beam diameter is kept constant at 1.5 mm, percentage overlapping taken as 80%.

Table: 3 Experimental parameters for single track

Sl. No.	**Powder composition**	**Exp. No.**	**P_{peak} (kW)**	**F (Hz)**	**T_{on} (ms)**	**P_{avg} (W)**	**Speed (mm/s)**
1	TiO_2 : B_4C	1.1	2	7	12	168	2.1
2	(Ratio of 4.3:1) wt %	1.2	2.5	8	8	160	2.4
3	Thickness of initial coating = 150 µm	1.3	3	7	8	168	2.1
4	**Sample 1**	1.4	3.5	6	8	168	1.8
5	TiO_2 : B_4C : Al	2.1	2	7	12	168	2.1
6	(Ratio of 59:14:27) wt %	2.2	2.5	8	8	160	2.4
7	Thickness of initial coating = 150 µm	2.3	3	7	8	168	2.1
8	**Sample 2**	2.4	3.5	6	8	168	1.8
9	TiO_2 : B_4C : Al	3.1	2	7	12	168	2.1
10	(Ratio of 35: 8: 57) wt %	3.2	2.5	8	8	160	2.4
11	Thickness of initial coating = 300 µm	3.3	3	7	8	168	2.1
12	**Sample 3**	3.4	3.5	6	8	168	1.8
13	TiO_2 : B_4C : Al	4.1	2	7	12	168	2.1
14	(Ratio of 30: 7: 63) wt %	4.2	2.5	8	8	160	2.4
15	Thickness of initial coating = 300 µm	4.3	3	7	8	168	2.1
16	**Sample 4**	4.4	3.5	6	8	168	1.8

For the analysis of coating with multiple tracks, 70 % side overlapping was taken. Wider area of coating produced with multiple tracks was used for XRD analysis. Due to multiple tracks better mixing of coating material with each other and also with the substrate material takes place. Overlapped tracks were developed with process parameters listed in Table 4.

Table: 4 Experimental parameters for overlapped coating

Sl. NO.	**P_{peak} (kW)**	**F (Hz)**	**T_{on} (ms)**	**P_{avg} (W)**	**Speed (mm/s)**
1	2	10	8	160	3
2	2.5	8	8	160	2.4
3	3	7	8	168	2.1
4	3.5	6	8	168	1.8

3.4.4 Preparation of laser coated samples for various analysis

To measure the microhardness and microstructural analysis laser coated samples were polished with 220, 600, 1200 grade SiC polishing paper at the cross section. Final polishing was done with diamond paste suspended polishing cloth.

3.4.5 Analysis of prepared samples

After preparation of the coated samples Optical microscopy and FESEM analysis were done for microstructure study. XRD analysis was done for identification of coating material. The microhardness was taken in similar way as discussed for first phase of experiment.

Chapter 4

Result and Discussion

- TiC coating on Al substrate (first phase of experiment)
  - Images after laser coating of TiC on Al substrate
  - Optical Images of the TiC coated Al samples at the cross section
  - Microhardness Analysis for first phase of experiment
- TiB_2-TiC-Al_2O_3 coating on Al substrate (second phase of experiment)
  - Images of samples after laser coating
  - Microhardness analysis of second phase of experiment
  - Microstructure analysis of the coated zone
  - Microstructure comparison
  - XRD analysis of the laser coated samples

4.1 TiC coating on Al substrate (first phase of experiment)

4.1.1 Images after laser coating of TiC on Al substrate

After performing first phase of experiment images of some of the TiC coated Al samples are shown in Figure10.

