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Mechanical Properties of TiN Coatings Deposited at Different Temperatures by IBAD Process

TiN coatings were deposited on hot working steel substrates by ion beam assisted deposition technique. The deposition process was conducted at two different temperatures 50 and 400 ºC. The influence of applied deposition temperature on the mechanical properties, adhesion strength and surface morphology of TiN coatings was studied. The mechanical properties, i.e. hardness, modulus of elasticity and coating strength were characterized by nano-indentation technique. Adhesion strength was evaluated by generally accepted scratch test technique. In addition, HRC adhesion test was utilized to compare adhesion of different coatings qualitatively. Surface morphology was analyzed by atomic force microscopy before and after the film deposition. The coating deposited at higher temperature displayed higher hardness, and also higher critical loads were obtained during scratch test, when compared to coating deposited at lower temperature. The ion bombardment during the deposition process enhances the adatom mobility allowing the deposition of coatings with high hardness and adhesion strength even at low temperatures.

Keywords: *TiN, IBAD, deposition temperature, AFM, surface roughness.*

1. INTRODUCTION

Hard coatings are deposited by a large variety of PVD deposition techniques, where a lot of process parameters are controllable in order to produce a desirable coating. The process parameter that is distinctive for all these techniques and withal one of the most important is the deposition temperature. Deposition temperature is one of the key parameters affecting the coating growth and the one that also affects the substrate properties [1-4]. Coating mechanical properties like hardness, elastic modulus and coating/substrate adhesion are dependent on the deposition temperature. It is well-documented that most of the coating mechanical properties are improved as the deposition is carried out at higher temperatures, [1]. When coatings are deposited onto heat sensitive substrates, the control of heat that is introduced by the deposition process is crucial. Lowering the deposition temperature raises another difficulty since the coating grows in condition with less energy – lower adatom mobility [3]. The lack of energy is compensated when a low-temperature deposition process is carried out under constant ion beam bombardment, which is feasible with Ion Beam Assisted Deposition (IBAD) [4,5]. In addition, IBAD offers a control over a wide range of deposition parameters, which favors this process in the production of coatings with improved quality. Coatings produced by IBAD are characterized by high density, high purity, and high hardness, good adhesion, good corrosion resistance and low intrinsic stresses. Such coatings are widely applied on elements in semiconductor industry but there is also a great potential in the application of these coatings on tools and machine parts subjected to severe friction and wear [6]. This arises from the fact that coatings produced by the IBAD process have low friction coefficient, very good tribological behavior and corrosion resistance as a result of fine coating texture and appropriate crystallographic orientation. Additionally, such coatings are produced with very small roughness, high precision and good reproducibility [7,8]. In comparison with other deposition techniques this process provides coatings with better performances [6,8]. Bearing all this in mind implies that the IBAD process conducted at a high temperature can result with coatings exhibiting great properties.

The goal of this research was to investigate the influence of deposition temperature on the structure and properties of TiN coatings deposited by IBAD technology.

2. MATERIALS AND EXPERIMENTAL

Studied TiN coatings were produced in an Ion Beam Assisted Deposition (IBAD) chamber with a base pressure of $1.5 \cdot 10^{-6}$ mbar. The coatings were deposited at two substrate temperatures: sample 1 – low temperature ~ 50 ºC and sample 2 – high temperature 400 ºC. Hot-working steel (X38CrMoV51) disks were used as a substrate material. Prior to coating, the substrates were hardened and prepared to the same grade of surface roughness. Before the coating process substrates hardness was measured and a value of 460 HV was determined. Samples were grounded using a 2000 grit paper before the process of fine-polishing with 1 μm grain diamond paste. Thickness of the coatings was calculated after abrading the coatings using CSEM “Calotest” instrument. The coating hardness and Young’s modulus of elasticity was assessed by the

