Plasma assisted techniques for deposition of superhard nanocomposite coatings

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Various techniques based on plasma application have been successfully used for deposition of superhard nanocomposite coatings. These techniques possess many varying parameters, which in turn influence the properties of a growing coating. Therefore it is important to reveal common regularities, if any, between the process parameters and properties of the coatings. The paper addresses this issue based on the results acquired by the application of plasma assisted CVD and PVD methods. Here it is shown how different deposition parameters, such as working gas pressure, bias and temperature, affect coating properties, mainly hardness. These parameters are found to have a complex influence and the effect caused by variation of one deposition parameter can be similar to that of another one. This presents an opportunity to improve other properties of the coating while maintaining the hardness.

Key words: superhard nanocomposite coatings, plasma assisted techniques, plasma assisted CVD, magnetron sputtering, vacuum arc deposition

1. Introduction

By definition, superhard materials are those which reveal a hardness value higher than 40 GPa. Designing of nanostructured coatings requires the consideration of many factors, such as the interface volume, crystallite size, surface and interfacial energy, texture, strain, etc., all of which depend significantly on deposition methods, parameters and conditions [1–10]. The well known generic concept for the design of superhard nanocomposites is based on thermodynamically driven segregation in binary (ternary, quaternary) systems, where the hardness reaches 50 GPa and even higher values [11–18]. The segregation can in some cases be completed by post-annealing resulting in hardness increase [19–22]. Another approach to reach high hardness is based on the formation of a coating consisting of a hard transition metal nitride and a soft metal which does not form thermodynamically stable nitrides [23–25], and these systems often show lower thermal stability revealing a decrease of the hardness upon annealing.

To fulfil the requirements for successful production of superhard nanocomposite coatings, various techniques based on plasma assistance are used. The techniques contain a wide range of varying parameters, and this paper concerns both the techniques and how the deposition parameters influence the characteristics of the deposited coatings.

2. Deposition techniques

Plasma assisted chemical vapour deposition (PACVD) and physical vapour deposition (PVD) techniques are within those widely used for deposition of superhard nanocomposite coatings. They both have advantages and disadvantages over each other which are briefly discussed below. In addition, some other techniques based on laser ablation, electron or ion beam bombardment, etc. are utilised for production of nanostructured coatings which demonstrate advanced mechanical properties [26–33].

2.1. Plasma assisted CVD

In PACVD process, coatings are deposited by breaking down of gaseous precursors resulting in the appearance of active radicals, which then form a coating on a substrate. The application of glow, arc or another type of discharge helps to deposit dense coatings with relatively low compressive stress. A high deposition rate and uniform deposition for complicated geometries are the advantages of PACVD [33–35]. Accurate control over the composition of a growing coating by varying of flow rates of the gases used in PACVD is more convenient and reproducible than controlling evaporation or sputtering rate in PVD. However, PACVD coatings have the disadvantage of being prepared by means of highly corrosive gases. Furthermore, a low deposition temperature is required for some applications, which is difficult to realise in PACVD.

Thus, PACVD techniques ensure an intensive bombardment of the substrate by forming species and provide high particle surface mobility sufficient for the phase segregation, and various coatings with advanced mechanical properties have successfully been deposited using this technique [3, 4, 19, 37–43].

2.2. Magnetron sputtering

Reactive magnetron sputtering is one of the most studied and broadly used techniques for deposition of a wide range of coatings. Numerous studies, both theoretical and experimental, have been performed to find out how process parameters affect the deposition rate, structure, stress, etc. [44–51].

Precise control and determination of the grain size is important for nanocomposites and many PVD process parameters affect it, including substrate temperature, bias voltage, discharge current, and partial pressure of reactive gas. The conventional reactive magnetron sputtering is far less dangerous and a low-temperature technology. Co-sputtering from single element targets allows independent regulation of each source thus enabling adjustment of

chemical stoichiometry of the coating. A wide range of nanocomposites has been synthesized using the sputtering method [52–66].

