



CVD diamond deposition under atmospheric conditions on steel with a silicon intermediate layer

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Abstract

In order to realize dry metal forming, the requirements of the surface layer, e.g. to load-bearing capacity and tribological properties are increasing. Therefore, the feasibility of chemical vapour deposition (CVD) of diamond onto tool steel 1.2379 under atmospheric conditions without a vacuum chamber is investigated, so that there is no limit according to the size of the tool.

For the deposition of CVD diamond coatings, a laser-based plasma CVD process combined with a physical vapour deposition (PVD) process is used. It is shown that a PVD silicon layer serves as diffusion barrier for the subsequent deposition of a CVD diamond layer. The diffusion barrier as well as the CVD diamond layer is analysed by laser microscope measurements, scanning electron microscopy, and energy-dispersive X-ray spectroscopy. The crystal structure of the diamond films is verified by Raman spectroscopy and laser microscope measurements.

To visualize the coating system, a focused ion beam is used to generate a cross-section. The local deposition of a CVD diamond layer onto tool steel without the need for a vacuum chamber is evidenced by these investigations.

Keywords: CVD diamond, PVD coating, diffusion barrier, steel

1 Introduction

In the process of metal forming, it is common practice to use lubricants. However, from an economic as well as an ecological point of view, there exists a strong demand to avoid lubricants in metal-forming processes. In order to realize dry metal forming, the requirements of the surface layer are increasing in relation to load-bearing capacity and tribological properties [1]. One approach is to coat the tool surface with a wear-resistant layer. For this approach, carbon-based coatings like diamond like carbon (DLC) are especially investigated [2].

Polycrystalline diamond coatings are also a candidate as tool-coating material for pioneering work on lubricant-free metal forming. The deposition of polycrystalline diamond coatings onto steel has already been successfully researched by various scientists [3]. Direct deposition of polycrystalline diamond onto steel substrates was investigated by Buijnsters et al. [4], with the conclusion that diffusion barrier layers are essential in the deposition of high-quality and adherent polycrystalline diamond coatings on steels. Several different materials that could serve as a diffusion barrier have been investigated, such as CrN [5], TiC/TiN [6], and SiC [7]. The thickness

of the diffusion barrier varies in the different researches. For the case of silicon interlayers, thicknesses between 0.5 μm [8] and 2 μm [9] can be found in the literature.

All processes applied for the successful deposition of polycrystalline diamond coating onto a steel substrate take place in a vacuum chamber. According to the dimensions of forming tools and their complex geometries, a chamber-free deposition process is required for the application of local wear protection.

2 Methods

CVD diamond coatings are deposited by a laser-based plasma CVD process combined with a PVD process (see Fig. 1). The process was explicitly described by Schwander [10].

The cold-work tool steel X153CrMoV12 (1.2379) in annealed condition with a hardness of 240 HV0.5 is used as the substrate material. The steel substrate is heated up to 250 °C prior to deposition. Afterwards the substrate is heated up to the deposition temperature in the range of 800 °C to 850 °C by an argon-plasma flame with 2.3 standard litre per minute (slm) of hydrogen with a power supply of 4 kW. The preheating is applied until a constant surface temperature is measured and then kept

constant for two minutes. In this way the thermal expansion of the steel substrate takes place before coating deposition. Hydrogen is introduced to the plasma flame to prevent oxidation of the steel substrate.

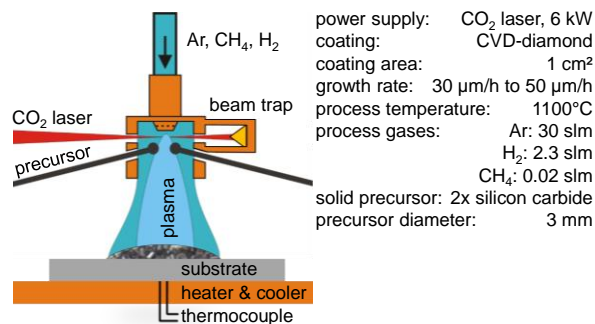


Fig. 1: Setup of the laser-based plasma chemical vapour deposition (CVD) process combined with physical vapour deposition (PVD).

Two silicon carbide precursors, with a diameter of 3 mm, are fed with a velocity of 0.09 mm/min for 7.5 min, which leads to a deposition rate between 1 mg/min and 1.5 mg/min. During deposition the substrate is constantly moving 10 mm back and forth in the y-direction to achieve a more homogeneous silicon-coating surface.