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Hardness Agilent Nano Indenter G200. Hardness was calculated for the two indentation loads applied, 5 mN and 10 mN. The Coating adhesion was evaluated by the "Revetest" scratch tester. The tests were carried out by sliding the diamond tip against the coatings at the rate of 10 mm/min and by progressive increasing the load with 100 N/min rate until the full delamination of the coating occurred. Critical loads which led to typical coating failures were determined by light optical microscopy. Those critical loads are denoted as follows: L_{c1} – first crack formation, L_{c2} – more serious crack formation, L_{c3} – first chipping, L_{c4} – coating detachment and L_{c5} – full delamination. Standard HRC adhesion tests were carried out by utilizing standard Vickers hardness tester. Rockwell indentations were made by applying a 150 kg force. In order to compare the coatings produced, Rockwell indents were qualitatively analyzed by light optical microscopy (LOM). Surface roughness of the samples was evaluated before and after the deposition process by VEECO di-CPII atomic force microscope (AFM). All images were acquired in contact AFM mode using a symmetrically etched silicon-nitride probe. In the case of surface roughness determination the scan size used was 90 μm^2. On the other side, in order to determine the grain size the scans were taken on the areas of 5 μm^2. Scan rate and set point were kept at 1 Hz and 225 nN respectively.

3. RESULTS AND DISCUSSION

Besides the deposition temperature, during deposition of both coatings all parameters were kept constant. Nevertheless, those processes resulted with coatings having different thickness. The sample 1 coating has 1600 nm in thickness, though sample 2 coating has 1050 nm in thickness.

The hardness of both coatings was determined at two different loads with respect to the penetration depth which was kept below 10 % of the coatings thickness. Considering the hardness of commercially deposited TiN coating both coatings examined in this study exhibited very high hardness. Such high hardness is achieved by additional ion bombardment during the film growth. Argon ions deliver energy to adatoms on the growing surface increasing their mobility thus enabling them to achieve the state with lowest energy [4]. Additional heat induced to the substrates, improves the deposition process taking it closer to the thermodynamic equilibrium [5]. The hardness results obtained for both coatings are presented in Figure 1, and modulus of elasticity is depicted by Figure 2. Depositing the coating at 400 ºC temperature resulted with considerably harder coating (29 GPa) than the low-temperature one. In surface engineering, concerning the coating hardness, it is well known that an increase in indentation load leads to decrease in hardness [8,9]. Such decrease is induced by the effect of the substrate material that is usually much softer than the coating. This effect is less pronounced in the case of high-temperature deposited coating, which is less sensitive to load increase, Fig. 1. In other words, sample 2 coating has a greater potential for practical application in the field of wear resistant materials due to its higher bearing capacity.

