

**COATING OF Cr-V LEDEBURITIC STEEL
WITH CrN CONTAINING 7 % OF Ag**

Pavel BÍLEK, Peter JURČI, Mária HUDÁKOVÁ, Jana BOHOVIČOVÁ

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. CrAg7N-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 coatings have an average thickness of 4.3 μm. They grew in a very well visible columnar manner, but, individual silver agglomerates were visible along the columnar crystals, also. The average size of silver agglomerates lies well below 50 nm, e.g. one can suggest that they are capable to be solved and release the Ag atoms to be migrated to the free surface during thermal exposition. The coatings had a good adhesion on the surface – the first critical loads, established by scratch-testing method, ranged between 30 and 39 N.

KEY WORDS

CrN-Ag coatings, Surface morphology, 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].

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

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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 basic CrN-compound. Silver containing transition metal nitrides films have been extensively studied in recent years [13].

The current paper deals with the development of adaptive nanocomposite CrAgN coatings on the Vanadis 6 Cr-V ledeburitic tool steel. It describes and discusses the microstructure and the basic coating characteristics like hardness, Young's modulus and adhesion for coating with 7 % content of silver.

EXPERIMENTAL

The substrate material was the PM ledeburitic steel Vanadis 6 with nominally 2.1 % C, 1.0 % Si, 0.4 % Mn, 6.8 % Cr, 1.5 % Mo and 5.4 % V and Fe as a balance and soft annealed to a hardness of 21 HRC.

The samples used for the investigation 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 temperature 530 °C) to final hardness of 60 HRC and then finely ground and polished with diamond suspension up to a mirror finish.

The conditions for CrN/Ag-coatings were reported elsewhere [14]. The output power on the Cr cathode was 5.8 kW and that on the Ag cathode was 0.21 kW.

The measurement of roughness was carried out on mirror finish samples and on samples with coatings by laser scanning confocal microscope Zeiss LSN 700. The analyses of the substrate microstructure, PVD-coatings investigation and the fractography were carried out using a JEOL JSM-7600F field emission scanning electron microscope (SEM) in BE-detection regime. Energy dispersive spectroscopy (EDS) was done on the same device at an accelerating voltage of 20 kV and standard working distance of 15 mm. For the examinations of the substrate, standard metallographic specimens were prepared and etched with Villela-Bain reagent. PVD layers were prepared for observation via a special method based on deep cooling of the samples in liquid nitrogen and subsequent breaking.

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 Nanohardness tester TTX 2 CSM Instruments equipped with a Berkovich indenter. The indentation depth was kept to 10 % 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 coating was 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. A standard Rockwell diamond indenter with a tip radius of 200 μm was used. Five measurements were made on each specimen and the mean value and standard deviation of adhesion represented by the L_{c1} , L_{c2} , L_{c3} and L_{c4} critical loads, respectively, was calculated. The critical loads were determined by recording the signal of acoustic emission as well as by viewing the scratches on the SEM micrograph. The L_{c1} critical load corresponding

to the occurrence of the first inhomogeneities in the coating. The L_{c2} and L_{c3} corresponding to another damages on the edge of the track. And finally the L_{c4} critical load was determined as the load when all of the coating was removed from the substrate.

RESULTS AND DISCUSSION

The microstructure of the substrate material after applied heat treatment is shown in Fig. 1. The material consists of a matrix with fine carbides uniformly distributed throughout the matrix. SEM micrograph (Fig. 1a) shows that the matrix is formed with fine tempered martensite. The EDS-maps of chromium and vanadium (Fig. 1b and 1c) show that the carbides are of two basic types. Large particles, having a size up to $2\ \mu\text{m}$, are the M_7C_3 carbides, and the finer formations are the MC carbides. It was recently established at [15,16] that M_7C_3 phase is chromium based that underwent dissolution in the austenite during heat processing, being responsible for the saturation of the austenite with carbon and alloying elements, which leads to high hardness of as-heat-treated material. Almost whole amount of MC phase remained undissolved. After the heat treatment, the average hardness of the material was $60 \pm 0,3$ HRC and the roughness of surface before and after deposition was $R_a < 0,01\ \mu\text{m}$.

