

**OVERVIEW OF Cr<sub>2</sub>N AND Cr<sub>2</sub>N/Ag COATINGS ON Cr-V  
LEDEBURITIC STEEL: MECHANICAL PROPERTIES  
AND ADHESION**

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**ABSTRACT**

*Samples made from Vanadis 6 PM ledeburitic tool steel were surface machined, ground and mirror polished. Prior the deposition, they were heat treated to a hardness of 60 HRC. Cr<sub>2</sub>N- and Cr<sub>2</sub>N/Ag-coatings were deposited by magnetron sputtering technique, using pure Cr and Ag targets, in a composite low pressure nitrogen/argon atmosphere and at a temperature of 500 °C. The contents of silver in Cr<sub>2</sub>N/Ag coatings were established 3, 7, 11 and 15 wt. %. Incorporation of silver in the Cr<sub>2</sub>N-matrix influence the growth rate, namely from the content of 11 wt. %. The nanohardness and Young's modulus do not change until the content of 11 wt. % where slightly increased but further increasing of silver led to decreasing these values rapidly. The best adhesion was established for coatings with 3 and 7 wt. % of silver.*

**KEY WORDS**

*Cr<sub>2</sub>N/Ag coatings, growth rate, nanohardness, Young's modulus, adhesion*

**INTRODUCTION**

Chromium nitrides (CrN) have been extensively investigated in the applications of protective coatings due to their high hardness, good wear resistance as well as excellent corrosion and high temperature oxidation resistance (1-5). They gained great scientific interest and industrial popularity due to those properties in copper machining, aluminium die casting and forming, and wood processing (6). However, in many applications, the requirements on coated material surface cannot be met by such a single coating. A further development to adapt some of their properties to a desired value for specific applications is to produce composite coatings, where different material properties are combined and some new desired properties could be created (7-9).

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The effect of self-lubrication has gained a great scientific importance in last few years. The main idea to develop self-lubricating and multi-purpose coatings is based upon the fact that commercially available lubricants (sulphides, oxides, graphite) exhibit considerable shortcomings and cannot be used effectively in tooling applications over sufficiently wide temperature range (10-12). Soft noble metals on the other hand, posse stable chemical behaviour and can exhibit self-lubricating properties due to their low shear strength. Noble metal particle bring several benefits to the layer properties compared to metal oxides or graphite. They are stable up to relatively high temperatures, have low hardness and do not behave as abrasive particles. A common disadvantage of noble metals is their high cost, but this can be optimized to an acceptable level. Self-lubricating effect is based on incorporation of small amount of noble metals, mostly silver, into the basic CrN-film. Silver is completely insoluble in CrN and forms nano-particles in CrN matrix. Silver containing transition metal nitrides films have been extensively studied in recent years [13].

The current paper deals with the development of adaptive nanocomposite Cr<sub>2</sub>N/Ag coatings on the Vanadis 6 Cr-V ledeburitic tool steel. It compares growth rate, basic mechanical properties as are nanohardness and Young's modulus and adhesion of the coatings Cr<sub>2</sub>N with different content of silver, nominally 3, 7, 11 and 15 wt. %.

## **EXPERIMENTAL**

### ***Material and processing***

The substrate material was the powder metallurgical ledeburitic steel Vanadis 6 with nominally mass fraction: w(C) 2.1 %, w(Si) 1.0 %, w(Mn) 0.4 %, w(Cr) 6.8 %, w(Mo) 1.5 %, w(V) 5.4 % and Fe as a balance and soft annealed to a hardness of 21 HRC. The samples used as experimental material for deposition were plates with dimensions of 50 mm x 10 mm x 10 mm, heat treated (austenitized at a temperature of 1050 °C, quenched in flow of nitrogen gas and double tempered for 2 hours at a temperature of 530 °C) to final hardness of 60 HRC and then finely ground and polished with diamond suspension up to a mirror finish.