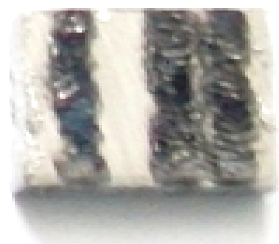
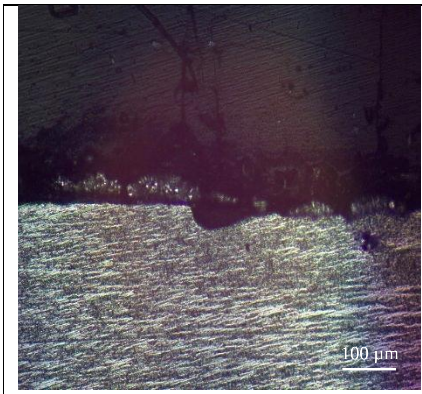
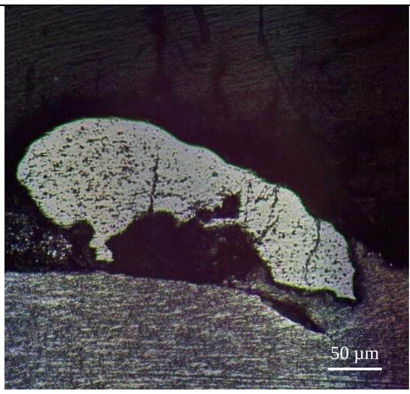
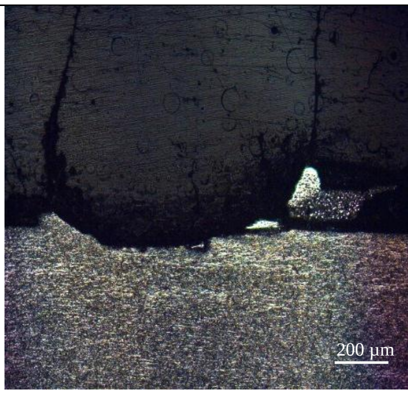
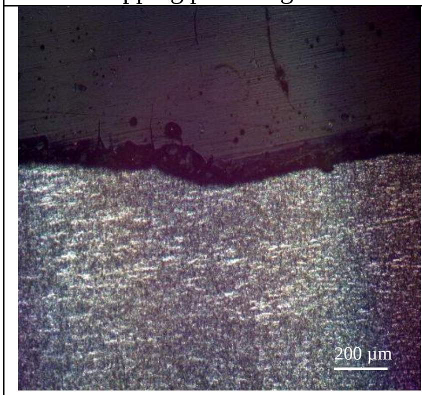
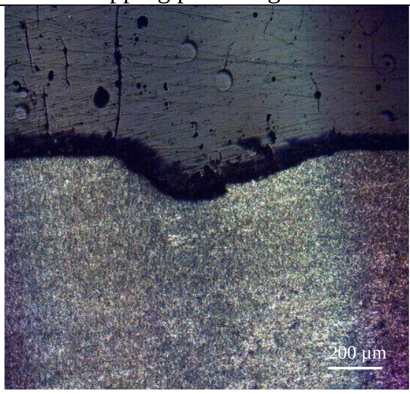
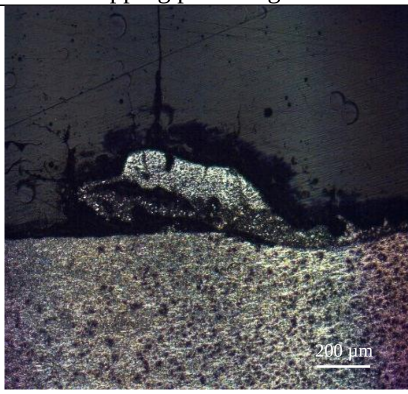
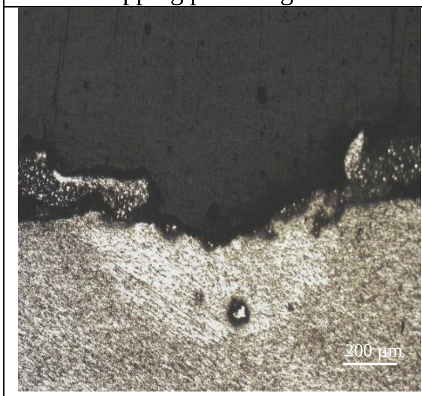
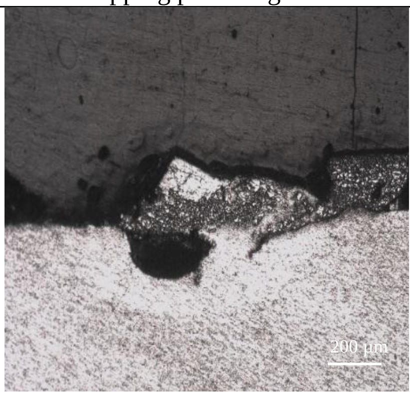
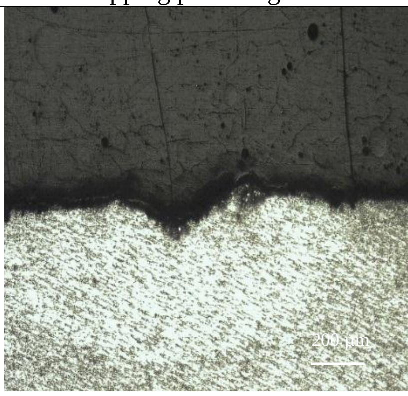
 P_{peak} = 1 kW, F = 14 Hz, T_{on} = 12 ms Overlapping percentage = 60 %, 70 %, 80 %	 P_{peak} = 1.5 kW, F = 8 Hz, T_{on} = 14 ms Overlapping percentage = 60 %, 70 %, 80 %
 P_{peak} = 2 kW, F = 6 Hz, T_{on} = 14 ms Overlapping percentage = 60 %, 70 %, 80 %	 P_{peak} = 2 kW, F = 7 Hz, T_{on} = 12 ms Overlapping percentage = 60 %, 70 %, 80 %
 P_{peak} = 2.5 kW, F = 8 Hz, T_{on} = 8 ms Overlapping percentage = 60 %, 70 %, 80 %	 P_{peak} = 3 kW, F = 6 Hz, T_{on} = 9 ms Overlapping percentage = 60 %, 70 %, 80 %

Fig. 10: Laser coating of TiC on Al with different parameters

From the above figure it is clear that coating of TiC on Al substrate formed which is not so uniform. Coating is better when laser processing was done at higher power as compared to lower power. At lower power, less heat is generated due to which bonding between TiC and Al substrate found weak, therefore some of the coating material removed from the substrate surface.

4.1.2 Optical Images of the TiC coated Al samples at the cross section

 P_{peak} = 2 kW, F = 8 Hz, T_{on} = 10 ms Overlapping percentage = 60 %	 P_{peak} = 2 kW, F = 8 Hz, T_{on} = 10 ms Overlapping percentage = 70 %	 P_{peak} = 2 kW, F = 8 Hz, T_{on} = 10 ms Overlapping percentage = 80 %
 P_{peak} = 2 kW, F = 6 Hz, T_{on} = 14 ms Overlapping percentage = 60 %	 P_{peak} = 2 kW, F = 6 Hz, T_{on} = 14 ms Overlapping percentage = 70 %	 P_{peak} = 2 kW, F = 6 Hz, T_{on} = 14 ms Overlapping percentage = 80 %
 P_{peak} = 2 kW, F = 7 Hz, T_{on} = 12 ms Overlapping percentage = 60 %	 P_{peak} = 2 kW, F = 7 Hz, T_{on} = 12 ms Overlapping percentage = 70 %	 P_{peak} = 2 kW, F = 7 Hz, T_{on} = 12 ms Overlapping percentage = 80 %

Images taken from optical microscopy of TiC coated samples are shown in fig. 11 (a and b)

Fig. 11(a): Optical images of TiC coated samples at cross section

From the optical images of the coated samples of first phase of experiment, it is found that a non-uniform TiC coating on Al substrate was formed. In some cases coating was found not properly bonded with Aluminium substrate. No specific trend on the thickness or structure of the coating was observed. Laser absorptivity of Al substrate is very less due to which melting depth of substrate material become less and diffusion of TiC on Al substrate reduces. TiC alone is not suitable for coating material on Al substrate by pulsed laser due to mismatch in properties of coating and substrate material. At low power range due to less adhesion, TiC is removed from the substrate surface.