On the other hand, high compressive stress is commonly observed in coatings deposited by magnetron sputtering at low pressures where it typically reaches 4–6 GPa and higher (e.g., [66–72]). Specifically, this stress is often responsible for the high hardness and therefore the hardness can decrease during annealing due to stress relaxation.

2.3. Vacuum arc deposition

Similar to magnetron sputtering, great attention has been paid to cathodic vacuum arc deposition and many studies have been performed on different types of cathodes, magnetic filters, etc. [73–85]. In contrast to PACVD and magnetron sputtering, where the glow discharge plasma of a background/reactive gas is used, in the cathodic vacuum arc deposition, a highly ionized plasma of the cathode material is produced by cathode spots moving on the cathode surface [74, 75]. This technique has some advantages over magnetron sputtering: a higher ratio of ionized particles to neutrals reaching a substrate, higher particle energy and the total particle flux resulted in reduction of stress in the growing coating [84, 86, 87]. As an example, Choi *et al.* [88] used a hybrid system of arc ion plating (Ti cathode) and sputtering (Si cathode) for the deposition of Ti-Si-N coatings and it was found that the mean particle energy of Ti ions is almost two times higher than that of Si ions, since the charge distribution of Ti ions was shifted to Ti^{2+} and Ti^{3+} states, while for Si the main charge state was Si^{+}.

For this reason, the plasma arc, often combined with other PVD or even CVD processes, is extensively used for deposition of superhard nanocomposites in research laboratories and industry [88–97].

2.4. Comparison of PACVD- and PVD-produced coatings

Generally, if the technique used can provide high flux and activity of the forming species, proper stoichiometry of a growing coating, and weak points are somehow avoided or at least diminished, there should be no difference in what particular method of deposition is applied.

Karvankova *et al.* showed [4] that the nc-TiN/a-BN coatings deposited by means of PACVD revealed the value of 45–55 GPa due to the formation of stable nanostructure. The same coatings deposited by vacuum arc evaporation of Ti and introducing $B_3N_3H_6$ at a bias of -100 V had a biaxial compressive stress exceeding 5 GPa, which relaxed upon annealing and led to a decrease of the hardness from initial 45–55 GPa to ~30 GPa. In contrast, in study by Procházka *et al.* [5], nc-TiN/a-Si_3N_4 coatings were deposited by PACVD and magnetron reactive sputtering facilities and the latter was found to be very capable of producing thermally stable superhard (hardness $\geq$ 45 GPa) nanocomposites if high enough nitrogen pressure and temperatures are applied.

The nc-($Ti_{1-x}Al_x$)N/a-Si_3N_4 nanocomposite coatings reported by Männling *et al.* [19] were deposited by vacuum arc evaporation at a temperature of 300°C. The crystallite size and hardness of different samples showed a variation of about 1.5–6 nm and 30–40 GPa, respectively. Upon annealing at 600–800°C in a reactive gas, all samples revealed a more or less pronounced increase in hardness and structural relaxation towards a uniform crystallite size of 3–4 nm. These results are in agreement with the idea of the spontaneous formation of an optimum nanostructure with high hardness and thermal stability when the elemental composition and nitrogen activity are adjusted appropriately and the temperature is sufficiently high to allow self-organisation to occur.

3. Influence of system configuration and deposition parameters on the hardness

3.1. Magnetic field arrangement

As known, magnetic field arrangement can strongly affect plasma chemistry making it possible to control the charge state of the particles arriving to the substrate [98]. Furthermore, under low energy ion bombardment, effectively controlled by applied magnetic field, the radiation damage in the subsurface region is reduced, while the ad-atom mobility is enhanced. A comparison of different plasma PVD processes given by Strauss and Pulker [87], including magnetron sputtering and vacuum arc, deals exactly with the problem of how to increase both the ion/atom arrival ratio and energy of the particles by extra magnetic fields.

