Surface & Coatings Technology 465 (2023) 129594

Contents lists available at ScienceDirect

Surface & Coatings Technology

journal homepage: www.elsevier.com/locate/surfcoat

High temperature friction and galling properties of nanolayered (Cr,V)N coatings and effect of V content

B. Podgornik [a,*], M. Sedlaček [a], B. Šetina Batič [a], M. Čekada [b]

[a] Institute of Metals and Technology, Lepi pot 11, 1000 Ljubljana, Slovenia
[b] Institute "Jožef Stefan", Jamova c. 39, 1000 Ljubljana, Slovenia

ARTICLE INFO

Keywords:
(Cr,V)N coating
Galling
High-temperature tribology
Hot forming
Self-lubrication

ABSTRACT

Chromium nitride (CrN) coating is considered as one of the best candidates for wear protection in many forming application where adhesive wear and galling dominate. However, its relatively high coefficient of friction against soft metals hinders its applicability. Vanadium nitride (VN), on the other hand has attracted increasing interest as VN is easily oxidized to form Magneli phase vanadium oxides with easy slipping shear planes, on one hand leading to self-lubricating properties but also to deteriorated wear resistance. This can be overcome by forming CrVN coatings. However, there is a lack of information how such coatings perform in terms of galling resistance and V-concentration in typical forming conditions and against soft metals.

Therefore, the aim of this work was to study friction properties of nano-layered PVD (Cr,V)N coatings at room and elevated temperature and how V-content influences on friction and galling resistance against typical work materials. Nanolayered (Cr,V)N coatings with V in concentrations from 15 to 30 % were deposited by industrial DC magnetron sputtering system and tested using Load-Scanner against AA2024 aluminum alloy and low-carbon steel at room and elevated temperature of 300 °C and 600 °C, respectively. Results were evaluated in terms of coefficient of friction level and stability, critical loads for galling initiation and volume of adhered work material. Results show that (Cr,V)N coatings do not necessarily improve galling resistance, being strongly dependent on V concentration and contact temperature. For forming Al alloys positive results are obtained with coatings containing 20–25 at.% V and for low-carbon steels above 25 at.%, with marked improvement obtained only at elevated temperatures.

1. Introduction

Manufacturing, including materials production, machining and metal-forming is responsible for about 28 % of global green-house gas (GHS) emissions [1] and has a large environmental impact [2]. It is the largest material and energy using sector, requiring large amount of energy at every production step, from the excavation of ore, materials production, manufacturing, assembly, recycling and disposal [3]. It accounts for approximately 37 % of global GHG emissions associated with required energy production [1]. Manufacturing also produces large volume of waste, both in production including lubricants, cutting and cooling fluids, etc. and at the end-of-life disposal. Due to increase in industry demands and society needs the global consumption of materials, energy needs, emissions and waste are likely to double if the current trends continue [4]. In order to move toward green, environmentally friendly production, with the metal-forming representing a huge part we need to eliminate or at least reduce use of hazardous lubricants, improve wear resistance and prolong life-time of tools as well as reduce energy consumption by reducing friction.

Metal-forming, especially hot-forming is a very demanding operation, with the tools being exposed to a complex combination of cyclic thermal, mechanical, chemical, and tribological loads [5], which result in different wear mechanisms influenced by a variety of parameters [6]. However, tool life in hot-forming is greatly affected by abrasive wear and adhesive wear, also known as galling [7]. More than 70 % of tools fail due to abrasive wear and galling [5]. Oxide layers formed on the work-piece surface and constant flow of "fresh" work-piece material into the contact result in the generation of hard abrasive particles and abrasive wear while high contact temperatures, which can exceed 600–700 °C affect tool hardness and contact surface reactivity, especially against soft metals causing galling [8]. Thus, the key factor affecting the efficiency of tools and consequently the quality and

* Corresponding author.
E-mail address: bojan.podgornik@imt.si (B. Podgornik).

https://doi.org/10.1016/j.surfcoat.2023.129594
Received 19 December 2022; Received in revised form 28 April 2023; Accepted 1 May 2023
Available online 7 May 2023

properties of the produced parts is the thermo-mechanical and tribological interaction between the tool surface and the work-piece material. To overcome abrasive wear, the tool surface should be hard and to overcome galling it should be lubricious across a broad temperature range.

Wear resistance of tools is traditionally improved by using tool steels with better fracture toughness vs. hardness ratio, more efficient lubrication and better tool design [9]. However, tool wear and galling resistance can be further enhanced by different surface engineering processes and techniques, including thermo-chemical processes, laser surface texturing, deep cryogenic treatment and especially by hard coatings [10]. Traditional hard coatings like TiN, TiAlN and CrN, greatly outperform tool and high speed steels when it comes to cutting and cold-forming, especially under starved lubrication and dry conditions [11]. However, at elevated temperatures and against soft metallic materials they show a relatively high coefficient of friction and a high tendency for galling [12]. In order to move forward, to green, lubricant-free or near-lubricant-free production we need different approach. Surfaces with high hardness, high temperature resistance and low friction across a broad temperature range are required, i.e. high-temperature self-lubricating wear resistant coatings [13].

As mentioned, typical hard ceramic coatings show high friction and high adhesion tendency against soft metals, which may result in severe adhesive wear and galling of coated tool if not lubricated [14]. On the other hand, Diamond-Like Carbon (DLC), hard amorphous carbon thin films and MoS_2-based hard coatings show excellent wear, anti-galling and self-lubricating properties in many different machine component, machining and cold-forming applications [15]. However, in spite of excellent tribological properties at room temperature DLC coatings lose their tribological performance at temperatures above 300 °C [16], while low thermal and thermo-dynamical stability of MoS_2 makes the processing and stability of self-lubricating MoS_2-composites rather difficult at high temperatures [17]. Adding a third element to transition metal nitride coatings is an effective method to further improve their mechanical properties and oxidation resistance [18], but can also affect their self-lubricating performance through the formation of high-temperature lubricious oxides [19]. In this respect, vanadium nitride (VN) has attracted increasing interests as VN is easily oxidized above 500 °C to form Magnéli phase vanadium oxides (V_2O_5) with easy slipping crystallographic shear planes and a low melting point (around 670 °C), leading to self-lubricating behavior [20]. On the other hand, the intensive oxidation of VN and out-diffusion of V at elevated temperatures, combined with tribo-chemical reactions considerably deteriorates coating wear resistance [21]. However, combining addition of vanadium to CrN coating to form (Cr,V)N [22] and multilayering [23] have proven to be an efficient way to simultaneously improve coating's tribological performance and strength at high temperatures.

Although, quite a few investigations on the effect of nanolayering and V content for (Cr,V)N coatings have been carried out in the last decade, they are mostly focused on oxidation resistance [19,24] and abrasive wear, deermined by a pin-on-disc tribometer against ceramic counter-material, either at room temperature [23,25,26] or very high temperatures of up to 900 °C [22]. There is a lack of information how these coatings perform in terms of galling resistance in typical hot-forming conditions and against soft metals. Therefore, the aim of this work was to study friction properties of nano-layered PVD (Cr,V)N coatings at room and elevated temperature range of 300 °C to 600 °C and how V-content influences on friction and galling resistance against a typical work material (i.e. aluminum alloy and low-carbon steel).

2. Experimental details

2.1. Material and coatings

Steel used in this investigation as a reference and substrate material was commercially available hot work tool steel AISI H11 (wt%, 0.37 % C, 1.0 % Si, 0.38 % Mn, 5.15 % Cr, 1.30 % Mo, 0.40 % V) from SIJ Metal Ravne d.o.o., Slovenia, commonly used in hot-forming applications. From the material delivered in forged and soft annealed condition cylindrical specimens (ϕ10x100 mm) were prepared by turning and grinding. Specimens were then vacuum heat treated according to steel producer specifications (austenitization @1020 °C for 20 min, quenched in N_2 gas @ 1.05 bar and 3 °C/s, and double 2 h tempered @580 °C) to hardness of 50 HRC (525 HV) and surface polished to average surface roughness Ra = 0.15 μm.

Coatings deposition was performed by DC magnetron sputtering in a CC800/9 (CemeCon) industrial unit equipped with four unbalanced magnetron sources, arranged in the corners of a chamber. By using one chromium, one vanadium and a pair of Cr/V triangular targets (Fig. 1) set of four nanolayered CrN/(Cr,V)N/VN coatings with varying Cr and V content (varying along the chamber's vertical axis) were deposited in a single process. The chromium and vanadium concentration varied from 39 to 30 at.% and 16 to 27 at.%, respectively (Table 1). Steel cylinders were mounted on a three-fold rotating substrate holder thus assuring nanolayered coatings with a uniform layer thickness distribution (~10 nm). A binary CrN coating was also deposited in the same unit using only Cr targets and used as a reference. Prior to the deposition all the samples were ultrasonically cleaned and sputter-etched for 75 min (bias 650 V, pressure 0.35 Pa, mixed argon and krypton atmosphere, as recommended by the equipment producer to make the process more stable). Coating deposition was carried out at the substrate temperature of 450 °C, the total operating pressure of 0.5 Pa, target power 2.5 kW, bias 120 V, cathode voltage 400 V, and the flow rates of nitrogen and argon of 80 and 200 ml/min, respectively.

In tribological-galling tests two typical work materials in the form of cylinders (ϕ10x100 mm) were used as a counter material. First one was normalized low carbon steel S235J2 used for welding constructions and hot forming with a hardness of 135 HB (142 HV) and average surface roughness Ra of about 1 μm. The other was high strength AA2024 Aluminum alloy in T4 condition with a hardness of 155 HB (163 HV) and a similar average surface roughness Ra of 1 μm, which is commonly extruded and widely used in aircraft industry.

2.2. Tribological testing

Tribological testing was performed under progressively loading dry sliding conditions using load scanning test rig (Fig. 2), aimed at simulating galling damage in hot-forming. The test configuration involves two crossed cylinders (ϕ10x100 mm) which slide against each other at an angle of 45° under a constant speed and gradually increasing normal load, obtained by spring based system. Through specific setup each point along the contact path of both cylinders corresponds to a unique load without any pre-loading history and with fresh surfaces constantly coming into the contact. This allows analysis of the coefficient of friction and wear as a function of the applied load as well as determination of critical loads for galling initiation and transfer layer build-up [27].

