STRUCTURAL CHANGES OF PVD COATED CR-NI STEEL AFTER HEAT LOAD

Stanislav KRUM[a], Jakub HORNÍK[a], David TONDL[a], Františka PEŠLOVÁ[b], Maxim PUCHNIN[a], Evgenyi ANISIMOV[a]

[a] *Czech Technical University in Prague, Faculty of Mechanical Engineering, Department of Material Engineering, Prague, Czech Republic, EU,*
s.krum@seznam.cz, jakub.hornik@fs.cvut.cz, tondl@ipp.cas.cz, maxim.puchnin@fs.cvut.cz, evgenyi.anisimov@fs.cvut.cz
[b] *Alexander Dubcek University of Trencin, Faculty of Industrial Technologies in Puchov, Puchov, Slovakia, EU, frantiska.peslova@fpt.tnuni.sk*

Abstract

The paper deals with evaluation of PVD functionally graded coatings based on Cr-Al-N, TiN and Ti-Al-N. Coatings were deposited in the following combinations: CrAl/CrAlN, Cr/CrN/CrAlN, nitriding/Cr/CrN/CrAlN, nitriding/TiN/AlTiN and nitriding/AlTi/AlTiN. As main criteria for coatings properties and quality comparison methods of scratch test and nanohardness measurement were selected. Subsequently, coatings CrAlN and TiN were designed as protection against high temperature oxidation of Cr-Ni steel (X16CrNiSi25-20) exposed to the temperature of 850 °C for 6 and 12 hours duration. Detailed microstructural analysis of the coating - substrate interface including EDS microanalysis of the elements distribution in the coating and the substrate was performed. Scratch test of selected coating after heat exposure was carried out in order to determine adhesion. From simulated tests it is evident that PVD coating CrAlN fulfils the role of protection. In the case of TiN there occurred intensive subsurface degradation of the coating connected with decohesion and subsequent cracking off the coating.

Keywords: PVD coating, FGM, CrNi austenitic steel, heat load, CrAlN

1. INTRODUCTION

PVD coatings based on nitrides of Cr, Ti, Al and their combination are commonly used as protective barrier on material surfaces or layers against oxidation, heat transfer, wear and corrosion [1, 2, 3]. These relatively common coating elements are sometimes modified by a small amount of rarer element [4]. The advantages of this method are wide spectrum of possible coating composition, high deposition purity and coating thickness uniformity. Due to the relative low adhesion of single nitrided layer with the distinct interface caused predominantly by the hardness difference, the layer combination reducing this effect must be created. Major application of these procedures is the preparation of functionally graded materials (FGM). These systems could eliminate certain disadvantages of conventionally prepared coatings (cracks, lower adhesion) [1,2,3]. The combination of coatings or layers and coatings reduce the influence of high difference in properties of substrate and coatings [5]. The final coating consists of multiple interlayers with gradiently increasing hardness and adhesion of the system. In this case the effect of functionally graded interlayer of coating CrAlN and TiAlN properties were evaluated. As the next step the influence of thermal load on CrNi steel microstructure and evaluation of behaviour of substrate surface and subsurface layer after depositing coating of Cr-Al-N, TiN and Ti-Al-N types was performed. The methods used were hardness testing and scratch test adhesion evaluation [6]. Coatings were selected on basis of literature research of the material [1-3,7]. Cr-Ni steel is used for machine parts exposed to corrosion, thermal and mechanical load. That is why the coating is expected to provide a barrier and thusly slow down or eliminate substrate degradation. Coated and uncoated material was exposed to thermal load during various time intervals.

2. EXPERIMENTAL

The commercial sub-ledeburitic powder metallurgically produced tool steel Vanadis 23 and corrosion resistant austenitic steel Dominial ZF 2 (**Table 1**) were selected as the base material for the testing of adhesion properties of deposited coatings. Steel heat treatment realized at Prikner Ltd. Consisted of vacuum quenching from 1020 °C followed by triple tempering at temperatures of 560 °C, 580 °C and 560 °C. Final achieved hardness was 64 HRC.

Table 1 Typical chemical composition of Dominial ZF 2 and Vanadis 23

Steel	Chemical composition (wt.%)									
	C	Mn	Si	Cr	Ni	Mo	V	W	P	S
Dominial ZF 2 W. Nr.: 1.2782, DIN: X16CrNiSi25-20	0.08	0.57	2.0	24.24	20.98	-	-	-	0.025	0.012
Vanadis 23 1.3344, DIN S5-5-3, AISI M3:2)	1.8	0.4	0.45	4.15	-	3.55	3.25	9,5	0.003	0.003

The combination of layers and coatings CrAl/CrAlN, Cr/CrN/CrAlN, nitriding/Cr/CrN/CrAlN, nitriding/TiN/AlTiN and nitriding/AlTi/AlTiN in accordance with **Table 2** were deposited on Flexicoat 850 (Hauzer) equipment. Parameters of the deposition of all coatings and layers were prior optimized on test batches. For coating following parameters were used: the power of cathod 4 kW, BIAS voltage 75 V, UBM coils 3 A and temperature 450 °C. Plasma nitrided layer as a hardened underlayer was created using following parameters: temperature of 510 °C and time of 4 h.