Ribeiro and co-workers [99] deposited Ti-Al-Si-N coatings on high-speed steel substrates by DC reactive sputtering with the aim to understand the evolution of the mechanical properties as a function of different magnetic fields at the substrate position, which allowed the variation of the ion/atom ratio of the particle flux arriving at the substrate surface. A significant density increase of the coatings was observed in the presence of the external magnetic field. The same system was used for deposition of Ti-Si-N coatings and it was found that, in addition to the ion/atom ratio and deposition rate, variation of the magnetic field near the substrate markedly affected the substrate temperature resulting in the formation of the stable nc-TiN/a-Si_3N_4 nanocomposite [58]. The importance of the ion flux provided by a proper arrangement of the magnetic field was emphasized by Kim *et al.* [60], where superhard Ti-Al-Si-N coatings were deposited by reactive sputtering.

3.2. Spatial arrangement of the target and substrate

A confocal arrangement of the target and substrate provides more uniform deposition over a lager area, as compared to the parallel one [100]. Furthermore, such an arrangement, combined with rotation of the substrate, results in the formation of less texture pronounced structures which is often beneficial. Thus, substrate rotation of 10 rpm and confocal arrangement of the two magnetron sources was applied during formation of superhard Ti-Al-Si-N coatings by Kim *et al.* [60].

The results of the formation of Ti-Si-N coatings by reactive sputtering from Ti and Si targets reported by Rebouta and *et al.* [55] showed that the highest hardness values for samples positioned far from the target were obtained for coatings prepared at lower deposition rates, while for those positioned closer to the targets, the best hardness value was obtained at a higher applied current, i.e. higher deposition rate.

The idea of rotating substrate during deposition about an axis lying on the substrate surface was proposed and realized by Lee *et al.* [101] with the aim to reduce the compressive stress. Here, deposition of TiB_2/TiC nanoscale multilayers was performed with a non-reactive unbalanced magnetron sputtering system using TiB_2 and TiN targets. Substrate rotation was found to generate lower intrinsic stress (less than 2 GPa against 4–7 GPa at no rotation). At certain times during the rotation cycle, energetic neutral particles bombarded the growing coating at oblique angles, thus giving rise to more efficient momentum transfer and hence greater mobility of surface ad-atoms. In addition, there was no deposition for half a rotation cycle. Therefore, there was more time available for migration of surface species to fill in voids resulting in a denser structure [102]. The hardness of rotated coatings reached values of 60 GPa and even slightly increased after 1 hour of annealing in argon at 1000ºC, while the hardness of non-rotated ones was well below 40 GPa. The twofold rotation was utilized by Willmann and co-workers [95] for deposition of Al-Cr-N nanocomposites by vacuum arc which helped to obtain more uniform coating properties.

3.3. Reactive gas pressure

Reactive gas pressure is easy to monitor and vary and its effect on the growing coating characteristics is hard to overestimate. To provide sufficient particle activity at the substrate, the reactive gas pressure has to be of high value (e.g., Ref. [5, 13]). Furthermore, at low pressures the deposition rate of the active gas species is also low and contamination of a growing coating with impurities becomes an issue. On the other hand, when increasing the

pressure in sputtering systems, one also increases the number of collisions between the particles, thus reducing the energy of the particles arriving to the substrate (e.g., Ref. [64, 103]). One more drawback of the high pressure comes from poisoning of the target that drastically affects the sputtering rate. Therefore, there is an optimum pressure value that provides the best mechanical properties of the coating.

The microhardness of sputtered Zr-Ni-N [1] and Zr-Y-N [104] coatings studied by Musil and co-workers was found to strongly increase with increasing of nitrogen partial pressure revealing a maximum at ~0.03 Pa. For $Ti_{1-x}Al_xN$ coatings formed by magnetron sputtering of a TiAl target (Ref. [105]) the hardness exhibited a well developed maximum at the nitrogen pressure of 0.025 Pa and a minimum at 0.075 Pa, which was connected with dramatic changes of the structure of the coatings. Nevertheless, all these values of nitrogen pressure seem to be insufficient to provide the formation of the thermally stable structure. For instance, Karvankova *et al.* [4] found that the thermal stability of even the fully segregated binary TiN-BN system depended on the nitrogen pressure. Up to an order of magnitude higher nitrogen pressures than those mentioned above were used for deposition of various nanocomposites, such as nc-TiN/Si_3N_4 [58], Ti-Al-N-C [59, 72], Ti-Al-Si-N [60], Ti-Al-N [63], Ti-Al-V-N [64], W-Ti-C/N [65]. On the contrary, Mayrhofer *et al.* [61] deposited Ti-B-N coatings from a TiN-TiB_2 segmented target with no nitrogen gas used.

