

## CHARACTERIZATION OF HARD PROTECTIVE COATINGS BASED ON (Cr,Ta)N

### KARAKTERIZACIJA TRDIH ZAŠČITNIH PREVLEK NA OSNOVI (Cr,Ta)N

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By reactive sputtering at low temperatures (200°C) hard coatings (Cr,Ta)N with two different compositions: Cr<sub>0.58</sub>Ta<sub>0.42</sub>N and Cr<sub>0.17</sub>Ta<sub>0.83</sub>N were prepared. Basic mechanical properties were evaluated such as Vickers microhardness, adhesion and internal stress in the coating. Among electrical properties, electrical resistivity and thermal coefficient of resistivity were measured. Crystal structure was also determined. All measurements were compared with results, obtained for chromium nitride and tantalum nitride coatings, prepared in the same apparatus at similar conditions. Oxidation rate of the coatings was also measured. At temperatures above 800°C a protective layer of chromium oxide was detected which stops further oxidation. At lower temperatures on the other hand, no such layer forms and oxidation proceeds unrestrained.

Key words: hard protective coatings, reactive sputtering, chromium tantalum nitride, oxidation

Z reaktivnim naprševanjem smo pri nizkih temperaturah (200°C) pripravili trdi zaščitni prevleki (Cr,Ta)N z dvema različnima sestavama: Cr<sub>0.58</sub>Ta<sub>0.42</sub>N in Cr<sub>0.17</sub>Ta<sub>0.83</sub>N. Izmerili smo osnovne mehanske lastnosti (mikrotrdoto po metodi Vickers, adhezijo in notranje napetosti v plasti), električne lastnosti (specifično električno upornost in temperaturni koeficient upornosti) ter določili kristalno strukturo. Rezultate meritev za obe ternarni nitridni prevleki smo primerjali s tistimi za prevleki iz kromovega nitrida in tantalovega nitrida, pripravljene v isti napravi pri podobnih pogojih. Merili smo tudi oksidacijsko odpornost prevlek. S fizikalnega stališča je zanimivo oksidacijsko obnašanje Cr<sub>0.58</sub>Ta<sub>0.42</sub>N. Pri temperaturah nad 800°C smo opazili zaščitno plast kromovega oksida, ki prepreči nadaljno oksidacijo. Pri nižjih temperaturah ta plast ne nastane in oksidacija poteka neovirano.

Ključne besede: trde zaščitne prevleke, reaktivno naprševanje, krom tantal nitrid, oksidacija

## 1 INTRODUCTION

Hard protective coatings based on binary transition metal nitrides have been in industrial use for over 15 years, the most widespread being the TiN coating. In recent years however, there is an emphasis on the development of multicomponent (ternary and quaternary) and multilayer nitride coatings.

In this paper measurements of structural, mechanical, electrical and oxidative properties of ternary nitride coatings based on (Cr,Ta)N are presented. The aspect of this research was to check whether the ternary coating (Cr,Ta)N possessed advantages of both binary coatings, CrN and TaN. The main advantage of CrN coating is a good resistance against oxidation, TaN coating on the other hand has high microhardness and a low temperature coefficient of resistivity. CrN<sup>1</sup> and TaN<sup>2</sup> coatings have been investigated considerably, which is not the case for the (Cr,Ta)N coatings<sup>3,4,5</sup>. As the solubility of chromium and tantalum is low<sup>6</sup>, the (Cr,Ta)N phase is thermodynamically unstable, but it can still be synthesized by physical vapour deposition (PVD).

## 2 EXPERIMENTAL PROCEDURE

All coatings were deposited by reactive sputtering in a Sputron (Balzers A.G., Liechtenstein) plasma-beam sputtering apparatus at a temperature of 200°C. Two

coatings with different chromium-to-tantalum ratios were deposited: Cr<sub>0.58</sub>Ta<sub>0.42</sub>N and Cr<sub>0.17</sub>Ta<sub>0.83</sub>N. The atomic ratio was determined by energy-dispersive X-ray (EDX) analysis, the microstructure and the crystal structure were studied by X-ray diffraction (XRD) and transmission electron microscopy (TEM), the surface of the coating and the fracture cross section were analyzed by scanning electron microscopy (SEM). The adhesion of the coatings was measured by the Revetest scratch tester. For the oxidation studies the samples were oxidized in a tube furnace in oxygen flow. The roughness, the thickness and the internal stress of the coatings were measured by Taylor-Hobson Talysurf 2 profilometer, whereas the weight-gain during oxidation was measured by a precise microbalance (Mettler Toledo UMT2).

