



Development of an in situ Plasma Treatment of X155CrMoV12 for a (Cr,Al)N PVD Tool Coating for Dry Metal Forming in Cold Forging.

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Abstract

Cold forging processes are of great importance in production engineering due to the high material utilization and the associated energy and resource efficiency. Liquid and solid lubricants are used in order to perform cold forging processes successfully. These lubricants are often questionable due to ecological, economic, and legislative reasons. For these reasons, dry metal forming exhibits an increased research potential in surface engineering. The absence of lubricants in dry metal forming contributes significantly to the waste reduction in manufacturing processes and to the goal of a lubricant-free factory. Coated metal forming tools may enormously reduce tool and workpiece wear in cold forging or deliver special functions even in the absence of the lubricants. However, the abdication of lubricants goes along with the requirement that the dry tribological system has to withstand the increased tribological loads. In this contribution a (Cr,Al)N PVD tool coating and an in situ plasma etching process are developed to ensure a sufficient adhesion strength on the tool material X155CrMoV12 (DIN 1.2379, AISI D2). Such a plasma treatment of the substrate is necessary for the coating to withstand increased tribological tool loads in dry metal forming.

Keywords: dry metal forming, (Cr,Al)N, HPPMS, plasma etching

1 Introduction

Cold forging processes are of great importance in production engineering due to the high material utilization and the associated energy and resource efficiency [1]. Cold forged parts are typically used within the drive technology, e.g. as driving shafts. In order to perform cold forging processes successfully, lubricants and often harmful additives are used, which are questionable due to ecological, economic, and legislative reasons [2]. There is an increasing interest for reducing these factors by using biodegradable lubricants and/or physical vapor deposition (PVD) coatings for cold forging. Regarding to this interest many studies were done within the Collaborative Research Center 442 (SFB 442) entitled ‘Environmentally friendly tribological systems’, which has been established by the German Research Foundation (DFG). Lugscheider et al. developed a multilayer (Ti,Hf,Cr)N PVD coating for cold metal forming applications using the arc ion plating technique [3]. Bobzin et al. enhanced this coating with a CrN toplayer for the interaction with

a biodegradable lubricant for environmentally benign metal forming [4]. As a next step, the avoidance of lubricant usage is the focus of many ongoing projects in metal forming which contributes significantly to the waste reduction in manufacturing processes and to the goal of a lubricant-free factory [5]. The state of the art mainly covers sheet metal forming processes, but reveals the potential of tool coatings to withstand the tool loads in dry metal forming as well. Compared with sheet metal forming cold forging is characterized by higher contact pressures and surface expansion of the workpiece [6]. The tribological conditions in cold forging process can lead to contact pressures of more than 3000 MPa [7]. Furthermore, the avoidance of lubricants results in a dry tribological system which has to withstand increased tribological loads [8]. In this term, the coating for dry metal forming should have a very high adhesion to the substrate material even at increased loads in order to enhance the tool life. The ternary system (Cr,Al)N is a promising candidate for these applications due to its high hardness and good

abrasion wear resistance [9]. Previous experimental investigations of (Cr,Al)N in both, lubricated contacts [10] and in dry running conditions [11] showed good tribological results as well. A promising approach towards the reduction of friction forces and thus towards reduced wear rate of tools is the application of self-lubricating coatings. Therefore, the existing (Cr,Al)N coating was enhanced by incorporation with vanadium (V) and tungsten (W) for the friction reduction in tool applications for high temperatures between 600 °C and 800 °C by means of magnetron sputtering (MS) [12]. Besides these, as solid lubricants molybdenum disulfide (MoS₂) and tungsten disulfide (WS₂) are interesting especially for lubrication at lower temperatures. Therefore, the current study focuses on a nanocomposite coating (Cr,Al)N + XS₂ (X = Mo, W) with disulfides. In this context, the (Cr,Al)N hard matrix serves the purpose of wear protection while the disulfides particles in the matrix provide for reduced friction in dry running. The overall approach within the priority program „Dry metal forming – sustainable production through dry processing in metal forming” (SPP 1676) is shown in Fig. 1. The Surface Engineering Institute (IOT) focusses on the development of (Cr,Al)N PVD coatings with self-lubricating disulfides while the Laboratory for Machine Tools and Production Engineering (WZL) works on the development of surface structures on workpieces to minimize friction and tool loads.