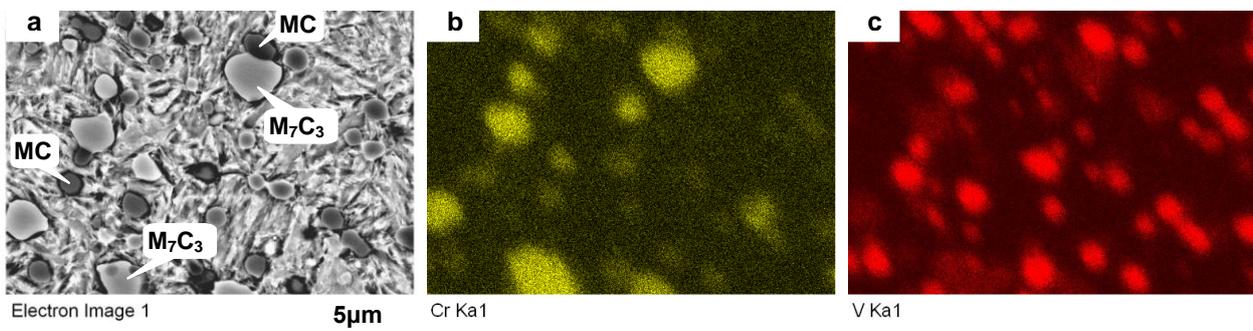


Fig. 1 Microstructure of PM ledeburitic steel Vanadis 6 substrate after heat treatment: a-overview (SEM-BSE), b-EDS map of chromium from Fig. 1a, c-EDS map of vanadium from Fig. 1a.

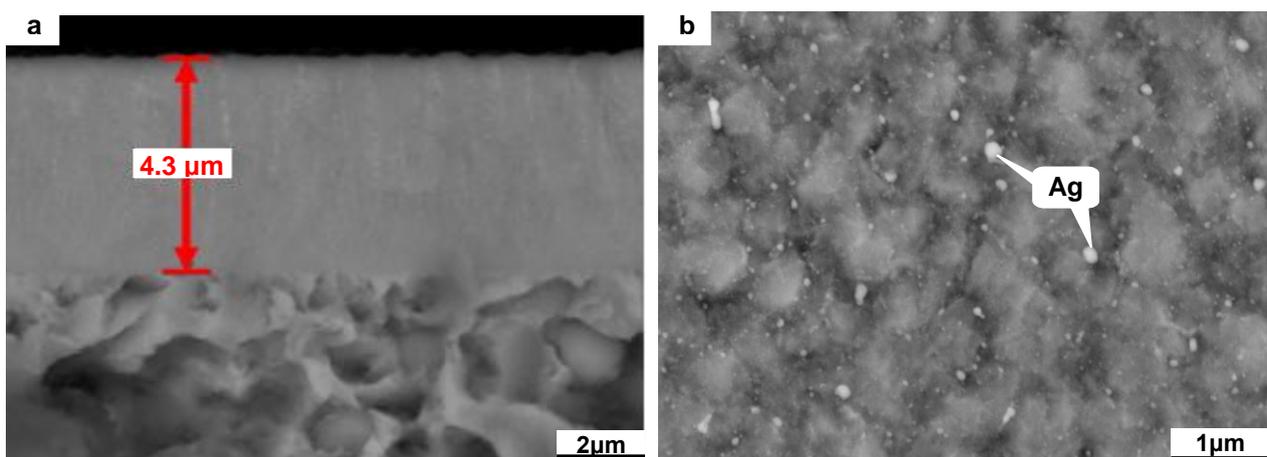


Fig. 2 SEM micrographs showing the microstructure of CrAg7N coating: a-fracture, b-surface overview with Ag particles.

