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RESEARCH PAPER

Tribological properties in electrodeposition of Ni-TiO$_2$ composite coating on tungsten carbide cutting tool

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ABSTRACT

In this paper tribological and electrochemical surface properties of Tungsten Carbide cutting tool substrate coated with Ni-Tio$_2$ composite layer via electrocodeposition technique have been studied. The failure modes mechanism was observed via optical microscopy. Results from X-ray Diffractrometry (XRD) analysis revealed that the peaks of XRD pattern corresponding to Ni and TiO$_2$. During electrodeposition effect of current density, pH vale of watt's solution on microhardness of the composite layer have been studied. The grain structure of composite layer is characterized using scanning electron microscopy (SEM). Microhardness of the composite layer was investigated using Vickers microhardness tester. The surface morphology of Ni-Tio$_2$ coated layer shows the deposition of fine grained structures at low currents with higher microhardness value and better adhesiveness with substrate. Moreover at constant temperature and time of deposition, the coating thickness increases with increase in current.

KEY WORDS : Microhardness, Electrocodeposition, Composite layers

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INTRODUCTION

Metal cutting puts extreme demands on the tool and tool material through conditions of high forces, high contact pressures, high temperatures, and intense chemical attack by difficult-to-cut work materials. In addition, the tool geometry and cutting conditions in terms of sharp edges, cyclic engagement, and presence of cutting fluid will add to the severity. Most often cutting tools are used close to their ultimate resistance against these loads, especially to the limiting thermal and mechanical stresses. In spite of the increasing use of high performance tool materials such as CVD and PVD coated carbides tool, cermets, ceramics, cubic boron nitride, and diamond coated tool. Tungsten carbide coated tool are still frequently used in tools for metal cutting applications. The relatively high strength and the possibility of economic manufacturing of tools with complicated geometries still justify the use of W-C tools in many cutting operations. The introduction of powder metallurgical grades in combination with Electro Slag Heating (ESH) and Physical Vapour Deposition (PVD) coating technologies has further improved the performance of cutting tools. Since the successful introduction of the PVD-TiN coating in the late seventies, the academic research on W-C metal cutting tools has been concentrated to developing even better coating materials and techniques for their deposition. Efforts have been made to enhance the cutting tool life of W-C cutting tools; nano coating Technology via Electrodeposition process has been employed.

Protective coatings on cutting tools have been in use for a little more than three decades. The search for wear resistant materials has since been redirected to encompass other material properties rather than just hardness. Davim (2011) reported that cutting performance is also dependant on both the cutting tool and the machine tool system. Cutting tool performance is dependent on tool material, cutting tool geometry and hard coatings. Rich *et al.*(2004) discussed that early hard coatings were deposited via chemical vapour deposition (CVD) and Physical vapour deposition (PVD) via magnetron sputtering process has been used for coating cutting tools. Kim *et al.*(2010) discussed that magnetron sputtering is preferred to the CVD process due to the contamination that occurs in the latest. Single layer such as TiN, TiC, CrN, DLC, Ti-O_2 and AlN coatings played an important role a few years ago, due to of their mechanical and tribological properties. Romero *et al.*(2004) and Chu *et al.*(1995) have reported that nowadays, those coating are being mixed, designed and improved in a way of heterostructures thin films and multilayered coatings with periods in the range of nanometers, which are one of the advanced coating concepts more commonly investigated during the last two decades, together with nanocomposites. Veprek (1999) discussed that the nano-composite coating ranges from 3-10 nm in size have been selected from nitrides, carbides, borides and oxides, and are imbedded in an amorphous or crystalline matrix. The large volume of grain boundaries provide ductility through grain boundary sliding along grain/matrix interfaces. Veprek (2001) reported that these coatings have been at times reported to have hardness up to 100GPa. A graded interface layer could be applied between the coating and the tool to increase adhesion and to relieve stress. Electrodeposition offers some unique advantages over other techniques such as improved appearance, corrosion resistance and physiochemical properties of surfaces (hardness, electrical and thermal conductivity, solderability etc.) which find its potential applications in fabrication of advanced components for micro/nano electromechanical systems (MEMS/NEMS). Fine structure growth and easy control of the coating thickness to fractions of a micrometer is possible via electrodeposition. The aim of this work is to evaluate the influence of Ni-Tio_2 composite coatings deposited onto tungsten carbide cutting tool substrate through electrodeposition technique. Ni-TiO_2 composite coating was employed to investigate the microhardness behavior, adhesion with substrate and coating thickness with different currents at constant temperature and deposition time.