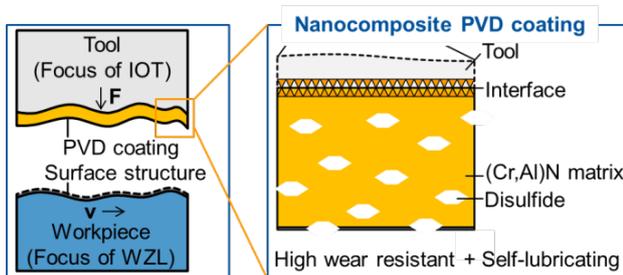


Figure 1: Illustration of the proposed dry tribological system. Legend: F = Normal force, v = sliding velocity.

The main focus in this study was set on the advances regarding the development of an in situ plasma treatment of the substrate for (Cr,Al)N PVD coatings deposited by means of high-power pulsed magnetron sputtering (HPPMS) technology. A maximum adhesion strength between the (Cr,Al)N coating and the substrate material X155CrMoV12 (DIN 1.2379, AISI D2) was pursued to withstand the tribological loads in dry metal forming. The surfaces of the non-treated metallic substrates are characterized by very inhomogeneous contamination layers consisting of dust, water, oil and metal oxides. Cleaning of the substrate surface by ion etching prior to the deposition is common practice [13] for a better adhesion of the coating on the substrate. According to this term, two different etching approaches are applied, namely *middle frequency (mf) argon (Ar) etching* and *chromium (Cr) ion etching* by HPPMS technology. (Cr,Al)N coatings on differently treated surfaces are tested inter alia by scratch tests. The evaluation of scratch resistance shows differences regarding the plasma etching processes.

Future works will cover the further development of the wear-resistant (Cr,Al)N PVD tool coating as well as the self-lubricating aspects by embedding disulfides into the matrix of (Cr,Al)N, see Fig. 1.

The structure of the paper is as follows. Firstly, experimental details on the deposition process of the (Cr,Al)N and the plasma treatments as well as on the analytical methods for the characterization of the coatings are presented in the Section 2. Afterwards, the results and discussion follow in Section 3. Concluding, the scientific findings are summarized and an outlook for future investigations is given in Section 4.

2 Experimental procedure

2.1 Deposition process of the (Cr,Al)N coating

The investigated coatings in this study were deposited on X155CrMoV12 substrates using an industrial CC800/9 Custom coating unit from CemeCon AG, Würselen, Germany. The unit is equipped with two conventional MS cathodes and two HPPMS cathodes. Furthermore, it has another high voltage supply to produce substrate bias in HPPMS mode. Figure 2 shows the schematic of the coating deposition setup. A Cr target (500 x 88 mm²) on HPPMS cathode no. 4 with 20 pieces of diameter 15 mm aluminum (Al) plugs (CrAl20) was used for the deposition (purity: Cr 99.9 % and Al 99.5 %). A pulse length of 200 μs was applied. A repetition frequency of 500 Hz was chosen. A constant mean power of 5 kW was applied. Argon flow was kept constant at 200 sccm. Nitrogen flow was controlled over the total pressure of 570 mPa. Conventional direct current (dc) bias of -120 V was performed on substrate. During deposition, the samples were rotated in a twofold motion. Before deposition, two kinds of etching variants were performed, namely *mf Ar ion etching* and *HPPMS Cr ion etching*, see Section 2.2.

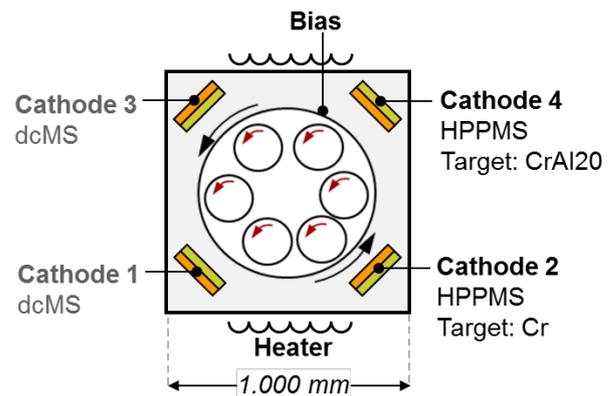


Figure 2: Schematic of the coating deposition setup (top view).