The thickness of CrAg7N coating was $4.3\ \mu\text{m}$ (Fig. 2a). The film grew in a well visible columnar manner. This type of layer growth is typical for magnetron-sputtered CrN films at a

wide range of processing parameters, as reported previously [17]. This result is in a good agreement with reported results at [14]. The addition of 7 % Ag into the CrN does not change the commonly known columnar morphology of such types of films and in addition, the thickness of the film was practically the same as that of the pure CrN and coatings with 3 % of Ag [14]. SEM micrograph in Fig. 3a, made from the fracture of coating in the BE-detection regime, and corresponding EDS mapping of Cr, respectively Ag, Fig. 3b, respectively Fig. 3c show that silver forms individual grains along columnar manner and on the surface (Fig. 2b) at higher concentration. The average size of silver agglomerates lies well below 50 nm. Various authors have reported [18, 19] that individual silver agglomerates along the columnar crystals are capable to be solved and release the Ag atoms to be migrated to the free surface during thermal exposition and it could be responsible for self-lubrication effect (Fig. 3b and 3c).

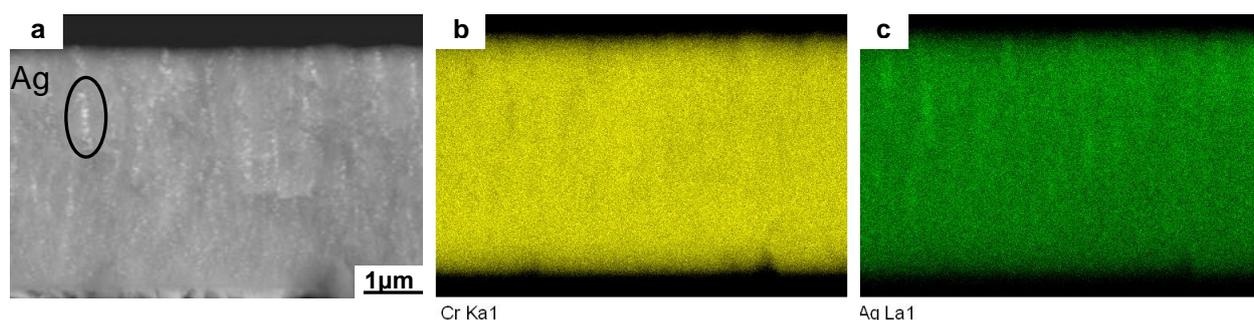


Fig. 3 SEM micrograph of fracture of CrAg7N coating: a-detail with Ag particles, b-EDS map of chromium from Fig. 3a, c-EDS map of Silver from Fig. 3a.

The nanohardness of CrAg7N coating was 16.17 ± 1.93 GPa. This value is comparable to early reported results [14] for pure CrN and coating with 3 % of Ag, how it is see in Table 1. Silver is very soft and could cause softening of the coating. However, no substantial effect of Ag addition on hardness was observed.

Similar behaviour can be found for measurement of Young's modulus E , Table 1. With addition 7 % of Ag in CrN coating Young's modulus little increase, but this difference could be explains by standard deviation of measurement and higher deposition temperature in comparison with previously work [14]. However, this slight increase in E is rather surprising because normally, a decrease of E is expected with an Ag – addition. Further examinations are required to better clarify this phenomenon.

