High temperature friction behavior of CrV$_x$N coatings

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Abstract

The object of this research is to deposit CrV$_x$N coatings with different content of Vanadium (V) by ion-sputter deposition to gain fundamental knowledge on the friction behavior of these coatings under high temperature and to analyze stick-slip phenomenon. The results of stick-slip tests under low sliding velocities are compared with real contact conditions. Here, an entirely new method is established to approach this problem at different scales by combining high-temperature friction study of coatings (Fraunhofer Institute for Mechanics of Materials IWM), and micro-tribology for stick-slip analysis (Holon Institute of Technology, HIT). The tribological experiments at Fraunhofer IWM were performed using a oscillating friction-wear test rig (SRV4, Optimol Instruments) in the temperature range of 25 to 700 °C. To study stick-slip phenomena, a new ball on flat device with a heated chamber for experiments at up to 500 °C was developed at the HIT. It was shown that an addition of V up to 27 - 35 at.% in CrV$_x$N coatings increases the hardness, fracture toughness and decreases the grain size. These parameters correlate with improved tribological properties of coatings with high content of V. At room temperature CrV$_x$N coatings feature strong sticking effects in the friction experiments. High values of the stick-slip parameters are explained by mechanical interlocking and adhesion on contact spots due to softening of surface layers of balls, high roughness and transfer of thick iron oxide films on the surface of the coatings. Low values of the wear and stick-slip parameters under friction of Cr$_{0.65}$V$_{0.35}$N at high temperatures (T = 500 - 700 °C) is associated with the formation of V$_2$O$_5$ oxide phase providing easy shearing of tribofilms in the interface of rubbed surfaces.

Keywords: Friction and wear; High temperature coating; Stick-slip
1. Introduction

The interest in high-temperature tribological behavior of ceramic and ceramic coatings has been a subject of intensive research in recent years [1 - 10]. The lubricating properties of high-temperature coatings are mainly determined by oxidation within the frictional contacts. Usually, surface films of contaminations or oxides effectively reduce the friction of ceramics [11]. The formation of lubricious surface oxides is associated with the so called Magnéli phases [12]. Possible candidates for the formation of these phases are W, Mo, Ti and V [13, 14]. The lubricating effect of Magnéli phases was revealed in high temperature studies of oxidized VN [15]. The authors suggested that oxides of the type, $V_nO_{2n-1}$ and $V_nO_{3n-1}$, form a Magnéli phase thus providing improved lubricious properties. On the other hand, Ouyang et al. [16] and some other authors [e.g. 17, 18] noted that only oxides of the type, $V_nO_{2n-1}$, form the Magnéli phase, and that the VO$_2$ and V$_2$O$_5$ oxides cannot be considered as Magnéli phases. At the same time, it was proved that the VO$_2$ and V$_2$O$_5$ oxides are also easily sheared thus providing high lubricity at high temperatures of 500 - 600 °C [16]. Recently, the friction and wear behavior of some ceramics at high temperatures were studied [19 - 22]. AlCrN is characterized by high resistance to oxidation in comparison to CrN and TiAlN [19]. The influence of the V content on structure and properties of AlCrN coatings was studied by Franz [19]. At temperatures close to 700 °C, friction and wear are mainly determined by oxidation and diffusion of V. It was shown that for supersaturated Ti-Al-V-N films the coefficient of friction was reduced to about 0.2 - 0.3 at 700 °C compared to the room temperature values of 0.6 - 0.8 [23, 24].