EXPERIMENTAL PROCEDURE

Selection of deposition current details :

Ni-TiO_2 coating has been deposited on Tungsten carbide cutting tool (WC) triangular bit (22 mm side) by electrocodeposition process. Cyclic cathodic scan was drawn using potentiostat (GAMRY Reference 600) in electrocodeposition of Ni-TiO_2 bath at room temperature. The potential was swept between -1.0 to -1.45 V vs SCE. The suitable current densities of 15, 25 and 85 mA for the deposition were selected from this curve. The steady state potentials corresponding to the above deposition current densities are estimated from the galvanostatic plot. Ni/TiO_2 composites were electrodeposited from an organic free Watts' nickel electrolyte with suspended TiO_2 nano-particles on the triangular shaped bits as shown in Fig. A.

Fig. A : Systematic arrangement of electrocodeposition of Ni-TiO_2 coating

All the chemicals used were of analytical grade with high purity purchased from Merks. A specially designed three electrode electrodeposition cell was used for electrodeposition of Ni-TiO_2 where cutting tool was working electrode, Ag/AgCl as reference electrode and Pt wire act as counter electrode (anode). The distance between Ag/AgCl refrence electrode and working electrode is 1 cm. The particle size of TiO_2 particles was about 50 nm. It was used without any pretreatment and maintained in the bath in suspension by continuous magnetic stirring with a rate of 210 rpm in order to maintain a uniform concentration of particles in the bulk solution. Before starting the electroplating, the electrolyte was placed in ultrasonic bath during 20 min to prevent the TiO_2 particle agglomeration. The composition of the plating solution, as well as the plating conditions, is given in Table 1.

EXPERIMENTAL FINDINGS AND ANALYSIS

Effect of current density on microhadrness of Ni-TiO_2 coatings :

The mechanical properties like hardness and thickness of the deposits are important for industrial applications and for this purpose microhardness and thickness measurements of the samples were carried out by applying 1.0 Kg-force load using Vickers hardness tester (Mitutoyo). The measurements show that the microhardness is influenced by change in current density as shown in Table 1. The measurements were carried out three times for each sample to confirm the reproducibility of the results and the maximum indentation depth was of the order of 1 micron.

Table 1 : Experimental conditions for the preparation of Ni/TiO_2 composite electrodeposits

Solution composition (Electrolyte watts)		Electrode position conditions	
$NiSO_4.6H_2O$	300 g/l	pH of electrolyte	4.4± 0.1
$NiCl_2.6H_2O$	45 g/l	Temperature (°C)	300
H_3BO_3	40 g/l	Substrate	Tungsten Carbide Bit
Ti-O_2 powder	6 g/l	Average current density (mA/cm_2)	15, 30, 45

The morphological characterization of as prepared samples were done using scanning electron microscope (JEOL JSM 6510 LV) at an accelerating voltage of 20 KV as shown in Fig. 1, 2 and 3 .The change in structures of composite layer is observed with change in current density at constant time of deposition because of change of grain size of TiO_2 particles co-deposited with nickel. Fine closed grained structures are observed at low current as shown in Fig. 1, 2 and 3.

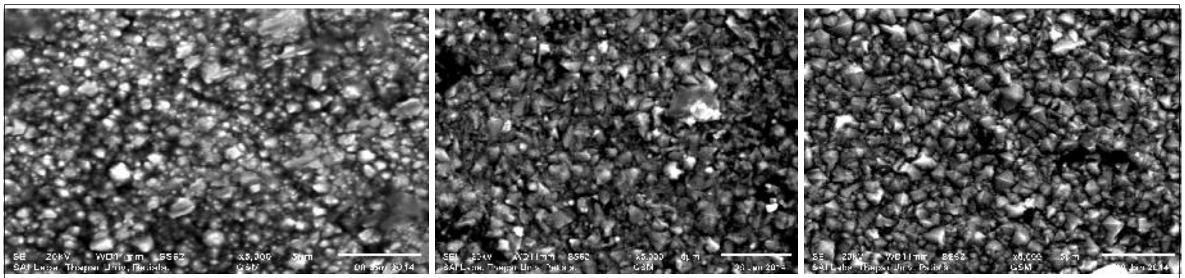

Fig. 1 Fig. 2 Fig. 3

Fig. 1-3 : Showing SEM photomicrographs of Ni/TiO_2 composite layer at 15, 30 and 45 mA current

It is clear from the figure that the SEM results that at lower current *i.e.* at 15mAmp fine closed grain structure is observed whereas the course grain structure is observed at 30 and 45 mAmp current intensity.