MECHANICAL PROPERTIES DETERMINED FROM NANOINDENTATION MEASUREMENTS, VALUES FOR CrN AND CrAg3N ARE FROM PREVIOUS WORK

Table 1

Coating	Hardness [GPa]	Young's Modulus [GPa]
CrN	16.79 ± 1.49	244 ± 15
CrAg3N	15.97 ± 1.44	241 ± 9
CrAg7N	16.17 ± 1.93	263 ± 17

After the scratch test, the failure of CrAg7N coating is with semi-circular tensile cracking (Fig. 4a), results documented Table 2. The coatings show a very brittle behaviour. Even at the beginning of track are many cracks visible, but the coating is stable and has a good adhesion. The first inhomogeneities accompanied with the signal of acoustic emission occurred at a load 34.5 N (L_{c1}), (Fig. 4b). With increasing load more damages on the edge of track are visible, L_{c2} (Fig. 4c) and at load 52.9 N (L_{c3}) (Fig.4c) occurred break substrate through the coating on

the edge of the track. At the load 79 N all coating is removed from surface of substrate as documented SEM micrograph in BE-detection regime (Fig. 5a). Corresponding EDS maps of chromium (Fig. 5b), silver (Fig. 5c), iron (Fig. 5d) and vanadium (Fig. 5e) show an interface where CrAg7N coatings crossing to substrate, steel Vanadis 6. On the surface of coating after exposure are visible crushed particles of Ag (Fig. 5f), which are probably responsible for better friction properties.

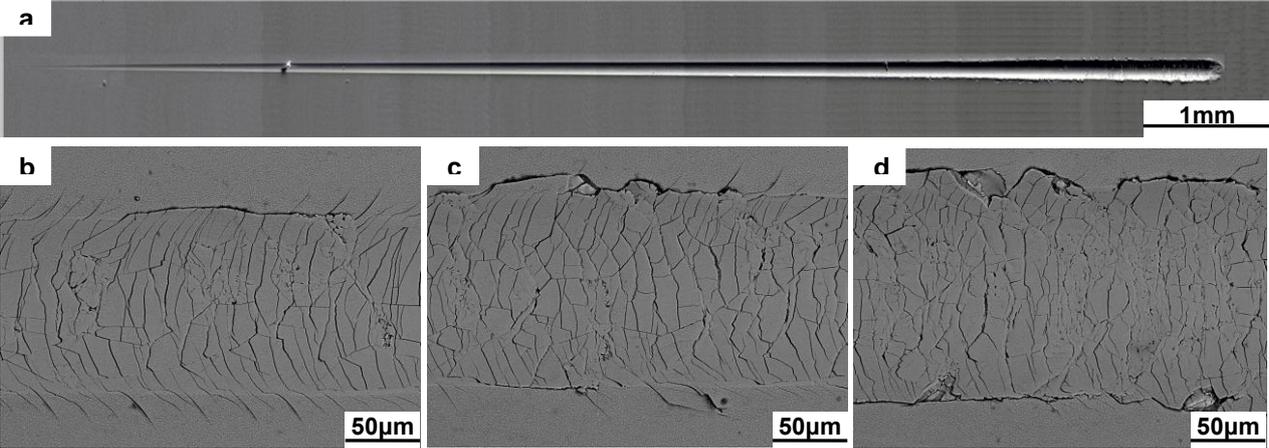


Fig. 4 Electron microscopy showing the failures after scratch testing: a-overview, b- L_{c1} , c- L_{c2} , d- L_{c3} .

ADHESION PROPERTIES DETERMINED FROM SCRATCH TEST Table 2

Coating	L_{c1} [N]	L_{c2} [N]	L_{c3} [N]	L_{c4} [N]
CrAg7N	34.52 ± 3.31	44.36 ± 1.58	52.85 ± 1.62	79.04 ± 2.19