In the current investigation upper coated or uncoated hot-work tool steel cylinder was representing stationary tool loaded against a moving lower cylinder made out of work material. Sliding speed was set to 0.01 m/s and load range from 200 to 1400 N, resulting in substantial plastic deformation of both work materials. First set of experiments was done at room temperature and relative humidity of about 50 %. Second set was executed at elevated temperatures. In the case of galling tests against S235J2 low-carbon steel, coated cylinder was heated to 150 °C, as typically used in forming applications and low-carbon steel cylinder to 600 °C by using heating elements installed in the specimen holders. In the case of AA2024 alloy, lower Al cylinder was heated to 300 °C and upper coated one again to 150 °C.

Before testing both specimens were ultrasonically cleaned in ethanol and dried in hot air. For each material combination and testing conditions at least three parallel tests on three different specimens were performed to obtain statistically relevant data. During testing coefficient

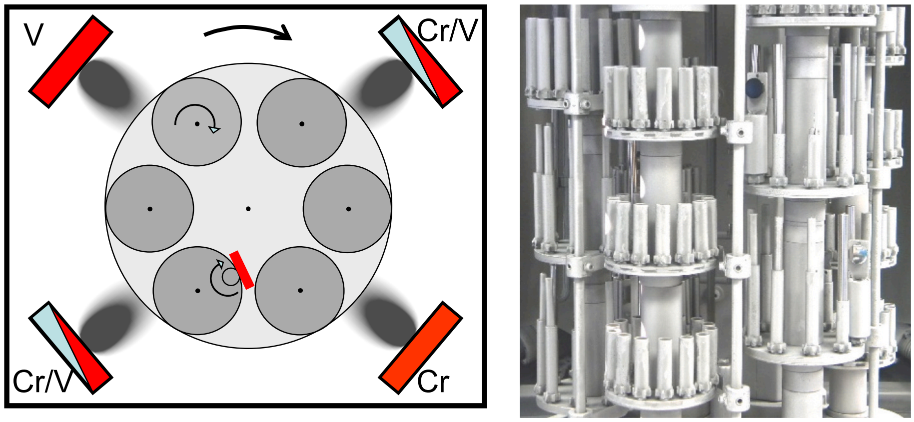


Fig. 1. DC magnetron sputtering targets distribution and deposition layout.

Table 1
Characteristics of the deposited (Cr,V)N coatings.

Coating	V_{EDS} [at.%]	Cr_{EDS} [at.%]	t [μm]	Ra [μm]	Lc [N]	HV
CrN	0	50	3.0	0.168	94	1800
CrVN-1	15.9	38.9	3.2	0.216	90	2060
CrVN-2	19.5	35.9	2.9	0.214	88	2120
CrVN-3	23.1	32.8	2.5	0.208	87	2240
CrVN-4	26.7	29.8	1.9	0.226	89	2380

of friction, normal load and position were recorded continuously and wear tracks analyzed after the completion of the test.

2.3. Wear tracks analysis

Wear track analysis involved measurement of the volume of adhered work material using optical 3D focus-variation measuring instrument, Alicona InfiniteFocus G4 and subtraction method (material above the reference plane of unworn coated cylinder). SEM/EDS analysis of the wear tracks was performed in FIB-SEM microscope Zeiss Crossbeam 550, Germany, equipped with EDS detector (EDAX, Octane Elite). Specific sections of the wear track were removed from the coated specimen surface by first performing rough removal (30 keV/20 nA) and finishing by fine polishing (30 keV/2 nA) in order to perform EDS depth analysis and obtain EDS depth maps. The X-ray photoelectron spectroscopy (XPS) of the selected wear tracks was performed using a PHI VersaProbe XPS spectrometer (Physical Electronics) equipped with a monochromatic Al Kα X-ray source. The XPS spectra were analyzed using the CasaXPS [28] software. The spectra were calibrated using the C 1 s peak of the adventitious carbon as a reference, and the Shirley background subtraction method was used to remove the background signal. The peak fitting was performed using a mixed Gaussian-Lorentzian function and ref. [29] used to perform deconvolution of the relevant peak components.

3. Results and discussion

3.1. Coatings characteristics

Coatings composition determined on the FIB cross-sections using HR-EDS, thickness (standard CSEM calotest), average surface roughness (Alicona Infinite Focus G4 optical 3D focus-variation instrument), adhesion critical load (Revetest Scratch tester) and HV microhardness are provided in Table 1. The reference binary CrN coating with a typical columnar structure had a thickness of 3.0 μm, hardness of about 1800 HV, average surface roughness of 0.17 μm and critical load for a rapid increase in the scratching force of 94 N. In the case of (Cr,V)N coatings, although having nanolayered structure they all show more of a single layer character without sharp interfaces and distinctive changes in composition between layers (Fig. 3), as shown by HR-EDS mapping and line scan analysis (Fig. 4). However, depending on the specimen's vertical position in the deposition chamber concentration of V and Cr varied between the four (Cr,V)N coatings deposited (Table 1). Vanadium content has been increased from 16 to 27 at.%, corresponding to reduced Cr concentration (from 39 to 30 at.%), while nitrogen concentration of about 45 at.% was detected in all coatings. (Cr,V)N coating with the lowest concentration of V (15.9 at.%; CrVN-1) displays the largest thickness of about 3.2 μm, average surface roughness of 0.22 μm and microhardness of about 2060 HV. Increase in V concentration on one hand results in reduced coating thickness but on the other hand in increased coating hardness, as shown in Table 1 and also reported by V. Perfiljev et al. [30]. For the highest concentration of V (CrVN-4; 26.7 at.%) coating thickness was 1.9 μm, average surface roughness 0.23 μm and microhardness almost 2400 HV. The difference in coating thickness can be explained by different sputtering yield of Cr and V, being approx. 2.5 times higher for the chromium (16.7 nm/min) than for the vanadium

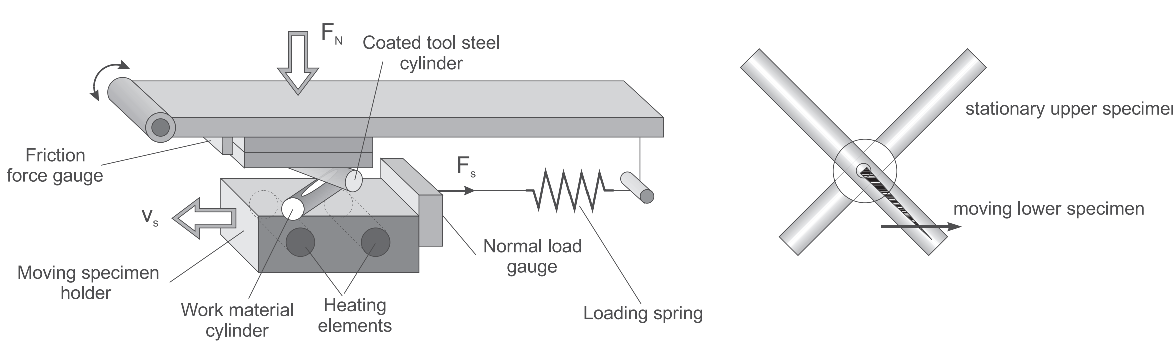


Fig. 2. Load-scanning test configuration.

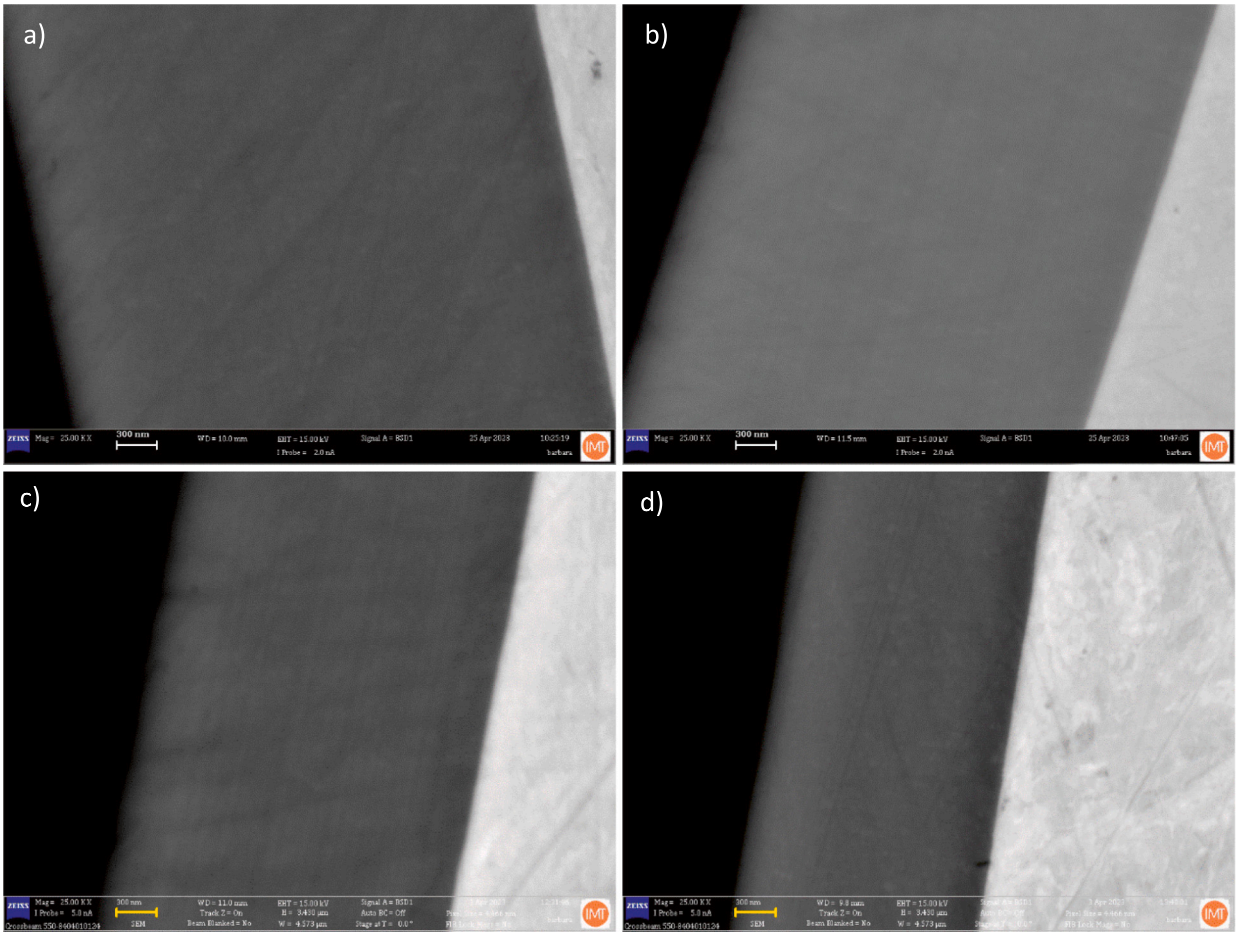


Fig. 3. SEM micrographs of polished (Cr,V)N coatings cross-sections; (a) CrVN-1, (b) CrVN-2, (c) CrVN-3 and (d) CrVN-4.