The diamond nucleation is carried out with a dispersion consisting of 200 ml of isopropanol and 210 mg of diamond powder with an average crystal size of 0.25 μm to 0.50 μm from the company Microdiamant AG. The dispersion is applied to the silicon coating by spraying with a superfine nebulizer.

The CVD diamond coating is deposited for 40 minutes. In 2007, Chen et al. published work showing that a higher ratio of methane to hydrogen enhances the diamond nucleation [11]. In contrast, a lower ratio of methane to hydrogen leads to a higher growth rate of microcrystalline grains. Therefore, deposition is carried out for the first five minutes with a higher methane-to-hydrogen ratio of 2.5 % to increase the nucleation rate. Afterwards, the polycrystalline CVD diamond layer is deposited with a ratio of 1.0 % to achieve a higher growth rate. The temperature measured by thermocouples underneath the substrate was regulated to 690 °C during deposition by feedback control. Detailed implementation of the feedback control was published by Prieske et al. in 2015 [12]. This regulated temperature results in a surface temperature of 1050 °C measured by IMPAC pyrometer IGAR 12-LO.

3 Results

3.1 Deposited silicon layer

The PVD coating is deposited by evaporation of solid silicon carbide precursor. In this way, a silicon layer is deposited, which is verified by energy dispersive X-ray spectroscopy (EDX), as shown in Fig. 2. The iron and chromium signals arise from the work tool steel X153CrMoV12 substrate, which contains 12 % chromium.

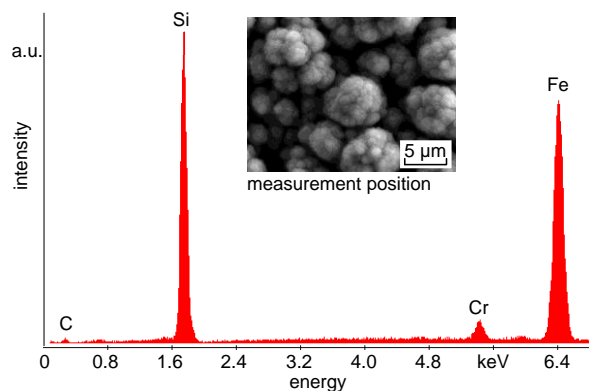


Fig. 2: EDX spectroscopy of the PVD layer obtained by evaporation of solid silicon carbide precursor.

The surface structure of the deposited silicon intermediate layer is shown by scanning electron microscope (SEM) measurements in Fig. 3a and 3b, which reveal the cauliflower-like structure of the silicon surface. To prove that the silicon diffusion barrier is a closed layer that covers the steel surface completely, backscattered electron microscopy (BSE) measurements are executed, which are shown in Fig. 3a and 3c. The result shows that a closed layer is successfully deposited, because the steel appears in bright white colour in the BSE measurements.

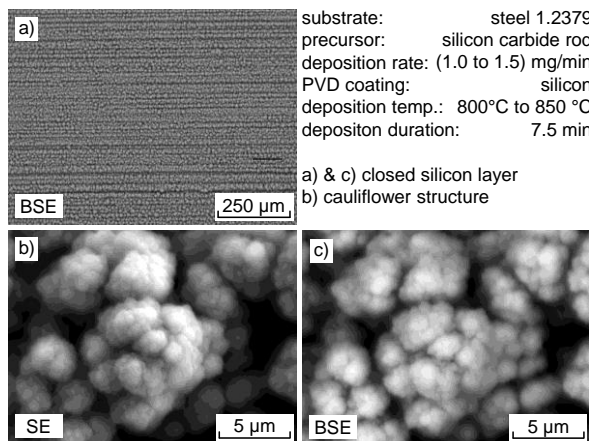


Fig. 3: a) BSE microscopy of deposited silicon coating, b) close-up SEM, and c) BSE microscopy of the silicon layer.

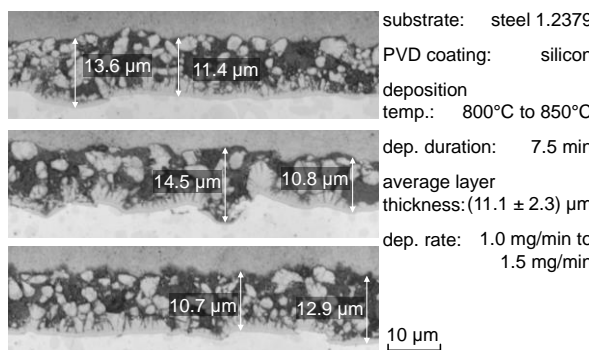


Fig. 4: Cross-section of silicon layer on steel to determine the layer thickness.