All specimens were hardened and tempered to a hardness of 60 HRC and polished to a mean roughness of Ra ≈ 0.025 μm. Prior to deposition, the specimens were cleaned in a multi-stage ultrasonic bath which contained alkaline solvents.

2.2 Variation of the in situ plasma treatments

A proper plasma treatment of the substrate is crucial for the development of the coating with maximum adhesion strength on substrate material. This section describes the comparative development of the in situ plasma treatment of the tool material X155CrMoV12.

For the deposition of (Cr,Al)N coatings with different pre-treatments of the substrate the etching process itself and different parameters in each processes were varied. In a first step, the influence of the etching duration ($t = \{20, 40, 60\}$ min), bias voltage ($V = \{550, 600, 650\}$ V) and Ar pressure ($p = \{250, 300, 350\}$ mPa) within mf Ar gas ion etching are investigated, see Fig. 3. Totally, nine samples (S1-S9) were etched with Ar ions. Two of the three parameters were kept fixed during the variation of the third parameter.

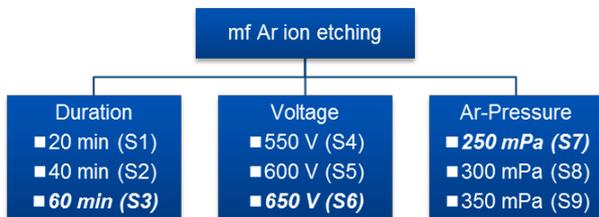


Figure 3: Variation of the process parameters within mf Ar ion etching.

In a second step, the influence of the Cr ion etching by HPPMS technology was evaluated. For this purpose, a Cr target (purity: 99.5%) on HPPMS cathode no. 2 was used for emitting the ions, see Fig. 2. Substrate bias was varied between dc and HPPMS technologies. The frequency ($f = \{500, 350, 200\}$ Hz) and the power ($P = \{2.5, 3.5, 4.5\}$ kW) were varied in the dc bias mode, whereas pulse length ($l = \{50, 100, 200\}$ μ s) and an offset configuration were varied for the HPPMS bias mode, see Fig. 4. Totally, eleven samples (S10-S20) were etched with Ar ions.

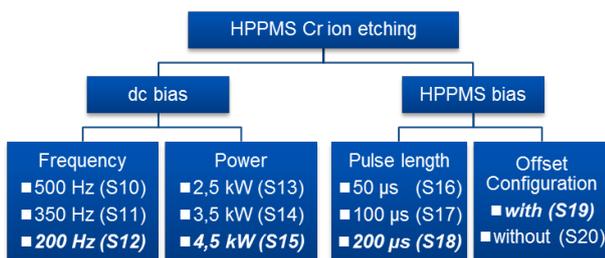


Figure 4: Variation of the process parameters within HPPMS Cr ion etching.

Macak et al. carried out some optical emission studies in HPPMS discharges in [14], which showed that the pulse duration consists of different phases. It was found that at the beginning of the pulse (between 0-40 μ s) gas ions dominated the plasma, while later metal ions were dominating (between 40-100 μ s) and finally as time elapsed (after 100 μ s) gas-metal ion composition with a lower intensity was the case. According to this findings, a pulsed offset bias in

HPPMS modus was used in addition to the variation of the listed parameters. In Fig. 5 an exemplary cycle of HPPMS offset bias is shown. The on-time was kept constant at 60 μ s after an off-time of 50 μ s. Total pulse length was 200 μ s. This setting allowed focusing on metal ions.

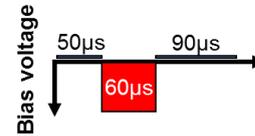


Figure 5: Example of a cycle of pulsed offset bias in HPPMS modus.

2.3 Analytical methods for the characterization

Morphology: morphology of the samples was analyzed using scanning electron microscopy (SEM) of type DSM 982 Gemini (Carl Zeiss GmbH, Jena, Germany).

