To Study the Mechanical Properties and Electronic Structure of Laser Treated Materials

A Thesis Submitted to

Devi Ahilya Vishwavidyalaya, Indore

For the degree of

Doctor of Philosophy

in

Instrumentation

Faculty of Engineering Science

By

SHEETAL SONI

School of Instrumentation

Devi Ahilya Vishwavidyalaya, Indore

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Certificate by the Supervisor

This is to certify that the work entitled **"To Study the Mechanical Properties and Electronic Structure of Laser Treated Materials"** is a piece of research work done by **Ms. Sheetal Soni,** under my supervision and guidance for the degree of Doctor of Philosophy from Devi Ahilya Vishwavidyalaya (DAVV), Indore (M.P.), India. The candidate has put-in an attendance more than 200 days with me.

To the best of my knowledge and belief the thesis:

1. embodies the work of candidate herself.
2. has duly been completed
3. fulfills the requirements of the ordinance relating to the Ph.D. degree of the university and
4. is up to the standard both in respect of contents and language for being referred to the examiner.

Signature of the Supervisor

Dr. Ratnesh Gupta

Signature of the Head U.T.D./Principal

Declaration by the candidate

I, Sheetal Soni, declare that the thesis entitled, **"To Study the Mechanical Properties and Electronic Structure of Laser Treated Materials"** is my own work conducted under the supervision of **Dr. Ratnesh Gupta** at **School of Instrumentation, DAVV, Indore**, **India**, approved by the research degree committee. I have put more than 200 days of attendance with the supervisor at the institute.

I further declare that to the best of my knowledge the thesis does not contain any part of any work, which has been submitted for the award of any degree either in the university or in any other university/Deemed university without proper citation.

Signature of the supervisor Signature of the candidate

Signature of the Head U.T.D./Principal

Dedicated to lord Krishna

&

My Parents

Mr. Jagdish Prasad Soni & Mrs. Krishna Devi Soni

1742

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CERTIFICATE

Ph.D. Course Work

Subject : INSTRUMENTATION **Faculty :** ENGINEERING SCIENCE

Enrolment No. : DS/08/5050 **Roll No. : Ph.D/2013/03**

This is to certify that **Ms. Sheetal Soni daughter** of **Mr. Jagdish Prasad Soni** has successfully completed the Ph.D. course work conducted at **School of Insterumentation, D.A.V.V. Indore**. from **Jan 2013** to **June 2013**. The Ph.D. course work is as per UGC Regulation 2009 and Ph.D. Ordinance of the University. The credits and the grades earned by the candidate are as follows :

S. No.	Course Title	Credits	Grade	Credits X Grade
1	Research Methodology	5	B+	40
2	Computer Application	3	B	21
3	Rewiew of Literature	3	A	27
4	Comprehensive Viva- Voce	4	A	36
		15		124

Semester Grade Point Average (SGPA) : 8.26 **Percentage : 77.54**

(Percentage Marks = 8.4 X SGPA + 8.1)

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May 07, 2015 *Sheetal Soni*

Preface

Coatings are used to enhance the properties of components and products in such diverse area as cutting tools hard coatings, wear and oxidation resistant biological coatings, miniature integrated electronics, micro-mechanical systems and coatings for optical devices. Laser nitriding and carbonitriding is more prominent techniques to form coatings on metals and alloys to improve the hardness, wear and corrosion resistance of the same. Laser nitriding and carbonitriding of metals such as iron, titanium and stainless steel is interesting area in both research and industry. On a time scale of hundreds nanoseconds, high intensity pulsed laser irradiation in ambient nitrogen and/or methane atmospheres transform the surface of the metals to micron thick metal nitride/carbonitride layer, which greatly improve the metal surface mechanical and tribological properties.

These properties are often originating from their rock salt structure and covalent bonding characteristic. Early reports showed that the mechanical properties can be determined more than by bonding than conventional microstructural features. This thesis focuses on the fabrication of the laser nitriding and carbonitriding of titanium metal. Since laser fluence and pressures of ambient gases are two most crucial factors determining the efficiency of laser nitriding/carbonitriding, hence the experiments focus on the influences of the ambient nitrogen and/or methane pressure and pulsed laser fluence on laser irradiation process. The central theme of this thesis is concerned with the mechanical properties of laser treated nitrides and carbonitrides of titanium. Since the properties of these nitrides and carbonitrides is depends on the bonding characteristic, we have emphasize on the investigation of electronic structure and bonding characteristics with chemical analysis. The primary tools used to

analyze the coatings are nanoindentation and photoelectron spectroscopy (PES) with emphasis put on the resonant photoemission spectroscopy. In this thesis, we have utilized the facility of synchrotron radiation source, which is the principal tool to utilize different X-ray and electron spectroscopy to fulfill the goal of present thesis project. Thus, the objective of this study is to apply resonant photoemission of the valence band and its CIS plots to gain insight into electronic bonding and correlate their findings to macroscopic mechanical properties.

The investigation of the influence of the laser fluence and pressures of ambient gas atmospheres have revealed that the 6.8 J/cm^2 and higher pressure of the ambient gases is superior compared to other parameters. Thesis also emphasize on the oxidation resistance behavior and its improvement by using post Ar treatments on these coatings.

We have investigated the structural, mechanical, electronic and transport properties of laser irradiated binary and ternary alloys (titanium nitrides and carbonitrides) as a function of ambient gas pressure (N_2 and/or CH_4) and laser energy density. To study their structural properties, X-ray diffraction (XRD) using lab source and in-plane and out of plane angle dispersive XRD in the grazing incidence geometry using synchrotron radiation source have been done. Electrical transport and mechanical measurements have been performed using pressure contact four-probe technique and nano indentation technique, respectively. Chemical composition and oxidation states have been investigated by X-ray photoelectron spectroscopy (XPS). The electronic structure and bonding behavior of the samples was studied using RPES and SXAS techniques. The thesis is divided into six chapters. In the following, we present a chapter wise brief description.