## 3 RESULTS AND DISCUSSION

### 3.1 Physical properties

CrN as well as TaN crystallize in a face-centred cubic lattice with a NaCl (B1) structure. XRD and TEM analyses proved that this is also the case for both (Cr,Ta)N coatings and we can predict, that the face-centred cubic structure is retained for all Cr:Ta ratios. The lattice parameters for both ternary coatings are between the values for CrN and TaN coatings (see Table 1). At both (Cr,Ta)N coatings the grain size was approximately 50 nm.

**Table 1:** Basic physical properties of CrN, (Cr,Ta)N and TaN coatings

coating	t ( $\mu\text{m}$ )	a (nm)	HV <sub>0.025</sub> L <sub>c</sub> (F <sub>t</sub> ) (GPa)	$\sigma$ (N)	$\rho$ (MPa)	$\rho$ ( $\mu\Omega\text{cm}$ )	TCR ( $10^{-6}\text{K}^{-1}$ )
CrN	2,39	0,418	17.7	86	490	1000	-1150
Cr <sub>0.58</sub> Ta <sub>0.42</sub> N	2,68	0,426	20.0	84	1450	480	-180
Cr <sub>0.17</sub> Ta <sub>0.83</sub> N	2,30	0,431	18.6	68	1370	270	-230
TaN	2,62	0,438	24.7	72	1490	430	-100

t = thickness

a = lattice parameter

HV<sub>0.025</sub> = microhardness with a load of 25g (substrate hardness HV<sub>2</sub>=6.5GPa)

L<sub>c</sub>(F<sub>t</sub>) = adhesion critical force for scratching force jump

$\sigma$  = internal stress

$\rho$  = specific electrical resistivity

TCR = temperature coefficient of resistivity

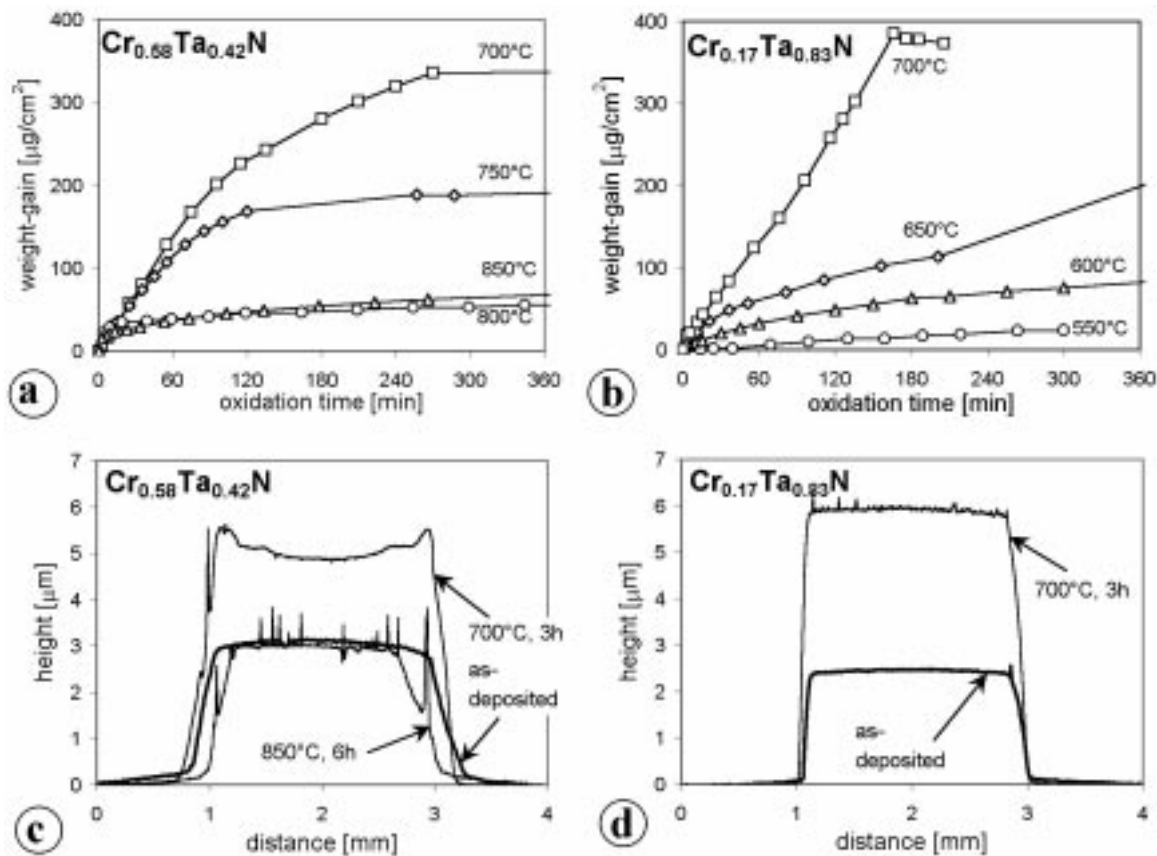
Among mechanical properties, microhardness, adhesion and internal stress were studied. Vickers microhardness was measured on coatings deposited on 100Cr6 (DIN) tool steel at loads between 25g and 2kg. Adhesion of the coating-substrate system was measured by the scratch test on the coatings deposited on OCR12 (DIN X210Cr12) tool steel. It was found out that the most reproducible parameter is the critical force for the total delamination of the coating, which correlates with the rapid