Chemical composition: the chemical composition of the coatings was determined using glow discharge optical emission spectroscopy (GDOES) in radio frequency (rf) mode as a function of etching time. A GDOES profiler type JY 5000 RF (HORIBA Jobin Yvon Ltd., Kyoto, Japan) equipped with an anode of 4 mm in RF modus was used. Furthermore, energy dispersive X-ray diffraction (EDX) line-scans were performed for the investigation of the chemical composition between the sheltered and etched surfaces of an uncoated specimen.

Mechanical properties: a NanoindenterTM XP by MTS Nano Instruments, Oak Ridge, Tennessee, USA, with a Berkovich indenter was applied for this purpose. The penetration depth was kept below 10 % of the top layer thickness. Calculations of the Young's modulus are based on Oliver and Pharr's equations [15]. A constant Poisson's ratio of $\nu = 0.25$ was assumed.

Adhesion strength by scratch tests: adhesion strength was quantitatively evaluated by scratch testing according to DIN EN 1071-3:2005 [16]. Scratch test conditions were identical in each case, applied load 10-70 N, speed 0.5 mm/min, loading rate 10 N/min. and scratch length 4 mm. During scratch testing various coating flaws such as cracking and spalling can be observed. Critical loads were examined by means of light microscopy (Keyence VHX-100, Keyence GmbH, Neu-Isenburg, Germany). As a measure of the adhesion between coating and the substrate the critical loads (L_{c_i}) are determined at which the first signs of different coating failures are noted. There are different critical failures modes: adhesive rupture, surface buckling, adhesion/cohesion, forward cracking and rearward cracking. L_{c_1} is the load at which the undisturbed scratch shows first signs of failure in form of plastic deformation at scratch track's edge. At L_{c_2} the coating starts to delaminate and the substrate material will be partly visible. At last, L_{c_3} means the last at which the coating is completely torn apart. This is a major coating damage failure.

Adhesion strength by Rockwelltest: Rockwell indentation (HRC) with a load of 1,471 kN according to VDI guideline 3198 [17] was used. Rockwell

indentations distinguish between different adhesion classes (HF) of HF 1 (very good adhesion) and HF 6 (insufficient adhesion).

3 Results and discussion

Exemplary cross section fracture of the HPPMS (Cr,Al)N coating (sample 10) is shown in Fig. 6. Cross section fractures of the other samples confirmed that the morphology does not change according to pre-treatment if the parameters of the coating deposition kept fixed. It can be clearly seen that the coating has a fine columnar morphology.

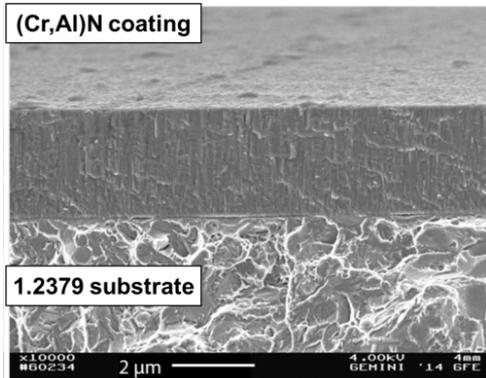


Figure 6: SEM cross section fracture of the (Cr,Al)N coating (S10).

The coating thickness is 2.60 μm , which corresponds to a deposition rate of 0.52 $\mu\text{m}/\text{h}$. The chemical composition of the deposited coatings as measured by GDOES shows no differences regarding to pre-treatment as well. Exemplary results are as follows: $X_{\text{Cr}} = 31$ at.-%, $X_{\text{Al}} = 11$ at.-% and $X_{\text{N}} = 58$ at.-% (sample 10), see Fig. 7. Cr:Al ratio is 74:26 (at.-%).

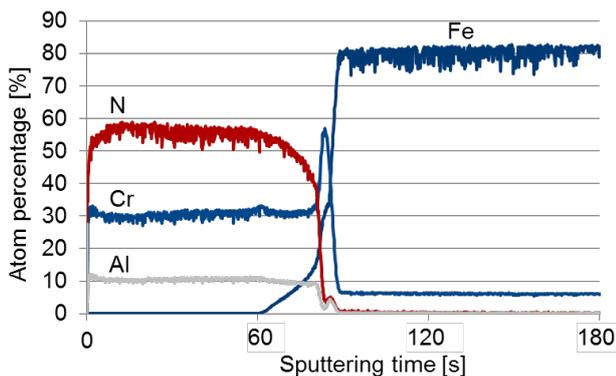


Figure 7: GDOES investigation of the (Cr,Al)N coating (S10).