(6.0 nm/min) [19]. However, all (Cr,V)N coatings show acceptable adhesion, evaluated by measuring the critical loads for rapid increase in the scratching force (Lc ≈ 90 N), similar columnar structure with reduced grain size trend and granular surface morphology (Fig. 5), as the V-concentration increases. As indicated by XRD analysis (not shown here), all (Cr,V)N coatings crystallized in a face-centered-cubic lattice with a B1 (NaCl) structure and in the form of solid solution, as also reported by others [19,24,26].

3.2. Room temperature tests

Results for room temperature galling tests are shown in Figs. 6 and 7. When tested against low-carbon steel (Fig. 6a) hardened hot-work tool steel shows initial friction of about 0.15 at 200 N load, which then gradually increases with load up to about 0.25 at the maximum load of 1400 N. The same is true for the volume of work material adhered to the tool steel surface, which is gradually increasing with load (Fig. 6b); from $6.5\cdot10^2$ μm^3/mm^2 to $7.5\cdot10^2$ μm^3/mm^2. More severe galling, indicated by sharp increase in friction is observed at loads above 1150 N. Binary CrN coating shows similar friction level and behavior, but higher galling tendency, with first signs of severe galling observed at a load of 1000 N and volume of adhered material as compared to uncoated tool steel being increased for up to 15 %, especially at high loads. CrVN-1 coating, containing 16 at.% of V shows much more unstable friction, fluctuating between 0.3 and 0.45 and about 20 % increased amount of adhered work material. Increased galling tendency is clearly seen for the whole load range investigated (Fig. 8b). Increasing V-content from 16 to 23 at.% has more or less negative effect, showing very unstable friction and increasing amount of adhered work material. However, by increasing V-content to 27 at.% (CrVN-4) very stable coefficient of friction between 0.15 and 0.2 is obtained up to the load of 1200 N and the smallest amount of work material adhered to the coated surface in the initial stages of sliding (<$6.0\cdot10^2$ μm^3/mm^2; Fig. 8c). Although quite high loads were used during galling tests (200–1400 N), no coating cracking, spallation or flaking were observed within the wear tracks, as shown in Fig. 9, regardless of the coating and V-content used. As confirmed by Fig. 9, the main wear mechanism is adhesive wear, with low carbon steel transfer and adhesion mainly starting at the coating's imperfection sites. Therefore, changes in galling resistance cannot be related to coating failure but more to the coating composition, higher hardness and especially smoother topography (Fig. 5).

In the case of room temperature tests against aluminum alloy friction behavior among different coatings is more similar, as shown in Fig. 7a. For all surfaces coefficient of friction in the investigated load range (200–1400 N) is between 0.2 and 0.25. However, while uncoated hot-work tool steel shows relatively stable friction and up to $7.5\cdot10^2$ μm^3/mm^2 of adhered work material, binary CrN and especially CrVN-1 coating with the lowest V-content have more unstable friction and between 20 % and 40 % higher galling tendency, as indicated by increased volume of adhered work material (Fig. 7b). By increasing V-concentration in the (Cr,V)N coatings galling resistance improves, with V-content of 20 at.% (CrVN-2) providing the most stable friction and the least amount of aluminum alloy adhered on the coating surface (~$6.0\cdot10^2$ μm^3/mm^2). However, as the V-concentration in the (Cr,V)N coating exceeds 25 at.% (CrVN-4) coefficient of friction again gets unstable and adhesion of work material picks up, reaching volume as high as $11.5\cdot10^2$ μm^3/mm^2 (Figs. 7b and 8d). Again no coatings failure in the form of cracking, spallation or flaking could be detected (Fig. 10).

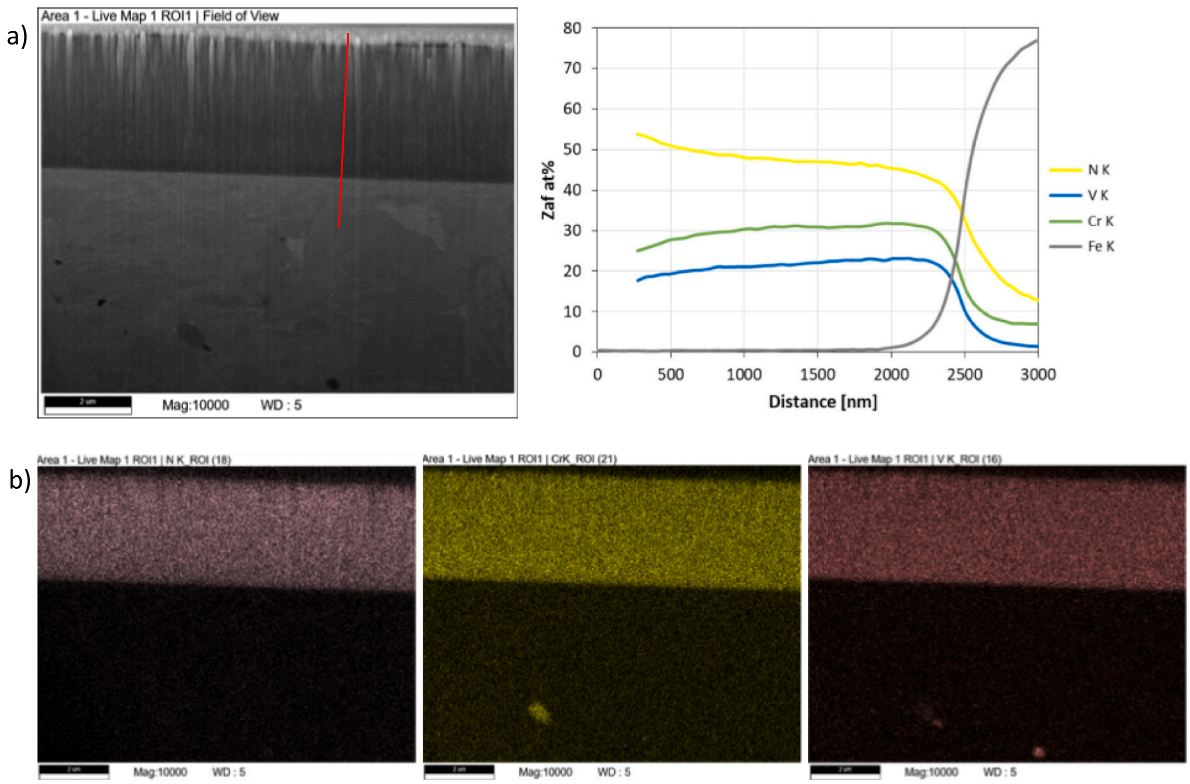


Fig. 4. (a) EDS Line profile and (b) EDS mapping for CrVN-3 coating.

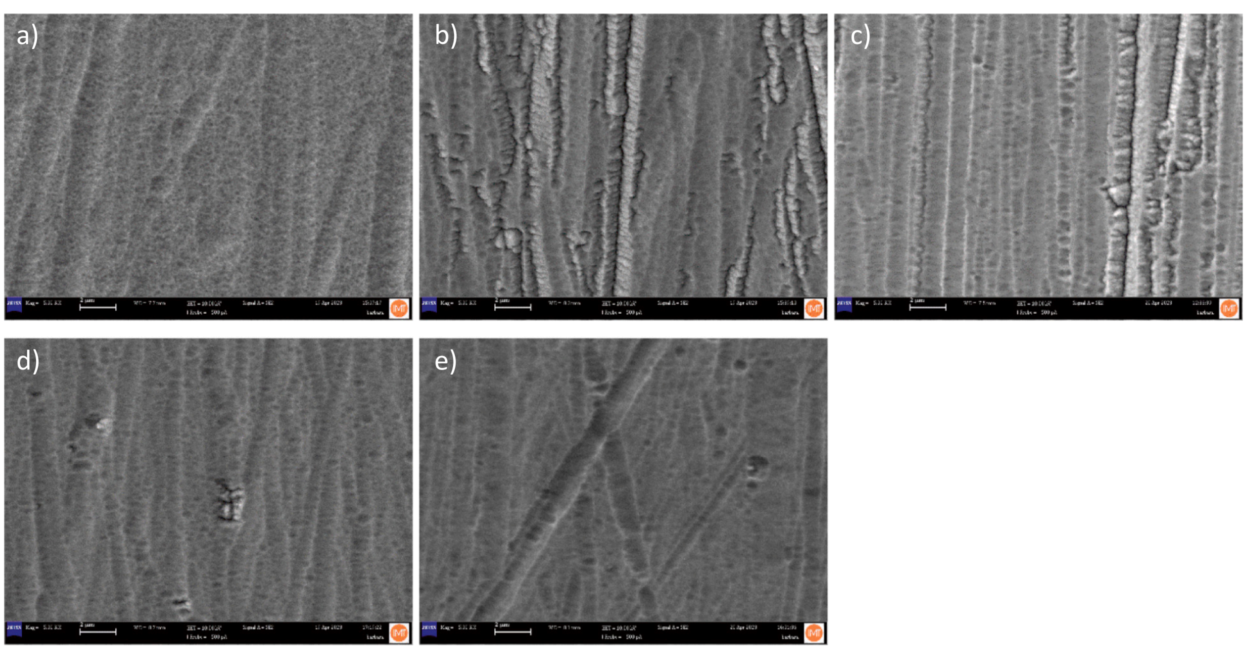


Fig. 5. Surface structure of (a) CrN, (b) CrVN-1, (c) CrVN-2, (d) CrVN-3 and (e) CrVN-4 coatings.