Comprehensive study and analysis of stick-slip phenomena is a key to understanding the formation and destruction of high temperature wear protection coatings [25]. Generally, friction processes can be broken down to stick-slip processes with different frequency and amplitude fluctuations of the friction force associated with adhesion on the pinned islands. The problems of stick-slip motion are carefully studied on the molecular level. Molecular dynamic computer simulation [26, 27], friction experiments using SFA technique [28 - 31] and the study of sliding friction [32, 33] provide a better understanding of the nature of molecular collisions on a nano-scale level. Molecular dynamic simulations of the stick-slip and wear of fcc crystalline and polycrystalline Ag were performed [34] and atomistic analysis of scratching was analyzed. On the macro-scale, the transition from static to kinetic friction of unlubricated or oil lubricated steel/steel, steel/ceramic and ceramic/ceramic pairs at room temperature was studied by Hwang and Zum Gahr [35]. As can be seen, a notable amount of research work is devoted to stick-slip phenomena on the nano- and macro-scale levels at room temperature. The mechanism of stick-slip motion at micro and macro-scale levels at elevated temperature is still a subject of debate. Furthermore, the development of a stick-slip model for coatings at high temperature can give interesting insights for the micro-scale description and understanding the physical mechanisms involved in friction of ceramic composite coatings. The present work was carried out by two teams: Fraunhofer Institute for Mechanics of Materials, IWM, Germany (macro-scale friction) and Holon Institute of Technology (HIT), Israel (micro-scale friction, stick-slip phenomena). The investigations focus on four main objectives: first, to deposit CrV$_x$N coatings; second, to evaluate friction and wear properties of coatings during stick-slip tests; third, to study friction and wear
properties of coatings under relatively high sliding velocities and temperatures; fourth, to compare the results of stick-slip tests with typical contact conditions in real applications.

2. Experimental

2.1 Design of Coatings

The CrN and CrVₓN coatings were provided by the Fraunhofer Institute for Surface Engineering and Thin Films IST in Braunschweig, Germany. The coatings were prepared by reactive DC magnetron sputtering in the unbalanced mode using a HTC 1000/4 (ABS) coater (Hauzer Techno Coating, Venlo, The Netherlands). As substrate material HS-6-5-2C (DIN 1.3343, heat treated to a hardness of HRC = 63 and polished) was used. The process chamber has a volume of 1 m³. Deposition was carried out by using typical deposition parameters of bias voltages between -100 and -300 V and coil currents of the magnetrons up to 6 A (for 2 targets). Targets made of chromium and vanadium where the target power for chromium was constant 3 or 6 kW and variable for the doping elements depending on the requested metal content. The sputter gas was a composition of argon and nitrogen whereas the N₂ content was kept below 50 % at a gas pressure 0.3 Pa. The resulting deposition temperatures varied from 100 to 450 °C, deposition rates were between 0.6 and 1.8 µm/h. After plasma etching of the substrate surface using argon as process gas, an adhesive layer of chromium was deposited using 2 targets. The top layer was formed with additional nitrogen in the process atmosphere. The fraction of doping elements in the considered coatings was adjusted while controlling the power of the additional metallic targets. The coating procedure is described in more detail by Paschke et al. [36].

2.2 Stick-slip tests

Stick-slip tests were performed using ball-on-flat arrangement (Fig.1).

Fig. 1. General view of the ball-on-flat rig. The temperature chamber is not shown here.
The effect of vanadium (V) content in CrV\(_x\)N (x = 0 at.%, 12 at.%, 27 at.%, 35 at.%) coatings on stick-slip behaviour under friction was studied in the temperature range of T = 25 - 500 °C. Based on the results of preliminary stick-slip experiments performed at room temperature, the stiffness parameter of two parallel springs k, the normal force F\(_N\), and the sliding velocity v were set to k = 2400 N/m, F\(_N\) = 0.5 N (P\(_{\text{contact}}\) = 1020 MPa) and v = 0.3 mm/s. A bearing steel ball with a diameter of 2 mm and hardness, H\(_V\) = 8 GPa, is used for sliding against the flat coated samples for 500 cycles at different temperatures. The length of the wear track is 1 mm, Stick-slip effects were investigated by reducing the sliding velocity after 500 cycles of sliding to v = 0.001 mm/s during a half cycle, i.e. unidirectional movement along the 1 mm wear track. The amplitude (A), the difference between the maximum and minimum values of the friction force in steady state, the static force F\(_s\) (at the beginning of friction) and the kinetic (average value) of the friction force F\(_k\) were chosen for description of stick-slip as schematically shown in Fig. 2. A slope of the static force line, F\(_s\), characterizes the full stick. If a slope of the friction force with time does not correspond to full slip, this means that the stick is accompanied by creep process [37].

