Growth and photoemission studies of titanium carbide coating by laser carburizing

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Abstract: Carburizing of metals is well known technique to modify the tribological properties like hardness and corrosion resistance of metal surfaces. Besides this the electronic structures of nitrides and carbides of titanium metal have great importance from both fundamental and technological point of view. Resonance photoemission electron spectroscopy is a well-known technique to reveal the electronic structure of these alloys. In the present work titanium carbide (TiC) coating has been synthesized by laser carburizing on commercial available pure titanium sheet in a controlled methane atmosphere. X-ray diffraction studies reveal the formation of TiC phase after laser treatment. The hardness of TiC was performed by nano-indentation and its electronic structure has been characterized by x-ray and valence band photoelectron spectroscopy. The measured hardness is six times higher than the pure Ti substrate. Resonance photoemission spectrum of TiC gives maxima at 46 eV, which is a characteristic feature of Ti 3d states in the valence band of TiC coating.

1. Introduction
TiC belongs to the family of refractory metals and hence exhibits similar properties. Due to its extraordinary chemical, thermal and physical properties it has been used in cutting tools, space technology, microelectronics, aerospace industry and biomaterial since last two decades. These fascinating properties of TiC make it very motivating to study theoretically as well as experimentally. Aforementioned properties of TiC mainly are governed by on its growth, electronic structure and bonding characteristics [1-4]. Carburizing of titanium metal and its compound to form a coating of TiC implant in a metallic substrate has been extensively studied with an aim to enhance its tribological properties. Plenty of work has been carried out for investigating the various properties of TiC coatings prepared from different methods i.e. gas carburizing, chemical vapour deposition (CVD), physical vapour deposition (PVD), evaporation, ion plating and sputtering [4-8] the literatures involving the fabrication of TiC coating in CH4 atmosphere prepared by laser carburizing and resonant photoemission study of Ti 3d states in TiC are still scarce. Resonant photo emission spectrum (RPES) of the Ti 3d character in Ti, TiN, TiCN and TiO2 has been observed previously [9-11], i.e. above the photon energy of Ti 3p absorption edge. Although various techniques are employed for the fabrication of TiC coatings on different substrate, laser processing in gaseous atmosphere is relative new technique to modify near surface region of metals and alloys; however the formation of TiCN on pure titanium sheet via laser
carbonitriding had already been reported earlier [12-13]. In this work TiC coating was fabricated on pure titanium sheet by laser carburizing.

2. Experimental Methods

2.1 Formation of TiC coating by laser carburizing
Pure commercial sheet of titanium was polished by SiC grinding paper and diamond paste. We have used pulsed Kr-F excimer laser of wavelength 248 nm to irradiate polished titanium sheet at laser energy density of 6.8 J/cm² in the controlled atmosphere of CH₄ gas (2 bar pressure). The reacting chamber has been evacuated to a pressure of 10⁻² mbar and we have flushed the chamber with the pressure of CH₄ gas three times before achieving the 2 bar pressure of CH₄ for laser irradiation.

2.2 Characterization on coated film
As prepared laser irradiated TiC coating was characterized with different characterization techniques to reveal its hardness, microstructure, chemical analysis and bonding characteristics. The micro-hardness of the coated film was investigated by nano-indentation hardness measurements. Phase analysis of the coating was characterized by XRD with monochromatic Cu Kα (λ= 1.5406 Å) radiation source. The core level photoelectron spectrum was studied by x-ray photoelectron spectroscopy (XPS) using Al Kα excitation source of energy 1486.6 eV. Before the performance of XPS study, Ar+ ion etchings performed at 3 keV in the preparation chamber to eliminate the atmospheric contamination on the specimen. To perform valence band photo electron spectroscopy (VBS), we have used BL-1 beam line of INDUS-I, RRCAT, Indore with the incident energy ranging from 30 eV-60 eV. XPS and VBS measurements have been done one after another in the same chamber without breaking the vacuum.