Regarding the mechanical properties as universal hardness (HU) and the modulus of indentation (E_{IT}), it must be stated that the $\text{HU}^3/E_{\text{IT}}^2$ ratio characterizes the resistance of the material to plastic deformation [18]. Therefore, a high HU and a low E_{IT} are aimed for a tribological application. In the case of (Cr,Al)N matrix the mechanical properties are strictly dependent on the Cr:Al ratio. The determination is done on the basis of previous investigations [19]. Mechanical properties do not show differences regarding the pre-treatment art

either. Exemplary results (sample 10) are as follows: $\text{HU} = 28.6 \pm 2.8$ GPa and $E_{\text{IT}} = 365.1 \pm 25.8$ GPa.

Scratch tests on all samples were done in order to evaluate the adhesion strength between the substrates and the specimens. Critical loads at which the coating failure occurs were determined and compared with each other. The specimens which show better adhesion strength between the coating and the substrate in each variation group are shown in Fig. 3 and 4 as bold and italic characters. Figure 8 shows exemplary an investigation of scratch tracks and a Rockwell indentation test by means of light microscopy. The arrow indicates the direction of the scratches. Table 1 summarizes the results of all specimens regarding adhesion strength. As mentioned before, the last at which the plastic deformation occurs at the scratch track's edge is determined by L_{C1} . This value is not interesting for the purposed application. Therefore, the focus was on the L_{C2} and L_{C3} loads.

		Variation	Sample	L_{C2} [N]	L_{C3} [N]	Rockwell HF	
mf Ar ion etching	Duration	20 min	S1	30	30	2	
		40 min	S2	40	40	2	
		60 min	S3	40	50	1	
	Voltage	550 V	S4	30	30	2	
		600 V	S5	30	40	2	
		650 V	S6	40	50	1	
	Ar-Pressure	250 mPa	S7	40	50	2	
		300 mPa	S8	40	40	2	
		350 mPa	S9	30	40	2	
HPPMS Cr ion etching	dc bias	500 Hz	S10	20	30	3	
		350 Hz	S11	30	30	2	
		200 Hz	S12	40	40	2	
	Power	2,5 kW	S13	20	30	3	
		3,5 kW	S14	30	30	2	
		4,5 kW	S15	40	40	2	
	HPPMS bias	Pulse length	50 μs	S16	30	40	3
		100 μs	S17	40	40	2	
		200 μs	S18	40	50	2	
Offset	with	S19	50	60	3		
	without	S20	40	50	2		

Table 1: Investigation of the specimens regarding adhesion strength between (Cr,Al)N coating and substrate.

The in Fig. 8 observed critical scratch loads L_{C2} and L_{C3} for this compound are 40 N and 50 N, respectively. At L_{C2} interfacial decohesion of the coating along the

scratch track borders occurs. At 50 N an adhesive failure of the coating is visible.

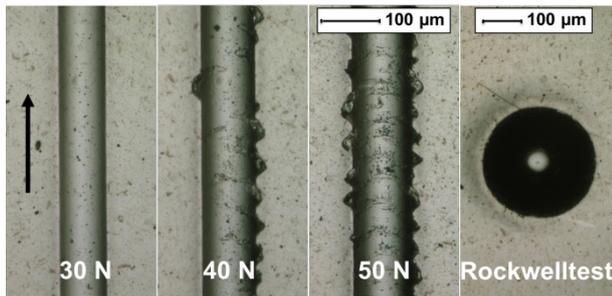


Figure 8: Scratch tracks at different loads and rockwelltest of the (Cr,Al)N coating (S6).

Considering the results in Table 1, the (Cr,Al)N coating exhibits the ideal critical loads on the X155CrMoV12 substrate with the variation of the following parameters in the mf argon ion etching: a duration of 60 min, a voltage of 650 V and a Ar pressure of 250 mPa. This pre-treatment will be used for the future studies on the further development of the (Cr,Al)N coating.

