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CHARACTERIZATION OF DEFECTS IN PVD TiAlN HARD COATINGS

KARAKTERIZACIJA DEFEKTOV PVD TiAlN TRDIH PREVLEK

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PVD hard coatings are continuously gaining their importance in different fields of applications. In industrial use, they are often exposed to corrosive environments. Hard coatings possess inherently good corrosion resistance, but the substrate-hard coating systems may suffer from a severe corrosion attack due to the defects (craters, pin holes) in the coatings. On the sites, where defects extend through the coating, pitting corrosion can take place. These sites are drawbacks in the applications of hard coating.

A PVD TiAlN hard coating was prepared on cold-work, tool-steel (AISI D2) substrates by sputtering using unbalanced magnetron sources. The growth defects incorporated into the coating were studied after the deposition and corrosion experiments. We used two methods: (1) scanning electron microscopy (SEM) for general overview of the coating topography and 2D-characterization of defects, and (2) scanning electron microscopy with a focused ion beam (SEM-FIB) for making serial cross-sections through the selected defects in order to provide images for a 3D-reconstruction of defects. In this work we tried to investigate the formation of a defect at a specific location and find out whether the selected defect causes pitting corrosion.

Keywords: PVD hard coating, defect, 3D-reconstruction, FIB, SEM

PVD trde prevleke pridobivajo pomen na različnih področjih uporabe. Pri različnih aplikacijah so pogosto izpostavljene korozijskemu okolju. Trde prevleke so kemijsko inertne in same po sebi korozijsko obstojne. Med njihovo pripravo pa nastane v njih veliko defektov (kraterji, "pinholi"). Nekateri od njih segajo do podlage. Na teh mestih pride do jamičaste korozije, kar pa je z vidika uporabe neželeno.

TiAlN-prevleko smo nanesli na podlago orodnega jekla D2 po postopku naprševanja z neuravnoteženim magnetronskim izvirom. Defekte, ki so nastali med pripravo plasti, smo preučili po korozijskem preizkusu. Za analizo smo uporabili dve metodi. Vrstični elektronski mikroskop (SEM), s katerim smo pridobili splošni pregled prevleke, kot tudi 2D-karakterizacijo defektov. Kot drugo metodo smo uporabili fokusiran ionski curek, ki je integriran v klasični SEM, s katerim smo izvedli serijo rezov izbranih defektov za njihovo 3D-karakterizacijo. V delu smo poskušali na specifičnih mestih ugotoviti mehanizem nastanka defektov in ugotovljali, ali povzročajo jamičasto korozijo.

Ključne besede: trde PVD-prevleke, defekti, 3D-rekonstrukcija, FIB, SEM

1 INTRODUCTION

In hard coatings, macro- and microdefects typically appear during the deposition[1–5]. The most common macrodefects are: (a) large and shallow craters with diameters greater than 5 μm, (b) nodular defects (spherical droplets, conical features) with diameters in the range of 1–5 μm and (c) disk-like holes arising from droplet wrenching and pin holes[1,2]. The defects smaller than 1 μm can be regarded as microdefects. Their main representatives are: (I.) small micro-sized holes (so-called pin holes) extended through the entire thickness of a coating and (II.) small islands generated by the built-in particles with a diameter of slightly less than 1 μm. These surface imperfections in the coatings can cause local stresses, higher friction, sticking of the material, local loss of adhesion and pitting corrosion. All these facts are drawbacks in the application of hard coatings. Therefore, it is very important to reduce their concentration. However, the question is how to deposit denser and less defective coatings.

In this paper we tried to investigate the formation of a defect at a specific location and find out whether such a defect can cause pitting corrosion. For scientific and technological reasons, this topic remains very important also for further investigations and our main goal was to make a contribution to the researched area by using microstructural characterization and 3D-reconstruction of defects.

2 EXPERIMENTAL WORK

The industrial unbalanced sputtering system CC800/7 (CemeCon) was used for the deposition of the TiAlN hard coating. The sputtering system was equipped with four unbalanced magnetron sources that were positioned pairwise at the two sides of the vacuum chamber. A cold-work, high-chromium, high-carbon-type, tool-steel D2 (OCR12VM) was used as the substrate material. The substrates were polished to R_a = 9–15 nm, ultrasonically cleaned in detergents, rinsed in deionized water and dried in hot air. The final cleaning was performed by ion etching. The RF bias with the maximal power of 2000 W was applied in CC800/7 for 85 min. During the deposition, the bias voltage and the substrate temperature were 125 V and 450 °C. The thicknesses of the coatings were around 4 μm and a 2-fold rotation was used during the sputtering.

The growth defects integrated into the hard coating were studied after the corrosion test. The corrosion experiment was performed in a 0.1 M chloride solution at pH = 6.8 using a PARSTAT 2263 device for electrochemical impedance spectroscopy. The immersion time was 24 h. The defect morphology and the distribution of defects were studied with field emission scanning electron microscopy (SIRION NC400, FEI).