PVD systems based on vacuum arc discharge usually utilize similar values of pressures but the ionization ratio of the incoming particle flux to a substrate is higher for arc sources, therefore particle activity is also higher. Lim *et al.* [90] carried out the deposition of Ti-Al-N coatings, and the nitrogen pressure was kept at 0.075 Pa while the flow rate of nitrogen was varied. The latter was found to help reducing stress in the coating to the level of 1.5–2 GPa. A number of coatings, Ti-Si-N, Ti-Al-Si-N, Ti-Al-V-Si-N, and Zr-Si-N, deposited by Martin *et al.* [94] at the nitrogen pressure of 0.8 Pa revealed the hardness up to 42 GPa. However, they also exhibited high compressive stress up to 7 GPa. By a hybrid method of arc ion plating and

magnetron sputtering, Cr-Si-C-N coatings were produced with the hardness of ~43 GPa and low friction (Jeon *et al.* [91]), while the working pressure was as high as ~0.07 Pa. Choi *et al.* [88] and Park *et al.* [92] reported on deposition of superhard Ti-Si-N and Ti-Al-Si-N coatings by the same technique resulting in the hardness of the coatings ~55–60 GPa at the total pressure of only 0.07–0.08 Pa. A similar technique was used for deposition of Ti-Cu-N in pure nitrogen atmosphere of 0.4 Pa, which demonstrated the hardness of 45 GPa and friction coefficient of 0.3 [106], though the coatings could not be classified as "classical" nanocomposites. In study by Karvankova et al [4], the deposition of nc-TiN/a-TiB_2 was carried out at a zero nitrogen pressure but with the use of borazine ($B_3N_3H_6$). In turn, the high nitrogen pressure of 3.5 Pa was applied for deposition of Al-Cr-N coatings by Willmann *et al.* [95].

The working pressure in PACVD is much higher than that in PVD systems. Thus, the total pressure of ~100 Pa was applied for deposition of Ti-Si-N coatings [16, 38], 133 Pa for Ti-Si-C [40], 200 Pa for TiN/Ti-B-N multilayers [42], 200 to 240 Pa for Ti-Si-C-N [39], 300 Pa for nc-TiN/a-BN/a-TiB_2 [43], etc., and even if nitrogen fraction in the total pressure is only ten percent or so, it is still about two orders of magnitude higher than that in sputtering systems.

However, high pressures required for successful formation of the superhard nanocomposites have their own drawbacks, namely poisoning of both the targets and growing coating.

A common problem during PVD coating formation is a decrease in the deposition rate (actually, sputtering rate) due to poisoning of the target. In study by Musil *et al.* [1], the deposition rate of Zr-Ni-N was found to decrease from 2.25 nm/s at no nitrogen to ~0.75 nm/s at the nitrogen pressure of 0.05 Pa due to the covering of the target surface with a ZrN_x nitride possessing a lower sputtering rate. Composition measurements carried out by Rebouta and co-workers [55], where steel substrates were coated with Ti-Si-N by reactive sputtering, revealed

a non-linear correlation between the Si content in the samples and the current applied to the Si target. As assumed, this behaviour resulted from some poisoning effect, especially in the case of low currents at the Si target. Poláková *et al.* [64] reported that the deposition rate was found to have a complex dependence on the nitrogen pressure, total pressure, substrate to target distance, and magnetron discharge current.