All Rockwell indentations exhibit adhesion classes between HF 1 and HF 3 regarding the classification by VDI guideline 3198 and these are all considered as acceptable. It can be said, that the HF classes of the coatings with Cr ion etching pre-treatment are lower comparing to the samples pre-treated with mf gas etching. But one of the aspects of the Cr ion etching treatment by HPPMS technology is the possibility of metal ion implantation into the surface which can lead to improvement of bonding force between the coating and the substrate surface [20]. In order to investigate this effect, an uncoated X155CrMoV12 specimen was sheltered in one half to prevent any treatment and the other half was Cr etched with the same parameters as by sample 19 (HPPMS Cr ion etching with HPPMS bias and offset configuration). Afterwards, the transition zone on the surface was analyzed by EDX line-scan, see Fig. 9. Existence of Cr on the etched surface is proven. Also SEM cross section fractions confirmed this observation, showing a thin Cr top-layer with a thickness of about 200 nm, see Fig. 10.

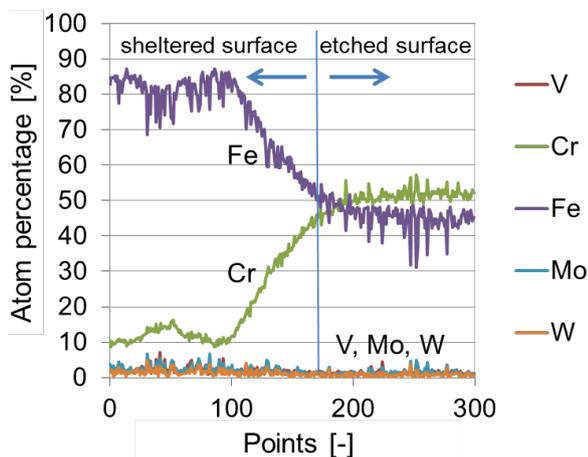


Figure 9: EDX line-scan of the sheltered and etched surface.

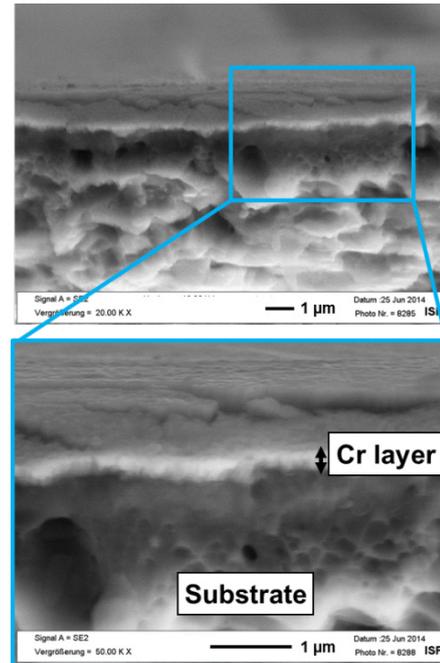


Figure 10: SEM cross section fracture of the etched surface.

4 Conclusion and outlook

The absence of lubricants in dry metal forming significantly contributes to waste reduction in manufacturing processes and to the goal of a lubricant-free factory. However, the avoidance of lubricant usage goes along with the requirement that the dry tribological system or coating has to withstand the increased tribological loads. In this contribution a plasma etching process is developed for the (Cr,Al)N PVD tool coating to ensure a sufficient adhesion strength on the tool material.

Since the results in this study only give a first impression of a very recent research, there remain topics to finish in the future. Firstly, (Cr,Al)N development by means of HPPMS technology will be completed. After that, the self-lubricating disulfides will be embedded into the (Cr,Al)N matrices. Application oriented wear tests using the Pin-On-Disc (IOT) and a novel Pin-On-Cylinder tribometer (WZL) will be performed to analyze the friction behavior which will constitute an important extension of this work. Also, the advances in surface structures on workpieces will be investigated to provide friction reducing surfaces in dry metal forming by experimental studies of surface structures by WZL in order to identify friction and, thus, tool load reducing surfaces compared with non-structured workpieces. Synthesized, these two approaches from two institutions will achieve a lubricant free cold forging.

Acknowledgements

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