Table 2 Details of coatings (layer composition and thickness)

Layer/coating	1	2	3	4
CrAl/CrAlN	CrAl: 150-200 nm	CrAlN: 2.5 μm		
Cr/CrN/CrAlN	Cr: 150-200 nm	CrN: 200-250 nm	CrAlN: 2,5 μm	
nitriding/Cr/CrN/CrAlN	Nitriding: 40 μm	Cr: 150-200 nm	CrN 200-250 nm	CrAlN 2.5 μm
TiN	TiN: 1.5 μm			
nitriding/TiN	Nitriding: 40 μm	TiN: 2.5 μm		
AlTiN	AlTiN: 2.5 μm			
nitriding/AlTi/AlTiN	Nitriding: 40 μm	AlTi: 200 nm	AlTiN: N flow gradient 10-20 sccm, cca 300 nm	AlTiN: 2 μm

Adhesion measurements were performed using the Reverest Xpress + (CSM Instruments) device with Rockwell indenter (tip angle 120°, tip radius 0.2 mm). The load was gradually increased from 1 to 100 N, with loading rate 100 N/min. The total length of each scratch was 10 mm and indentor moved at velocity of 5 mm/min. Scanning electron microscope JEOL JSM-7600F with EDX detector was used for the evaluation of microstructure and for analysis of microindentations on samples prepared according to standard metallographic procedures. Hardness of coatings was determined by means of Nanotest device (Micro Materials Ltd.). Total number of indentation cycles applied to each sample was 10 with a loading force corresponding to measurement in 15 % of the coating depth. Microindenter LecoM-400-G1 was also used for the evaluation of hardness using load of 1 kg or 200 g for each sample.

Table 3 Description of heat load

Coating	Duration	Temperature (°C)
nitriding/Cr/CrN/CrAlN	6 hours	850
nitriding/Cr/CrN/CrAlN	12 hours	850
TiN	Several seconds	900 - 1000

The coatings nitriding/Cr/CrN/CrAlN and TiN were deposited on X16CrNiSi25-20 Steel - high alloyed steel with austenitic structure. It has a great thermal stability and resistance against corrosion. Steel was quenched from austenitization temperatures of 1050 °C - 1100 °C. The coatings TiN and nitriding/Cr/CrN/CrAlN were subjected to the heat load (**Table 3**). Coatings of nitriding/Cr/CrN/CrAlN were heated in the furnace with a long dwell times. TiN was tested directly in application of glass moulding process. That is the reason of such a short thermal exposure.

3. RESULTS AND DISCUSSION

3.1 Hardness

Table 4 Hardness values of evaluated coatings

Coating	**Surface hardness**		**Substrate**
	H_{IT} (GPa)	**HV0.2**	
CrAl/CrAlN	24.1	2457	Vanadis 23
Cr/CrN/CrAlN			Vanadis 23
nitriding/Cr/CrN/CrAlN			Vanadis 23
nitriding/Cr/CrN/CrAlN			X16CrNiSi25-20
TiN	24,4	2208	X16CrNiSi25-20
nitriding/TiN			Vanadis 23
AlTiN	26.8	2733	Vanadis 23
nitriding/AlTi/AlTiN			Vanadis 23

Surface hardness of uncoated samples was measured by HV1 method. Surface hardness of coated samples was measured by nanoindentation (H_{IT}) or by HV0.2 method. H_{IT} is expressed as a quotient between maximal loading force and projected contact area at the load. Results of hardness measurements are in **Table 4**. Initial hardness of Vanadis 23 steel resp. X16CrNiSi25-20 is 284 HV resp. 750 HV.

The values of nanohardness of the TiN, CrAlN and AlTiN are very similar and relatively high (**Table 4**).

3.2 Adhesion

From the results in **Table 5** it is evident that using gradiently deposited multicoating that follows the chemical gradient from the base material to the surface coating layer has positive effect on final adhesion. Significantly increased adhesion was achieved when a 904itride layer was formed on base material (substrate). All samples containing nitride layer did not suffer from the delamination up to 100 N. Microstructural analysis using electron scanning microscopy was performed on samples of selected coatings. Morphology of intermediary phases and their size may influence coating adhesion.

