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Microhardness study of Ti(C, N) films deposited on S-316 by the Hallow Cathode Discharge Gun

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Properties

ABSTRACT

Purpose: The micro hardness properties of Titanium Carbonitride composite coated on SS-316 substrates were studied to achieve a desired harden surfaces.
Design/methodology/approach: Hollow Cathode Discharge gun (HCD–gun) was employed for deposition of the Ti(C, N) on SS-316. The evaporated and ionized metal (Ti) was coated as an under layer with 0.5 ampere beam current and 100 volt bias voltage. The reactant nitrogen and methane gasses were fed through inlet in to the chamber containing Ti element to form Ti (C, N) matrix with an optimized ratio.
Findings: In this work, Glow Discharge Optical emission Spectroscopy (GDOS) used for compositional analysis of the content elements. On the bases of this operation it was revealed the existence of Ti, C, N elements, X-ray diffraction (XRD) technique was utilized to investigate films crystalline structure. The investigation showed that samples with different stoichiometry have a fcc structure with (111) plan of reflection. The atomic ratio of carbon and nitrogen were measured using energy dispersive X-ray (EDX) analysis. The optimized value was funned to be $TiC_{0.87}N_{0.13}$. The atomic force microscopy (AFM) and scanning electron microscopy (SEM) were employed to study the films microstructure. A hardness of 3250 HV was obtained in the carbon content C/C+ N atomic ratio of 9 to 1 using a Vickers microhardness tester.
Research limitations/implications: As the study was carried out on a limited surfaces, we shall endeavor further attempt on large area deposition.
Practical implications: The tools coated in titanium accompanied by nitride and carbide has shown significant improvement. Good compatibility of Ti (C, N) compound makes these composite suitable in various technical and industrial applications.
Originality/value: It may be remarked that, the hardness obtained in this work is very encouraging and therefore, it is convenient to regard this as a privileged step taken in tool manufacturing aspect.
Keywords: Mechanical properties; Microhardness; Titanium carbonitride

1. Introduction

It has been recognized that substitution of uncoated tools by tools coated in titanium accompanied by nitride, charbonide and carbide have shown remarkable effect and extent [1-7]. They are contributed mainly in manufacturing of tools and new preparation method, on the bases of coating function. Their good mutual compatibility combined with important differences in mechanical properties make these compound [Ti(C, N)] well suited to various applications. Conventional arc process was most often used for deposition of Ti(C, N) on variety of substratum [8,9]. In different approach [10], it has given that maximum hardness of samples correspond to partial substitution of carbon in titanium carbide matrix, implies the role of carbon increment in improvement of hardness. By reviewing the articles, we find firstly few reports are available on Ti(C, N). Secondly, hardness of samples, substantially depend upon two factors that is the preparation techniques and control of stoichiometry of constituent. Harish and Rajam [11] have studied multilayer super lattice of titanium component as a class of super hard materials. That is to say, Ti(C, N) composition has a great potential of improvement. The attempt of this work is however, to attain well defined hard surface by using hollow cathode discharge gun deposition technique.

2. Experimental details

Deposition of titanium charbonide on stainless steel 316, was carried out in active CH4 and N2 ambient using hollow cathode discharge gun model DLKD-1800 with 15 KW power. Experimental set up and its schematic diagram is shown in fig 1(a) and 1(b) respectively. It is mainly consist of electron gun, plasma arc, graphite boat, anode electrode and vacuum chamber. Granules of titanium with 99.98 % purity supplied by the Merck company were put in the graphite boat which is mounted on a copper plate acts as an anode electrode. Substrates are washed thoroughly in a usual manner using ultrasonic bath, detergent, acid, alcohol and acetone and then, fixed in the fixtures. Prior to deposition substrates were bombarded by argon ions produced in electric discharged chamber to end-process of surface cleaning. The steered plasma with titanium arc target was operating with focused electron beam on boat to evaporate and ionize material. By applying 100 volt bias voltage to the boat, titanium films was deposited as the under layer with 0.5 ampere beam current. Finally, the reactant gasses of nitrogen and methane with total pressure of 2*10-3 torr were fed to the chamber via inlet as shown in fig 1(b). To study crystalline structure and phases present in the coating, X-ray diffraction analysis were carried out by PW 1840 model Philips with mono chromatic copper radiation (Cu Kα). An atomic force microscope (AFM) was used to reveal the surface topography. To investigate micro structural composition, scanning electron microscopy (SEM) XL-30 Philips was employed. By performing micro hardness tests by Wickers lits wetzelar MM6 model, information about the hardness of samples was gained. Finally, glow discharge optical emission spectroscopy (GD-OES) was utilized to qualitative study of coating elements.