![Fig. 2. Stick-slip curve under friction for CrN coating (V = 0 %) at room temperature during half of the cycle. A: the amplitude of oscillations of the friction force at steady state, mN; F\(_s\): maximal value of the friction force (static) in the beginning of friction, mN; F\(_k\): the average value of the friction force, mN.](image)

A relation between slip and stick during one single event was evaluated after the analysis of 3 identical curves. The same tests were carried out under different temperatures. The surfaces before and after the friction tests were analyzed by SEM, XRD techniques. The XRD patterns were recorded using a Scintag – X2 diffractometer with 45 kV operation voltage and CuK\(_{\alpha}\) radiation. The hardness and roughness parameters of coatings and the depth and width of the wear tracks as well as the size of the wear spot on the surface of the ball were measured. The hardness tests were performed using a Matsuzawa MXT-50 microhardness tester at a load of 1 N. The roughness parameters were measured using a Surtronic 3+ from Taylor Hobson. During the preliminary experiments, it was found out that
the friction behaviour of coatings with 0 % and 12 % and 27 % and 35 % of vanadium are almost the same. Therefore, the main object of this work was to study the friction and the stick-slip behaviour of CrN and Cr$_{0.65}$V$_{0.35}$N coatings at room (T = 25 °C) and high (T = 500 °C) temperatures.

2.3 Friction and wear of coatings using SRV4 test system

Tribological experiments were performed using a self-constructed pin-on-plate arrangement in a SRV4 test machine (SRV4, Optimol Instruments), Fig.3. One general drawback of the standard test setup is that only the lower part of the setup is heated. To realize well-defined thermal conditions, the upper part of the setup can be equipped with an additional heating. Pins (also made from HS-6-5-2C and heat treated to a hardness of HRC = 63) were machined with radii of 20, 40 and 80 mm in order to apply different contact pressures using the same normal force. Friction tests were carried out under 10, 30, 100 N normal force loadings, a displacement amplitude of 2 mm and test durations from 500 up to 4500 cycles with a constant frequency of 25 Hz and 50 % relative humidity. The tests were performed at the temperatures of 25, 500, 600 and 700 °C. The initial contact pressure was varied between 180 MPa and 660 MPa resulting from different normal forces and pin radii. The effect of Vanadium content on the friction and wear of coatings at different temperatures was studied. Preliminary results indicated a high reproducibility of results. Fig. 4 depicts the results of the friction tests of Cr$_{0.73}$V$_{0.27}$N at the temperature of 600 °C.

Fig.3. High temperature set-up for sliding experiments with various pins, (Optimol SRV4). The blue arrows at the pin bearing beam indicate the lateral movement during the sliding experiments.
Fig. 4. An example of the change of the friction coefficient during a sliding experiment (Cr$_{0.73}$V$_{0.27}$N vs. HSS steel ball, T = 600 °C, F$_N$ = 30 N).

3. Results

3.1 Morphology of virgin surfaces and the mechanical properties of CrV$_x$N coatings

SEM images of the virgin surfaces of CrVN coatings are shown in Fig. 5. The oval shaped grains of the CrN coating show an average grain size of about 500 nm, Fig. 5a. An essentially different surface structure is observed for the CrV$_x$N coatings, showing a relatively smooth surfaces with an almost amorphous structure, Fig. 5b-d. The results of the hardness and roughness measurements of coatings are depicted in Table 1.
Fig. 5. SEM images of the virgin surfaces of CrV\textsubscript{x}N coatings; a) x = 0 at.\%, b) x = 13 at.\%, c) x = 27 at.\%, d) x = 35 at.\%.