The Cr<sub>2</sub>N- and Cr<sub>2</sub>N/Ag-coatings were grown in a Hauzer-Flexicoat 850 magnetron sputter deposition system in a pulse regime with a frequency of 40 kHz. Two water cooled targets, positioned opposite one to another and at an angle of 45° with respect to the substrate surface normal, were used for the deposition. For the Cr<sub>2</sub>N-coatings, both targets were made from pure chromium (99.9 % Cr). For the Cr<sub>2</sub>N/Ag-coatings, an Ag target (99.98 % of purity) was used instead of one of the Cr target. In the case of the Cr<sub>2</sub>N-coatings, the cathode input power was 2.9 kW on each cathode. For the production of Ag-containing coatings, the output power on the Cr cathode was increased to 5.8 kW and that on the Ag cathode was in sequence 0.10, 0.21, 0.34 and 0.45 kW, respectively, regarding to preparation of coatings with silver content of 3, 7, 11 and 15 wt. %, respectively, in the Cr<sub>2</sub>N matrix (it responds to 1.2, 2.8, 4.4 and 6.0 at. % of silver, respectively). The processes were carried out in a low pressure atmosphere (0.15 mbar), containing nitrogen and argon in a ratio of 1:4.5. The samples were placed between the targets on rotating holders with a rotation speed of 3 rpm. Just prior to the deposition, the substrates were sputter cleaned in an argon low-pressure atmosphere for 15 min. The substrate temperature was 250 °C for the cleaning and 500 °C for the deposition. A negative substrate bias of 200 V was used for the sputter cleaning and that of 100 V for the deposition. The total deposition time was 6 h.

## ***Investigation methods***

X-ray diffraction patterns have been recorded using a Panalytical Empyrean diffractometer with Bragg-Brentano geometry and iron filtered  $\text{CoK}\alpha$  characteristic radiation ( $\lambda = 0.17903$  nm). Incident beam was equipped with parallel beam optics. Diffraction radiation has been collected with scintillation detector with  $0.27^\circ$  parallel plate collimator. Samples were measured at a room temperature and without sample spinning. The spectra were recorded over a two-theta range  $30 - 130^\circ\text{C}$ .

The thickness of the coatings was measured on the fracture surfaces of coated Charpy impact specimens. The material was immersed into liquid nitrogen for 20 min and then broken down. A scanning electron microscopy (SEM) in JEOL JSM 7600F was used for the analyses.

The nanohardness and the Young's modulus (E) values of the coatings were determined using the instrumented nanoindentation test under a normal load of 60 mN using a TTX 2 CSM Instruments nanohardness tester equipped with a Berkovich indenter. The penetration depth (and the loading) was chosen in order to not exceed one tenth of the coating thickness, to minimize the substrate effect. Fifteen measurements were made and the mean value and the standard deviation were then calculated.

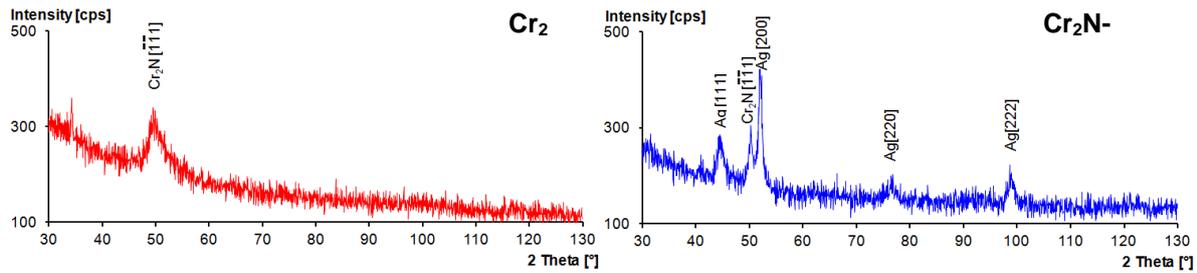
The adhesion of the films has been examined using a CSM Revetest scratch-tester. The scratches were made under a progressively increasing load from 1 N to 100 N, with a loading rate of 50 N/min. Standard Rockwell diamond indenter with a tip radius of 200  $\mu\text{m}$  was used. Five measurements have been made and the mean value and standard deviation of adhesion, represented by the  $L_{c1}$  and  $L_{c2}$  critical loads, respectively, has been calculated. The critical loads were determined by the viewing of the scratches on the SEM micrograph. The  $L_{c1}$  critical load corresponds to the occurrence of the first side cracking of the coating. And the  $L_{c2}$  critical load has been determined as a load when the film was completely removed from the substrate inside the scratch.