increase of the scratching force. The internal stress in the coating was evaluated from the deflection of a round silicon wafer covered with the coating<sup>7</sup>. The mechanical properties are listed in **Table 1**. (Cr,Ta)N coatings have a higher microhardness than CrN but lower than TaN coating. The adhesion is comparable to both binary coatings as well. The internal stress on the other hand is close to the value for TaN and three times higher than for CrN. High internal stress could be a disadvantage for a possible application.

Two electrical quantities of (Cr,Ta)N were also measured, the specific electrical resistivity and the temperature coefficient of resistivity (TCR). They are both comparable to the values for TaN. All coatings have a negative TCR i.e. they have a semiconductor character.

### 3.2 Oxidation

The oxidation of (Cr,Ta)N coatings was studied in a temperature range 550-850°C by measuring the weight-gain of the samples. The oxidation of tantalum-rich Cr<sub>0.17</sub>Ta<sub>0.83</sub>N coating at 550°C was negligible while at 600 and 650°C there was a steady parabolic growth as predicted by diffusion theory (see **Figure 1b**). At 700°C the oxidation proceeded swiftly in a linear manner and

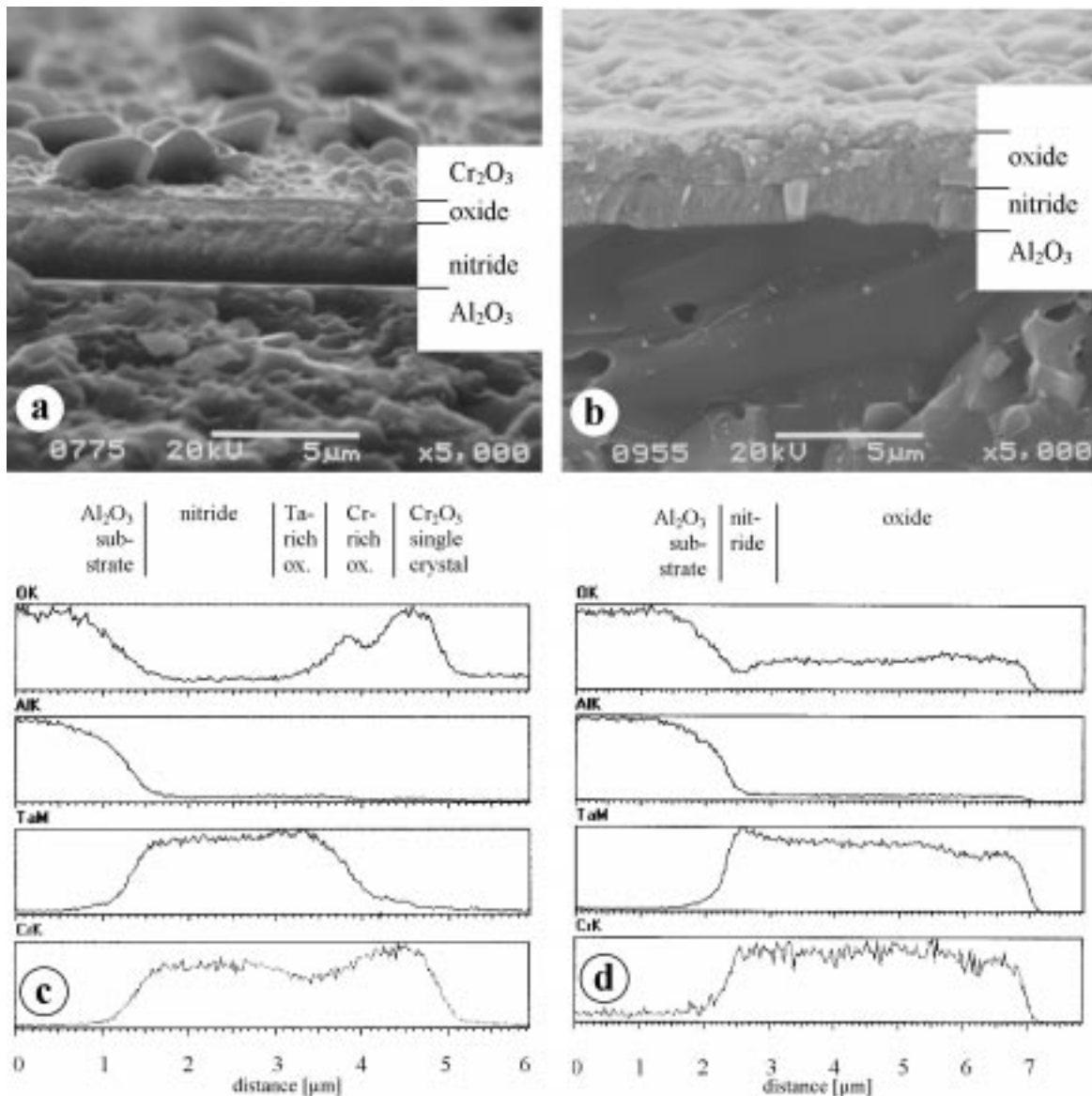


**Figure 1:** Weight-gain as a function of time at different oxidation temperatures: **a)** Cr<sub>0.58</sub>Ta<sub>0.42</sub>N; **b)** Cr<sub>0.17</sub>Ta<sub>0.83</sub>N. Coating thickness after oxidation at different temperatures: **c)** Cr<sub>0.58</sub>Ta<sub>0.42</sub>N; **d)** Cr<sub>0.17</sub>Ta<sub>0.83</sub>N  
**Slika 1:** Prirastek mase v odvisnosti od časa pri različnih temperaturah oksidacije: **a)** Cr<sub>0.58</sub>Ta<sub>0.42</sub>N; **b)** Cr<sub>0.17</sub>Ta<sub>0.83</sub>N. Debelina prevleke po oksidaciji pri različnih temperaturah: **c)** Cr<sub>0.58</sub>Ta<sub>0.42</sub>N; **d)** Cr<sub>0.17</sub>Ta<sub>0.83</sub>N

the whole 2.3  $\mu\text{m}$  thick coating was completely oxidized in 165 minutes.

The oxidation of chromium-rich  $\text{Cr}_{0.58}\text{Ta}_{0.42}\text{N}$  coating was studied at higher temperatures because  $\text{CrN}$  is more resistant to oxidation than  $\text{TaN}$ . At higher temperatures (800 and 850°C) the oxidation proceeded in a parabolic manner and relatively slowly (see **Figure 1a**). At lower temperatures (700 and 750°C) on the other hand, the oxidation was much faster and displayed a linear growth, which gradually reached a plateau. We emphasize the unexpected result that the oxidation rate at lower temperatures (700-750°C) was several times greater than at higher temperatures (800-850°C).

These results were confirmed by thickness increase measurements. We deposited the coatings in the shape of a belt 2 mm wide in order to measure the height of the step, which corresponds to the thickness of the coating. The cross sections over these structures are given in **Figures 1c and 1d**. The chromium-rich  $\text{Cr}_{0.58}\text{Ta}_{0.42}\text{N}$  coating thickness doubled after 3 hours of oxidation at 700°C, but after 6 hours of oxidation at 850°C there was hardly any increase at all (see **Figure 1c**). The only visible change is that the surface became much rougher than it used to be. The thickness increase of the tantalum-rich  $\text{Cr}_{0.17}\text{Ta}_{0.83}\text{N}$  coating after 3 hours of oxidation at 700°C was even more than double (see **Figure 1d**).