In agreement with work of L. Aissani et al. [31] and V. Perfilyev et al. [30] addition of V in high concentrations (~30 at.%) improves anti-galling properties of CrN coating at room temperature. This could be associated with the formation of some lubricious oxides on the surface. However, beside adhered work material and negligible surface oxidation wear track analysis (EDS and XPS) didn't show formation of any lubricious oxides. Therefore improved properties of (Cr,V)N coatings can be mainly related to higher hardness, toughness and smoother surface of the high V-containing coatings, which result in decreased adhesion and consequently to lower static and kinetic friction forces as well as the amplitude of the stick-slip behaviouor [30]. Regarding the effect of work material, as compared to low-carbon steel, aluminum alloy is very prone to galling, it experiences larger plastic deformation rates and shows lower strain hardening rate [32]. This resulted in a strong adhesion and formation of continuous layer of adhered work material on the coating surface (Fig. 10), thus masking the effect of V

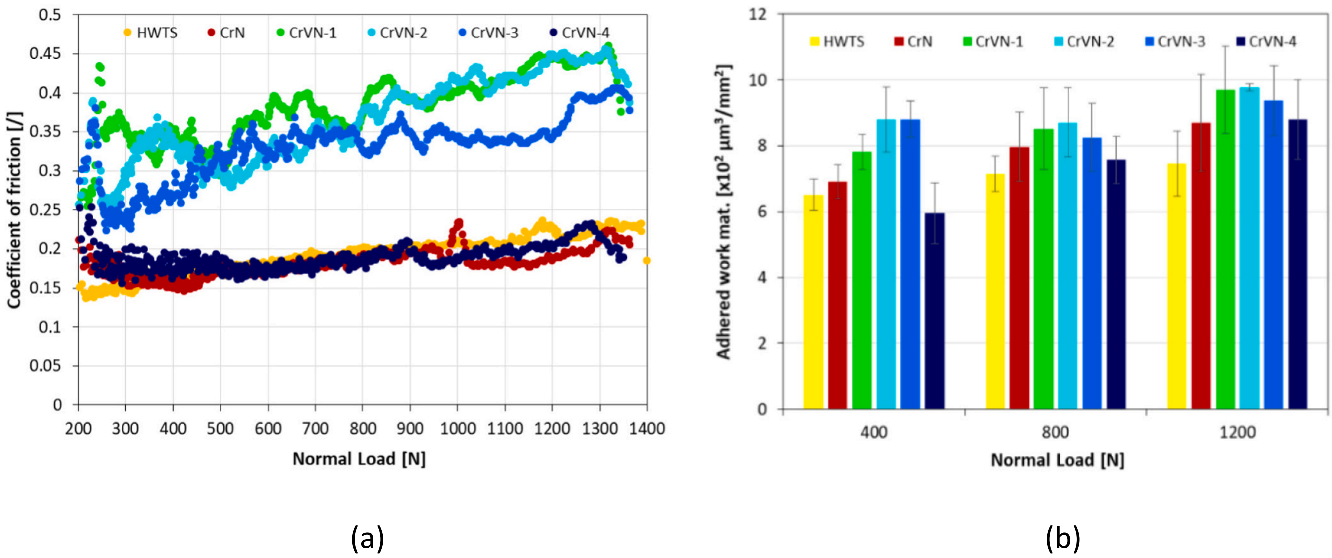


Fig. 6. (a) Coefficient of friction as a function of load and (b) volume of adhered work material for RT tests against low-carbon steel.

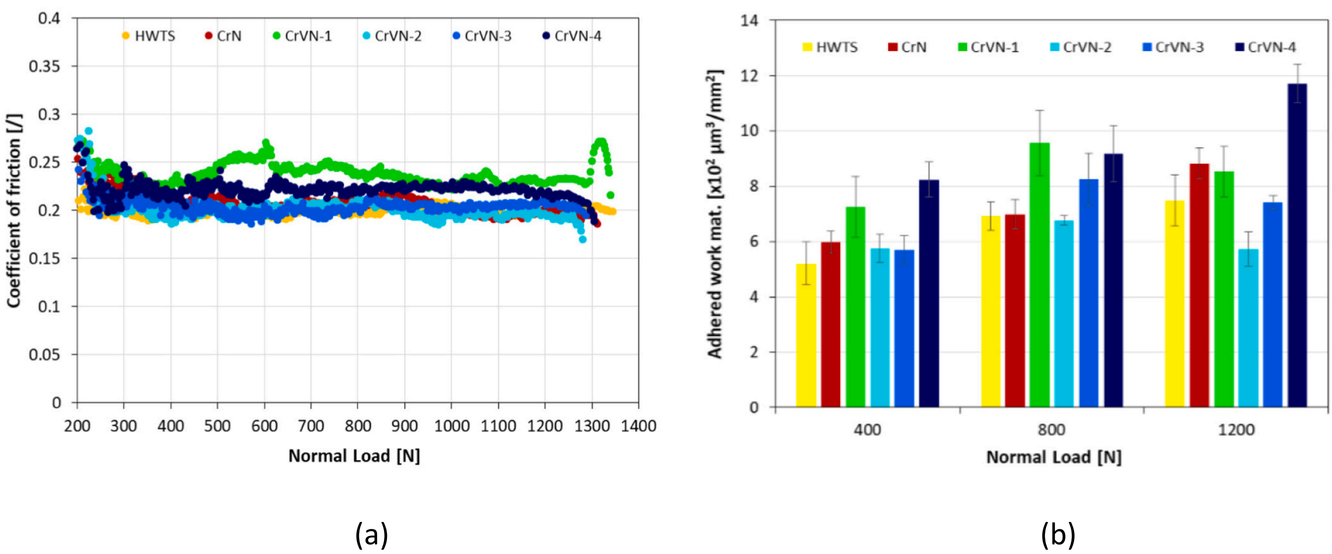


Fig. 7. (a) Coefficient of friction as a function of load and (b) volume of adhered work material for RT tests against AA2024 Al alloy.

content and shifting optimum combination of properties to medium V-concentrations of about 20 at.% (Fig. 7). In this case shearing took place within the layer of transferred Al alloy rather than at the coating interface, as indicated by smoother wear track of CrVN-2 coating (Fig. 10a).

3.3. High temperature tests

At elevated temperature galling tests against low-carbon steel (600 °C) all coatings provide considerably improved galling resistance as well as lower and more stable coefficient of friction. In the case of uncoated hot-work tool steel coefficient of friction is above 0.9 (Fig. 11a) and volume of adhered work-material about two orders of magnitude larger than for room temperature (3.3–3.5·10^4 μm^3/mm^2; Fig. 11b). With the application of CrN based coatings coefficient of friction has been reduced down to about 0.4–0.5 and more or less maintained that level for the whole load range investigated, as shown in Fig. 11a. Coatings also provided greatly reduced adhesion of work material, being at the level of room temperature tests (~10·10^2 μm^3/mm^2), owing to their good high temperature properties, stability and oxidation resistance [33]. However, in this case addition and increased concentration of V has strong positive effect, providing more stable friction and reduced adhesion of work material. Higher the V-concentration bigger is the improvement, especially at high loads and deformation rates, reaching as high as 45 % (CrVN-4) compared to binary CrN coating (Fig. 11b). Wear track analysis (Fig. 12) also showed that by increasing V content the adhesion of work material is predominantly positioned at the surface irregularities.

On the other hand, when tested against Al alloy at 300 °C all surfaces show quite high and unstable friction (Fig. 13a) and high degree of adhered work material (Fig. 13b). As for room temperature tests no coating failure was detected (Fig. 14), with the unstable friction and high degree of work material adhesion being related to increased oxidation and high sticking tendency of Al alloys at elevated temperatures. For uncoated hot-work tool steel initial coefficient of friction at low loads is at the level of 0.15 but quickly becomes unstable and at the load of 700 N exceeds 0.5 also resulting in a large volume of adhered work material (30–40·10^2 μm^3/mm^2). Binary CrN coating shows similar