Fig. 1a. A view of Ion coating apparatus

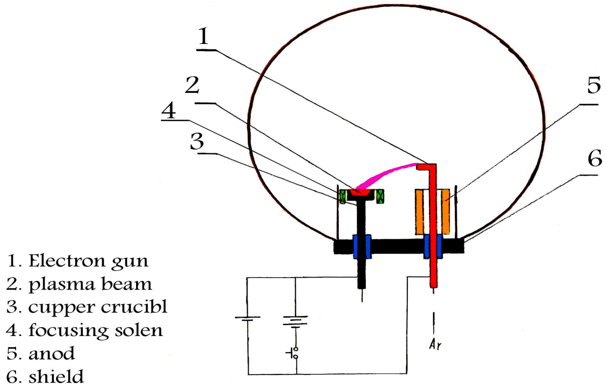


Fig. 1b. schematic diagram of Ion coating element.

3. Results and discussion

Compositional analysis of Ti(C, N) films coated on steel-316 is made by glow discharge optical emission spectroscopy. On the bases of this operation films were sputtered from target (i. e. coated sample) and then, elemental compositions are identified from top to bottom of the surface by optical emission spectroscopy process. As a function of sputtering time; depth profiling of samples reveal the existence of elements. Figs 3(a) and 3(b) represent TiC0.20N0.80 and TiC0.58N0.42 the non-stoichiometric carbon and nitrogen in Ti(C, N) constituent. We shall discuss in proceeding section the hardness of samples is improved remarkably by carbon content. In this work Ti, C and N are essential elements, while the others appeared in figs, are not dominant from the view point of present article.

Distribution of titanium in the both figs 3(a) and 3(b) is attributed to negative bias applied to the substrate. As Ti ion energy raises to about 200KV, more penetration of Ti towards the substrate is taken place as a result, physical and mechanical properties of near surface is improved.

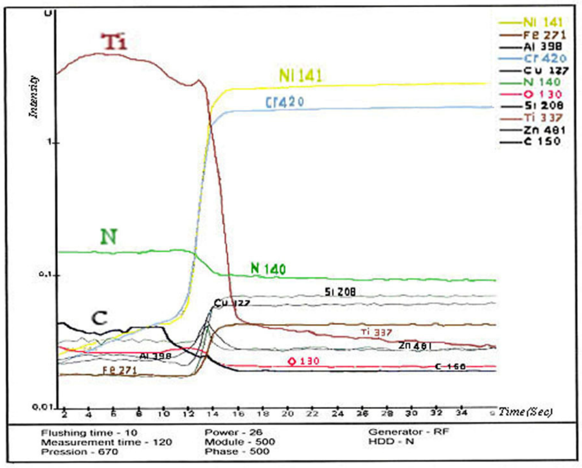


Fig. 3a. GD-OES analysis of TiC0.20N0.80 on stainless steel 316.

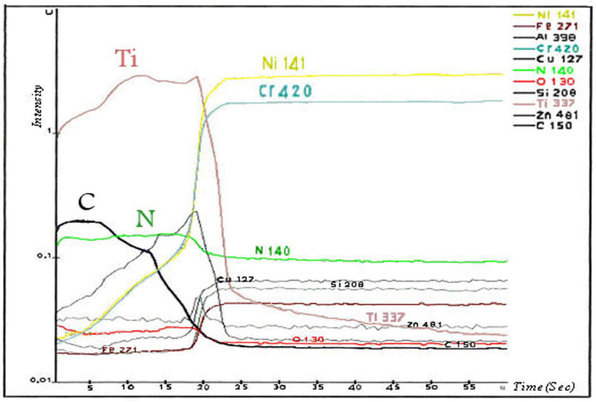
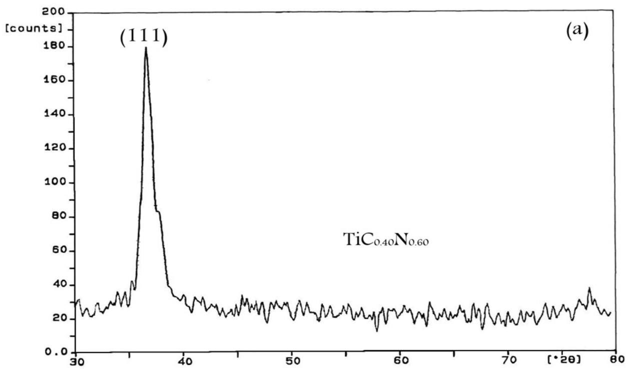
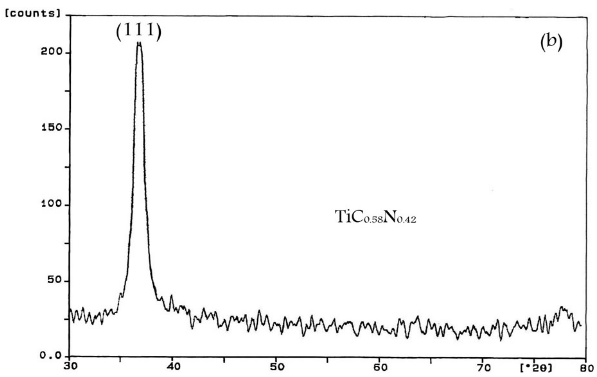