The codeposition of Ti with Ni was confirmed by Electron dispersion spectroscopy (EDS). The EDS result shows the peaks corresponding to Ti and Ni. Ni and Ti layers were polycrystalline exhibiting diffraction peaks corresponding to Ni phase structure and Ti.

It has been clear from EDS data (Table 2) that microhardness of the composite layer decreased if the percentage of Ti particle increases.

Table 2 : EDS Data for different current intensity

Current intensity (mA)	Microhardness (HV)	(%) age of Ti	(%) age of Ni
15	904.5	0.05	99.89
30	603.9	0.11	99.95
45	453.9	0.13	99.87

Effect of pH concentration in Watt’s solution on microhardness of Ni -TiO_2 coatings :

In electrodeposition pH value of the solution is a vital parameter control to maintain the process optimization. pH of the bath influences the hydrogen evolution voltage, the precipitation of basic inclusion and decomposition of the complex or hydrate from which the metal is deposited. In a complex bath, pH may influence equilibrium between various processes. When the anode is insoluble, oxygen evolution takes place at the anode :

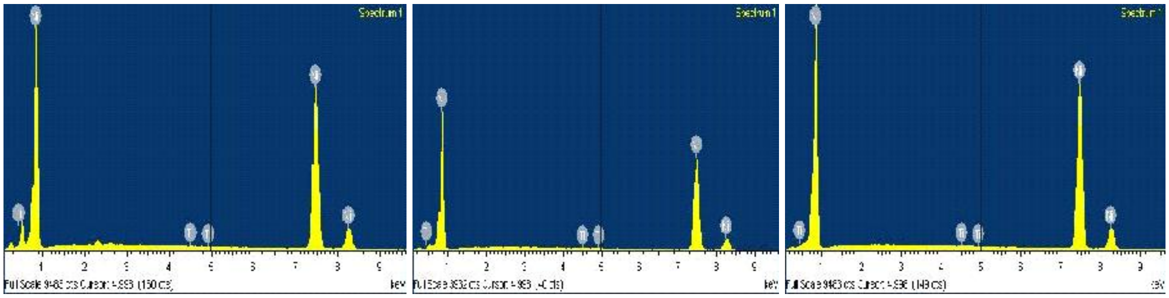

Fig. 4 Fig. 5 Fig. 6

Fig. 4-6 : Shows a typical EDS diffraction pattern of Ni-Tio_2 composite layer

$2H_2O \rightarrow O_2 + 4H^+ + e^-$

On the other hand, hydrogen evolution at the cathode is accompanied by the production of hydroxide ion :

$2H_2O + 2e^- \rightarrow 2OH^- + H_2$

If the current efficiency is greater at the anode than at the cathode, the bath becomes more alkaline. If the electrode efficiencies are similar, the pH of the bath remains unchanged. Hence, change in pH of a plating bath is a good indication of electrode efficiencies. The coating has been done at different value pH Concentration of Watt’s solution. Table 3 shows the microhardness of composite layer at different pH concentration at 15mAmp current.

Table 3 : Effect of pH on microhardness

Sr. No.	pH Concentration	Microhardness (HV)
1.	3.5	828.1
2.	4.5	1273
3.	5.5	908.2

Microhardness which is mainly effect of grain sized is influenced by the pH value of the solution. Fig.7-9 shows the SEM photographs of composite coating at 3.5, 4.5 and 5.5 pH concentration of the solution at a current intensity of 15 mAmp. It is clear from the SEM Photographs that fine closed grained structures are observed at pH concentration of 4.5 which corresponding to maximum microhardness of the composite coating. Similar findings were obtained by Saifullin (1977); Van Acker (2005);