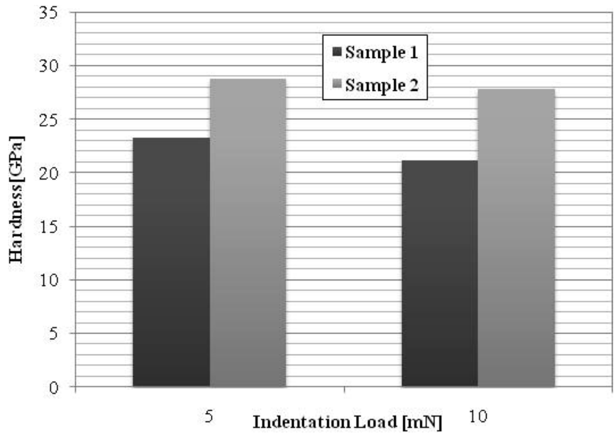

Figure 1. Hardness comparison of coatings deposited at different temperatures

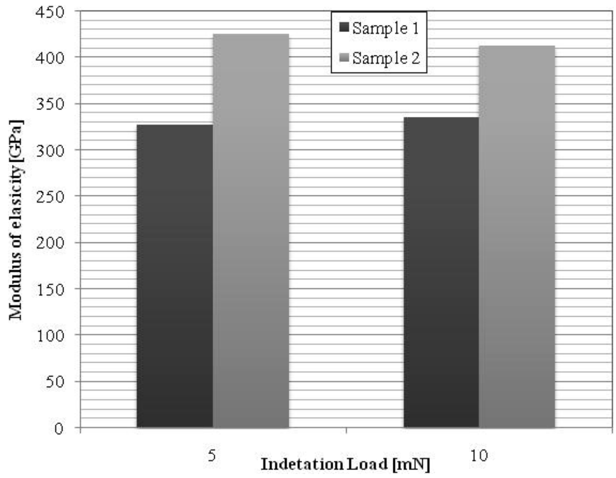

Figure 2. Comparison between modulus of elasticity of coatings deposited at different temperatures

If considering that the sample 1 coating grew in less favorable conditions, then the hardness achieved in this process is outstanding.

Sample 1 coating showed generally good adhesion, Fig. 3a, although the moments when the first cracks formed occurred fairly earlier than in the case of sample 2. First cracks were quickly followed by coating chipping (L_{c3}) that also occurred considerably earlier than in the case of sample 2, compare Fig. 3a and 3b. Surprisingly, the coating detachment occurred somewhat earlier at the sample 2 but this coating resisted a longer period before full delamination, which occurred at higher forces than at sample 1. It must be pointed out that adhesion is dependent on the coating thickness in a way that thicker coatings more adhere than the thinner ones [10].

Although the sample 1 coating thickness with the value of 1600 nm is larger than of sample 2 that is 1050 nm it displayed lower adhesion. Further, this proves the previous findings that the coating deposited at lower temperature has generally lower adhesion. As expected, the higher adhesion is in direct relation with the coating hardness. In order to depict the different behavior between two coatings, during the scratch test, the morphology of the wear tracks was investigated at the same normal load of 30 N. Examination of the scratch tracks by LOM is presented in Figures 4a and 4b. At this stage, ductile tensile cracking along the scratch track is evident in both cases but the extent of its appearance is different. The cracks are more frequent and the coating chipping is much more severe at the low-temperature deposited coating – sample 1. This means that the sample 2 coating resists greater plastic deformation before chipping formation, what is additionally proved by folded coating with fewer cracks on the scratch track edge, Fig. 4b. In both cases, none of the cracks extends outside the wear track which is a sign that their origin is not a buckling failure in front of the indenter. Both coatings displayed ductile failure modes during the scratch testing. The wear track morphology undoubtedly confirms that the higher deposition temperature enhanced the adhesion of TiN coating.

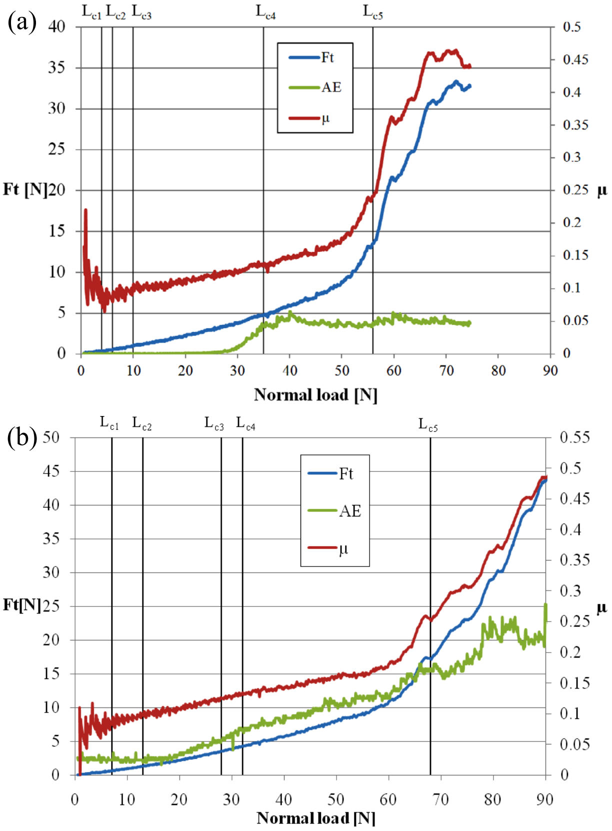

Figure 3. Scratch test plots: (a) sample 1 – deposited at low temperature (~ 50 °C) and (b) sample 2 – deposited at 400 °C