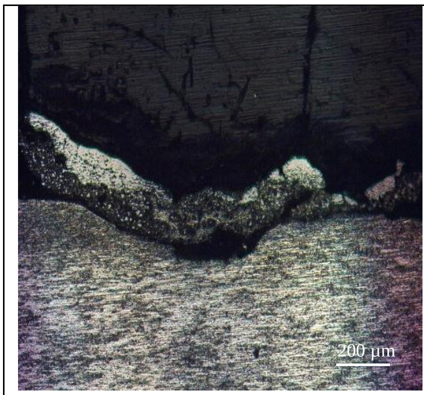
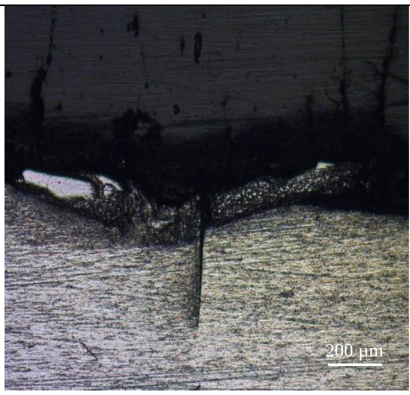
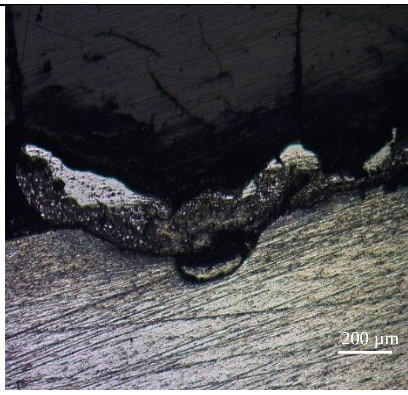
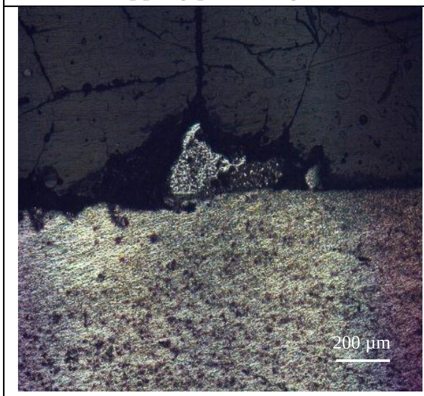
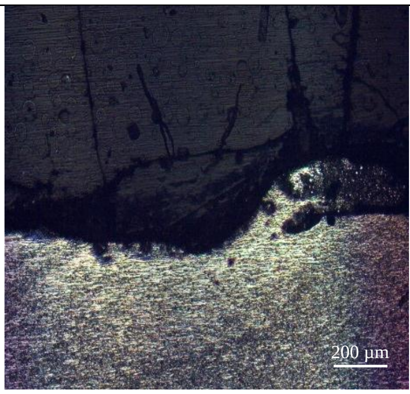
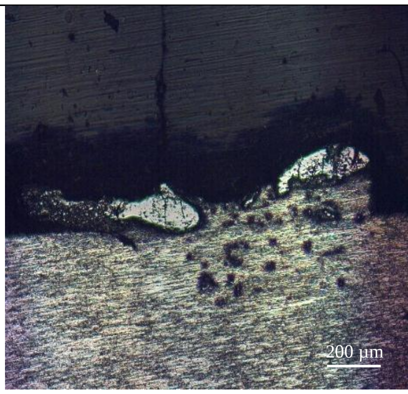
 P_{peak} = 2.5 kW, F = 8 Hz, T_{on} = 8 ms Overlapping percentage = 60 %	 P_{peak} = 2.5 kW, F = 8 Hz, T_{on} = 8 ms Overlapping percentage = 70 %	 P_{peak} = 2.5 kW, F = 8 Hz, T_{on} = 8 ms Overlapping percentage = 80 %
 P_{peak} = 3 kW, F = 6 Hz, T_{on} = 9 ms Overlapping percentage = 60 %	 P_{peak} = 3 kW, F = 6 Hz, T_{on} = 9 ms Overlapping percentage = 70 %	 P_{peak} = 3 kW, F = 6 Hz, T_{on} = 9 ms Overlapping percentage = 80 %

Fig. 11(b): Optical images of TiC coated samples at cross section

4.1.3 Microhardness Analysis for first phase of experiment

Hardness value measured at the coating cross section of the coated samples shows variation in the hardness which depends on the laser process parameters.

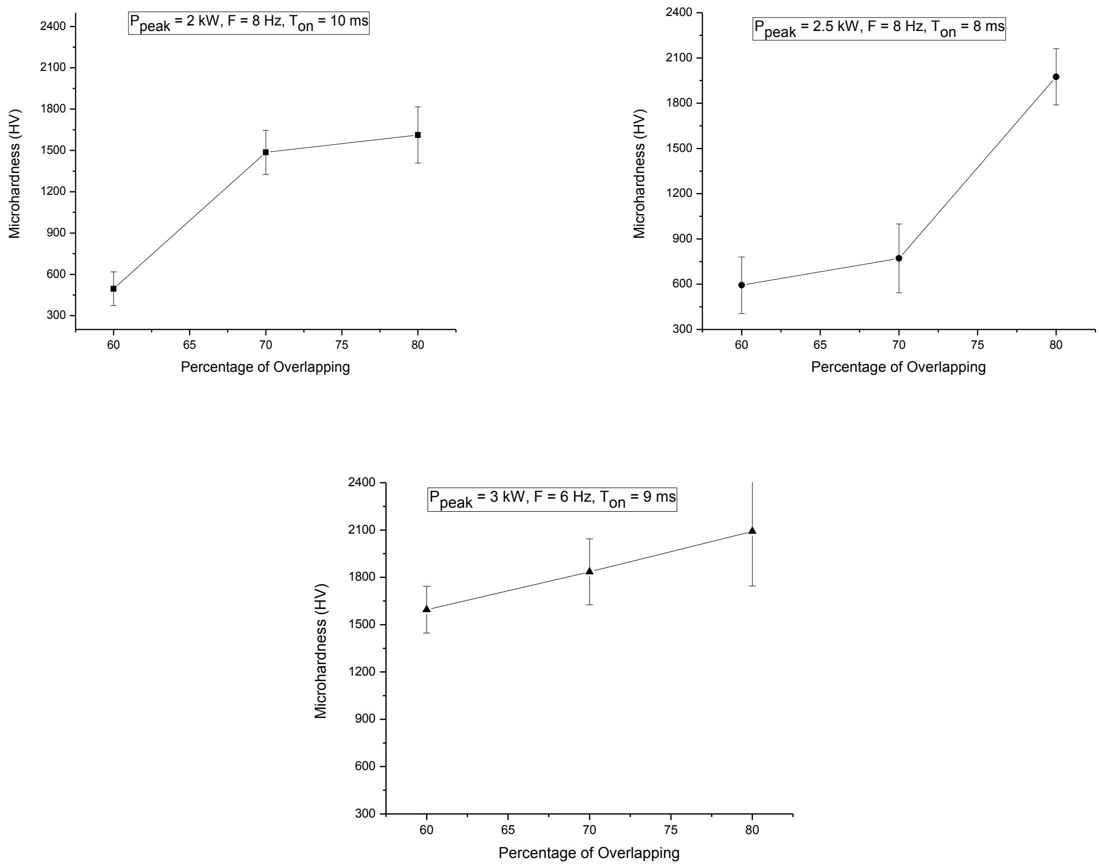


Fig. 12: Microhardness vs Percentage of Overlapping graph

Outcomes of first phase of experiment

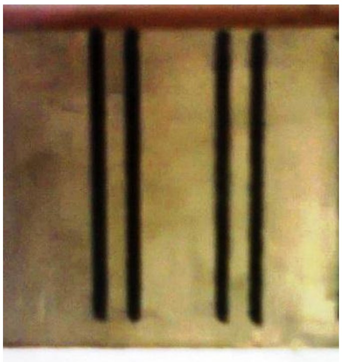
- TiC coating has formed on Al substrate by pulsed Nd: YAG laser process.
- Microhardness of coating found very high compared to substrate material.
- Microhardness increases with increase in percentage of pulse overlapping.
- For low peak power (1-1.5 kW) with high scanning speed (4-10 mm/s) coating layer of TiC did not form bond with Al substrate. Thus this low power range is unsuitable for formation of coating.