The second method for measuring adhesion of coatings was used Rockwell adhesion test – “Mercedes test”. It was used a Rockwell “C”- type diamond cone indenter with an applied load of 150 kg. Once the load has been removed the indents were examined by SEM and the adhesion of coatings was classified as HF 1 to HF 6, according to the amount of cracking and delamination of coating around the indent. Indents that are classified as HF 1 and HF 2 are regarded as having adequate adhesion. Indents that are classified as HF 3 and HF 4 still have acceptable adhesion and indents HF 5 and HF 6 have unacceptable adhesion.

## **RESULTS AND DISCUSSION**

Fig. 1 shows X-ray diffraction spectrum recorded from the as-deposited the  $\text{Cr}_2\text{N}$ - and the  $\text{Cr}_2\text{N}$ -11Ag-films. The  $\text{Cr}_2\text{N}$  film is composed only by  $\text{Cr}_2\text{N}$ -phase and it is evident that the  $\text{Cr}_2\text{N}$ -11Ag film is composed of metallic silver and  $\text{Cr}_2\text{N}$ -phase. Further, the width of the  $\text{Cr}_2\text{N}$  peak was decreased after incorporation silver in  $\text{Cr}_2\text{N}$  matrix. One can thus assume that the silver does not contain any significant stresses after deposition, e.g. during the deposition at  $500^\circ\text{C}$ , the silver underwent plastic deformation and internal stresses in the film were relieved effectively. This finding is in good agreement with the Köstensbauer's observations [14], where stress relieving in coatings commenced at  $380^\circ\text{C}$ .

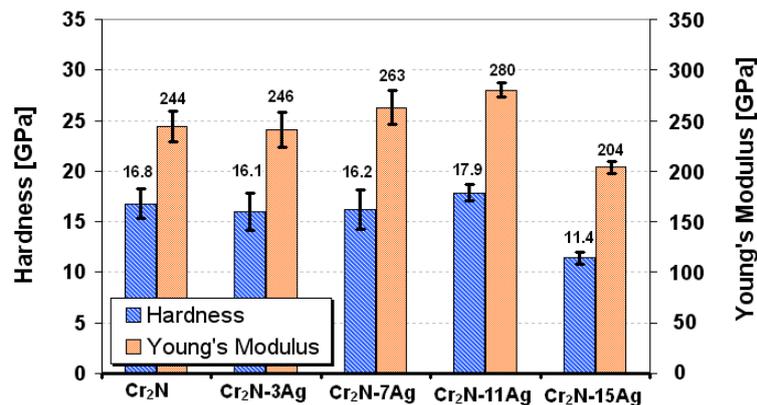
In Table 1 are results for measurement of thickness of the films with different silver content. It is clear that the growth rate of the films is accelerated by the addition of silver in the  $\text{Cr}_2\text{N}$  matrix. The starting point of increasing growth rate was found to be in film containing 11 wt. % of Ag. The growth rate further increased with increasing content of silver. It is in good agreement with investigations of group of Mulligan's researches (15).