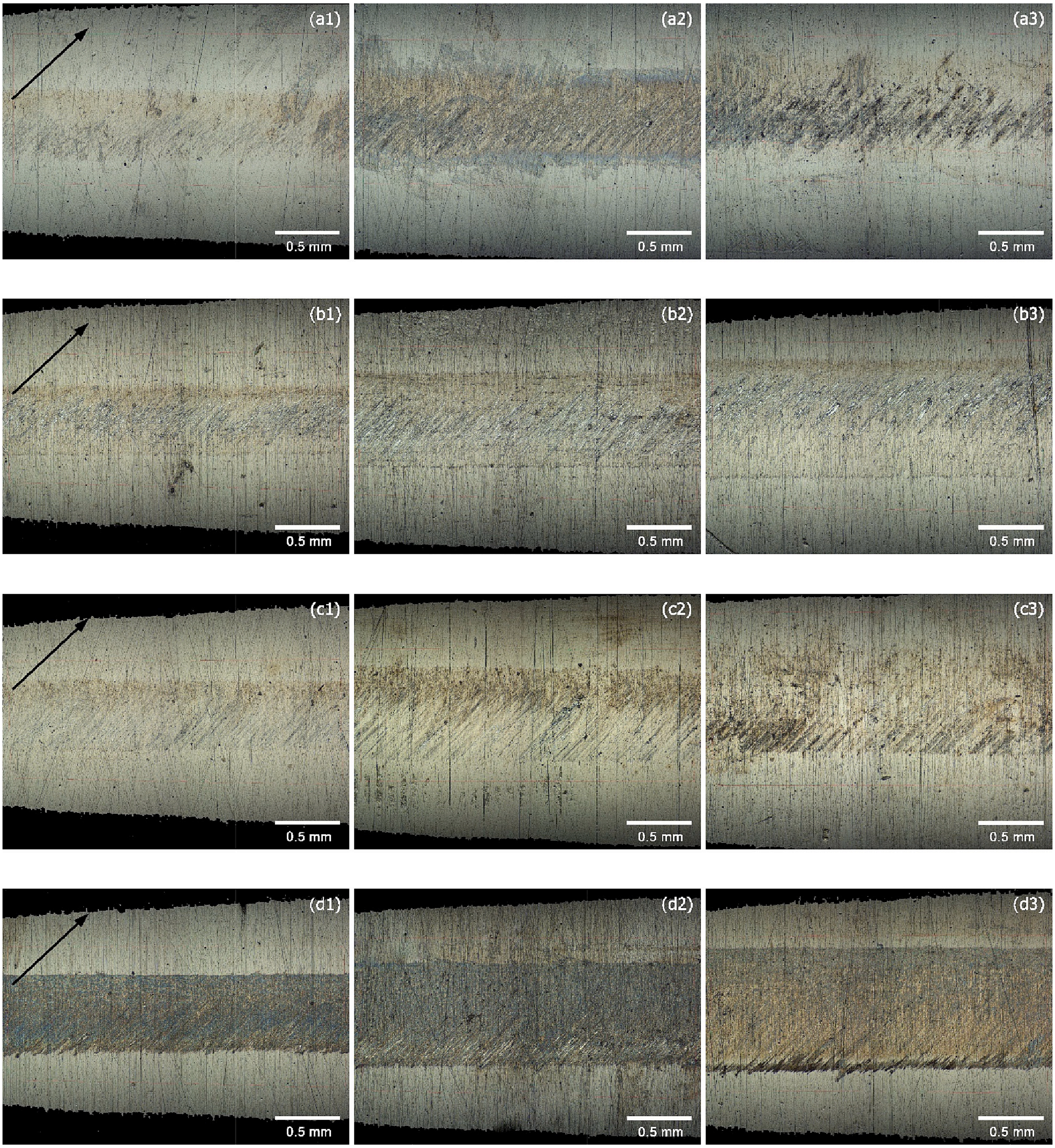
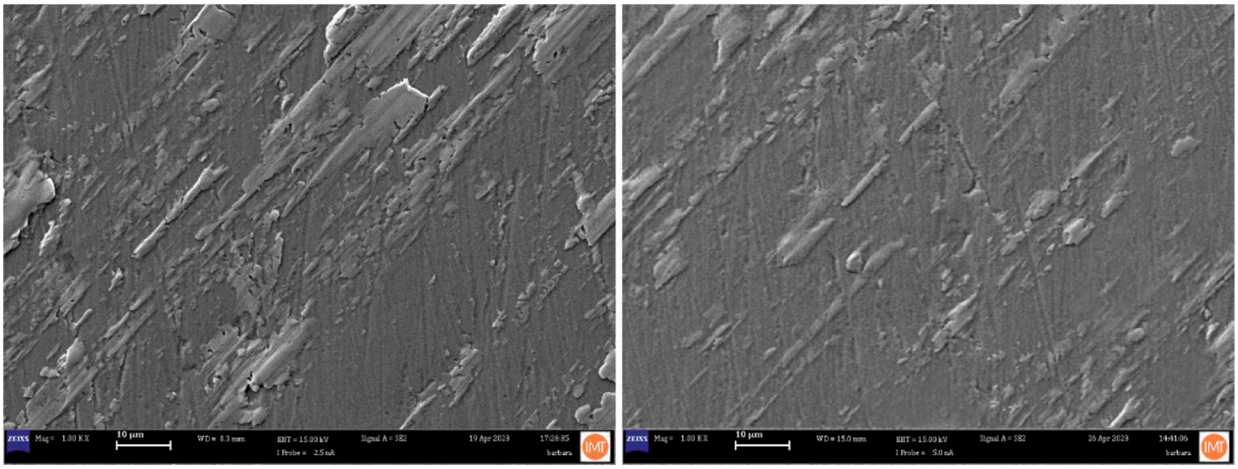


Fig. 8. Wear tracks on coated tool steel for room temperature tests: (a) binary CrN coating against low carbon steel, (b) CrVN-1 coating against low carbon steel, (c) CrVN-4 coating against low carbon steel and (d) CrVN-4 coating against Al alloy at three different loads (1–400 N, 2–800 N and 3–1200 N); arrow indicates direction of sliding.

unstable friction but provides up to three times better galling resistance, mainly due to prevented surface oxidation. Addition of V in lower concentrations (up to 20 at.%) has negative effect, increasing coefficient of friction above 0.6 and amount of adhered material to the level of uncoated hot-work tool steel, as shown in Fig. 13. This could be related to the reaction between aluminum oxides and vanadium oxides and formation of $AlVO_4$ oxide, which is a compound of high coefficient of friction [34]. However, as shown by E. Arisi et al. [35], $AlVO_4$ forms only at temperatures above 700 °C, while testing against AA2024 alloy was performed at 300 °C. Contact temperatures generated within the tribological contact could potentially reach 700 °C but would be greatly localized, thus having negligible effect. XPS analysis of wear tracks (Fig. 17) also didn't reveal any traces of $AlVO_4$ phase (V5+ component between 517.9 eV and 516.7 eV not being present). On the other hand, for (Cr,V)N coating with higher V-concentration of 23 at.% (CrVN-3) and smoother surface (Fig. 5, Table 1) very stable coefficient of friction was established in the whole load range investigated. Although friction is at a relatively high level of 0.5, this results in the lowest amount of adhered work material (15–30 % lower than CrN) and the best anti-galling properties. Further increase in V-content somehow deteriorates coating's properties, causing less stable friction and increase in tendency to pick-up work material (Fig. 12). In agreement with surface topography and roughness results, the best anti-galling behavior against Al alloy at elevated temperature shows CrVN-3 coating with the smoothest



(a) (b)

Fig. 9. SEM micrographs of room temperature wear tracks against low carbon steel at the load of 800 N; (a) CrVN-2 and (b) CrVN-4.

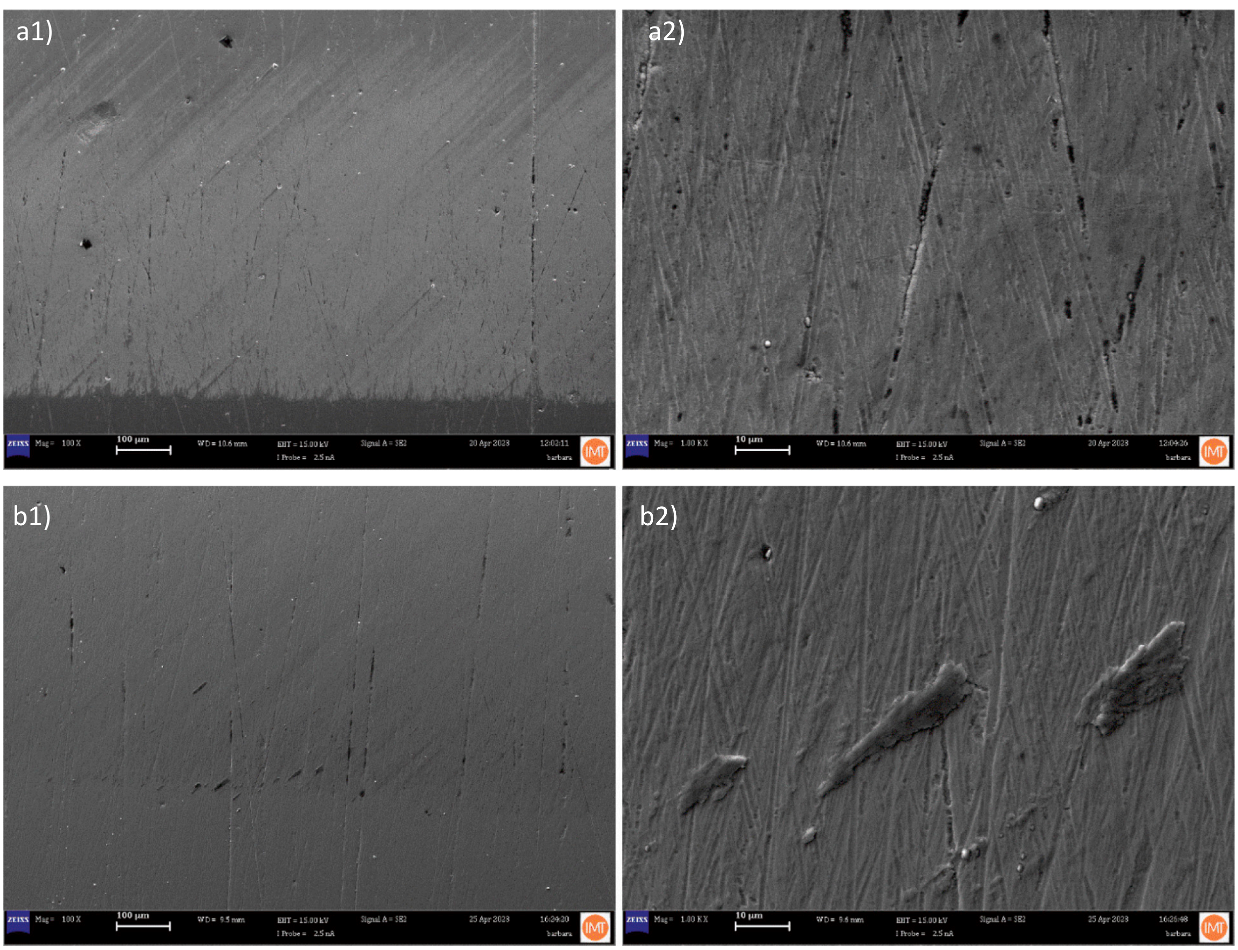


Fig. 10. SEM micrographs of room temperature wear tracks against AL alloy at the load of 800 N; (a) CrVN-2 and (b) CrVN-4.

surface.