Chapter-1: The first chapter mainly deals with the literature survey related to laser surface irradiation process for the synthesis of nitrides and carbonitrides and its advantages over conventional nitriding and carbonitriding techniques. This chapter also focuses on the early reports on the theoretical and experimental studies of these nitrides and carbonitrides films prepared by another synthesis process. This information becomes the basis for the topics presented in subsequent chapters. The chapter reviews fundamental aspects of laser-gas-plasma-metal interaction.

Chapter-2: This chapter deals with the different instrumentation and methods like sample preparation and characterization techniques employed during the course of this thesis work. Some necessary details about the instruments used and the basics of their working principle are presented. The experimental conditions along with the precautions are also discussed in this chapter. Sample preparation includes laser irradiation in the containing atmospheres i.e. CH_4 and/or N_2 gases at different ambient pressure and laser fluence to make binary or ternary alloys. The as prepared films of TiCN were further subjected to laser irradiation in Ar containing atmospheres to improve their oxidation resistance properties. Surface morphology has been carried out by AFM and SEM. Structural characterizations have been done by conventional XRD and grazing incidence XRD. The diffraction data has invariably been treated with "winfit formalism" to extract structural parameters and particle size. These parameters are obtained by Nelson-Riley plots and Scherrer formula. Bulk characteristic were measured by four probe resistivity (pressure contacts) and nano-indentation techniques to investigate the electrical and mechanical properties of laser irradiated films. We have used Jonsson and Hogmark model to simulate our hardness profile as a function of indentation depth in order to

know the hardness of the substrate and coating and thickness of the films, simultaneously.

In order to carry out electronic band structure, we have used synchrotron radiation source throughout the thesis work. Synchrotron radiation source (SRS) is currently a very powerful technique for detailed studies of many of the properties of condensed matter in material science. Such equipment is available at Indus 1 and Indus 2, RRCAT, Indore. The main advantages are the inherent high brightness and the tunable monochromatic beam, which allow the development of a high-resolution instrument. We have used different beamline of Indus -1 and Indus 2 synchrotron radiation facility in this thesis work. The basic theory of photoelectron spectroscopy (PES) and XPS have been reviewed. To understand the electronic structure and bonding characteristic, the theory of resonant photoemission spectroscopy and soft X-ray absorption spectroscopy have been studied in details.

Chapter-3: This chapter mainly deals with the study the growth of laser irradiated titanium nitrides films by varying nitrogen ambient pressure. The results of X-ray diffraction, high temperature resistivity and nano-indentation studies are presented. The X-ray diffraction data shows the formation of nano-crystalline fcc phase of TiN, the particle size increases as a function of nitrogen ambient pressure. Resistivity data shows the metallic behavior of prepared films and formed phase are stable at least upto the 500^0C. Hardness of the films was investigated by nano-indentation and it is higher for 8 Bar of nitrogen ambient pressure. To understand variation in hardness and resistivity, films were subjected to XPS, VBS and SXAS studies to correlate these properties with its electronic structure and bonding characteristic.

Chapter-4: We have divided this chapter in two parts; first part will discuss the resonant photoemission studies of TiN films by varying nitrogen ambient pressure at

the Ti *3p* absorption edge. While, the second part of this chapter mainly deals with the depth selective GIXRD, *in-situ* in-depth X-ray photoelectron and valence band spectroscopy to carried out elemental depth profile due to the limitation of the PES techniques (surface sensitive technique). We have sputtered the samples by 3 keV Ar^+ ion to etched the samples starting by 5 min to 160 min and taken the XPS and VBS's spectra each time. Result shows variation of concentration of nitrogen with depth which is also clear from the GIXRD (at different angle of incidence) and valence band spectra.

Chapter-5: In this chapter, we mainly deal with the fabrication of ternary TiCN films on titanium sheets by laser irradiation technique after understanding the binary TiN phase and see the effect of laser energy density and ambient gas pressure on the growth properties of TiCN. The major aim of this chapter is to correlate the mechanical properties of TiCN with its electronic band structure. Upto now, we have not seen any report on the fabrication of TiCN coatings by laser irradiation techniques. XRD techniques were employed to measure the structural parameters and particle size. Mechanical and electronic structure of these films was carried out by Nano-indentation, XPS, RPES and SXAS studies. High metallicity and high hybridization of metal Ti *3d* with non-metal *2p* orbitals leads to very high hardness for the sample prepared at 6.8 J/cm^2, laser energy density (compared to that of TiN prepared by same methods).

Chapter 6: This chapter describes the study of structural and electronic properties of as prepared and post Ar treated TiCN prepared at 4.0 J/cm^2. Topography of the specimens before and after Ar-treatment was characterized by atomic force microscopy (AFM). Structural and electrical properties were carried out by in-plane and out-of-plane XRD and high temperature resistivity, respectively. In the second

part, structural studies on temperature dependent annealing of as prepared and laser irradiated Ar have been presented. The studied range of temperature is 200ºC to 650ºC. Four-probe temperature-dependent resistance of the specimen has been measured from 25^0C to 500^0C under the $1X10^{-6}$ torr pressure, and the annealing of all the specimens have been done under the vacuum of $1X10^{-6}$ torr for 1 h. The study is aimed to investigate the oxidation resistance behavior of the TiCN films before and after the Ar treatment with the help of electronic band structure.

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