Another serious problem is the poisoning of the growing coating. Its influence on the superhard coating characteristics was thoroughly studied by Veprek and co-workers [5, 107], where nc-TiN/a-Si_3N_4 coatings were produced by PACVD, as well as PVD magnetron sputtering. Both the working gas containing chlorine and hydrogen (in case of PACVD) and oxygen were considered as contaminants in the coating. The high hardness could be obtained only when the impurity content of the coatings is kept sufficiently low, namely ≤0.5 at.% for chlorine and ≤0.05 at.% for oxygen. Already 0.1 at.% of oxygen resulted in a noticeable decrease of the hardness, and no superhard nanocomposites could be obtained when the oxygen impurity content reached ≥0.3 at.%.

3.4. Bias voltage and discharge current

One of the important parameters which control the stoichiometry and the formation of the nanostructure is the discharge current density at the substrate during deposition: as it was shown by Veprek *et al.* [3], at a "high" current density above 2.5 mA/cm^2 stoichiometric nc-TiN/a-Si_3N_4 was formed, whereas at a "low" current density of 1 mA/cm^2 the multiphase nanocomposites nc-TiN/a-Si_3N_4/a- and nc-$TiSi_2$ were obtained. Higher hardness of Ti-Al-V-N coatings was observed when the current density was increased from 0.5 to 1.5 mA/cm^2 (see Ref. [64]). As mentioned above, high ion current densities can be achieved by the application of additional magnet coils which focus ions to the substrate and provide a high level of ion bombardment, as was carried out for Ti-Si-N [58] and Ti-Al-Si-N [60] coatings.

The optimum values of bias voltage lie in the range of up to -150 V, e.g. -50 V for Ti-Al-N [63] and Ti-B-N [61], -80 V for Ti-Al-C-N [59], -100 V for Ti-Si-N [58] and Ti-Al-Si-N [60]. This is defined by several factors. In case of low deposition temperatures, very low bias values usually do not ensure sufficient particle energy needed for the formation of a stable nanocomposite structure. On the contrary, the microstructure and stress strongly depend on the energy delivered to the surface during coating growth, limiting the upper value of bias: for instance, Musil *et al.* [56] found that increase in bias from -50 V led to a change from columnar porous microstructure for the Al-Cu-N coatings in tension, through a very dense fibrous one for the coating in a low compression to that with many defects probably caused by the high compressive stress at bias of -150 V. Selective sputtering of a multi-component growing coating is the next reason: the hardness of Zr-Ni-N increased with increasing bias accompanied by a decrease of the Ni content due to preferential re-sputtering of Ni atoms from the surface of the growing coating [1]. High bias does not only result in compressive stress and preferential sputtering but also leads to a decrease in the deposition rate, as it was found by Andreasen and co-workers [108] where Ti-Cu-N nanocomposites were synthesized by sputtering of $Ti_{80}Cu_{20}$ targets.

Nevertheless, relatively high bias values are not always necessary for successful formation of superhard coatings. Thus, Nose *et al.* [57] reported that the hardness of RF sputtered Ti-Si-N coatings with low Si content increased with increasing negative bias voltage reaching a maximum of 42 GPa in a range of -10 to -30 V, though the coatings consisted of columnar grains and could not be attributed to the nanocomposite ones consisting of nc-TiN embedded in a-Si_3N_4. Procházka *et al.* [5] did not apply the bias for deposition of superhard nc-TiN/a-Si_3N_4 coatings in pure N_2 atmosphere. Instead, the high substrate temperature of 630ºC provided energy for formation of the proper structure.

A fundamental problem in the formation of superhard coatings is the stress generated in the coating during growth, which is controlled by the delivered energy. The problem is an

issue mainly for PVD sputtered coatings where the required particle activity is due to bias application. In Ref. [56], it was found that with increasing bias the macrostress continuously changed from tension to compression and at bias of -80 V Al-Cu-N coatings with zero stress were formed exhibiting a quite high hardness of ~40 GPa. It is thermal stability that suffers from hardening by the bombardment with energetic particles, resulting in a drastic decrease in hardness values upon annealing. This issue was discussed by Veprek *et al.* [4, 19, 24, 89]. Possible ways to reduce the stress, thus in some cases reducing hardness too, include a proper selection of both technique and working parameters, such as confocal arrangement of the target and substrate and their relative rotation and higher deposition temperature, respectively. In paper [94] where deposition of Ti-Si-N, Ti-Al-Si-N, Ti-Al-V-Si-N, and Zr-Si-N coatings by vacuum arc was reported high compressive stress in the coatings appeared to decrease upon addition of Si.