Fig. 6. XRD spectra for CrV\textsubscript{x}N coatings measured at room temperature before and after exposure at 500 °C in air. The pure CrN coating shows only slight oxidation, indicated by a small Cr\textsubscript{2}O\textsubscript{3} peak at 2\theta = 57°, whereas there is a remarkable change of the phase composition of the V containing coating indicated by the formation of CrN, Cr\textsubscript{2}N and V\textsubscript{2}O\textsubscript{5}.

Fig. 6. XRD patterns of CrV\textsubscript{x}N coatings at different temperatures: 1) V = 0 at.\%, T = 25 °C; 2) V = 35 at.\%, T = 25 °C; 3) V = 35 at.\%, T = 500 °C; 4) V = 0 at.\%, T = 500 °C.
Table 1. The effect of vanadium content on hardness ($H_V$) and roughness ($R_a$, $R_z$) of the coatings.

<table>
<thead>
<tr>
<th>CrV,N ($x = %$)</th>
<th>Hardness [GPa]</th>
<th>Roughness parameters [µm]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Average</td>
<td>StDev</td>
</tr>
<tr>
<td>0</td>
<td>11</td>
<td>0.25</td>
</tr>
<tr>
<td>12</td>
<td>12</td>
<td>0.6</td>
</tr>
<tr>
<td>27</td>
<td>14.5</td>
<td>0.5</td>
</tr>
<tr>
<td>35</td>
<td>15</td>
<td>0.7</td>
</tr>
</tbody>
</table>

These measurements show a continuous increase from the minimum hardness of 11 GPa at 0 % Vanadium to a maximum hardness of 15 GPa for the coating with 35 % Vanadium. The roughness of the surface $R_z$ also increases with rising Vanadium content. In order to evaluate the brittleness of the coatings, Vickers indentation tests with a load of 1 N were carried out. SEM images of the indentation zones reveal crack propagation around the indents in the CrN coating while no cracks were observed around the indent on the surface of Cr$_{0.65}$V$_{0.35}$N coating, Fig. 7. Thus, in addition to the higher hardness, the CrV$_{35}$N surface features also a higher fracture toughness than the CrN coating.

Fig. 7. SEM images of the surfaces of CrN (a) and Cr$_{0.65}$V$_{0.35}$N coatings after indentation ($F = 1$ N). The white arrows indicate the cracks originating from the indentation.

3.2 Study of stick-slip phenomena under friction of CrV$_x$N coatings

The stick-slip-experiments were carried out for the coatings without Vanadium and with maximum content of Vanadium ($x = 35$). The friction behavior of these coatings was investigated at 25 °C and 500 °C (Fig. 8).
The coefficient of friction is for both modifications of the coating significantly higher at room temperature than at 500 °C. The presence of Vanadium in the coating does not show any distinct influence on the friction coefficient at room temperature, where $\mu$ is roughly 0.76 ± 0.02. Though, at 500 °C the friction coefficient drops more strongly for the Vanadium doped coating. The wear coefficients of the ball specimens that were used as counter bodies are shown in Fig. 9. Wear coefficient, K is significantly higher under friction of the CrN coating in comparison to the $\text{Cr}_{0.65}\text{V}_{0.35}\text{N}$ coating. An increase in the temperature led to strong wear of the ball specimen in combination with the V-free coating. It has to be noted that the amount of wear at room temperature as well as at high temperature is very low for the coating with 35 % of V.
The typical wear marks on the ball specimen surfaces that were in contact with CrVₓN coatings at different temperatures are shown on Fig. 10. A majority of black wear particles around the spot and in the track indicate a strong oxidation of these surfaces, Figs. 10a. Significantly smaller size of the contact spot and the lower amount of wear particles in the wear mark vicinity indicate a decrease of wear with increasing content of V (Fig. 10b). Strong plowing in the contact spot occurs under friction for CrN at high temperature (Fig. 10c). The surface damage of the ball and the wear track are significantly smaller under friction with Cr₀.₆₅V₀.₃₅N coating (Fig. 10d). SEM images of the wear tracks and positions of corresponding EDX analyses on the surfaces of CrVₓN coatings tested at room and high temperatures are shown in Fig. 11.
Fig. 10. Wear marks on the surface of steel ball specimen after stick-slip-experiments with CrV\textsubscript{N} coatings at different temperatures and vanadium contents: (a) $x = 0\%$, 25 $^\circ$C; (b) $x = 35\%$, 25 $^\circ$C; (c) $x = 0\%$, 500 $^\circ$C; (d) $x = 35\%$, 500 $^\circ$C.