In Figure 5 HRC indents are presented in order to evaluate the coatings according to HRC adhesion test standard. Crack pattern and extent of chipping indicate that both coatings falls into the HF2 group of adhesion strengths quality. This is a group of coatings with very good adhesion to the substrate. Examining the HRC indents additionally proves the conclusions drawn from the scratch test results. The coating deposited at 400 °C (sample 2) exhibited higher adhesion. Under the applied load sample 2 coating plastically deformed, what prevented chipping formation on the folded edges of the indent, as it was not the case with sample 1 coating, presented in Figure 5a.

Overall, a low-temperature deposited coating displayed better mechanical characteristics than the TiN coatings produced by other deposition processes, conducted at low temperatures. Such conclusion is drawn when comparison is made with results published by other researchers [6,8,11,12].

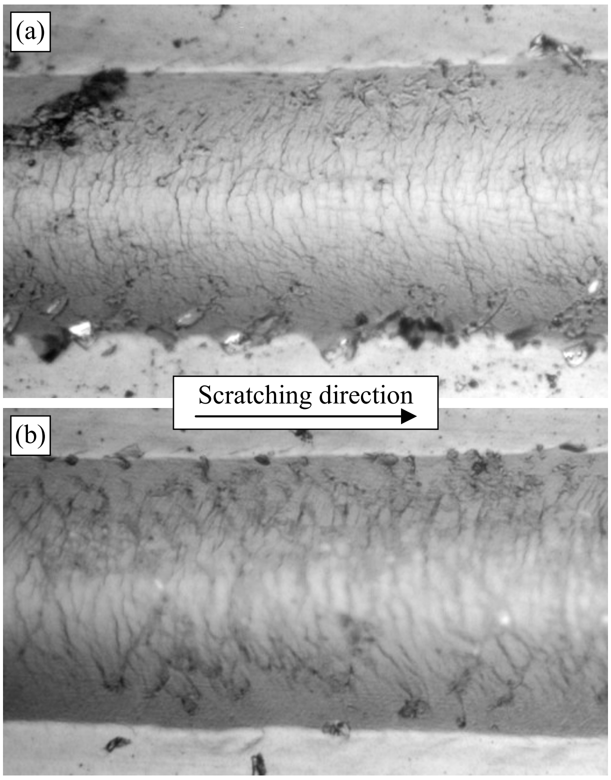

Figure 4. Scratch tracks morphology at 30 N load: (a) sample 1 – deposited at low temperature (~ 50 °C) and (b) sample 2 – deposited at 400 °C