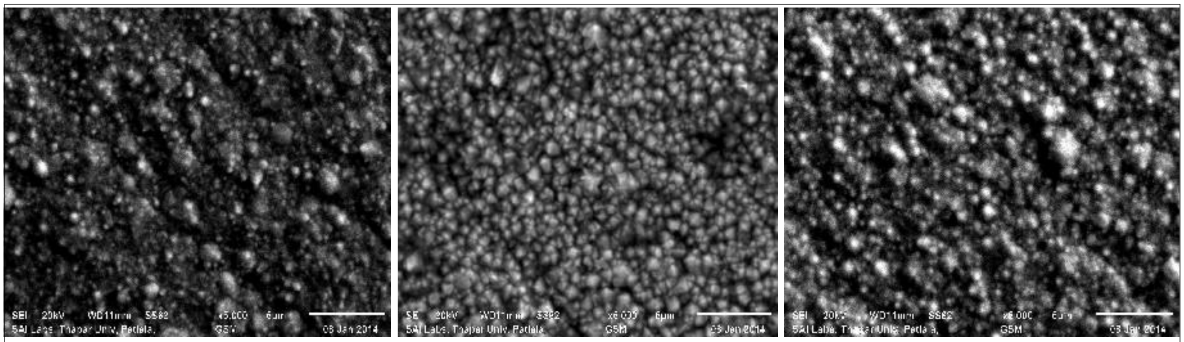

Fig. 7 Fig. 8 Fig. 9

Fig. 7-9 : Showing SEM photomicrographs of Ni/TiO_2 composite layer at 3.5, 4.5 and 5.5 pH concentration of Watt's solution

Liao *et al.* (2000) and West (1984).

Coating thickness :

The mechanical properties like hardness and thickness of the deposits are important for industrial applications and for this purpose microhardness and thickness measurements of the samples were carried out by applying 0.5 Kg-force load using vickers hardness tester (Mitutoyo). The measurements show that the microhardness is influenced by change in current density at constant temperature, pH value and stirring of the bath solution as shown in Table 1. The measurements were carried out three times for each sample to confirm the reproducibility of the results and the maximum indentation depth was of the order of 1 Micron. As shown in the Fig. 10 and 11, the increase in microhardness is observed at low current and constant temperature because of lattice strains produced by the lattice defects and fine grained deposits whereas, the coating thickness increases with increase in current applied. Coating thickness is also increased with increase in current.

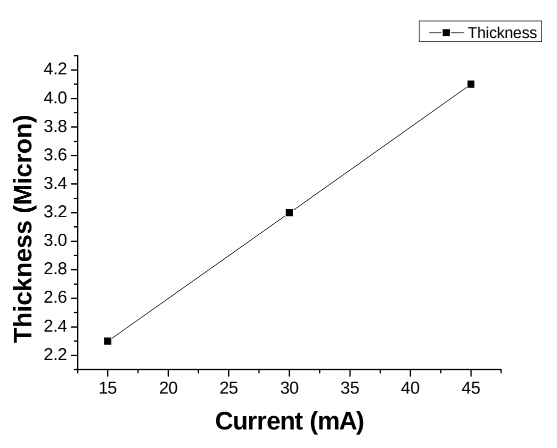

Fig. 10 : Showing effect of current on the coating thickness

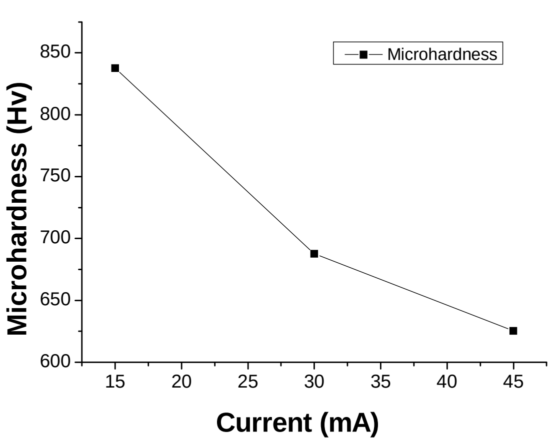

Fig. 11 : Showing effect of current on microhardness of coating

Conclusion :

Electrodeposition is a versatile route to deposit composite coatings of Ni-TiO$_2$ on the surface of cutting tool. In this method coating one metal on top of a different metal is deposited to modify its surface properties. It is one of the challenged processes for improvement of the surface. Specially, it is used for the improvement of mechanical properties such as wear and hardness properties of the coating surface. From the tribological study of composite layer following conclusions are drawn:

- The microhardness of Ni-TiO$_2$ coatings decreases due to increase in grain size and decrease in tungsten content. Highest microhardness value is obtained at 15mA current.
- The surface morphology of Ni-TiO$_2$ coating was found crack free at lower current densities however some fine cracks has appeared at high current densities, which means that Ni-TiO$_2$ coating are prone to cracking at higher current density.
- pH value of the electrolyte bath influences the hydrogen evolution voltage. Microhardness which is mainly effect of grain sized is influenced by the pH value of the solution. Higher microhardness value (1273 Hv) is obtained at pH 4.5 at lower current density.

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