Fig. 11. SEM images of the wear tracks of CrV\textsubscript{N} coating, (a) $x = 0\%$, 25 $^\circ$C; (b) $x = 0\%$, 500 $^\circ$C; (c) $x = 35\%$, 25 $^\circ$C; (d) $x = 35\%$, 500 $^\circ$C. The numbers indicate the locations for EDX element analyses presented in Table 2.
Table 2. The results of EDX analyses (at.%) in the wear tracks of CrV\textsubscript{x}N coatings. The analysis of oxygen and nitrogen has been excluded.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>25 °C</th>
<th>500 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>x = 0 %</td>
<td>x = 35 %</td>
</tr>
<tr>
<td>Coating 1</td>
<td>V Cr Fe Ni</td>
<td>V Cr Fe Ni</td>
</tr>
<tr>
<td>Track 2</td>
<td>- 65 31 4</td>
<td>- 54 40 6</td>
</tr>
<tr>
<td>Track 3</td>
<td>- 98 2</td>
<td>- 81 17 2</td>
</tr>
<tr>
<td>Debris 4</td>
<td>- 44 49 7</td>
<td>- 27 66 7</td>
</tr>
</tbody>
</table>

Strong transfer of ball specimen material (Fe, Ni) to the surface of CrN occurs under friction at room temperature. Friction of Cr\textsubscript{0.65}V\textsubscript{0.35}N coating at room temperature is also accompanied with the transfer of material from the ball but the content of Fe and Ni is lower in comparison to the coating without V. The wear particles in both cases show a content of Fe close to 50 at %. The high temperature tests of CrN are accompanied with strong transfer of the components of the steel ball on the surface of the coating. Heating of CrV\textsubscript{35}N leads to the formation of V\textsubscript{2}O\textsubscript{5} phase like compositions, Fig.6. However, the transfer of ball specimen material is still observed but in a much smaller amount. The results of X-ray analysis of Cr\textsubscript{0.65}V\textsubscript{0.35}N coating after heating at temperature, T = 500 °C are shown in Fig.11. As can be seen, the Vanadium presences on the surface of Cr\textsubscript{0.65}V\textsubscript{0.35}N at temperature of 500 °C. The V\textsubscript{2}O\textsubscript{5} oxide structure near the worn surface and in the wear track is shown in Fig. 12.

![Image](image1.png)

Fig.12. V\textsubscript{2}O\textsubscript{5} oxide structure near the worn surface (a). V\textsubscript{2}O\textsubscript{5} tribofilm in the wear track after friction test of the coating at temperature of 500 °C (b).
The effect of V content and the temperature on the amplitude of friction force has also been studied and is shown in Fig. 13. Notably, high friction of coatings is accompanied by low values of force amplitude. The converse effect is observed for the coatings rubbed at high temperature that show relatively low coefficients of friction.

![Fig.13. The effect of Vanadium content and the temperature on the force amplitude of stick-slip under friction of coatings during 500 cycles.](image)

3.3 The friction tests using SRV4 system

The stick-slip experiments were carried out with 500 cycles. Thus, the results from SRV4 experiments were analyzed for the same number of cycles. The results of the friction tests are shown in Fig. 14. The maximum values of the friction coefficient were obtained under friction at room temperature. Oxidation of Chromium and the transfer of ball material to the surface of CrN coating are responsible for the high COF of $\mu = 0.8$ at room temperature (Fig. 15). A similar result is observed for friction of the $\text{Cr}_{0.65}\text{V}_{0.35}\text{N}$ coating at room temperature ($\mu = 0.8$). The drop of the COF at high temperature is not as significant as observed in the stick-slip setup (s. fig. 8).