In the case of high temperature galling tests against low-carbon steel clear trend of improved tribological behavior of (Cr,V)N coatings with increased V-concentration can also be related to more intense formation of lubricious V-type oxides (VO_2 and V_2O_5) as indicated by the EDS analysis of the wear track cross-sections and increased concentration of oxygen (Fig. 15). According to N. Fateh et al. [36] and V. Perfilyev et al. [30] easy sheared VO_2 and V_2O_5 oxides are formed on the surface of VN and (Cr,V)N coatings around 500 °C thus providing good lubricity and reduced stick-slip effect. XPS analysis of the wear track shown in Fig. 16 confirmed formation of VO_2 and V_2O_5, as indicated by small peak between 517 and 516 eV [37] and peak fitting with three components, corresponding to nitride and two oxide states of vanadium (V4+ 516.8–515.9 eV and V5+ 517.9–516.7 eV). Further TEM analyses are

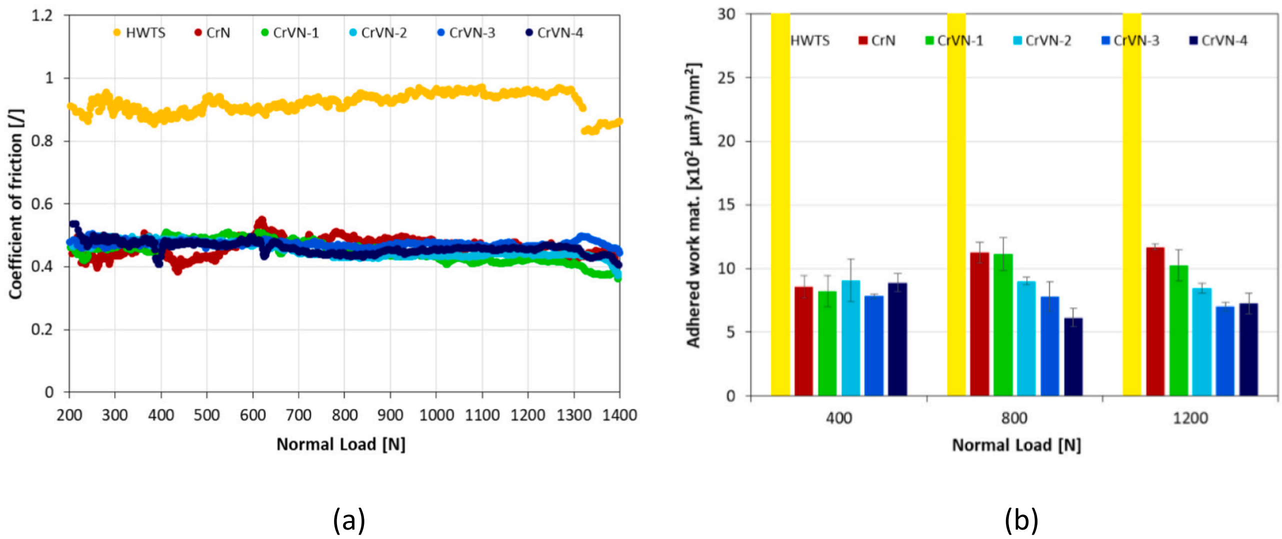


Fig. 11. (a) Coefficient of friction as a function of load and (b) volume of adhered work material for high temperature tests against low-carbon steel (600 °C).

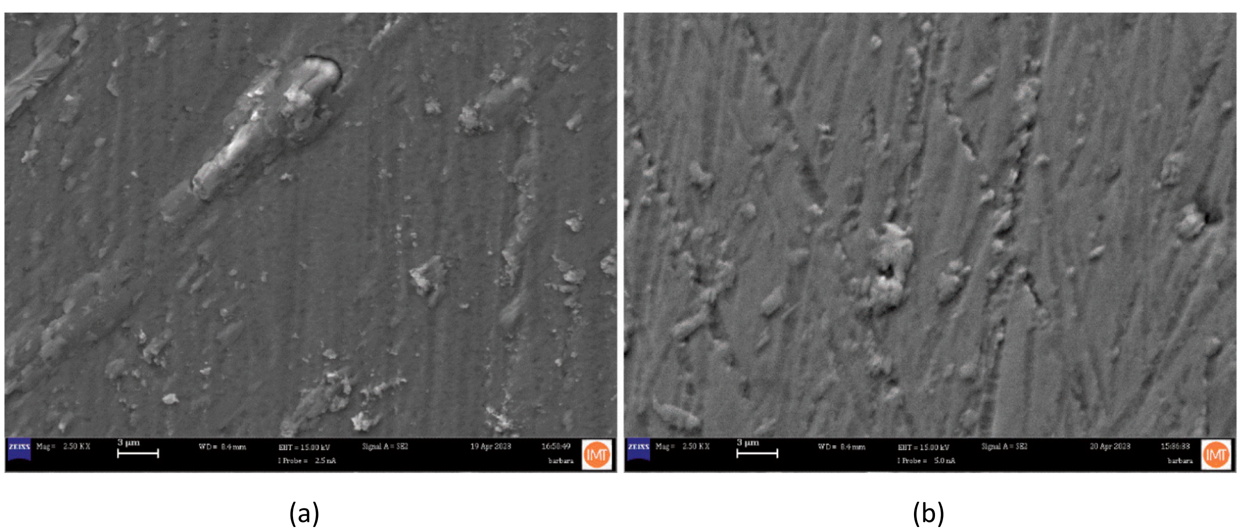


Fig. 12. SEM micrographs of high temperature (600 °C) wear tracks against low carbon steel at the load of 800 N; (a) CrVN-1 and (b) CrVN-4.

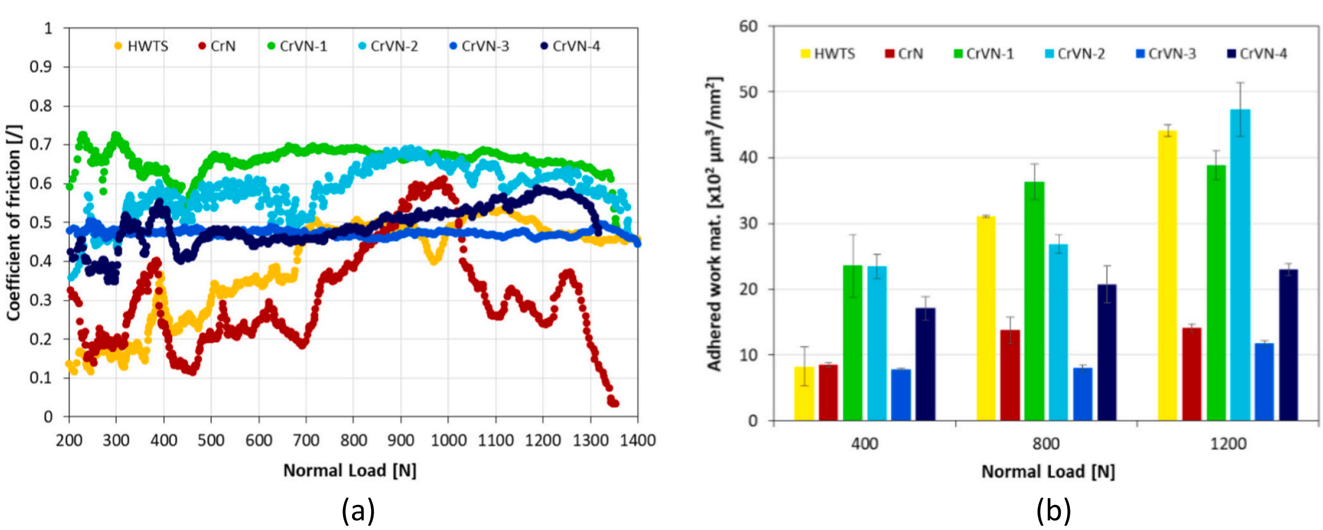


Fig. 13. (a) Coefficient of friction as a function of load and (b) volume of adhered work material for high temperature tests against Al alloy (300 °C).

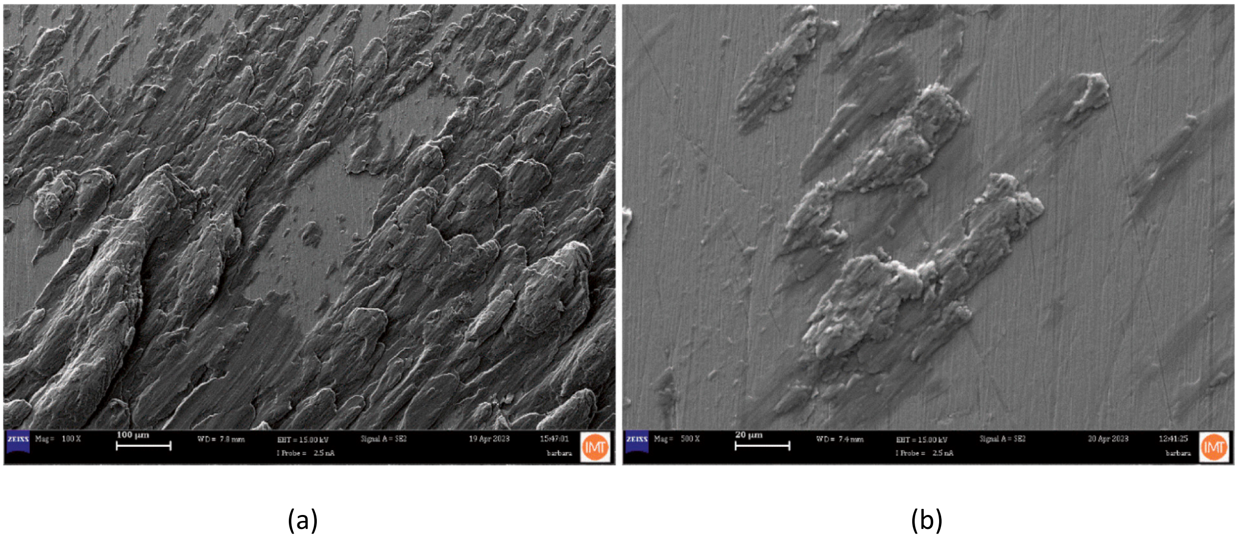


Fig. 14. SEM micrographs of high temperature (300 °C) wear tracks against Al alloy at the load of 800 N; (a) CrVN-1 and (b) CrVN-3.