To determine the average thickness of the deposited silicon layers, cross-section polishes are done and visualized by laser scanning microscope measurements. In Fig. 4 it is shown that the average thickness of the PVD silicon layer is 11.1 μm with a standard deviation of 2.3 μm .

3.2 Deposited CVD diamond layer

In Fig. 5a, it is shown by an SEM measurement that the deposited silicon layer serves as a diffusion barrier for the subsequent deposition of a CVD diamond layer. The polycrystalline structure can be seen as well as the locally closed diamond layer. In the BSE measurements in Fig. 5b and 5c it is visible that the CVD diamond layer is not a completely closed layer, because the silicon layer can be detected between the single diamond crystals. The silicon layer appears white due to electric charging by the electron microscopy.

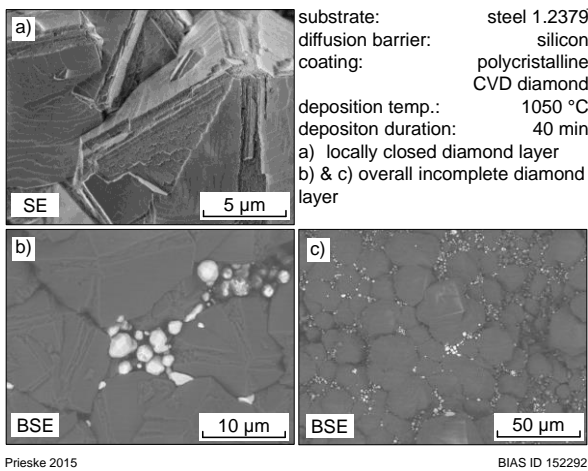


Fig. 5: a) SEM of a locally closed diamond layer; b) and c) BSE microscopy of CVD diamond layer on silicon diffusion layer.

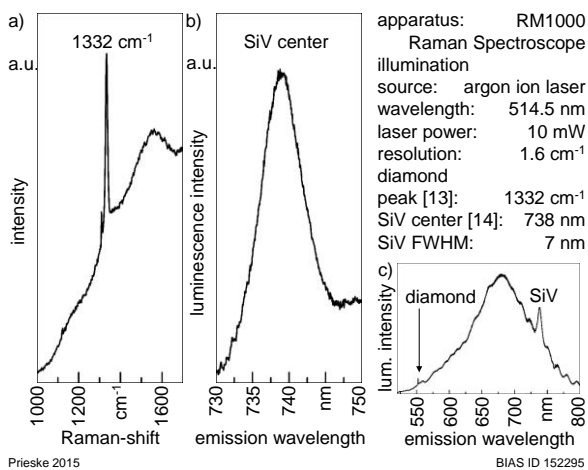


Fig. 6: a) Raman spectroscopy, b) close-up of photoluminescence peak of the SiV centre, and c) photoluminescence spectra measurement on a single diamond crystal.

The crystals that can be seen in Fig. 5 are proven to be diamond by the sharp peak at 1332 cm^{-1} in the Raman spectroscopy measurement [13], which can be seen in Fig. 6a. Fig. 6b shows the results of the recorded photoluminescence, which shows a peak at 738 nm with a full width at half maximum of 7 nm. That recorded signal

shows that silicon-vacancy centres (SiV) exist inside the diamond crystals [14].

To visualize the coating system, a focused ion beam (FIB) is used to generate a cross-section, which is shown in Fig. 7a. The average thickness of the coating composition can be calculated as approximately 31 μm . On closer observation (Fig. 7b) of the transition between the silicon coating and the CVD diamond layer, the interdigitation of the two coatings can be seen. At the transition between steel substrate and silicon layer, a gap can be detected.

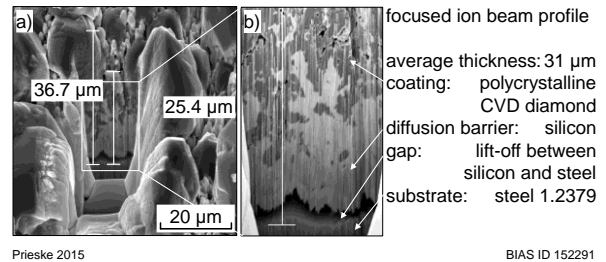


Fig. 7: a) FIB profile of a CVD diamond coating on a steel substrate with a silicon diffusion barrier; b) close-up of the profile.