Whereas the coefficients of friction are similar for the both types of coatings, the wear coefficient, K, of the steel balls is significantly lower for the $\text{Cr}_{0.65}\text{V}_{0.35}\text{N}$ coating than for the coating without Vanadium for both room and high temperature (Fig. 16), which is in good agreement with the results of the stick-slip tests (s. fig. 9).
Fig. 14. The effect of Vanadium content and temperature on the friction coefficients of CrV,N coatings (initial contact pressure, $p = 415$ MPa, i.e. a normal force of 30 N ) in SRV experiments after 500 oscillation cycles, i.e. a sliding distance of 2 m at a sliding velocity of 100 mm/s.

Fig. 15 SEM image of the wear track of CrN coating after SRV testing at room temperature.
After 1250 cycles, the wear track was found to be completely covered by a bright layer and featuring a maximum wear depth of 2.4 µm. Whilst the coating remained almost unharmed after 1250 cycles, it was completely worn off after 2500 cycles (Fig. 17). The results of EDX analyses of the worn surface after 2500 cycles are given in Table 3. It can be seen that the vanadium content in the layer decreases and signals of iron and carbon are present, indicating that the coating is worn through. A focused ion beam cut through the wear track of a specimen shows that the Cr$_{0.73}$V$_{0.27}$N coating is still present, Fig. 18. The remaining coating thickness is about 1.5 ± 0.5 µm. The sum of the remaining coating thickness and the wear depth of about 2.4 µm correspond well to the initial coating thickness of 3.8 µm. From this image the exact interface could not be determined. The EDX line scan in the insert to Figure 18 is along the yellow line. The vanadium content is highest at surface of the coating and the iron content increases from the surface to the interface and substrate. After reaching the interface the chromium content decreases rapidly. The oxygen content remains nearly constant.
Fig. 17. The profiles of the wear tracks of Cr$_{0.73}$V$_{0.27}$N coatings after friction during 1250 cycles (50 s) and 2500 cycles (100 s).

Table 3: EDX analyses of the layers in the wear tracks of friction tests

<table>
<thead>
<tr>
<th>Number of cycles</th>
<th>C [at.%]</th>
<th>N [at.%]</th>
<th>O [at.%]</th>
<th>V [at.%]</th>
<th>Cr [at.%]</th>
<th>Fe [at.%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1250</td>
<td>-</td>
<td>16.0</td>
<td>10.8</td>
<td>22.0</td>
<td>21.9</td>
<td>-</td>
</tr>
<tr>
<td>2500</td>
<td>7.1</td>
<td>14.5</td>
<td>23.0</td>
<td>4.5</td>
<td>49.6</td>
<td>1.2</td>
</tr>
</tbody>
</table>

Fig. 18. (a) SEM image of a FIB cut and (b) EDX line scan in the wear track of Cr$_{0.73}$V$_{0.27}$N coating, T = 600 °C, t = 50 s, F = 30 N, $p_i = 415$ MPa).

Figure 18 shows the area in front of the wear track after testing at 700 °C. The coating outside the wear track exhibits needle-shaped crystals of different sizes, fine crystals near the wear track and large crystals at larger distance from the wear track. The crystals are oriented
radially from the wear track and happen to be larger with increasing distance from the wear track. This behavior is an evidence for crystal growth at higher temperatures since the heat dissipation through the ball and ball holder lowers the contact temperature in comparison to the non-contact specimen surface. Between the areas of the small and large crystals there is a transition zone of about 100 to 200 µm, into which the larger crystals extend. In this transition zone one can see also some craters. This area is indicated in Figure 19 by a square and magnified in Fig. 20. Some of the craters are spalled and that thereunder is a layer with another slightly different but finer structure. The different appearances are investigated further by EDX analyses. The results are given in Table 1. The corresponding areas for this analysis are indicated in Figure 20 by the numbers 1, 2 and 3. The higher oxygen and vanadium contents at location 1 indicate that the crystallites are composed of V$_2$O$_5$ as expected also from the literature. This phase should be the cause for low friction coefficient under friction at high temperatures. However, the effect of Magnéli phase is diminished by strong transfer of the steel ball material to the coated surface.