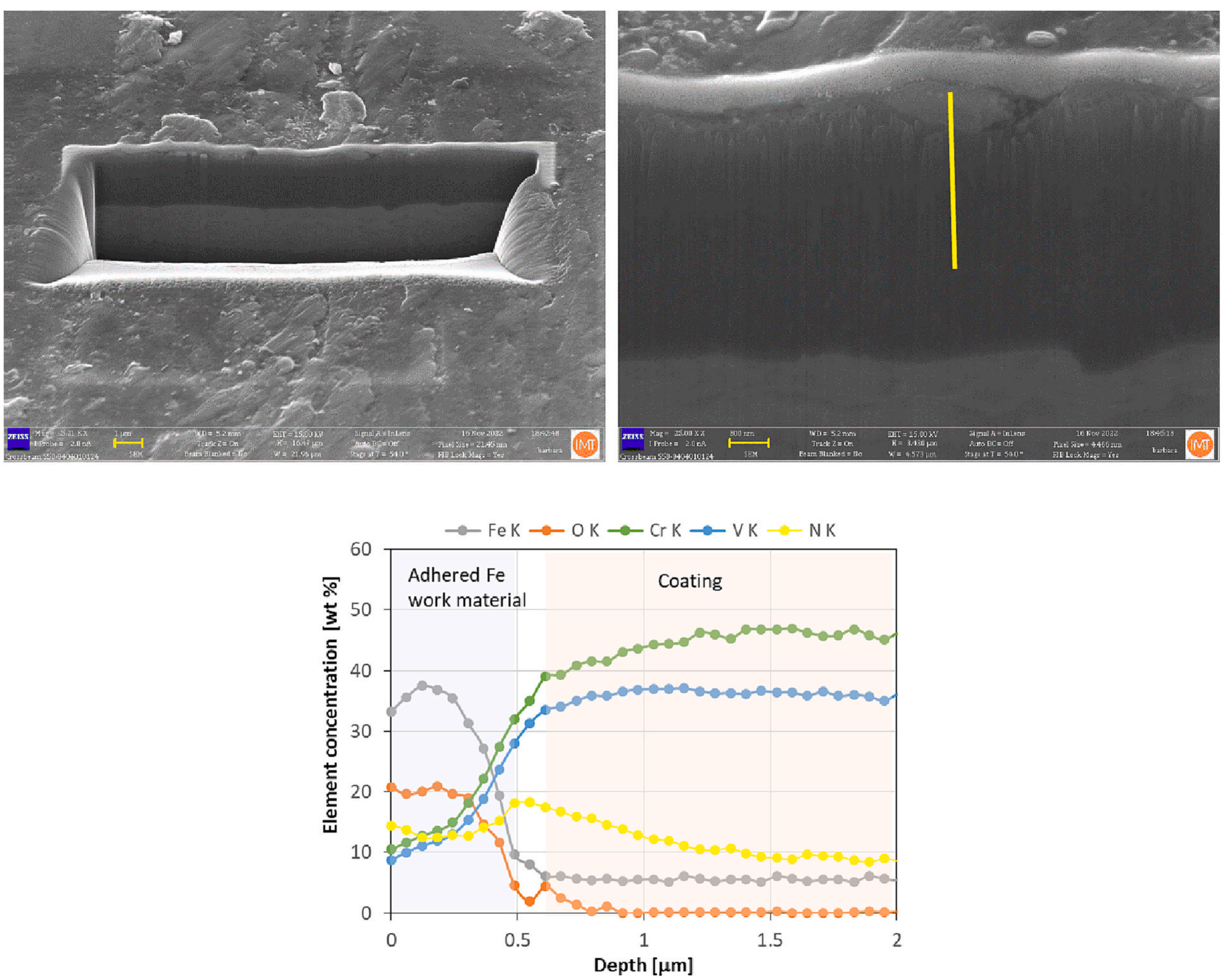


Fig. 15. SEM/EDS line analysis of high temperature wear track (CrVN-4/S235J2 @600 °C, F_N = 800 N).

planned for detailed analysis and identification of oxides formed locally in different areas of the wear track. Improved friction properties are thus mainly attributed to formation and easy interface shearing of these oxide layers in the wear track during deformation and plastic smearing.

On the other hand, for high temperature tests against Al alloy performed at 300 °C, temperature is in general too low to allow direct formation of lubricious oxides [20]. However, as indicated by XPS analysis (Fig. 17) VO_2 oxides (peak at 515.9 eV) are present within the contact zone. In this case improvement in friction and galling properties is down to combined effect of increased hardness and change in surface

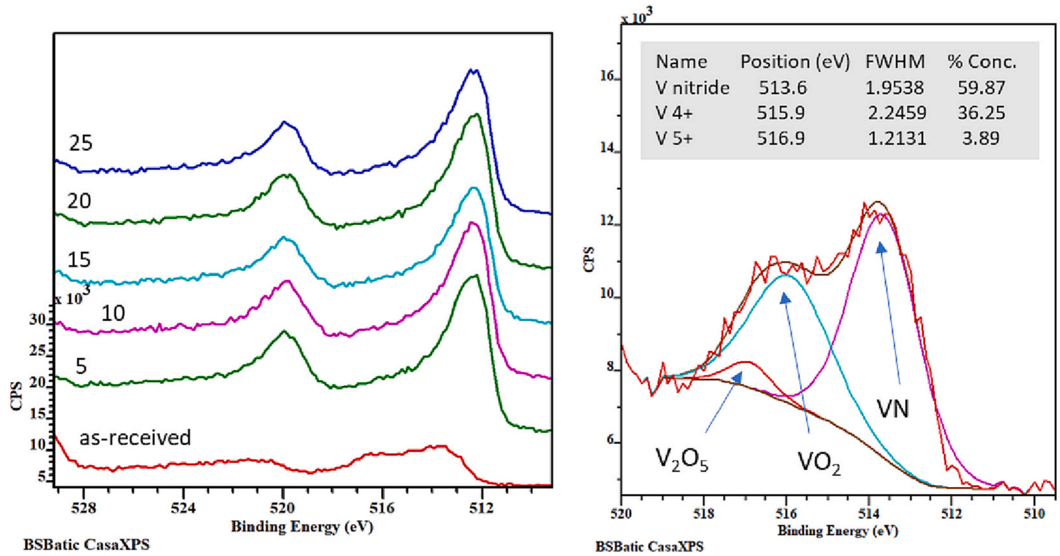


Fig. 16. V 2p XPS peak and peak fitting of the CrVN-4/S235J2 @600 °C wear track (F_N = 800 N; as-received and sputtered for 5, 10, 15, 20 & 25 min @2 kV Ar + ions).

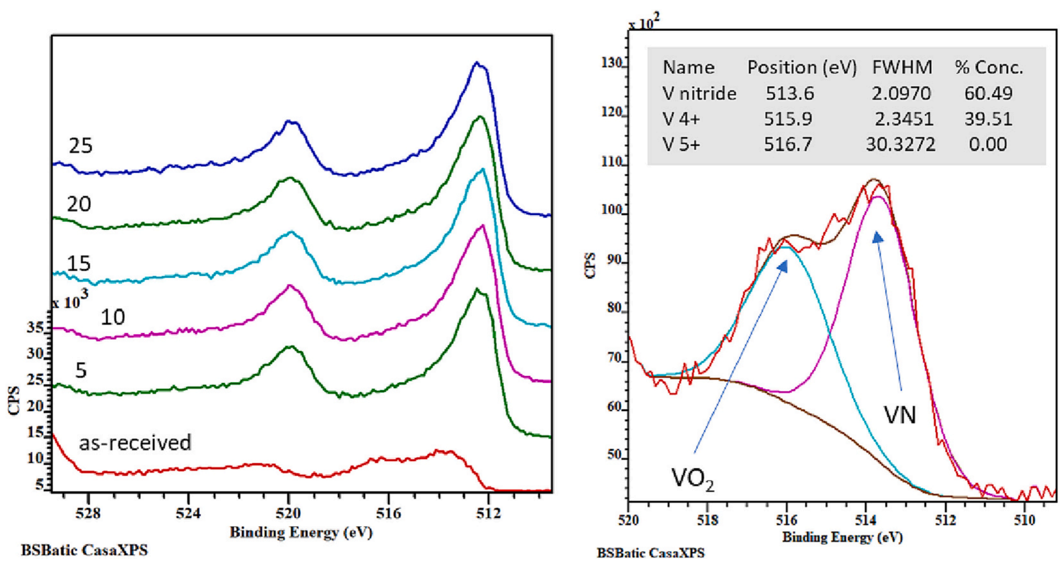


Fig. 17. V 2p XPS peak and peak fitting of the CrVN-3/AA2024 @300 °C wear track (F_N = 800 N; as-received and sputtered for 5, 10, 15, 20 & 25 min @2 kV Ar + ions).

morphology of (Cr,V)N coatings, and local micro-formation of some lubricious oxides due to high contact pressures, material shearing and elevated contact temperatures. At low V-concentrations (< 20 at.%) formation of lubricious oxides is suppressed while at high concentrations (> 25 at.%) increase in coating roughness and hardness will again promote work material transfer and galling. V-content also has a direct effect on lubricious oxides formation in tribo-contact with Al, and higher the V/Al ratio (i.e. higher V-content) higher is the possibility for some localized micro lubricious oxides formation [20].

4. Conclusions

Results of this investigation focused on the effect of V-concentration on the galling resistance of nanolayered (Cr,V)N coatings under room and elevated temperature conditions can be summarized in the following conclusions:

- At room temperature and against low-C steel binary CrN coating provides similar friction behavior and galling resistance as hardened hot-work tool steel. Addition of vanadium in general has negative effect, resulting in higher and more unstable friction, as well as increased adhesion of work material to the coating surface. However, at high V-concentrations above 25 at.%, combination of increased hardness and finer coating structure provides more stable friction up to the load of 1200 N and improved galling resistance.
- In the case of AA2024 aluminum alloy optimum V-concentration providing smoother friction and improved galling resistance is between 20 and 25 at.%, although not being considerably different as compared to uncoated hot-work tool steel and binary CrN coating. Shift in best V-concentration toward lower concentrations can be related to aluminum alloy showing larger degree of plastic deformation and being more prone to galling, thus shearing taking place within the layer of transferred material instead at the coating interface.