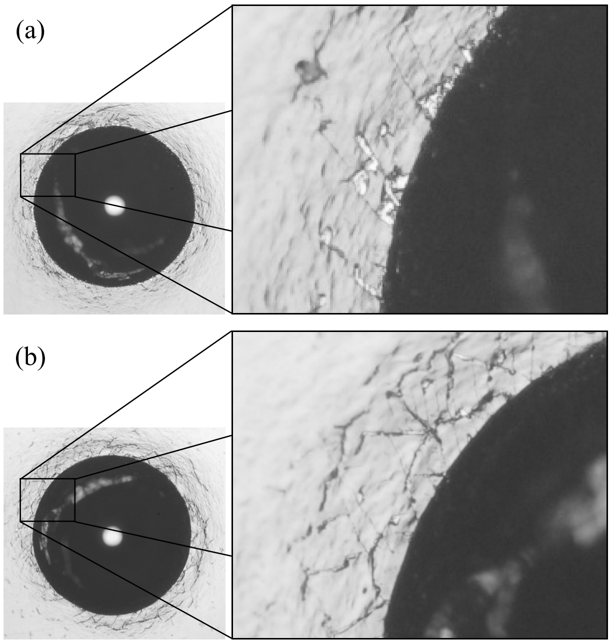

Figure 5. HRC indent: (a) sample 1 and (b) sample 2

Surface roughness has a very important role in tribological and corrosion behavior of coated parts [8]. For full understanding of the coating behavior during exploitation, it is essential to identify the wear mechanisms dependent on the surface roughness. Additionally, surface roughness has a large influence on the coating/substrate adhesion, which is a crucial characteristic of a coated system. Concerning previous discussion, surface analyses were carried out by AFM in order to determine the influence of deposition temperature on the coating roughness. After both deposition processes, increase in surface roughness was observed. The higher the deposition temperature, the more increased the surface roughness, see Table 1.

Table 1. Surface roughness of the samples before and after the deposition process

	R_a [nm]	R_q [nm]
Samples before the deposition	3.96	3.02
Sample 1 (~ 50 ºC)	9.3	7.2
Sample 2 (400 ºC)	12.06	9.04

There is a vast number of parameters that influence the roughness after the deposition, such as the ion beam energy [5,13], ion to atom arrival ratio [13], film thickness [14,15,16], grain size [15,16], coating texture [14,16], and others. In this study, all process parameters were kept constant except the temperature (heat) which directly affects the adatom mobility. This implies that increase in surface roughness is attributed to increased adatom mobility, which leads to aggregation of large crystal grains [17]. In percentage, the increase of roughness is around 30 %, which is actually a considerable value but certainly not sufficient to affect the properties of coatings applied on tools subjected to micro and macro wear. However, such increase in surface roughness is important in the field of ultra-precise engineering applications like in Micro-electro-mechanical systems (MEMS) or semiconductor elements [7,18].

Different heat input during the process of deposition resulted not only with different surface roughness but also with different TiN grain sizes. The 5 μm^2 scan of the coating surface revealed that sample 1 consists of larger grains, see Fig. 6. It is well known that increase in adatom mobility increases the grain size of the deposited coating. However, this was not the case in this study, what indicates the existence of a limit in this process. When the energy becomes greater than the surface energy, the process of desorption appears and the adatoms are desorbed [19]. This suggests that there exists a maximum temperature when the grain size of TiN is maximal. A maximum temperature is obviously below 400 ºC. Determining the exact temperature is a subject of our future research. Higher hardness and higher adhesion strength of the coating is clearly a consequence of denser coating structure comprised of smaller grains.

4. CONCLUSIONS

From the present study, the following conclusions are drawn:

- The deposition process carried out at 400 ºC resulted with TiN coating exhibiting very high hardness up to 28.5 GPa. This coating has higher hardness than the one deposited in the same conditions but at low temperatures (~ 50 ºC);
- For both coatings ductile failure modes were observed during scratch testing. Such behavior is preferred in applications of highly loaded wear resistant coatings. The coating deposited at higher temperature displayed higher adhesion, withstanding a greater amount of plastic deformation before cohesive and adhesive cracking;
- Both deposition processes increased the surface roughness. It was found that surface roughness increased in a greater extent when the coatings were deposited at high temperatures (400 ºC). Generally, when coatings are deposited by IBAD technology it is expected that increase in process temperature will result with increase in surface roughness;
- AFM microscopy revealed that, in fact, the higher hardness and the higher adhesion of a high-temperature deposited coating is attributed to the coating smaller grains.