- Also it was observed that in high power range (2-3.5 kW) with low scan speed (1.5-3 mm/s) as a result of high percentage of overlapping coating is achieved with high bonding strength.
- At high power TiC is melted and formed a solidified coating on the Al substrate.
- TiC alone is not suitable for coating material on Al substrate by pulsed laser due to mismatch in properties of coating and substrate material.
- So it is recommended to use some other material with TiC to get proper bonding on Al substrate.

4.2 TiB_2-TiC-Al_2O_3 coating on Al substrate (second phase of experiment)

4.2.1 Images of Samples after laser coating

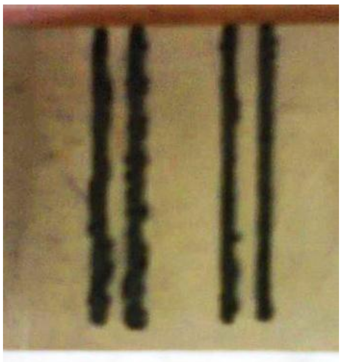
Fig. 13 shows laser coated samples of second phase of experiment with single track and overlapping track by using different powder compositions and process parameters.



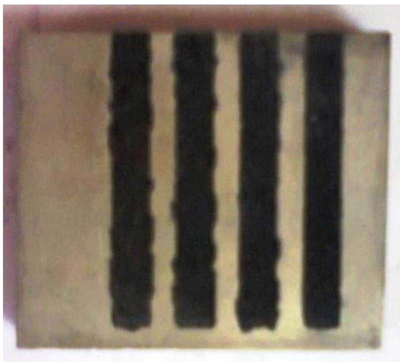
(a) Single track

(b) Overlapping track

Sample 1



(a) Single track



(b) Overlapping track

Sample 2

Fig. 13: Laser coated samples

4.2.2 Microhardness analysis of second phase of experiment

Hardness value measured at the cross section of the coated samples shows variation in the hardness which depends on the process parameters and powder composition. For samples 1 and 2 microhardness decreases with increase in the power and for samples 3 and 4 microhardness increases with increase in the power considering other parameters like pulse duration and frequency kept constant. Differences in variation of hardness with respect to power were mainly due to the initial thickness of the coating material.