**Fig. 1** X-ray diffraction patterns from the  $Cr_2N$ - and the  $Cr_2N$ -11Ag-films in as-deposited state

THICKNESSES OF THE  $Cr_2N$ - AND THE  $Cr_2N$ /Ag-FILMS AND MECHANICAL PROPERTIES DETERMINED FROM NANOINDENTATION MEASUREMENTS, (\*) PREVIOUS INVESTIGATIONS (16-19) Table 1

Coating	$Cr_2N$ *	$Cr_2N$ -3Ag*	$Cr_2N$ -7Ag*	$Cr_2N$ -11Ag	$Cr_2N$ -15Ag*
Thickness [ $\mu m$ ]	4.3	4.2	4.3	4.7	6.3
Hardness [GPa]	$16.79 \pm 1.49$	$16.13 \pm 1.83$	$16.17 \pm 1.93$	$17.86 \pm 0.79$	$11.43 \pm 0.61$
Young's modulus [GPa]	$244 \pm 15$	$246 \pm 17$	$263 \pm 17$	$280 \pm 7$	$204 \pm 6$



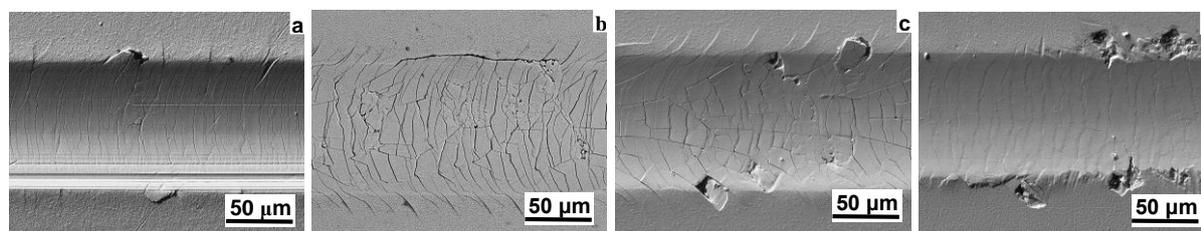
**Fig. 2** Mechanical properties determined from nanoindentation measurements of the  $Cr_2N$ - and the  $Cr_2N$ /Ag-films

Table 1 and Fig. 2 show the results from the nanoindentation measurements. The nanohardness of the pure  $Cr_2N$  was  $16.79 \pm 1.49$  GPa. The incorporation silver in  $Cr_2N$  matrix does not change the nanohardness until content of 7 wt. % of Ag. The nanohardness of the  $Cr_2N$ -11Ag film was  $17.86 \pm 0.79$  GPa and there is evident slight increase in hardness. This could be explained by refinement of the  $Cr_2N$  grains, in terms of the size of individual crystallites, in comparison with previous results of the pure  $Cr_2N$  film (20). On the other hand, the film containing 15 wt. % Ag had much lower hardness [16]. This could be attributed to silver, which is very soft in nature. Results for Young's modulus show the same tendency as for the nanohardness.

Table 2 and Fig. 3 document results from scratch-testing. All films were observed for the first symptoms of coating failure, located at a side of the scratch as abruptness of coating ( $L_{c1}$ ). It is evident, that the  $Cr_2N$  films with addition of 3 and 7 wt. % of Ag, respectively, had the best adhesion. Further increasing of content of silver led to decreasing of critical load  $L_{c1}$  and the failure became more serious. The films containing 3, 7 and 11 wt. % of Ag, respectively, had a critical load  $L_{c2}$  around 80 N. The film containing 15 wt. % of Ag had  $L_{c2} = 67.4$  N. The lowest  $L_{c1}$  (24.5 N) and  $L_{c2}$  (42.7 N) was found to be the film without silver.