The focused ion beam (SEM-FIB) installed in a conventional scanning electron microscope (QUANTA 200 3D, FEI) was used to prepare different cross-sections through the defect. The primary opening (required for further observations of cross-sections) with the dimensions of 20 μm × 10 μm × 10 μm was ion milled with a 20-nA beam current, while the acceleration voltage of ions was 30 kV. Then the cross-sectioning was executed with the medium-high beam current (5 nA). The next step was polishing, which was divided into two stages. First, there was rough polishing with a 3-nA beam current and an exposure time of around 3 min, while the second one was fine polishing with a 1-nA beam current for another 3 min. At the end of the polishing, the specimen was tilted and an image of the cross-section was taken using low ion-beam current (10 pA). After the image acquisition the next slice of sample, with the thickness of about 1 μm, was removed by ion milling. The image of the new cross-section was acquired again by ions. This method was repeated until the entire area of the defect was examined.

The SEM-FIB cross-section images were put together into a 3D-image of the defect with the Avizo Fire 6.3 software. First, the images were imported into the software, where the voxel size and the slice thickness were defined. Then the images were arranged and aligned in such a way that a pixel of any picture represents the same site of interest on all the images. After that the voxel was cropped to a volume which contained only the defect, the coating and the part of the substrate, where pitting corrosion took place. All the images were then labeled. During the next step, several algorithms (resampling, surface generation and smoothing) were used for the 3D-image processing. Finally, a 3D-reconstruction was performed utilizing the same software[6].

3 RESULTS AND DISCUSSION

A corrosion test of TiAlN on a D2 substrate, using electrochemical spectroscopy, was carried out in a chloride medium. After that a characterization of defects was performed.

As a very useful tool for cutting and examining internal structure of defects, we applied focused-ion-beam milling. We prepared cross-sections through the growth defects by ion-beam milling (**Figures 1** and **2**). After several cuts of different defects we found out that with a non-destructive top-view examination (SEM, LM) it is almost impossible to determine which defect can cause pitting corrosion, because we cannot observe if there is any direct diffusion path (pin holes, crevices, columnar grain boundaries) through the coating that enables a corrosion attack on the substrate[4,7].

To reveal the problem we analyzed two typical defects. **Figure 1** shows a crater that was formed in the TiAlN coating on the D2 tool steel, while **Figure 2** displays a spherical droplet on the same substrate. From these two images it is difficult to conclude that corrosion

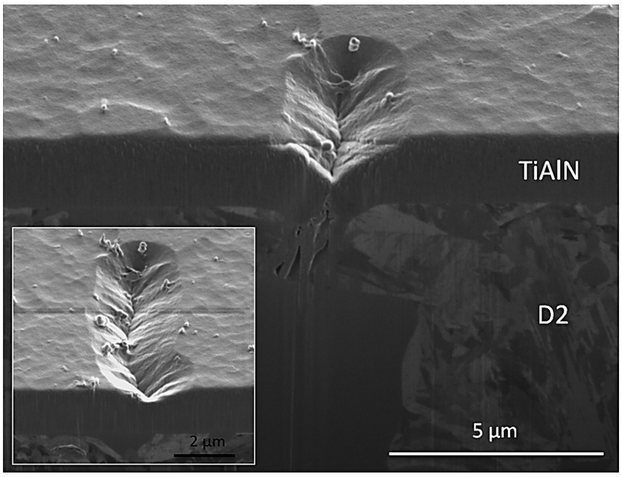

Figure 1: SEM image and FIB cross-sectional micrograph of the same growth defect (crater) on a sample TiAlN/D2 tool steel
Slika 1: SEM- in FIB-slika prereza defekta (kraterja) na vzorcu TiAlN/D2 orodnega jekla

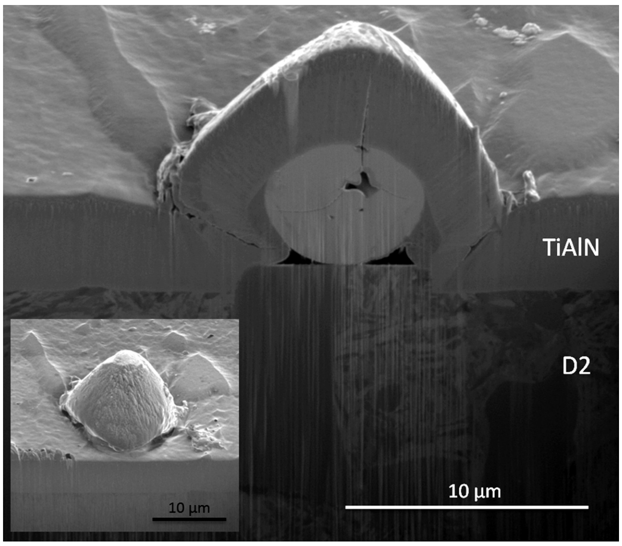

Figure 2: SEM-micrograph and an FIB cross-section image of a spherical droplet on a sample TiAlN/D2 tool steel
Slika 2: SEM- in FIB-slika prereza sferične kapljice na vzorcu TiAlN/D2 orodnega jekla