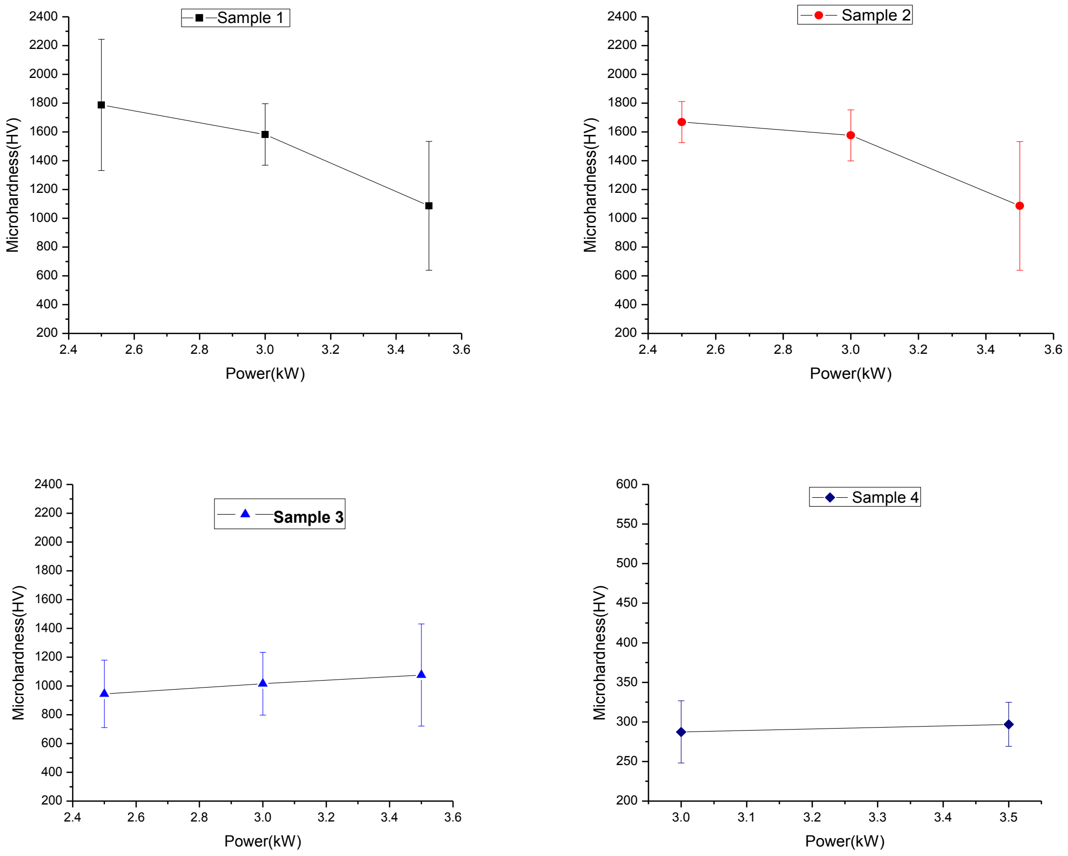


Fig. 14: Microhardness vs Power graph

From the graph of sample 1 and 2 it is concluded that

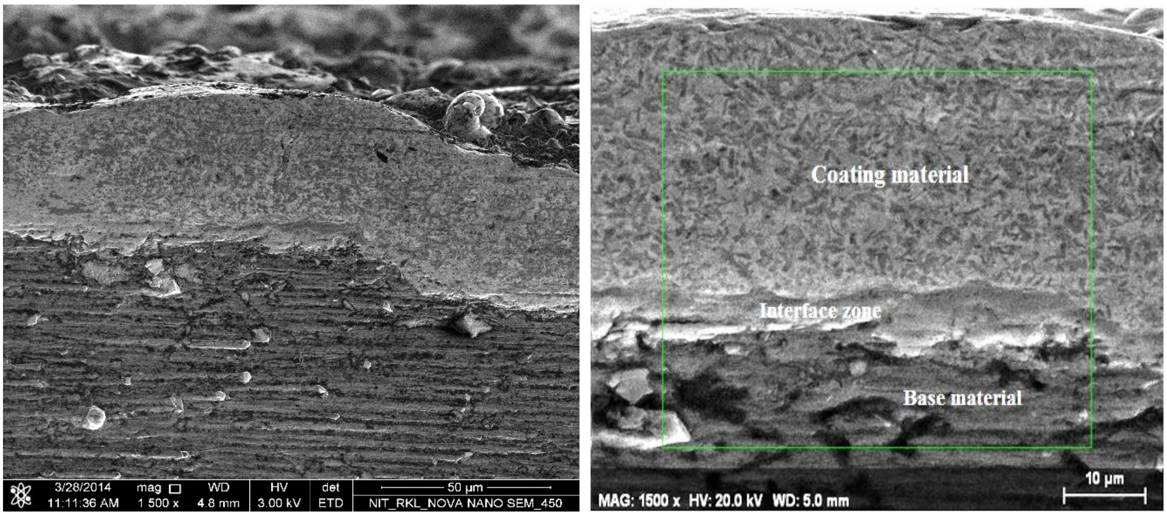
- Sample 1 has more hardness as compare to sample 2 due to the presence of less amount of Al in sample 1 compared to the sample 2.
- Microhardness decreases with increase in the power considering other parameters like pulse duration, frequency and pulse overlapping kept constant.
- Since a relatively thin layer (150 µm) of the coating material was deposited by preplaced method on the base material so there are more chances of mixing of the coating material with the base material when power increases. Thus hardness decreases with increase in the power.

Similarly from the graph of sample 3 and 4 it is concluded that

- Sample 3 has more hardness as compare to sample 4 due to the presence of less amount of Al in sample 3 compared to the sample 4.
- Microhardness increases with increase in the power considering other parameters like pulse duration, frequency and pulse overlapping kept constant.
- Thick layer (300 µm) of the coating material was deposited by preplaced method on the substrate surface due to which very less amount of power reaching to the base material. So there are more chances of mixing of the coating material with itself rather than with the base material. That results into better mixing of initial powders and formation of more TiC and TiB_2 which corresponds to the increase in hardness value with increase in the power.

4.2.3 Microstructural analysis of the coated zone

The FESM micrograph of coated sample processed with peak power of 2.5 kW, frequency of 8 Hz, pulse duration of 8 ms and powder mixture composed of TiO_2 and B_4C in Ratio of 4.3:1 is shown in the Fig. 15. From the figure it is seen that a uniform coating is achieved upto some region. A coating layer of around 50 microns has been formed on the Al substrate.



(a) (b)

Fig. 15: FESEM Micrograph of the coating at power of 2.5 kW, frequency of 8 Hz and pulse duration of 8 ms.

When we concentrate our analysis in the coated zone we observed that there is an interface zone between the coating material and substrate material. It is clear from the figure that there is no crack formation in the interface zone. So it can be concluded that better adhesive bonding of the coating material with substrate material took place.

Corresponding to the micrograph of Fig. 15 the EDS mapping of the coated zone is shown in Fig.16. Different elements of the coating material like Ti, C, B, and O are shown in individual images. From these images it is found that the interface zone is rich in Ti but C and B are present in a small amount. Since we have used TiO_2 and B_4C as the coating powder without any additional Al, there is no sign of the presence of Al in the interface zone.

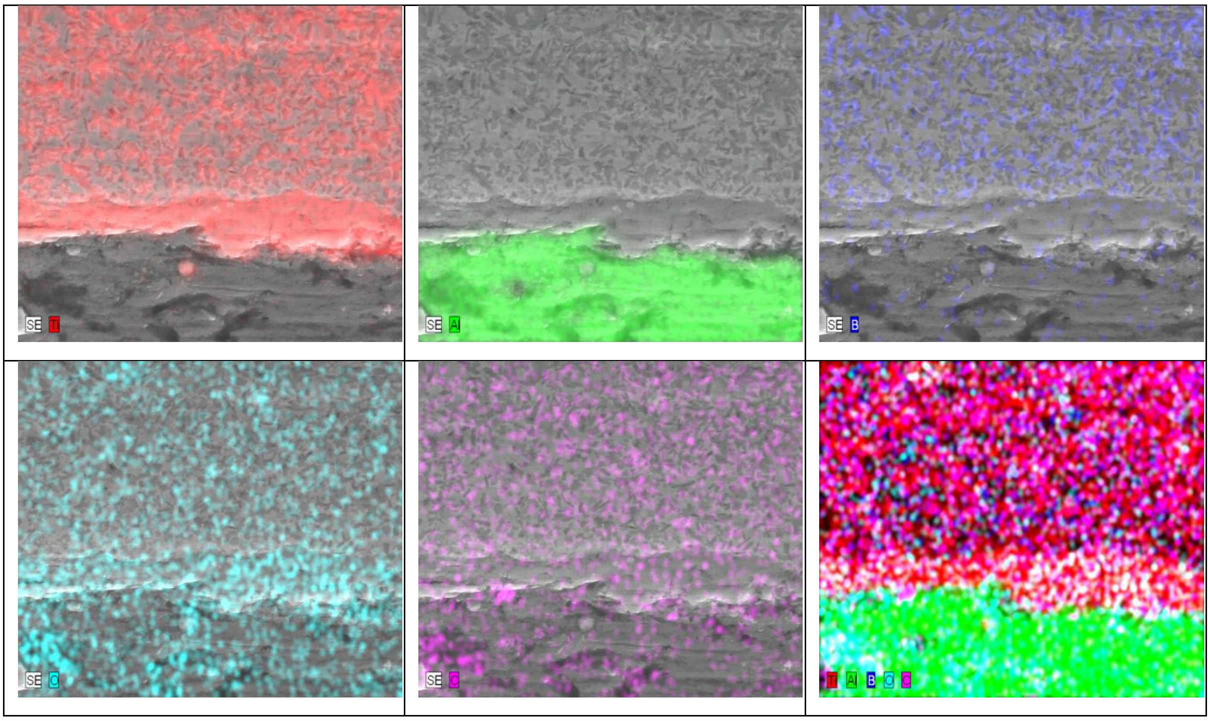
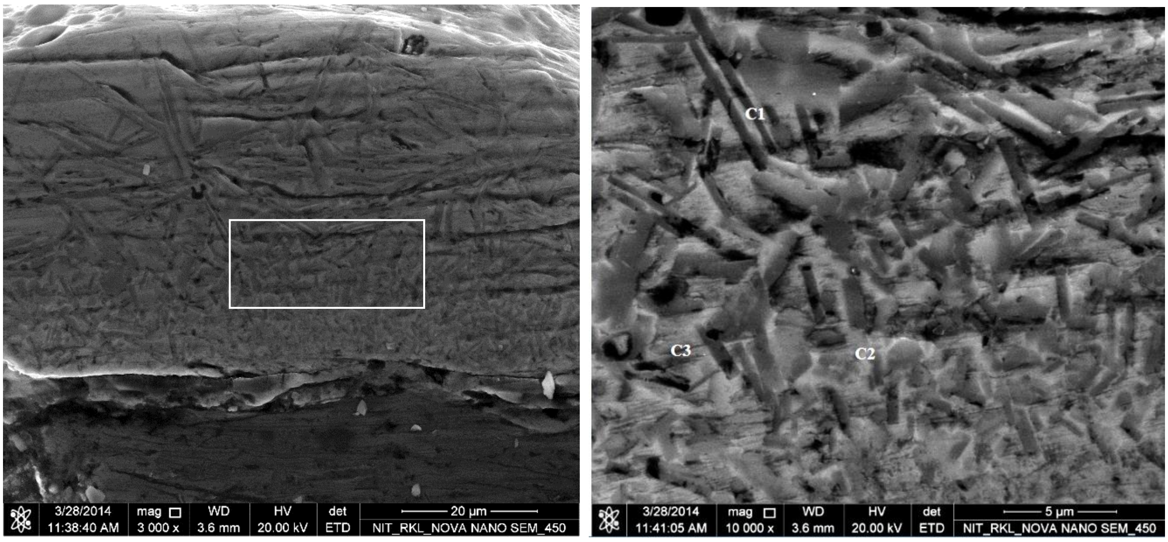