To investigate the influence of the applied surface temperature of 1050 $^{\circ}\text{C}$ for 40 minutes during the CVD process, hardness measurements were executed. As reference the hardness of the steel substrate in annealed condition was measured to $238 \pm 11 \text{ HV0.5}$ (Fig. 8b). In Fig. 8 the hardness of the steel substrate after the deposition process is shown. It can be seen that the steel substrate is locally hardened by the applied temperature profile of the deposition process. In the centre (measurement position 0 mm Fig. 8a) a maximum hardness of 777 HV0.5 was measured, which decreases towards the edges of the substrate. The coated area of 1 cm^2 is marked in Fig. 8a. Underneath the coated area the steel is hardened to a minimum hardness of 600 HV0.5. At the edges of the steel substrate the hardness did not change compared to the initial condition. The hardness also decreases with increasing distance, vertically to the coating surface. In a distance of 2.75 mm a decrease of the hardness of 200 HV0.5 was determined.

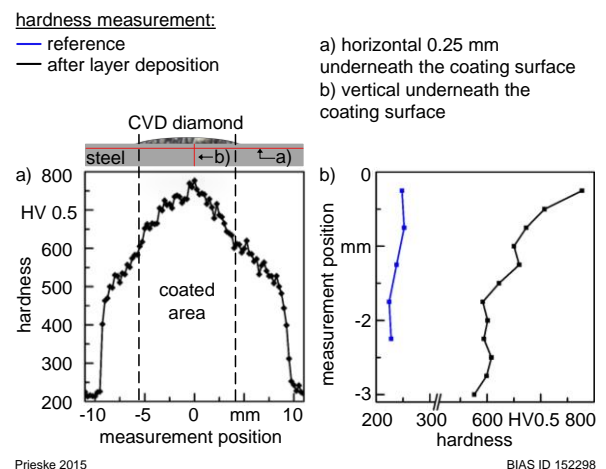


Fig. 8: Result of hardness measurement a) horizontal and b) vertical underneath the coating surface.

4 Discussion

The results show that the laser-based plasma CVD combined with a PVD process enables the deposition of a coating combination under atmospheric conditions with the same machine. The deposition of an intermediate layer (diffusion barrier) is essential for the deposition of polycrystalline diamond onto steel substrates, as shown by the researches of Buijnsters et al. in 2007 [4]. It is shown that the vaporization of solid silicon carbide precursors in the PVD process leads to the deposition of a silicon coating on the steel substrate. With a deposition duration of 7.5 minutes, a closed silicon coating with an average layer thickness of $11.1 \mu\text{m} \pm 2.3 \mu\text{m}$ is achieved. The silicon surface shows a cauliflower-like structure. The large variety of interlayer materials used for deposition of diamond onto steel such as, for example, CrN [5], TiC/TiN [6], SiC [7], or Al [15] show that there are several materials that have the ability to serve as a diffusion barrier.

CVD-diamond deposition onto the silicon coating evidences the function as a diffusion barrier, as was also confirmed in 2010 by Álvarez et al. [9], who used a vacuum chamber process (ion beam deposition) to deposit the silicon coating. Due to the way of diamond seeding, by spraying with a superfine nebulizer, a low seeding density was reached, which might be the reason for not achieving a completely closed CVD-diamond layer, even after a coating thickness of $31 \mu\text{m}$. The purpose of choosing this way of seeding, instead of using an ultrasonic bath, was to avoid any restriction of the substrate dimension.

The reason for the lift-off between the silicon interlayer and the steel substrate (see Fig. 7b) is the tensile residual stress, which arises during cooling down of the steel substrate, according to the unequal coefficients of thermal expansion. The adhesion of the silicon coating to the steel substrate needs to be improved and the tensile residual stress reduced, before transferring the coating system into an application.

The deposition temperature has a huge impact on the hardness of the steel substrate as was determined in Fig. 8. The CVD deposition temperature is above the austenitizing temperature, so that the rapid cooling down (in 100 s from $1050 \text{ }^\circ\text{C}$ to $350 \text{ }^\circ\text{C}$) of the steel substrate, after the extinction of the plasma flame, leads to a hardening underneath the coated area.