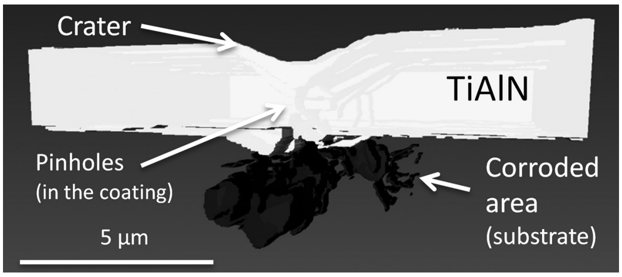

Figure 3: 3D reconstruction of a corrosion volume under a TiAlN coating on a site where a crater with pin holes was present
Slika 3: 3D-rekonstrukcija korodiranega območja pod TiAlN-prevleko na mestu, kjer se je nahajal krater s "pinholi"

took place, but when we continue with a series of slices, we can realize that the crater extends through the whole coating and originates in a small hole on the surface of the D2 tool steel (**Figure 1**). It is known that PVD processes have a poor ability to cover small pits or holes with a low aspect ratio (where depth is similar to their width) due to the shadowing effect.

Spherical droplets (**Figure 2**) are created as a result of arcing. The arc tendency during the deposition or etching cycles is increased with impurities on substrates, shields, fixtures, turntables and targets. Arcs are the origin of microdroplet formation. Some of these microdroplets can be incorporated into the coating during its growth or deposit on the surface of the substrate.

In our case a microdroplet was deposited on the surface of the substrate material during etching or at the beginning of the deposition cycle (**Figure 2**). This conclusion can be confirmed by the fact that the droplet is in contact with the uncoated surface and that the substrate surface under the droplet is untreated by ion etching due to the shadowing effect (the step on the surface).

Figure 2 shows that the region under the spherical droplet is not completely filled with coating due to the shadowing effect. Unexpectedly, the corrosion did not occur under it. After a detailed FIB analysis we recognized that pitting corrosion did not appear because there were no pin holes or porosities that could allow the solution to penetrate into the substrate. However, it is necessary to point out that corrosion was found under the other examined spherical droplets due to the existing pin holes.

The 3D image clearly shows that under the crater a pin hole extends through the entire thickness of the coating (**Figure 3**). It is known that corrosion takes place on the spots, where the solution can directly reach the substrate. Black pits on the image represent the corroded volume of the substrate. The calculated volume of the corroded area is surprisingly large (around 23 μm^3), while the volume of the crater is approximately two times smaller (12 μm^3). The corrosion products had a depth of 5 µm in the base material. On the spots where the corrosion has occurred, the substrate cannot provide sufficient support to the coating, so it can be damaged easily.

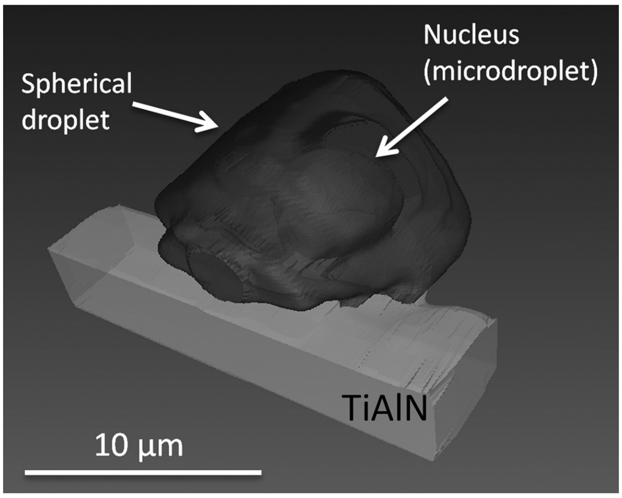

Figure 4: 3D-transparent image of a spherical droplet
Slika 4: 3D-transparentna slika sferične kapljice

A 3D rendering of a spherical droplet without a nucleus (microdroplet) is shown in **Figure 4**.

4 CONCLUSION

Growth defects (large and shallow craters or cone structures due to the inclusion in the middle of a dense coating layer) do not always present a break point for the corrosion resistance. We found that small pits on the substrate surface and growth defects lead to the formation of pin holes. It is well known that pin holes cause pitting corrosion.

Selected pits were analyzed by FIB in combination with SEM. In this way we obtained an insight into the pitting-corrosion process.

We can conclude that 3D imaging and analyzing provide new insights in understanding the growth-defect formation as well as its influence on the corrosion processes, which will help us solve challenging problems regarding the extension of the coating/substrate-system life time.

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