3. Result and Discussion

3.1 Structural characterization by XRD
The diffraction pattern of prepared TiC coating have shown in figure 1. Some of the diffraction peak of the specimen belongs to FCC TiC (JCPDS PDF#32-1383) compound and rest of them corresponds to α-hcp Ti phase due to the higher penetration depth of Cu Kα in the material used in θ-2θ geometry. There is no peak belongs to any phase of titanium oxide.

![Figure 1. XRD patterns of TiC coatings at methane ambient pressure of 2 bar.](image1)

![Figure 2. Micro-hardness depth profile of TiC coatings at methane ambient pressure of 2 bar.](image2)

3.2 Hardness measurement
In the nano-indentation technique a diamond indenter used to indents the coating surface on the application of force F. The force F increases from 0 to F, then return to 0 continuously. The obtained hardness HU (N/mm²) is well-defined as the ratio of the applied force F and the area A(h). Figure 2
shows the composite hardness profile as a function of depth (indentation). From the fitting of the experimental data clearly suggest that the hardness of the TiC compound formed on the Ti substrate has higher value.

3.3 Chemical analysis by XPS:
Core level XPS spectrum of the constituents present in the coating were carried out to understand the chemical state and bonding states of the coated TiC film via laser carburizing. Core level spectra of Ti 2p region (figure 3(a)) clearly showed spin-orbit doublet Ti 2p\(\frac{3}{2}\) and Ti 2p\(\frac{1}{2}\) of Ti 2p for all the chemical bonds between carbon and titanium, hence further confirmed the formation of Ti-C phase. We have fitted Ti 2p spectra with three sets of peaks at binding energies corresponds to Ti 2p\(\frac{3}{2}\) and Ti 2p\(\frac{1}{2}\) doublet, peaks at 456.2 eV and 462.2 eV attributed to the Ti-C bonding [2]. Satellite peaks corresponding to TiC appeared at 458.7 eV and 464.7 eV for the Ti 2p\(\frac{3}{2}\) and Ti 2p\(\frac{1}{2}\) doublet, respectively. The difference between the doublet and corresponding satellite peak is approximately 2.1 eV and matches with the literature [14]. Production of satellite peaks may be related with the presence of different phases defined in the literature. The shake-up satellite is due to the sudden change in cumbic potential as the emitted photoelectron passes through the valence band. The loss in energy is equivalent to the difference in binding energy of main peak and shake-up peak [14-15].

Figure 3(b) shows the typical XPS core level spectra of C 1s region. The binding energy at 281.6 eV corresponds to C-Ti bond again indicating formation of Ti-C phase. However, intense peak at binding energy of 284.0 eV appeared, that has been attributed to presence of carbon in carbon matrix agreed well with the early reports [2]. Quantitative analysis of the component could not be carried out due to the excessive presence of the carbon in carbon matrix of the coated film.

3.4 Resonant photoemission of Ti 3d
It is well known that 3d electron states show strong resonant in the valence band to Ti and its interstitial compound between the photon energy range 40 eV to 50 eV. Figure 4 shows the energy distribution curves of valence band of TiC in the photon energy between 30 eV to 60 eV. One can clearly see that when we tuned the photon energy above 40 eV, the intensity variation of peak near Fermi edge changes rapidly. It shows maxima at 46 eV, this intensity increment is correlated with the result of resonance photoemission of Ti 3d character in the valence band of titanium and its compound [9-10].

4 Conclusion
Non-stoichiometric oxide free FCC phase of TiC has been formed during the laser carburizing on titanium sheet. The hardness of the coating is quite high in comparison to Ti substrate. XPS further confirmed the growth of TiC. RPES study reveals the resonant photoemission of Ti 3d states at 46 eV.
photon energy involved in the valance band of TiC. The hardness of the coatings depends on the strong hybridization of Ti $3d$ with C $2p$.

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