Fig. 16: EDS elemental mapping of the coated zone showing concentration of Ti, Al, B, C and O.

The portion above the interface zone is well mixed with the chief constituents of the coating material. Very less amount of Al is present in this region. So we can conclude that dilution of Al from the substrate to this coating region is less for using a pre-placed powder mixture without any Al at applied laser processing condition.

To determine microstructure of the coated sample FESEM analysis has been performed. Fig. 17 (a) shows FESEM micrograph of coated sample processed with peak power of 2 kW, frequency of 7 Hz, pulse duration of 12 ms and powder mixture composed of TiO_2, B_4C and Al in Ratio of 59:14:27.



(a) (b)

Fig. 17: FESEM micrograph of coated sample processed with peak power of 2 kW, frequency of 7 Hz and pulse duration of 12 ms

Corresponding to the micrograph of Fig. 17 (a) the high magnified view of the coated zone is shown in Fig. 17 (b). From this figure it is found that there are mainly three kinds of structures in the coating. First one is rectangular shaped particles (marked as C1) with deep grey shaded, second one is irregular shaped particles (marked as C2) with light grey. Besides rectangular and irregular particles, there also exist some white matrix zones (marked as C3).

From the EDS elemental mapping of the coated zone as shown in Fig. 18 it is found that particle C1 is rich in Ti and B, but there is a lack of Al in the rectangular shaped particles. So it can be concluded that rectangular shaped particles are TiB_x.

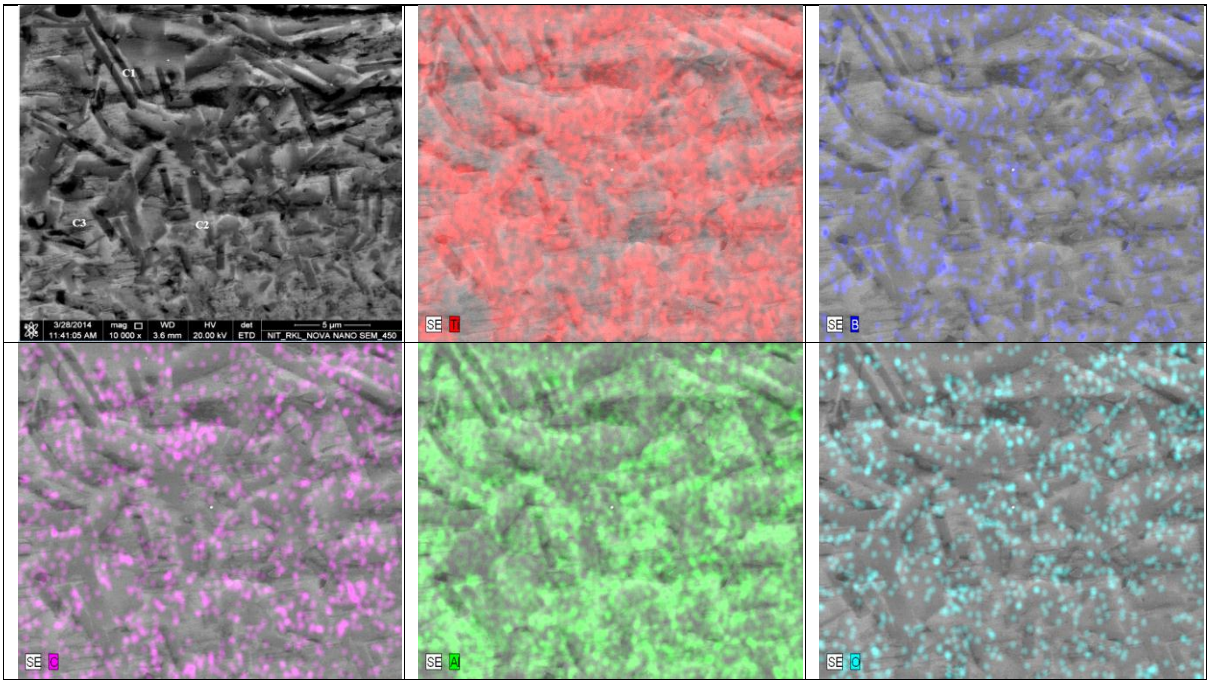
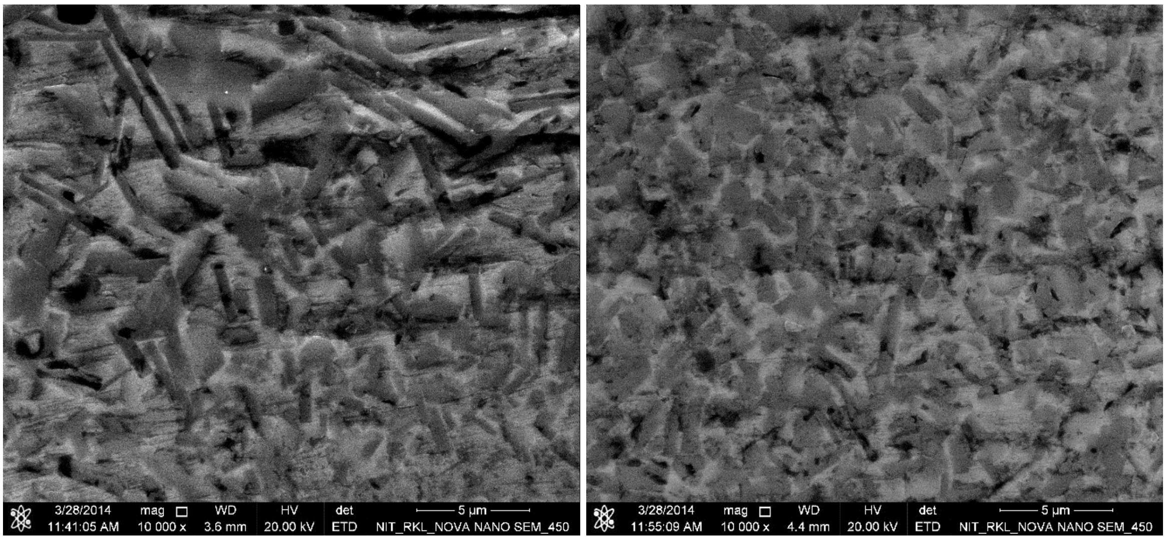