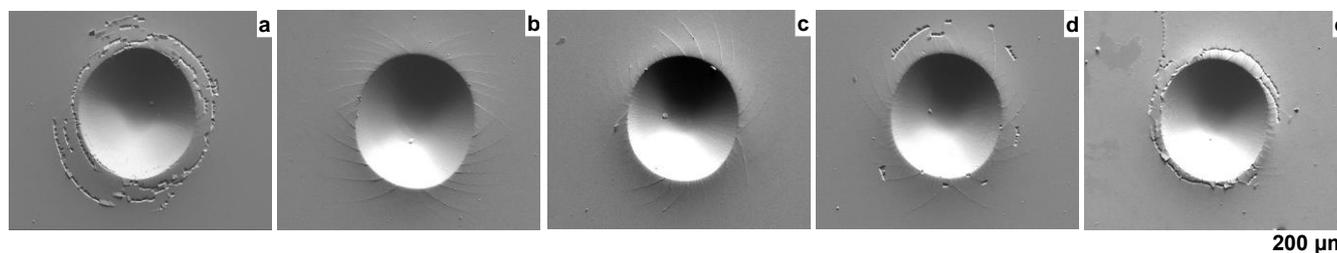
ADHESION OF THE Cr<sub>2</sub>N- AND THE Cr<sub>2</sub>N/Ag-FILMS DETERMINED FROM SCRATCH TEST, (\*) PREVIOUS INVESTIGATIONS (16-19) Table 2

Coating	Cr <sub>2</sub> N*	Cr <sub>2</sub> N-3Ag*	Cr <sub>2</sub> N-7Ag*	Cr <sub>2</sub> N-11Ag	Cr <sub>2</sub> N-15Ag*
L <sub>c1</sub> [N]	24.5 ± 1.7	46.9 ± 8.1	44.4 ± 1.6	37.1 ± 3.0	35.8 ± 2.7
L <sub>c2</sub> [N]	42.7 ± 4.4	82.6 ± 8.6	79.0 ± 2.2	80.2 ± 2.2	67.4 ± 3.8



**Fig. 3** SEM micrographs of the scratch documented critical load  $L_{c1}$ , (a) Cr<sub>2</sub>N-3Ag, (b) Cr<sub>2</sub>N-7Ag, (c) Cr<sub>2</sub>N-11Ag, (d) Cr<sub>2</sub>N-15Ag

Figure 4 documents the results from “Mercedes test”. These results were in good agreement with measurement of scratch test. The films with addition of 3 and 7 wt. % of Ag, respectively, have shown the best adhesion. Around the indents were observed cracking, but without any indications of delamination. Thus, these films could be classified as films with an adequate adhesion, mark HF 2. Around the indents of films containing 11 and 15 wt. % of Ag, respectively, were observed cracking and moreover the first delamination of the films. Film containing 15 wt. % of Ag had delamination more evident, but both of them can be classified as a films with an acceptable adhesion, mark HF 3. Finally the film without silver has been presented with considerable delamination around the indent and has been classified as HF 4.



**Fig. 4** SEM micrographs of the trails after “Mercedes test”, (a) Cr<sub>2</sub>N (b) Cr<sub>2</sub>N-3Ag, (c) Cr<sub>2</sub>N-7Ag, (d) Cr<sub>2</sub>N-11Ag, (e) Cr<sub>2</sub>N-15Ag

## CONCLUSION

The Cr<sub>2</sub>N- and the Cr<sub>2</sub>N/Ag-films were prepared by magnetron-sputter deposition method on the Vanadis 6 ledeburitic steel. The mechanical properties and the adhesion of the films have been evaluated. The main findings can be summarized as follows:

- The films were composed of the Cr<sub>2</sub>N-phase and metallic silver particles.
- The growth rate of the films is accelerated by the addition of silver into the Cr<sub>2</sub>N matrix after exceeding the content of 7 wt. % of Ag.
- The mechanical properties did not change dramatically until the content of silver achieved of 11 wt. %. Then, the both the hardness and the Young’s modulus increased, but only in limited extent. Further increasing of silver led to decreasing of mechanical properties dramatically.
- The addition of silver into the Cr<sub>2</sub>N matrix improved the adhesion and relieved the internal stresses. The best adhesion on the ledeburitic steel substrate was found for films with 3 and

7 wt. % of silver, respectively. Further increasing of silver in the Cr<sub>2</sub>N matrix led to decreasing of the adhesion.