Through these researches, the basic requirements for chamber-free deposition of CVD-diamond onto steel for the application of local wear protection are fulfilled.

5 Conclusion

The research results show that a closed silicon layer can be deposited onto cold-work tool steel X153CrMoV12 by the evaporation of solid silicon carbide precursors. It was verified that the silicon layer serves as a diffusion barrier, enabling the deposition of CVD diamond onto steel substrates. For the first time, CVD diamond with a preceding diffusion barrier was deposited with one machine under atmospheric conditions onto a steel substrate.

Acknowledgements

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References

- [1] F. Vollertsen, F. Schmidt: Dry Metal Forming: Definition, Chances and Challenges. *Int. J. Precision Engineering and Manufacturing – Green Technology* 1/1 (2014) 59-62.
- [2] G. Reisel, S. Steinhäuser, B. Wielage: The behaviour of DLC under high mechanical and thermal load. *Diamond and Related Materials* 13 4–8 (2004) 1516–1520
- [3] K. Kellermann, C. Bareiß, S.M. Rosiwal, R.F. Singer: Well adherent diamond coatings on steel substrates. *Advanced Engineering Materials* 10 7 (2008) 657–660
- [4] J.G. Buijnsters, P. Shankar, J.J. Ter Meulen: Direct deposition of polycrystalline diamond onto steel substrates. *Surface and Coatings Technology* 201 22–23 (2007) 8955–8960
- [5] J.G. Buijnsters, P. Shankar, W. Fleischer, W. van Enckevort, J. Schermer, J.J. ter Meulen: CVD diamond deposition on steel using arc-plated chromium nitride interlayers. *Diamond and Related Materials* 11 3–6 (2002) 536–544
- [6] R. Polini, F. Pighetti Mantini, M. Braic, M. Amar, W. Ahmed, H. Taylor, M.J. Jackson: Effects of Ti- and Zr-based interlayer coatings on the hot filament chemical vapour deposition of diamond on high speed steel. *Proceedings of the 32nd International Conference on Metallurgical Coatings and Thin Films, ICMCTF 2005, Thin Solid Films* 494 1–2 (2006) 116–122
- [7] H. Hei, Y. Shen, J. Ma, X. Li, S. Yu, B. Tang, W. Tang: Effect of substrate temperature on SiC interlayers for diamond coatings deposition on WC-Co substrates. *Vacuum* 109 (2014) 15–20
- [8] G. Cabral, J. Gäbler, J. Lindner, J. Grácio, R. Polini: A study of diamond film deposition on WC-Co inserts for graphite machining: Effectiveness of SiC interlayers prepared by HFCVD. *Diamond and Related Materials* 17 (2008) 1008–1014
- [9] F. Álvarez, M. Reinoso, H. Huck, M. Rosenbusch: Diamond deposition on siliconized stainless steel. *Applied Surface Science* 256 (2010) 3962–3966
- [10] M. Schwander, F. Vollertsen: In situ doping of diamond coatings with silicon, aluminium and titanium through a modified laser-based CVD process. *Diamond and Related Materials* 41 (2010) 41–48
- [11] G.C. Chen, H. Lan, B. Li, F.W. Dai, S.J. Askari, J.H. Song, L.F. Hei, W.Z. Tang, F.X. Lu: Growth feature of layered self-standing diamond films by DC arc plasma jet CVD. *Journal of Crystal Growth* 309 (2007) 86–92
- [12] M. Prieske, C. Wiegmann, M. Schwander, F. Vollertsen: Feedback control of the substrate surface temperature in a laser-induced plasma CVD process. *Dry Metal Forming OAJ FMT* 1 (2015) 1–4
- [13] A.C. Ferrari, J. Robertson: Interpretation of Raman spectra of disordered and amorphous carbon, *Physical Review B* 61 (2000) 14095–14107
- [14] T. Feng, B. D. Schwartz: Characteristics and origin of the 1.681 eV luminescence center in chemical-vapor-deposited diamond films. *Journal of Applied Physics* 73 3 (1993) 1415–1425
- [15] Y.S. Li, H.T. Ma, L.Z. Yang, Q. Yang, A. Hirose: Enhanced diamond CVD synthesis on steel by ion beam implantation and sputtering of Al. *Surface and Coating Technology* 207 (2012) 328–333