Fig.19. SEM image of the end of wear track after friction of Cr$_{0.65}$V$_{0.35}$N coating at high temperature (T = 700 °C), number of cycles, N = 4500 cycles, load, F = 30 N, initial pressure, p$_i$ = 415 MPa).
Fig. 20. SEM image showing details of an elongated crystal and crater structures in its vicinity. The numbers indicate the locations for EDX element analyses.

Table 1: EDX analyses of the surface structures as indicated in Fig. 20

<table>
<thead>
<tr>
<th>Location</th>
<th>O [at.%]</th>
<th>V [at.%]</th>
<th>Cr [at.%]</th>
<th>Fe [at.%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>70.2</td>
<td>29.8</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>55.6</td>
<td>20.4</td>
<td>23.5</td>
<td>0.5</td>
</tr>
<tr>
<td>3</td>
<td>60.5</td>
<td>20.2</td>
<td>19.3</td>
<td>-</td>
</tr>
</tbody>
</table>

4. Discussion

Typical stick-slip curves of CrN and Cr$_{0.65}$V$_{0.35}$N coatings in frictional contact with steel are shown in Fig. 21. A maximum value of the friction coefficient is observed under friction of both the two types of coatings at room temperature. In this case the value of the coefficient of static friction in the beginning of motion is close to the value of the coefficient of kinetic friction. This process is accompanied with small variation of the COF (amplitude), (Fig. 21, graph 1). This observation can be explained by oxidation of surface layers, strong adhesion between the surface of the steel ball and the transferred film of the ball material on the coated surface, Figs. 10a, 10b. The small amplitude is apparently associated with the formation of relatively smooth surfaces due to material transfer. A slope of the stick parts during friction at room temperature does not convenient to slope of the static force at the beginning of cycle (full stick). It means that the sticks are accompanied by creep. This phenomenon will be considered in more detail in our future work. In the case of pure CrN (V = 0 %) heating of contact pair leads to increased ductility of the ball, resulting in ploughing and strong adhesion in the wear scar of the ball, Fig. 10c. Friction of Cr$_{0.65}$V$_{0.35}$N coating at high temperature is accompanied with the transfer of the material of coating on the surface of the ball, Fig. 10d. The transfer and adhesion under friction at high temperature are responsible for large values of the amplitude of friction. (Fig. 21, graph 2). Static friction is
decreased at high temperature, especially when the oxide lubricating phase is present on the rubbed surface. The formation of soft transfer films in the friction contact at high temperature causes a decrease of the average friction coefficient which is not the case with friction at room temperature. High temperature friction of Cr$_{0.65}$V$_{0.35}$N coating is accompanied by formation the V$_2$O$_5$ lubricating phase. The presence of this phase lowers the average COF value as well as the amplitude of friction, (Fig. 21, graph 3). However, relatively high values of the amplitude and average values of the friction coefficient are associated mainly with transfer of the ball material to the coated surface.

![Graph showing stick-slip phenomena under friction of CrV$_x$N coatings at room (T = 25 °C) and high (T = 500 °C) temperatures: (1) $x = 0 \%$ and 35 \%, T = 25 °C; (2) and $x = 0 \%$, T = 500 °C; (3) $x = 35 \%$, T = 500 °C.]