It is generally accepted that higher residual stresses are associated with higher defect densities induced during ion bombardment. Therefore, when heavy elements are incorporated into the coating, a systematically lower residual stress is observed [109]. This is because higher activation energies are required for surface diffusion of less mobile heavier atoms than for more mobile lighter atoms, and at the same bias voltage less energy is available for defect formation in case of heavy atoms as a larger part of the energy is spent for moving atoms to their equilibrium position.

3.5. Substrate temperature

Similar to applied bias voltage, temperature provides the energy needed to make species on the surface mobile and therefore can to some extent substitute the bias (e.g., Ref. [5, 58]). Temperature affects the deposition rate (actually, the time of particle presence on the surface, which decreases with temperature increase), purity of the forming coating, as well as its chemical composition. An important role in the structure of the growing coating is also

attributed to the substrate temperature as high temperatures result in denser structures. All together, these parameters and processes influence the mechanical properties of a coating, e.g. hardness.

The importance of high temperatures to complete the segregation was discussed in review by Veprek *et al.* [13], supported by rough estimations of the diffusion coefficient for the forming species. It was stated that the low substrate temperatures of 200–300ºC are not sufficient as the diffusion coefficient is of orders of magnitude below the required value. Generally it is true, however, the lower the substrate temperature, the higher is the compressive stress generated during deposition by PVD, and this stress increases the diffusion coefficient. Furthermore, the factor which also increases diffusivity at low temperatures is a very high concentration of impinging energetic atoms and ions, so the diffusion coefficient starts to strongly depend on the local concentration making the particles more mobile. Finally, as mentioned in Section 3.2 (Ref. [101]), a proper rotation of the substrate could provide sufficient time for particles to diffuse to their advantageous positions.

Typical values of the substrate temperature lie in the range of 200–400ºC for PVD techniques, e.g. 150ºC [60], 250ºC [106], 300ºC [1, 61, 64, 88, 91, 92, 94], 350ºC [63, 97], 400ºC [59], rarely exceeding the value of 500ºC with low or no bias application (e.g., Ref. [4, 95]), and 500–600ºC for PACVD [4, 15, 16, 38–40, 42, 43]. The latter is not only because of "extra" energy required for PACVD to provide high surface mobility, but also because of purity issues, namely to make detrimental impurities volatile and force them to leave the surface. The higher temperatures would benefit from higher mobility of forming species but, on the other hand, reduce the deposition rate and cause strong degassing from the surrounding walls which would lead to poisoning of a growing coating. For example, in work of Lee *et al.* [38] where temperatures in the range of 400 to 900ºC were applied for PACVD Ti-Si-N coatings, the maximum deposition rate was observed at 600ºC, while the hardness exhibited maximum at 500ºC. Ribeiro *et al.* [58] found that superhardness of sputtered Ti-Si-N coatings

could be achieved either by application of high temperatures of about 500ºC or at low temperatures of 350ºC in combination with the increased energetic ion flux (owing to extra rectangular coils) arriving to the substrate.

4. Conclusion

In addition to the common regularities of the impact of plasma parameters on the properties of growing coatings, there are some specific features responsible for the formation of essentially superhard nanocomposite materials. It is not always possible to precisely distinguish which parameter has stronger influence, as the parameters often affect in combination rather than separately and their influence can drastically depend on the values of other parameters. Moreover, one parameter can be substituted with another one while revealing the same influence on the coating characteristics, for example, bias and temperature, and this fact gives new opportunities for the production of superhard coatings as it allows variation of the other characteristics whilst maintaining the same hardness value.

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