Table 5 Results of adhesion measurements (sratch test)

Coating	Load of the rating failure L_{C3} (N)	Substrate
CrAl/CrAlN	33.78	Vanadis23
Cr/CrN/CrAlN	38.89	Vanadis23
nitriding/Cr/CrN/CrAlN	> 100 (no failure)	Vanadis23
nitriding/Cr/CrN/CrAlN	> 100 (no failure)	X16CrNiSi25-20
nitriding/TiN	> 100 (no failure)	Vanadis 23
AlTiN	18.79	X16CrNiSi25-20
nitriding/AlTi/AlTiN	> 100 (no failure)	Vanadis 23

3.3 Heat load effect

Table 6 shows difference of hardness values between coatings that were exposed to an elevated temperature for 6 and 12 h. Nanohardness of the sample which was kept in furnace for 12 h is lowered.

Table 6 Change of properties after thermal load

Coating	Surface hardness H_{IT} (Gpa)	Surface hardness HV0.2	Substrate
nitriding/Cr/CrN/CrAlN after 6 h of thermal load	72.51	660	X16CrNiSi25-20
nitriding/Cr/CrN/CrAlN after 12 h of thermal load	53.24	670	X16CrNiSi25-20

Fig. 1 shows microstructure of TiN coated sample that has been used in application of glass moulding. It is clear that after long term service at elevated temperatures the coating remains undamaged. However, oxide layer is formed at substrate surface that is in contact with the coating. Character of the layer is porous and that is the reason of the coating possible failure at higher mechanical load. Initiator of active coated surface failure is potential occurrence of carbides or other intermediary phases causing roughness of both the surface and the coating. The presence of this layer causes lowering of adhesion between the base material and coating. Simultaneously, the matrix loss leads to insufficient load capacity and thus breaking of the coating. In that case the coating peels off.

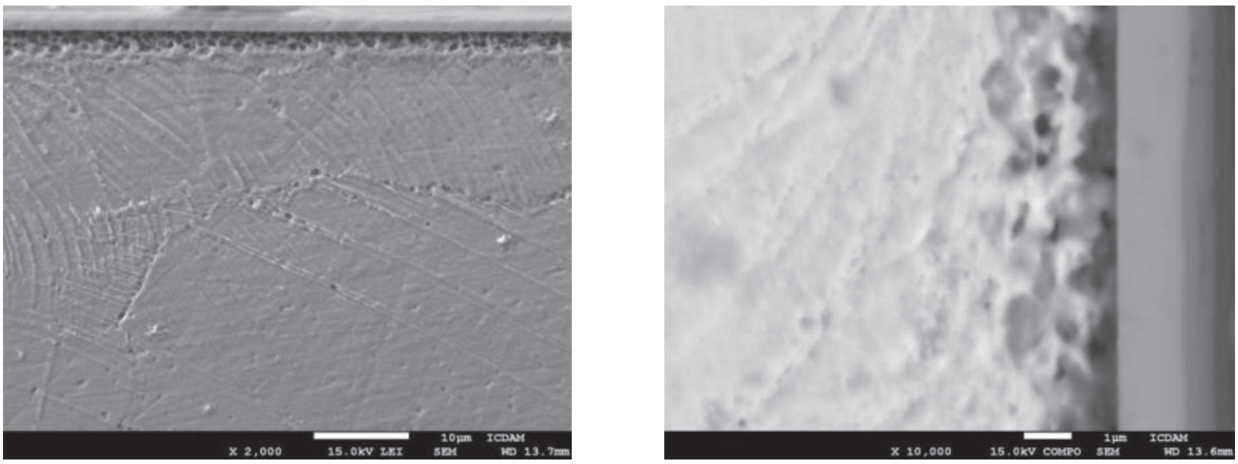
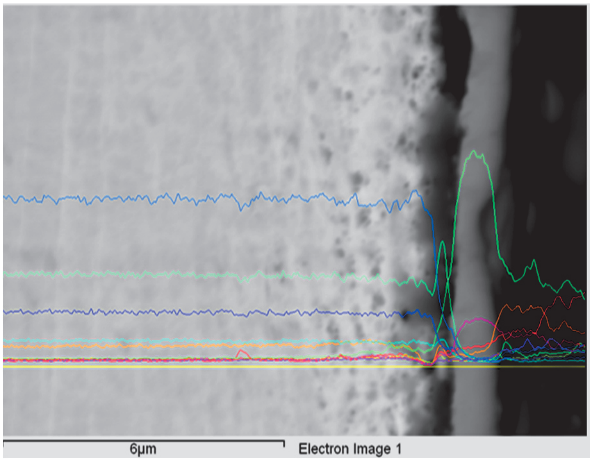
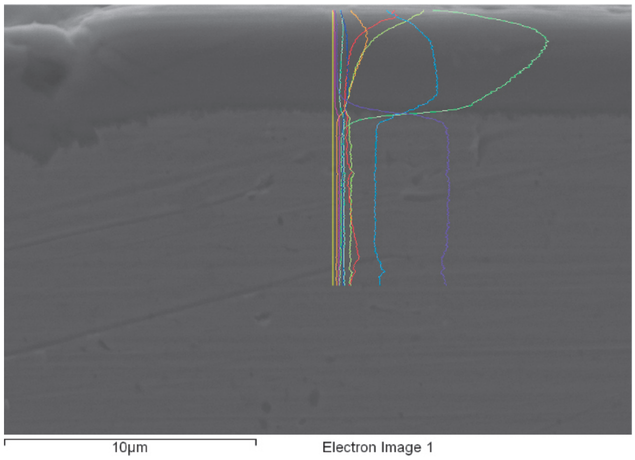


