Characterization of TiAlON Layers Deposited on Tungsten Carbide (WC) Substrate by Physical Vapor Deposition (PVD)

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ABSTRACT

Properties of thin films of titanium aluminium nitride (TiAlON) deposited on tungsten carbide substrate (WC-Co) by Magnetron Sputter Ion Plating (MSIP) were studied. Phase formation, phase transition, hardness and film structure are affected by the percentage of oxygen reactive gas. In this work the properties of the layers deposited at constant total vacuum pressure $10^{-2}$ mbar and constant percentage of nitrogen reactive of 20% and O$_2$ reactive gas ranging from 1 to 5% were studied. The investigations were carried out using, X-ray diffraction (XRD), Calotte measurement, nanoindentation, optical scanning microscope (OSM) and tribometer. The results show that the maximum hardness of the layer of TiAlON was 32 GPa.

Key Words: Physical Vapor Deposition PVD/TiAlON/ Nanohardness / XRD

INTRODUCTION

Nowadays the environmental and economical issues have become of great concerns. Dry cutting is one of applications which helps to avoid pollution and waste disposal cost. Optimizing the manufacture of cutting tools by the use of special alloys, adapting tool geometrics and coating is beneficial in this respect. The Magnetron Sputtering Ion Plating MSIP is a well known technology for developing complex and wear resistant coatings, such as TiAlN, by reactive sputtering. Adding reactive gases to the coating process such as a nitrogen and oxygen make it possible to generate metastable TiAlON coatings$^{(1)}$.

To improve wear resistance of tool for dry cutting applications, the deposition of TiAlON films of high oxidation stability is used$^{(2-5)}$.

Some research activities are concentrated on optimizing coating properties for improving the performance of tool dry cutting application. TiAlN-based hard coatings for dry cutting operations are well known for their high nanohardness even at elevated temperatures and for their good oxidation resistance$^{(6)}$. A further improvement can be achieved by depositing a layer of TiAlON on WC-Carbide substrate, at different percentage of O$_2$% and different pressures. TiAlN shows a high oxidation resistance up to 800°C while TiN up to 600°C only$^{(7)}$. The formation of a dense Al$_2$O$_3$ top layer increases diffusion and oxidation resistance of the TiAlN film. The amorphous state of Al$_2$O$_3$ can be stabilized up to 1100°C by adding nitrogen to deposit AlON$^{(6-9)}$. Further improvements concerning nanohardness and wear resistance can be achieved by adding titanium to deposit TiAlON$^{(10-11)}$. The presence of reactive gases during the coating process such as nitrogen and oxygen makes it possible to generate metastable TiAlON coatings$^{(12)}$.

The aim of his work is to improve wear resistance of tools for dry cutting applications through the deposition of TiAlON films by PVD.
Coating deposition:

The facility and devices used in the deposition and investigation of the formed layers in this work were as follows: Magnetron sputtering ion plating (Leyboled-Heraeus Z400), ultrasonic cleaner, lapping, grinding and polishing machines, nanohardness tester, XRD, optical scanning microscope (OSM), Colette test (ball wear test) and tribometer. Substrate was made ofWC/Co with dimensions of 10x10x5 mm. It is intended to be used in cutting tools. The nominal composition of the substrate was W 86.36, Co 8 and C 5.64.

The preparation of substrates for deposition was carried out in different steps: (a) polishing with grinding machine using diamond paper grade 800 - 4000, (b) using fine cloth and diamond suspension with 3μm until the surfaces were mirror like. Before the coating process, the specimens were cleaned and degreased in a four-stage ultrasonic cleaner using two hot alkaline solutions (T = 55°C, pH 8 and 11), then the specimens were rinsed with de-ionized water, dried by compressed nitrogen, and then stored in a heated cabinet at 70°C to avoid contamination with dust and humidity until deposition process.

The chamber of the MSIP was evacuated after introducing the samples to achieve a pressure of 6x10^{-5} mbar before introducing Ar gas for etching or N\textsubscript{2} reactive gas for depositing the layers. The polished and pre-cleaned substrates were plasma etched for 10 min by radio frequency (R.F) at 10^{-2} mbar Ar discharge and at 150W power. TiAlON layers were prepared by using Ti\textsubscript{0.75}Al\textsubscript{0.25} alloy as a target and N\textsubscript{2} as a reactive gas mixed with different percentages of high purity 99.9999% argon, at a vacuum pressure of 10^{-2} mbar.

The thickness of the formed layers was measured using Calotte instrument (CEME CON KALOTTEHE/L), which is a spherical abrasion method, for measuring the coatings thickness. The deposition rates were calculated from the corresponding deposition time and measured film thicknesses.

To measure the hardness of the layers, a nanohardness (Nano Indenter XP) tester was used. All investigations were conducted at loads from 10 - 20 milli Newton (mN) applied onto the sample. The hardness was calculated from the dynamic loading during measurements. The maximum depth of penetration of indenter was limited to 10% of coating thickness in order to reduce the substrate influence.