Fig. 3b. GD-OES analysis of TiC0.58N0.42 on stainless steel 316.

The phase composition of Ti(C, N) species has been studied by few workers. Y. Y. Guu et al. [9] have used cathodic arc ion plating and reported (111) preferred orientation, while in other report [10], the Ti(C,N) coated by activated reactive evaporation (ARE) have showed (200) texture. In our case, although samples are prepared under different stoichiometry of carbon and nitrogen, but, they possess preferred growth orientation of (111) corresponds to fcc structure. The XRD diffraction patterns are given in fig 4(a,b,c). Our investigation on different samples revealed that by increasing carbon content in the films i.e. C/C+N ratio 9 to 1, intensity of peak is increased {fig 4(c)}. XRD patterns of other stoichiometries, Ti0.40N0.60 and TiC0.58N0.42 are given for comparison in fig 4(a) and 4(b) respectively.





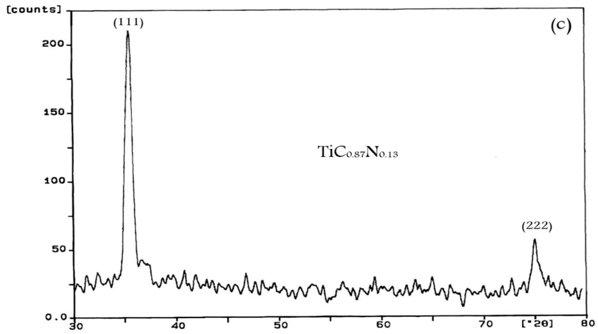
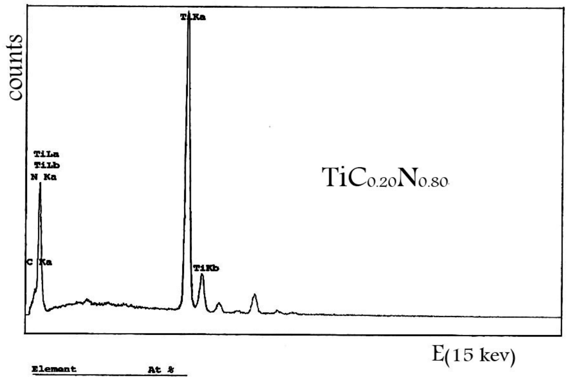
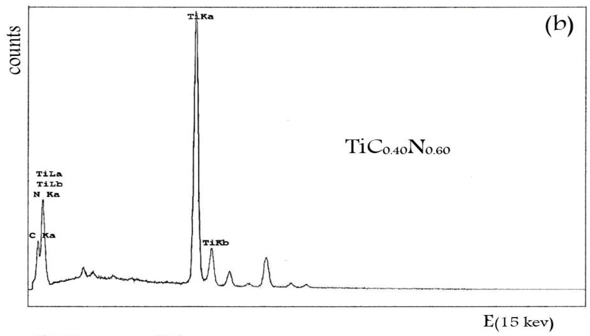


Fig. 4. X-Ray diffraction patterns of TiC_xN_y coatings on glass.