Cr<sub>2</sub>N/Ag films are promising way to increase its tribological properties. From the point of view of the mechanical properties and the adhesion, the content of silver in the Cr<sub>2</sub>N matrix should not exceed the 7 wt. % (2.8 at. % of Ag).

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### REFERENCES

1. BERTRAND, G., SAVALL, C., MEUNIER, C. 1997. *Surface and Coatings Technology*, 96, p. 323 – 329.
2. UMEHARE, J. XU, H., KOJIMA, I. 2001. *Applications of Surface Science*, 201, p. 208 – 218.
3. PRADHAN, SK., NOUVEAU, C., VASIN, A., DJOUADI, M.A. 2005. *Surface and Coatings Technology* 200, p. 141-145.
4. HAN, S., LIN, J.H., TSAI, S.H., CHUNG, S.C., WANG, D.Y., LU, F.H., SHIN, H.C., 2000. *Surface and Coatings Technology*, 133 – 134, p. 460 – 465.
5. MERCS, D., BONASSO, N., NAAMANE, S., BORDES, J-M., CODGET, C. 2005. *Surface and Coatings Technology*, 200, p. 403-407.
6. GAHLIN, R., BRONMARK, M., HEDENQVIST, P., HOGMARK, S., HAKANSSON, G. 1995. *Surface and Coatings Technology*, 76/77, p. 174 – 180.
7. HAUERT, R., PATSCHEIDER, J. 2000. *Advanced Engineering Materials*, 2, p. 247-259.
8. ZHANG, S., SUN, D., FU, Y., DU, H. 2003. *Surface and Coatings Technology*, 167, p. 113-119.
9. HOVSEPIAN, P., MUNZ, W. 2003. *Vacuum*, 69, p. 27-36.
10. MULLIGAN, C.P., BLANCHET, T.A., GALL, D. 2010. *Wear*, 269 p. 125-131.
11. AOUDI, S.M., PAUDEL, Y., SIMONSON, W.J., GE, Q., KOHLI, P., MURATORE, C. VOEVODIN, A.A. 2009. *Surface and Coatings Technology*, 203, p. 1304 – 1309.
12. ERDEMIR, A. 2005. *Surface and Coatings Technology*, 200 p. 1792 – 1796.
13. AOUDI, S.M., BOHNHOFF, A., SODERGREN, M., MIHUT, D., ROHDE, S.L., XU, J., MISHRA, S.R. 2006. *Surface and Coatings Technology*, 201, p. 418-422.
14. KÖSTENBAUER, H., FONTALVO, G.A., KECKES, J., MITTERER, C. 2008. *Thin solid Films*, 516, p.1920-1924.
15. MULLIGAN, C.P., BLANCHET, T.A., GALL, D. 2008. *Surface and Coatings Technology*, 203, p. 584-587.
16. BOHOVIČOVÁ, J., HUDÁKOVÁ, M., JURČI, P. 2012. In: *Proceedings of the 21st Int. Conference METAL*. Brno, p.918-924.
17. JURČI, P., DLOUHÝ, I. 2011. *Applied Surface Science*, 257 p.10581-10589.
18. P. BÍLEK, P. JURČI, M. HUDÁKOVÁ, J. BOHOVIČOVÁ, J. SOBOTOVÁ. 2013. In: *Proceedings of the 22nd Int. Conference METAL 2013*. Brno, p. 886-891.
19. JURČI, P., KRUM, S. 2012. *Materials Engineering*, 19, p. 64-70.
20. BEGER, M., JURČI, P., GRGAČ, P., MECIAR, S., KUSÝ, M., HORNÍK, J. 2013. *Metallic Materials*, 51, p. 1-10.