Fig. 1 TiN coating and porous subsurface layer of base material X16CrNiSi25-20.

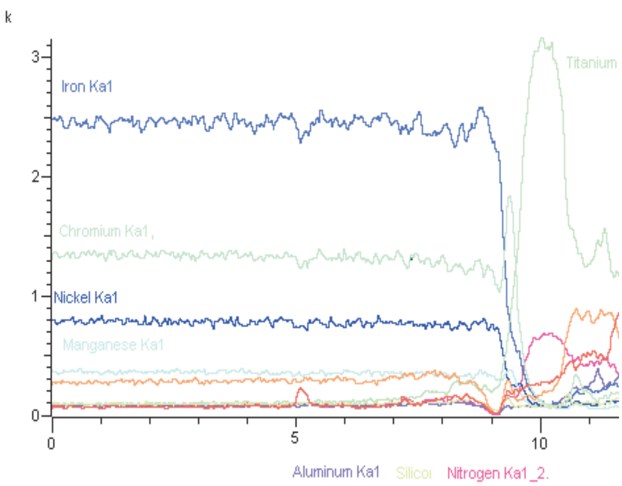
The result of chemical analysis of the coating and oxide layer is in **Fig. 2**. Chemical composition was determined by EDX (linear method and mapping). In the porous layer, Fe, Cr and Mn contents are lowered. At the same time increased concentrations of oxygen and nitrogen were detected. These facts point out to oxidation resp. corrosion process taking place under the TiN coating.



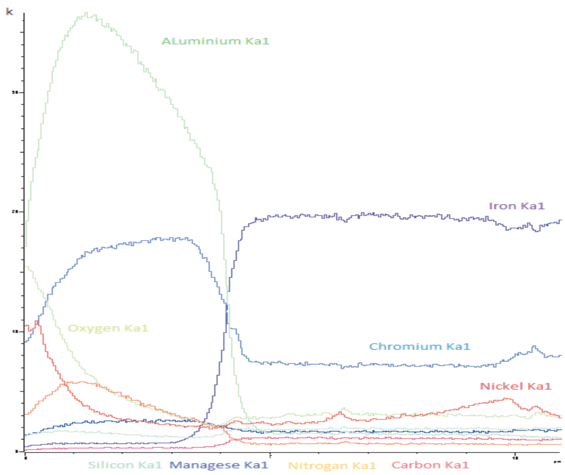
TiN coating and the subsurface layer after high temperature exposition during moulding process (900 - 1000) °C



Nitriding/Cr/CrN/CrAlN coating after 12 h of high temperature exposition at 850 °C



Concentration profiles in TiN coating



Concentration profiles in nitriding/Cr/CrN/CrAlN coating after 12 h of high temperature exposition

Fig. 2 EDX analysis of TiN and nitriding/Cr/CrN/CrAlN coating on X16CrNiSi25-20 steel after high temperature exposition

CONCLUSIONS

The application of pure metals as a material of “interlayers” improves the adhesion of the coatings by gradually approaching its composition to the substrate. Further improving of adhesion was reached using gradiently deposited multicoating that follows the chemical gradient from the base material to the final functional coating layer. Best results of adhesion improvement were achieved applying the nitriding process as hardened underlayer, which approaches hardness of the deposited coatings. The results will be applied in further FGM research.

During the operation of TiN coated parts formation of oxide layer under the surface takes place. It negatively influences adhesion between the substrate and coating and surface strength of the mould. Combination of X16CrNiSi25-20 substrate and TiN coating the coating does not fulfil desired protective function. Further work will be oriented on projecting and testing of glass mould coating composition, which would not have this negative effect. On the other hand from the hardness and adhesion testing it can be assumed that coating of consisting of nitride layer and Cr/CrN/CrAlN have a good protective function. Also it retains certain thermal stability.

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