Fig. 18: EDS elemental mapping of the coated zone showing concentration of Ti, Al, B, C and O for analysis of marked C1, C2 and C3 particles.

Similarly the EDS analysis for marked C2 structure indicates that irregular shaped particle C2 is rich in Ti and C but there is lack of Al in the irregular shaped particles. So it can be say that irregular shaped particles may be TiC_x. In addition, it can be seen from EDS elemental mapping of the coated zone that marked C3 structure is rich in Al and O which is the indication of formation of Al_xO_y.

4.2.4 Microstructure comparison

(a) Effect of laser power on microstructure of produced coating for same powder composition



(a) (b)

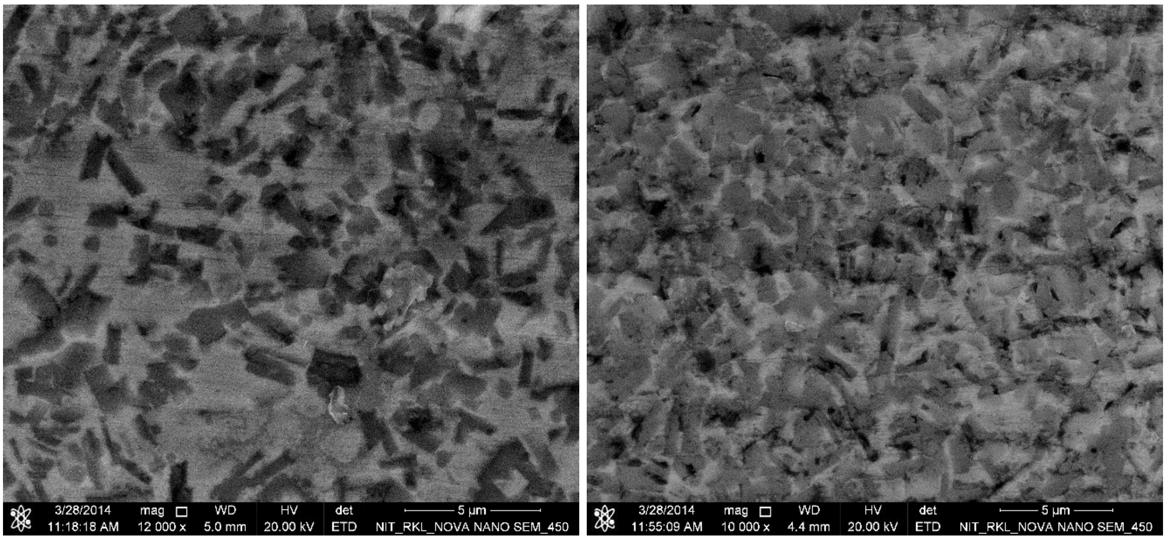
Fig.19: Morphology of reinforcement of the coating produced with (a) laser peak power of 2 kW frequency of 7 Hz and pulse duration of 12 ms and (b) peak power of 3 kW, frequency of 7 Hz and pulse duration of 8 ms.

Figure 19 shows the morphology of the coating produced with (a) laser peak power of 2 kW, frequency of 7 Hz and pulse duration of 12 ms and (b) peak power of 3 kW, frequency of 7 Hz and pulse duration of 8 ms. These two coatings performed with preplaced powder composition i.e. (TiO_2 : B_4C : Al) in the stoichiometric composition (Ratio of 59:14:27).

From the initial microstructure analysis it is found that the coated zone structure is composed of TiC_x, TiB_x and Al_xO_y. From the images it is found that, particle size shown in figure (b) is smaller than the particle size shown in figure (a) and also distribution of the particles are more uniform as compared to the first one.

Uniform distribution of the coating material takes place due to the diffusion of the particles at high temperature. So we can say that at higher temperature proper mixing of particles achieved that result into formation of relatively smaller size particles. These smaller reinforced particles further improve the mechanical properties of the substrate material.

(b) Effect of powder composition on microstructure of produced coating for same power range



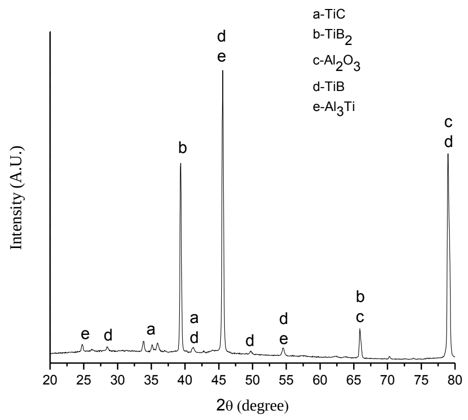
(a) (b)

Fig. 20: Morphology of reinforcement of the coating produced with (a) laser peak power of 2.5 kW, frequency of 7 Hz and pulse duration of 8 ms and (b) laser peak power of 3 kW, frequency of 8 Hz and pulse duration of 8 ms.