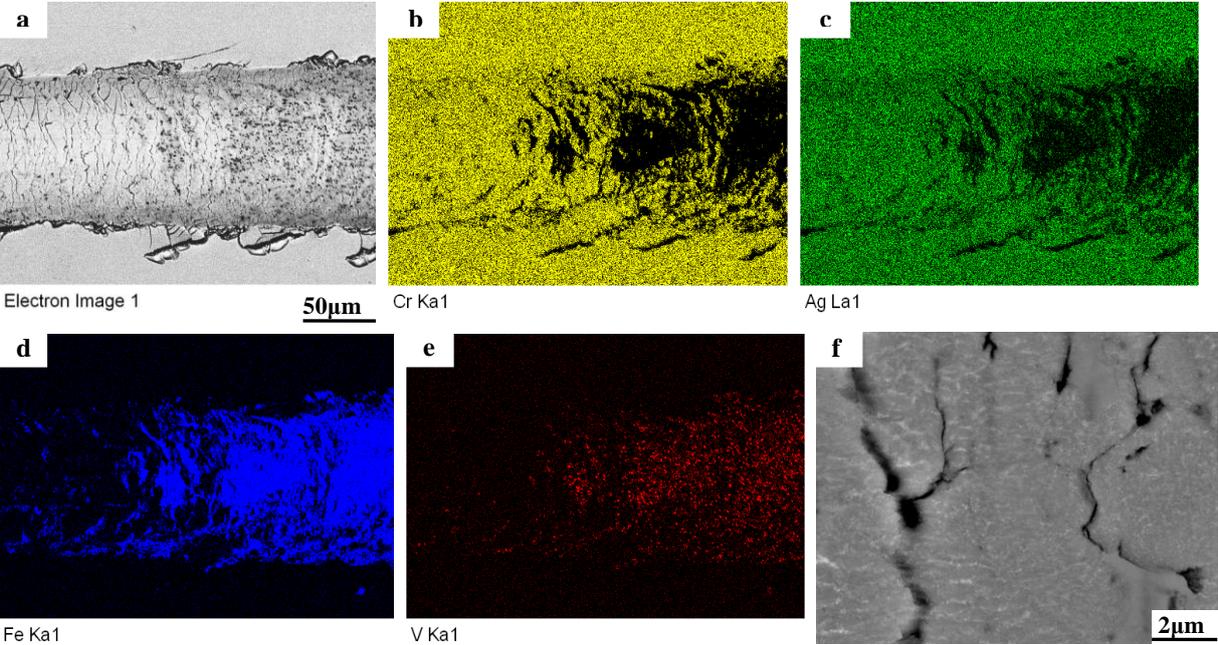


Fig. 5 Electron microscopy showing the failures after scratch testing: a- L_{c4} , b-EDS map of chromium from Fig. 5a, c-EDS map of silver from Fig. 5a, d-EDS map of iron from Fig. 5a, e-EDS map of vanadium from Fig. 5a, f-surface after test.

CONCLUSIONS

The effect of magnetron-sputtered CrAg7N-coatings on the mechanical behaviour of ledeburitic tool steel has been evaluated and an evaluation of the mechanical properties of the substrate/coating complex was done. The main findings can be summarized as follows: Coating deposited on the substrate grew in a typical columnar manner and had a thickness 4.3 μm . On the surface of coating and along the columnar crystal were visible individual silver particles with the size below 50 nm.

The addition of 7 % of Ag into the CrN film does not influence the hardness of the CrN negatively. On the other hand, the Young's modulus has been established to be slightly higher than that of CrN or CrAg3N, which can be considered as rather surprising, because an opposite effect could have been expected.

The adhesion of CrAg7N film can be evaluated as very good. This can be attributed to a good capability of the soft Ag particles to absorb the plastic energy, which makes it more resistive against delamination.

CrAgN coating of PM Cr-V ledeburitic steel Vanadis 6 is a very promising way to increase its tribological properties at intermediate temperature. The addition of 7 % of silver brings good adhesion properties without effect on hardness of coatings. More tribological test of that coating is required.

ACKNOWLEDGEMENTS

This publication is the result of the project implementation: CE for development and application of advanced diagnostic methods in processing of metallic and non-metallic materials, ITMS:26220120048, supported by the Research & Development Operational Programme funded by the ERDF. This research was supported by the grant project VEGA 1/1035/12.

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