The appearance color or Ti(C,N) constitution in C/C+N ratio is different and it is depended to carbon atoms concentration. In beginning, TiN is golden yellow, by increasing carbon content, then this gives a dark violet color. Fig 5(a,b,c) shows the compositional atomic ratio analysis by EDX for carbon and nitrogen constituents in TiC_xN_y films coated on SS-316. The ratio is, however, arranged by N_2:CH_4 mass flow rate. Our investigations on many species confirmed that 9 to 1 ratio between carbon and nitrogen elements correspond to very tough surface. References [12-14] also reported the micro hardness of Ti(C, N) composition was 3000 HV and depended upon the reactive gas ratio.



Element	At %
C K	9.59
N K	41.87
TiK	48.54
Total	100.00



Element	At %
C K	19.77
N K	29.41
TiK	50.82
Total	100.00

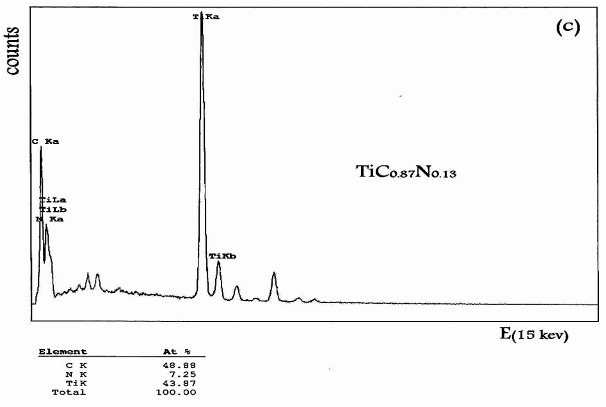


Fig 5. EDX analysis of TiC_xN_y coatings on steel 316.

Summery of atomic ratio related to lattice parameter and measured hardness is given in table 1. According to the table, it is clear that, changes in hardness of spices accompanied by changes in carbon and nitrogen atoms along with other lattice parameter. Therefore, the study can help us to explain surface phenomena. Different values are reported in the literature for different material preparation techniques [15]. In our case, satisfactory result is occurred at 3250 HV values.

Table 1. Summery of atomic ratio related to lattice parameter and distance between (111) planes.

Cu kα		λ=1.54056Å			
TiC_xN_y	2θ	d(Å)	a(Å)	C/C+N	Average hardness(HV)
$TiC_{0.12}N_{0.88}$	36.881	2.435	4.218	0.12	1500
$TiC_{0.20}N_{0.80}$	36.793	2.441	4.228	0.20	1750
$TiC_{0.40}N_{0.60}$	36.738	2.444	4.234	0.40	2100
$TiC_{0.47}N_{0.53}$	36.667	2.449	4.242	0.47	2410
$TiC_{0.58}N_{0.42}$	36.600	2.453	4.249	0.58	2680
$TiC_{0.70}N_{0.30}$	36.085	2.487	4.308	0.70	2930
$TiC_{0.87}N_{0.13}$	35.707	2.513	4.352	0.87	3250

Surface of Ti(C, N) films with $TiC_{0.47}N_{0.53}$ configuration were examined using atomic force microscope in the tapping mode to prevent any damage to the surface during scanning. Fig (6) and (7) show the three and two dimensional views respectively. As shown in the both figs, deposited films are homogenous, dense and well packed. Usually, roughness of surface mainly depends upon to the rate of growth, energy and flux impinging ions on the substrate. We were succeeded to prepare non-smooth layers with thickness about 1.2μ and average roughness of 197 Å. A column formed feature of typical $TiC_{0.47}N_{0.34}$ with average peak height 114Å is illustrated in Fig 6. Recalling data given in table (1), justifies our argument about contribution of carbon in connection with surface hardness in Ti(C, N) matrix.

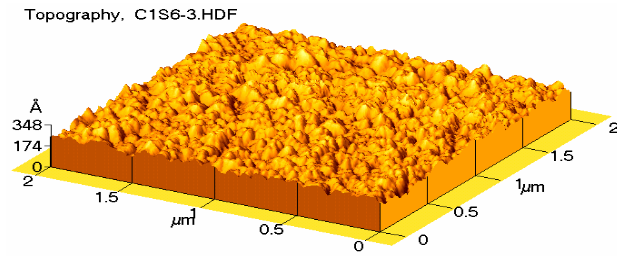


Fig. 6. three dimensional AFM image of $TiC_{0.47}N_{0.53}$ coating on glass.