The coatings structure was examined by XRD using CuK\alpha at 40V, 40mA radiation with incident angle 3°. Coating morphology was investigated by examining the cross-section of the deposited layer using optical scanning microscope (OSM).

A high temperature tribometer model CSM was used to measure the friction coefficient, each sample was tested at a load of 5N at room temperature. All experiments were made at a fixed velocity of 5 cm/s and each test was manually stopped as soon as reaching 200 meter sliding distance. With regard to the environment parameters, the relative humidity was kept at 50 %. Data acquisition from tribometer test were connected on-line to an excel file, which gave, at the end of the test, the mean value of the friction coefficient in steady state.

The layers of TiAlON were deposited by MSIP with generator pulses of frequency 29.999 KHz of set voltage 800V. The actual current was 0.3A, and the actual voltage range from 880V to 950V.
using variants. The target used was Ti_{75}Al_{25}. The oxygen percentage was reduced gradually while keeping the nitrogen percent at 20%.

**RESULTS**

**Mechanical Properties:**

Table 1 show the results of the mechanical properties obtained for TiAlON layers deposited at a vacuum pressure of $10^{-2}$ mbar inside the deposition chamber with different percentages of oxygen and constant percentage of N$_2$ (20%).

**Table 1: results of TiAlON.**

<table>
<thead>
<tr>
<th>Sample</th>
<th>O$_2$%</th>
<th>Thickness [µm]</th>
<th>L$_{cr}$ [N]</th>
<th>Impact No.$\times10^3$ at 500N</th>
<th>Hardness [GPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>108</td>
<td>10</td>
<td>1.3</td>
<td>20</td>
<td>500</td>
<td>18</td>
</tr>
<tr>
<td>107</td>
<td>5</td>
<td>0.78</td>
<td>20</td>
<td>500</td>
<td>16</td>
</tr>
<tr>
<td>109</td>
<td>3</td>
<td>0.79</td>
<td>20</td>
<td>500</td>
<td>22</td>
</tr>
<tr>
<td>110</td>
<td>1.5</td>
<td>1.39</td>
<td>70</td>
<td>500</td>
<td>29</td>
</tr>
<tr>
<td>111</td>
<td>1</td>
<td>1.24</td>
<td>50</td>
<td>750</td>
<td>32</td>
</tr>
</tbody>
</table>

From table 1 it can be seen that the hardness increases with decreasing the percentages of reactive (O$_2$). The maximum hardness recorded was 32GPa for the samples 111 at 1% of oxygen with 20% of nitrogen. This may be due to the formation of a new hard phase from Ti$_3$AlN (12-18) as shown from XRD Fig.2.

**Scratch test and Impact test:**

The adhesion strength is one of the major mechanical properties which must be taken into account in coatings technology. The maximum adhesion strength was recorded at a critical load of 70N for the layer deposited at 1.5% O$_2$ as shown in Fig. 1a, and line scan in Fig. 1b shows the intensity of elements W and Co % increased and Ti % in layer was decreased that means the coatings was removed.

The low hardness and poor adhesion strength of TiAlON coatings deposited at high percentages of oxygen may be due to oxygen contamination of the interface between the layer and the substrate (19-22).

Adhesion and cohesion of TiAlON layers tested by impact measurements shows that the maximum number of impact failure until removed of the layers is $75\times10^4$ at load 500N Fig.2c for sample 111.

a) Scratch test to samples 108,110 and 111 of TiAlON deposited at $10^{-2}$mbar

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b) Line scan at scratch test to sample 110 TiAlN shows the critical load 70 N

c) Calotte measurements to some samples TiAlON

d) Rockwell test to samples 108 and 110 TiAlON

e) Samples of TiAlON layers after impact tests at load 500N with number of impulses 5x10^5.

Fig.1- a, b, c, d and e are mechanical properties of the TiAlON samples.

XRD Analysis:

Figure 2 shows the XRD patterns of the TiAlON layers deposited at different O₂ percentages. The sample (111) deposited at 1 % O₂ was the only one to show a peak corresponding to TiALN at 2θ = 34°.
Wear test:

The tribology test made on sample 111 of TiAlON showed the layers had a relatively high friction coefficient as shown in figure (3). The mean friction coefficient is approximately ~ 0.75.

Fig 2- XRD to samples 111,110, 109,108 and 107 at 10^{-2} mbar, 20 %N, with different ratios of O_2 and WC/Co substrate without coating

CONCLUSION

TiAlON layers were deposited on WC at vacuum pressure 10^{-2} mbar at different percentages of O_2 as a reactive gas and constant percentage of N_2 of 20%. The hardness of the layer increased with decrease in the O_2 %. The maximum hardness and maximum scratch load of TiAlON layers are 28 GPa, 70 N respectively. The mean friction coefficient was 0.75. The layers of TiAlON deposited at different percentages of O_2 are amorphous but at 1% of O_2 a TiAlN phase is deposited, that explains the increase in hardness.
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