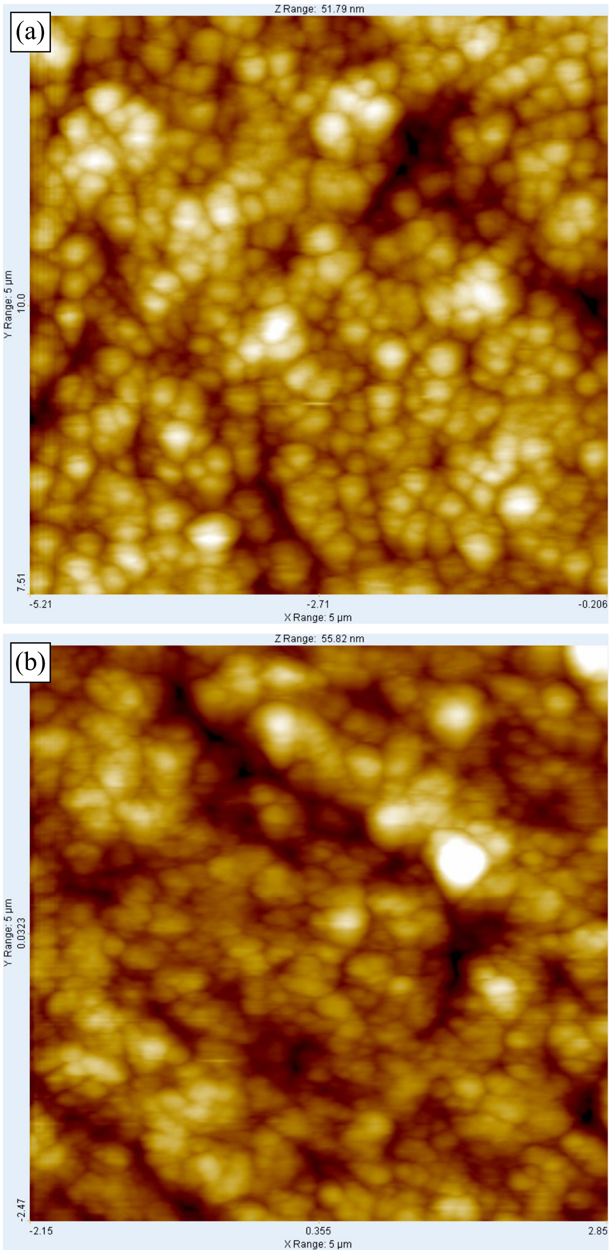

Figure 6. AFM images of coatings morphology: (a) sample 1 and (b) sample 2

A high-temperature deposited TiN coating undoubtedly exhibited better mechanical properties than the one deposited at low temperatures. On the other hand, the properties of TiN coating achieved by a low-temperature deposition are substantially better than of the same coatings produced in similar conditions by other techniques. This is what favors IBAD low-temperature deposited TiN coating in a field of wear resistant materials applied on thermally sensible substrates.

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МЕХАНИЧКЕ ОСОБИНЕ TiN ПРЕВЛАКА ДЕПОНОВАНИХ НА РАЗЛИЧИТОЈ ТЕМЕРАТУРИ УЗ ПОМОЋ *IBAD* ПРОЦЕСА

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TiN превлаке су депоноване на субстрате од челика за рад на топло техником депозиције подржане јонским снопом. Процес депозиције је изведен на две различите температуре и то на 50 и на 400 ºC. У

овом истраживању испитиван је утицај температуре депозиције на механичке особине, адхезију и морфологију површине TiN превлака. Карактеризација механичких особина попут тврдоће и модула еластичности је извршена техникама нано-индентације. Адхезија превлака је одређивана широко прихваћеном скреч тест (*scratch test*) техником, док су примењени и додатни *HRC* адхезиони тестови како би се извршило квалитативно поређење адхезије испитиваних превлака. Применом *AFM* микроскопа извршено је испитивање морфологије површина пре и након процеса депозиције превлака. У поређењу са превлаком депонованом на ниској температури, превлака депонована на високој температури је показала већу тврдоћу и бољу адхезију у виду већих критичних сила постигнутих током скреч тестова. Јонско бомбардовање током процеса депозиције узрокује већу покретљивост депонујућих атома чиме се поспешује добијање превлака са већом тврдоћом и адхезијом чак и на ниским температурама депозиције.