Comparison of the results from stick-slip analysis with the experimental data from oscillating wear experiments (SRV) shows good correlation of both methods for coefficients of friction at room temperature (Fig. 22). The difference between the methods is $\Delta \mu \approx 0.03$ and shows a small decrease of COF for an addition of 35 at.% vanadium. At 500 °C, however, the stick-slip-test-setup shows a decrease of COF from 0.6 (0 at.% V) to 0.45 (35 at.% V) whereas the SRV-setup records an increase from 0.55 to 0.65. This observation can be explained when the testing conditions are taken into account. First of all, the test parameters are not identical, especially the sliding velocity is much higher for the SRV-test, yet the normal force is smaller than in the stick-slip-experiment. Furthermore, the distance is two times higher for the SRV experiments. Consequently, the frictional power that is generated differs strongly for each tribological test setup, as can be seen from Table 2. Thus, it can be concluded that different wear mechanisms are activated depending on the power of friction. Especially here, a closer look at the wear track of the SRV-specimens reveals a significant amount of transferred material from the steel body to the coated surface. Additional, wear particles in the track can further increase the coefficient of friction.
Investigations with an increasing number of cycles up to 4500 cycles were only carried out in SRV tests. The friction coefficient increases as well in comparison to 500 cycles during low sliding velocity. This effect can be explained by a rise of the contact temperature under relatively high sliding velocity in the SRV tests causing oxidation of surface layers and intensification of the material transfer from the ball to the coated surface. The friction coefficients coincide well for friction at 500 °C. This correlation can be explained by the fact that the sliding velocity and duration do not affect the contact temperature significantly.

Table 2: Comparison of experimental conditions and resulting COF and frictional power.

<table>
<thead>
<tr>
<th></th>
<th>Average sliding velocity $v$</th>
<th>Sliding distance $s$</th>
<th>Normal force $F_N$</th>
<th>Contact pressure $p_i$</th>
<th>Coefficient of friction $\mu$</th>
<th>Frictional power $P_{frc} (=v<em>F_N</em>\mu)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stick-slip</td>
<td>0.3 mm/s</td>
<td>1 m</td>
<td>0.5 N</td>
<td>1020 MPa</td>
<td>0.6</td>
<td>0.09 mW</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.45</td>
<td>0.0675 mW</td>
</tr>
<tr>
<td>SRV4</td>
<td>100 mm/s</td>
<td>2 m</td>
<td>30 N</td>
<td>415 MPa</td>
<td>0.55</td>
<td>1650 mW</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.65</td>
<td>1900 mW</td>
</tr>
</tbody>
</table>
Fig. 22. The effect of number of cycles on the friction coefficient for CrN (V = 0 %) and Cr$_{0.65}$V$_{0.35}$N rubbed at the temperatures 25 °C and 500 °C and the sliding velocity, $v = 0.3$ mm/s (HIT) and frequency 25 Hz (IWM).

Good correlation between stick-slip and SRV tests is observed in the evaluation of the wear coefficients. A low wear coefficient under friction with Cr$_{0.65}$V$_{0.35}$N at room temperature can be explained by smooth surface of coating, their high hardness and toughness in comparison to coating without Vanadium. Maximum wear is observed for the CrN coating at high temperature. Softening of the steel ball, plowing, strong adhesive wear and transfer of ball material to the coated surface determines the high wear under this condition. The formation of a solid lubricant reduces the wear of ball and coating significantly.

5. Summary

1. The effects of vanadium content in CrV$_x$N coating and the temperature on pin-on-plate friction and wear properties and stick-slip phenomena have been studied.
2. Good correlation between SRV and stick-slip tests has been revealed.
3. The amplitude of the COF of CrV$_x$N against steel was analyzed in a wide temperature range.
4. The addition of Vanadium to the CrV\textsubscript{x}N coating (35 %) improves the tribological properties in terms of lower friction and wear for temperatures up to 500 °C. The changes of tribological properties at room temperature are associated with higher hardness, toughness and smaller grain size in comparison to CrN coating without V.

5. The low wear rate of Cr\textsubscript{0.65}V\textsubscript{0.35}N at high temperatures (T = 500 - 700 °C) is associated with the formation of a Magnéli phase in the tribological contact.

6. The coatings with high content of Vanadium are not useable for temperatures higher than 600 °C, since large crystals of Vanadium oxide are formed.

References