– For high temperature conditions of 600 °C, coatings with high temperature and oxidation stability provide two to three times better galling resistance, as well as lower and smoother friction. Addition of V results in further, up to 45 % improvement with the increased V-content having straight-forward positive effect obtained through smoother coating surface and intensified micro formations of lubricious oxides on the coating's contact surface.
– Testing against Al alloy at 300 °C turned out to represent the most demanding contact conditions, characterized by very unstable friction and high degree of galling and work material transfer. Binary CrN coating improves situation by about 50 % due too high temperature oxidation stability. Addition of V in general gives smoother friction but at higher level and thus results in an increased work material transfer. However, at 23 at.% optimum combination of increased surface hardness, smooth surface morphology and localized formation of some lubricious oxides resulted in the best tribological performance and galling resistance.

CRediT authorship contribution statement

B. Podgornik: Conceptualization, Supervision, Investigation, Tribological testing, Data analysis, Writing – original draft, Writing – review and editing.

M. Sedlaček: Wear volume measurement and analysis, Writing – original draft.

M. Čekada: Coatings development and deposition, Coatings characterization, Writing – review and editing.

B. Šetina Batič: SEM microscopy & XPS analysis of wear tracks, Writing – review and editing.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Bojan Podgornik reports financial support was provided by Slovenian Research Agency.

Data availability

Data will be made available on request.

Acknowledgements

The authors acknowledge the financial support from the Slovenian Research Agency (research core funding No. P2-0050 & P2-0056). Dr. Peter Panjan is greatly acknowledged for the help and info on coatings deposition.

References

[1] H. Ritchie, Sector by sector: where do global greenhouse gas emissions come from?, Our World in Data. https://ourworldindata.org/ghg-emissions-by-sector, 2020.
[2] E. Worrell, J. Allwood, T. Gutowski, The role of material efficiency in environmental stewardship, Annu. Rev. Environ. Resour. 41 (2016) 575–598.
[3] National Materials Advisory Board, The Role of Materials in Energy and the Environment. In: Materials in the New Millennium: Responding to Society's Needs. The National Academies Press, doi:10.17226/10187.
[4] E. Hertwich, R. Lifset, S. Pauliuk, N. Heeren, Resource Efficiency and Climate Change: Material Efficiency Strategies for a Low-Carbon Future, A report of the Int. Resource Panel, United Nations Environment Programme, Nairobi, Kenya, 2020.
[5] B. Podgornik, V. Leskovsek, Wear mechanisms and surface engineering of forming tools, Mater. Technol. 49 (2015) 313–324.
[6] H. Kim, N. Kardes, Friction and lubrication, in: T. Altan, A.E. Tekkaya (Eds.), Sheet Metal Forming – Fundamentals, ASM International, Metal Park, 2012, https://doi.org/10.31399/asm.tb.smff.t53400073.
[7] S.R. Schmid, W.R.D. Wilson, Tribology in manufacturing, in: B. Bhushan (Ed.), Modern Tribology Handbook, CRC Press, NY, 2000.
[8] K. Dohda, M. Yamamoto, C. Hu, L. Dubar, K.F. Ehmann, Galling phenomena in metal forming, Friction 9 (2021) 665–685.
[9] J.A. Schey, Tribology in Metalworking: Friction, Lubrication and Wear, ASM, Ohio, 1984.
[10] B. Podgornik, J. Vizintin, S. Hogmark, Improvement in galling performance through surface engineering, Surf. Eng. 22 (2006) 235–238.
[11] K.L. Rutherford, S.J. Bull, E.D. Doyle, I.M. Hutchings, Laboratory characterisation of the wear behaviour of PVD-coated tool steels and correlation with cutting tool performance, Surf. Coat. Technol. 80 (1996) 176–180.
[12] J. Heinrichs, S. Jacobson, Mechanisms of transfer of aluminium to PVD-coated forming tools, Tribol. Lett. 46 (2012) 299–312.
[13] A. Arjunan, A. Baroutaji, J. Robinson, A.-G. Olabi, Smart tribological coatings, in: A.-G. Olabi (Ed.), Encyclopedia of Smart Materials, Elsevier, 2022, pp. 414–425.
[14] M. Vilaseca, J. Pujante, G. Ramírez, D. Casellas, Investigation into adhesive wear of PVD coated and uncoated hot stamping production tools, Wear 308 (1–2) (2013) 148–154.
[15] C. Donnet, A. Erdemir, Tribology of Diamond-like Carbon Films: Fundamentals and Applications, Springer, NY, 2008.
[16] Dong Yangchun, Zheng Kailun, J. Fernandez, Li Xiaoying, Dong Hanshan, Lin Jianguo, Experimental investigations on hot forming of AA6082 using advanced plasma nitrocarburised and CAPVD WC: C coated tools, J. Mater. Process. Technol. 240 (2017) 190–199.
[17] K.P. Furlan, J.D. Biasoli de Mello, A.N. Klein, Self-lubricating composites containing MoS2: a review, Tribol. Int. 120 (2018) 280–298.
[18] L. Rapoport, A. Moshkovich, V. Perfilyev, I. Lapskera, M. Kugler, A. Kailer, A. Renz, T. Hollstein, High temperature friction behavior of CrVxN coatings, Surf. Coat. Technol. 238 (2014) 207–215.
[19] P. Panjan, A. Drnovšek, J. Kovač, P. Gselman, T. Bončina, S. Paskvale, M. Čekada, D. Kek Merl, M. Panjan, Oxidation resistance of CrN/(Cr, V)N hard coatings deposited by DC magnetron sputtering, Thin Solid Films 591 (2015) 323–329.
[20] R. Franz, C. Mitterer, Vanadium containing self-adaptive low-friction hard coatings for high-temperature applications: a review, Surf. Coat. Technol. 228 (2013) 1–13.
[21] Y. Mu, M. Liu, Y. Wang, E. Liu, PVD multilayer VN–VN/Ag composite coating with adaptive lubricious behavior from 25 to 700°C, RSC Advances 6 (2016), 6-53043–53.
[22] Xu. Wang Cuicui, Wang Zhenyu Beibei, Li Hao, Wang Li, Chen Rende, Wang Aiying, Ke Peiling, Tribological mechanism of (Cr, V)N coating in the temperature range of 500–900 °C, Tribol. Int. 159 (2021), 106952.
[23] Y. Qiu, B. Li, J. Lee, D. Zhao, Self-lubricating CrVN coating strengthened via multilayering with VN, J. Iron Steel Res. Int. 21 (5) (2014) 545–550.
[24] S. Petrović, B. Gaković, P. Panjan, J. Kovač, V. Lazović, C. Ristoscu, I. Negut, I. N. Mihailescu, Oxidation behaviour of composite CrN/(Cr, V)N coatings with different contents of vanadium induced by UV nanosecond laser pulses, Opt. Quant. Electron. (2018), https://doi.org/10.1007/s11082-018-1475-3.
[25] E. Contreras, Y. Galindez, M.A. Rodas, G. Bejarano, M.A. Gómez, CrVN/TiN nanoscale multilayer coatings deposited by DC unbalanced magnetron sputterin, Surf. Coat. Technol. 332 (2017) 214–222.
[26] Xu. Beibei, Guo Peng, Wang Zhenyu, Chen Rende, Ye Yumin, Shuai Jintao, Wang Aiying, Ke Peiling, Anti-wear Cr-V-N coating via V solid solution: microstructure, mechanical and tribological properties, Surf. Coat. Technol. 397 (2020), 126048.
[27] B. Podgornik, S. Hogmark, J. Pezdirnik, Comparison between different test methods for evaluation of galling properties of surface engineered tool surfaces, Wear 257 (2004) 843–851.
[28] N. Fairley, V. Fernandez, M. Richard-Plouet, C. Guillot-Deudon, J. Walton, E. Smith, D. Flahaut, M. Greiner, M. Biesinger, S. Tougaard, D. Morgan, J. Baltrusaitis, Systematic and collaborative approach to problem solving using X-ray photoelectron spectroscopy, Appl. Surf. Sci. Adv. 5 (2021), 100112.
[29] G. Silversmit, D. Depla, H. Poelman, G.B. Marin, R. De Gryse, Determination of the V2p XPS binding energies for different vanadium oxidation states (V5+ to V0+), J. Electron Spectrosc. Relat. Phenom. 135 (2–3) (2004) 167–175.
[30] V. Perfilyev, A. Moshkovich, I. Lapsker, A. Laikhtman, L. Rapoport, The effect of vanadium content and temperature on stick–slip phenomena under friction of CrV(x)N coatings, Wear 307 (1–2) (2013) 44–51.
[31] L. Aissani, C. Nouveau, M. Jade Walock, H. Djebaili, A. Djelloul, Influence of vanadium on structure, mechanical and tribological properties of CrN coatings, Surf. Eng. 31 (2015) 779–788.
[32] R. Dorward, Work Hardening and Annealing of Aluminum Alloys, in: K. Andrfeson, J. Weritz, J.G. Kaufman (Eds.), Aluminum Science and Technology, ASM Handbook, Vol. 2A, ASM International, Metal Park Ohio, 2018, pp. 279–291.
[33] T. Polcar, R. Martinez, T. Vítů, L. Kopecký, R. Rodriguez, A. Cavaleiro, High temperature tribology of CrN and multilayered Cr/CrN coatings, Surf. Coat. Technol. 203 (20–21) (2009) 3254–3259.
[34] K. Kutschej, P.H. Mayrhofer, M. Kathrein, P. Polcik, C. Mitterer, Influence of oxide phase formation on the tribological behaviour of Ti–Al–V–N coatings, Surf. Coat. Technol. 200 (2005) 1731–1737.
[35] E. Arisi, S.A. Palomares Sanchez, F. Leccabue, B.E. Watts, G. Bocelli, F. Calderon, G. Calestani, L. Righi, Preparation and characterization of AlVO4 compound, J. Mater. Sci. 39 (2004) 2107–2111.
[36] N. Fateh, G.A. Fontalvo, G. Gassner, C. Mitterer, Influence of high-temperature oxide formation on the tribological behaviour of TiN and VN coatings, Wear 262 (9–10) (2007) 1152–1158.
[37] C.-C. Wang, C.-L. Lu, F.-S. Shieu, H.C. Shih, Structure and photoluminescence properties of thermally synthesized V2O5 and Al-doped V2O5 nanostructures, Materials 14 (2) (2021) 359.