**Figure 2:** SEM micrographs of fractured samples: **a)**  $\text{Cr}_{0.58}\text{Ta}_{0.42}\text{N}$  coating oxidized for 6.5 hours at 850°C; **b)**  $\text{Cr}_{0.17}\text{Ta}_{0.83}\text{N}$  coating oxidized for 10 hours at 650°C; **c)** EDX line analysis of sample **a)**; **d)** EDX line analysis of sample **b)**. (The apparently dark lower sublayer of the nitride coating in **Figure a**) is an edge effect. The EDX line scans should be regarded as only qualitative because the lateral resolution is about 1  $\mu\text{m}$ )

**Slika 2:** SEM posnetka prelomljenih vzorcev: **a)** prevleka  $\text{Cr}_{0.58}\text{Ta}_{0.42}\text{N}$ , oksidirana 6,5 ur pri 850°C; **b)** prevleka  $\text{Cr}_{0.17}\text{Ta}_{0.83}\text{N}$  oksidirana 10 ur pri 650°C; **c)** EDX linijska analiza vzorca **a)**; **d)** EDX linijska analiza vzorca **b)**. (Navidezno temnejši spodnji sloj nitridne plasti na **sliki a**) je posledica robnega efekta. EDX linijska analiza ima zgolj kvalitativen pomen, ker je lateralna resolucija le okrog 1  $\mu\text{m}$ )

**Figure 2a** shows an SEM backscattered electron micrograph of the fracture cross section of the  $\text{Cr}_{0.58}\text{Ta}_{0.42}\text{N}$  coating, oxidized at  $850^\circ\text{C}$  for 6.5 hours. A clear two-layer structure is visible, the outer being the oxide and the inner the nitride. The oxide layer is relatively thin, as can be predicted from the weight-gain measurements (see **Figure 1a**). A remarkable feature are grains several micrometers in diameter. **Figure 2c** shows EDX compositional depth profiles of the sample presented on **Figure 2a** ( $\text{Cr}_{0.58}\text{Ta}_{0.42}\text{N}$  coating oxidized for 6.5 hours at  $850^\circ\text{C}$ ). Five regions can be distinguished: the  $\text{Al}_2\text{O}_3$  substrate, chromium-tantalum nitride, tantalum-rich oxide, chromium-rich oxide, and pure chromium oxide. The last peak in the signal corresponding to a grain is pure chromium oxide.

The roughness of the  $\text{Cr}_{0.58}\text{Ta}_{0.42}\text{N}$  coating oxidized at  $850^\circ\text{C}$  was 410 nm, but only 50 nm of the one oxidized at  $700^\circ\text{C}$ . This proves that the oxide grain growth is a high-temperature process.

**Figure 2b** presents the fracture cross section of the tantalum-rich  $\text{Cr}_{0.17}\text{Ta}_{0.83}\text{N}$  coating oxidized for 10 hours at  $650^\circ\text{C}$ . There are no oxide grains present. EDX analysis shows no variation of the Cr:Ta ratio (see **Figure 2d**), therefore the oxide layer composition can be considered depth-invariable.

The intriguing results of the oxidation of the chromium-rich coating point out that there are two mechanisms of oxidation: a low-temperature one ( $700\text{--}750^\circ\text{C}$ ) and a high-temperature one ( $800\text{--}850^\circ\text{C}$ ). The qualitative description of the processes are in our opinion similar to those described for  $\text{TiAlN}$ <sup>8</sup>. At high temperatures the mobility of chromium is high. The outward diffusion of chromium causes the formation of a chromium-rich oxide layer, whereas the inward diffusion of oxygen forms an oxide layer rich in tantalum. This is not unexpected, because the mutual solubility of chromium and tantalum is negligible<sup>6</sup>. After the chromium-rich oxide layer has grown thick enough, it behaves like a diffusion barrier and stops the further oxidation. At lower temperatures, on the other hand, the mobility of chromium is too low for such de-mixing to occur. A continuous oxide layer forms, which has no diffusion barrier properties.

The formation of oxide grains can be attributed to thermal relaxation of the structure. As the internal stress is high enough, excess material is extruded from the coating. The extruded element is chromium, because it has much greater mobility than tantalum. This is possible only at high temperatures, where the mobility of chromium is large enough.

#### 4 CONCLUSIONS

Two (Cr,Ta)N hard coatings with different atomic composition were prepared. Both coatings crystallize in a face-centred cubic lattice. The microhardness and adhesion values are between those for CrN and TaN whereas the internal stress, the specific electrical resistivity and the temperature coefficient of resistivity are comparable to TaN rather than CrN. At oxidation of  $\text{Cr}_{0.58}\text{Ta}_{0.42}\text{N}$  coating at  $800\text{--}850^\circ\text{C}$ , a two-layer structure forms which considerably slows the oxidation, while at  $700\text{--}750^\circ\text{C}$  the oxidation proceeds unrestrained because a homogeneous oxide layer forms with no protective ability. None of the observed properties brings us an advantage comparing to the CrN and TaN coating. But the oxidation behaviour, albeit of scientific interest, severely limits possible applications.

#### ACKNOWLEDGEMENT

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