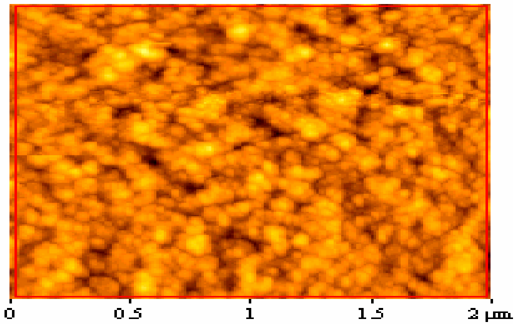


Fig 7. Two-dimensional AFM image of $TiC_{0.47}N_{0.53}$ coating on glass.

Coating morphology was obtained using scanning electron microscopy. The cross-section view or a typical Ti(C, N) sample is shown in Fig 8(a,b).

a)

b)

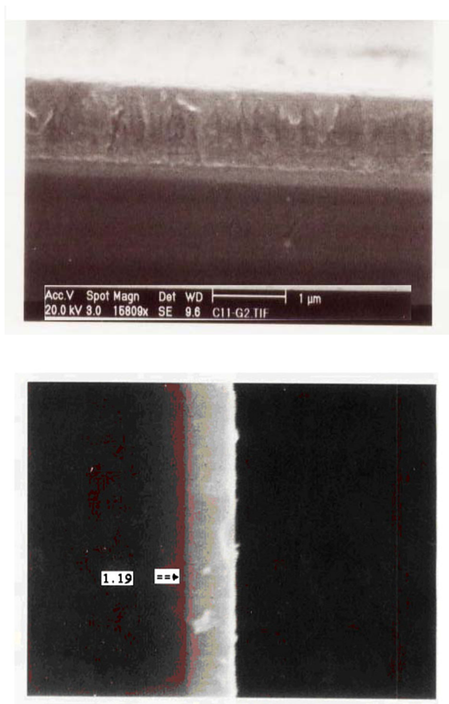


Fig. 8. SEM micrographs of $TiC_{0.47}N_{0.53}$ deposited on glass substrate with 1.19 μm thickness.

Fig 9 is the plot of hardness values as a function of carbon. As discussed before, hardness is increased as the carbon content in composition is increased. One reason for this event is that, in many metallic compounds, like oxides, nitrides, carbides and carbonitrides non-metals are replaced by carbon and nitrogen. In this way, metallic and ionic binding are being changed to covalent binding. It is known that hardness of covalent binding is much higher [16]. In addition, the penetration of ions in to the substrate gives rise to much harden samples [17]. Taking these under consideration, the results obtained in this study has proven to be acceptable.

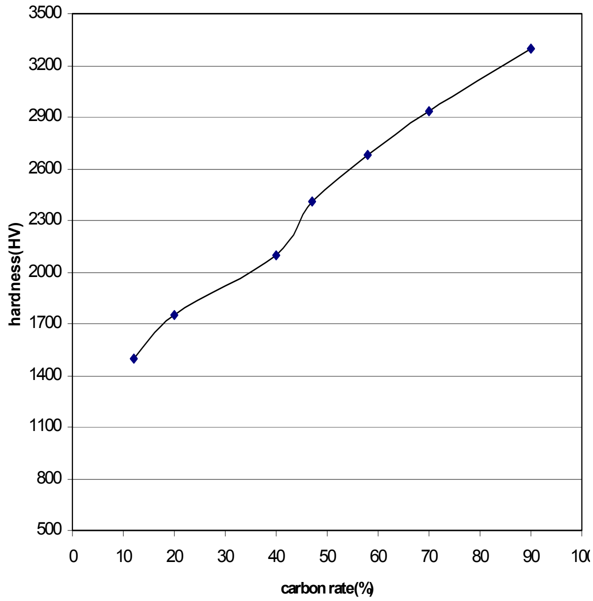


Fig. 9. micro hardness of Ti(C, N) with different carbon content.

4. Conclusions

The effect of carbon and nitrogen constituents in Ti(C, N) matrix was investigated in the films deposited on stainless steel 316 substrates using HCD gun. The non-stoichiometric samples were prepared by mass flow rate of N_2:CH_4 during coating process. It was found that, the dense and hard films with 3250 HV hardness can be obtained when the atomic ratio of C/C+N is to be 9:1. The XRD patterns of all species showed a dominant reflection along (111) plane. To obtain high quality Ti(C, N) films, it is necessary to apply bias voltage between substrate and crucible.

The AFM image of 1.2µm with average peak height of 114Å and average roughness of 197Å has been exhibited. Therefore, in the conclusion it can be said that, ion coating process is one of the suitable techniques for surface preparation and modification.

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