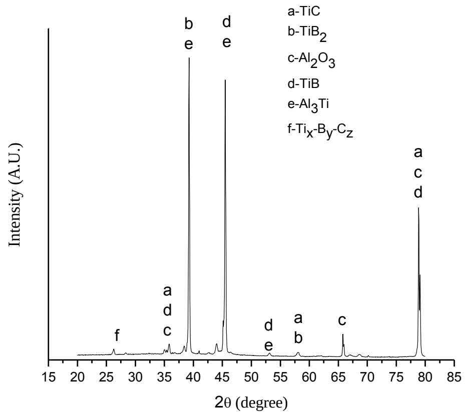
Fig. 20 shows the morphology of the coating having same process parameters i.e. peak power range of (2.5-3.0) kW, frequency range of (7-8) Hz and pulse duration of 8 ms but with different powder composition. Morphology of the coating shown in Fig.20 (a) for sample produced with initial powder mixture of (TiO_2: B_4C) with 4.3:1 ratio and shown in Fig.20 (b) for sample produced with initial powder mixture of (TiO_2 : B_4C: Al) with the ratio of (59:14:27).

From the initial microstructure analysis it is found that the coated zone structure is composed of TiC_x, TiB_x and Al_xO_y. From the images it is found that distribution of the particles shown in Fig.20 (b) are more uniform as compared to the first one. Here the processing parameters of both the coated samples are almost same and microstructural difference is due to the change in powder composition only. Sample coated with more Al content provides better mixing of coating material with the base material which results into formation of relatively smaller size particles. Due to more amount of Al in coated sample shown in Fig.20 (b) hardness value is less as compared to the first one.

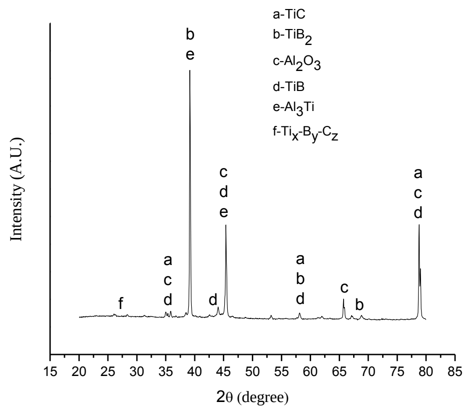
4.2.5 XRD analysis of the coated samples



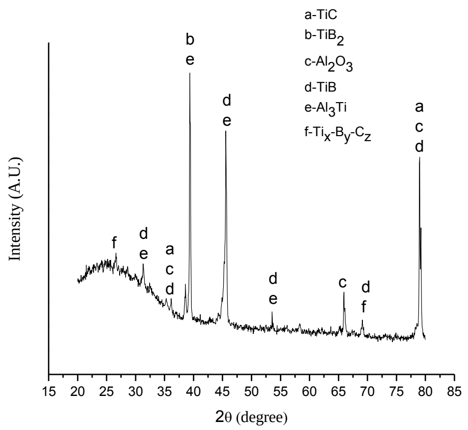
(a) Sample 1



(b) Sample 2



(c) Sample 3



(d) Sample 4

Fig. 21: X-ray diffraction profiles of the top surface of laser surface coated Aluminium samples showing the effect of powder composition and process parameters on the phase formation behaviour.

Fig. 21 (a) and (b) shows the XRD profiles of the top surface of laser coating produced with laser peak power of 2 kW, frequency of 7 Hz, pulse duration of 12 ms and scan speed of 2.1 mm/s using powder composition of TiO_2+B_4C (4.3:1 weight ratio) and TiO_2+B_4C+Al (59:14:27 weight ratio) respectively. Similarly Fig. 21 (c) and (d) shows the XRD profiles of the top surface of laser coating produced with laser peak power of 3 kW, frequency of 7 Hz, pulse duration of 8 ms and scan speed of 2.1 mm/s using powder composition of TiO_2+B_4C+Al (35:8:57 weight ratio) and TiO_2+B_4C+Al (30:7:63 weight) respectively.

From all the XRD plots it is clear that coating layer is composed of a numbers of compounds like TiC, TiB_2, TiB, Al_2O_3, Al_3Ti, Ti_x-B_y-C_z etc. therefore it can be say that, during laser processing these compounds are formed by reaction of TiO_2, B_4C and Al. For 1st case (a) where no extra aluminium powder was used in preplaced powder mixture, reaction occurred by using Al from substrate material.

Close comparison between the graphs shown in Fig.21 (a) and (b) indicates that there is no significant difference in phase formation, however difference in peak intensity was observed due to change in powder composition of preplaced layer. High intensity of Al_3Ti for sample 2 indicates that for same process parameters probability of Al_3Ti formation is higher when amount of Al in the initial powder mixture is more.

Similarly graphs shown in Fig. 21 (c) and (d) indicates almost same phase formation due to same processing parameter, but difference in peak intensity was observed due to change in powder composition of preplaced layer. Here, high intensity of Al_3Ti, Al_2O_3 for sample 4 indicates probability of Al_3Ti and Al_2O_3 formation is more due to higher amount of Al in the initial powder mixture.

Chapter 5

Conclusion and Future scope

- Conclusion
- Future scope

5.1 Conclusion

Following conclusions were obtained from present work:

- TiC alone is not suitable for coating material on Al substrate by pulsed laser due to mismatch in properties of coating and substrate material.
- In-situ formed $TiC+TiB_2+Al_2O_3$ coating shows strong metallurgical bond with the Al substrate without any crack formation as compared to the only TiC coating on aluminium substrate.
- Formation of TiC and TiB_2 by preplaced powder mixture due to localized laser heat improve the surface properties of the aluminium substrate like its hardness without actually affecting its bulk mechanical properties.
- The surface properties are highly affected by the laser process parameters and composition of preplaced powder in the different powder mixtures.
- Hardness value not only depends on the powder composition and processing parameters but also depends on the initial thickness of the preplaced powder.

5.2 Future scope

Future scope of the present work are as follows:

- Wear test for the coated samples can be done by ball on disc or adhesive type wear testing.
- This coating can be applied for actual environment.
- Different substrate material can also be tested for this coating composition.
- Use of continuous type high power lasers and sophisticated knowledge based controllers may produce uniform laser coating which is less susceptible to variations in process parameters.

Chapter 6
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