Layer arrangement for the formation of a coating on a surface of a substrate, coating method, and substrate with a layer arrangement

The invention relates to a layer arrangement for the formation of a coating on a substrate, a coating method for depositing a layer arrangement, as well as a substrate, in particular a tool having a layer arrangement in accordance with the present invention, according to the preamble of the independent claim of the respective category.

The production of efficient tools is mostly realized by the formation of a coating on their surfaces. An important class of such coated tools are in particular, among other things, cutting tools in various embodiments. Typical materials to be coated are, among other things, tool steel and hard metals.

A known problem concerned with the coatings of such materials is both, the high oxidation rate under the influence of air, even around 500°C, and the sag at relatively low temperatures (HSS ca. 550 °C, hard metal ca. 650 °C).

Thus, preferably ceramic cutting members for the working of steels are used, e.g. ceramic cutting members on the basis of cubic boron nitride. For example

for the high speed working of aluminum alloys and grey cast iron, SiN-ceramics are increasingly used. Thereby, ceramic materials prove to be more resistant in comparison to the metallic tool materials. A further improvement in performance can be achieved by a capable coating of the tools.

The hard coatings known from the state of the art are often based on classical compositions such as TiN, TiNC, CrN. These known hard coatings are limited with respect to their field of applications due to their special physical properties, especially with respect to their temperature load capacity. On the one hand, hardness is decreasing at elevated temperatures and on the other hand, oxidation occurs even at relatively low temperatures, leading to an increasing wear of the coating.

To avoid these problems essentially two classes of coatings have been developed being, both, oxidation resistant in a range up to 1000 C and have better properties with respect to hardness.

One class of coatings are Al-containing base layers such as AlTiN and AlCrN, wherein, dependent on specific requirements, additional elements can be alloyed. Typical composition are compositions of the type AlTiXNCO, wherein X is e.g. Cr or an other metal.

Another possibility known from the state of the art for improving the performance of coated tools is the combination of classical hard coatings acting as support layers with a finish-layer acting as a top-layer and having a respective function. In particular Si-coatings having a high Si content (10 at% or higher; at% means in the framework of this application „atom percent") of the type MeSiXNCO (X being an additional metal or B) such as TiSiN have to be mentioned which have an increased temperature load capacity.

In addition, it is for example also known to CVD-methods to deposit on indexable inserts oxidic ceramic-coatings such as Al_2O_3 using CVD-methods, in order to reduce wearing processes at elevated contact temperatures, in particular while turning on a lathe.

Under investigation are actually also boron-based coatings such as B_4C as well as cubic BN coatings. However, cubic BN has the decisive disadvantage that it is extremely difficult to prepare. This is mainly due to difficulties in connection with the growth of the coating as such, as well as due to high internal stress in the coatings.

Regarding high temperature materials, volumetric-ceramic materials on the basis of SiN have been developed in recent years having higher hardness and improved oxidation resistance in comparison with SiC and Si_3N_4. Their special properties result from complex covalent chemical bonds and are due to low oxygen diffusion rates within the amorphe structure of SiCN.

Up to now it was only partly possible to provide coatings which meet the constantly increasing requirements with respect to mechanical properties, such as hardness and toughness, tribological properties such as affinity to adhesion at elevated temperatures as well as friction, oxidation resistance and other characteristic properties, especially at extreme temperatures.

Moreover, the above described improved coatings are procedurally difficult to prepare, so that the coated tools are very expensive and, as a result, from the economical point of view, in many cases coating is not worth while and tools being coated in such a way have only a limited market.

It is therefore an object of the invention to provide an improved coating for a substrate, in particular for a tool, which overcomes the problems known from the state of the art, having in particular an improved tribological and oxidation behavior, improved mechanical properties, especially, but not only, with respect to the hardness, and can be also used under excessive temperature conditions.

It is a further object of the invention to provide a method which allows a very reliable and simple way of deposition of the coating according to the invention onto a substrate, wherein coating apparatuses, well known from the state of

the art, can be used so that the coating process itself is feasible in a very economical way.

The subject matters of the invention which satisfy these objects are characterized by the features of the independent claims of the respective category.

The respective dependent claims relate to particularly advantageous embodiments of the invention.

Thus, the invention relates to a layer arrangement for the formation of a coating on a surface of a substrate, in particular on the surface of a tool, wherein the layer arrangement comprises at least one hard layer having the composition $Si_aB_bMe_cN_uC_vO_w$ with a,b > 0 and 33 at% > c ≥0, preferably 25 at% > c ≥0, in particular 10 at% > c ≥0 and u,v,w ≥ 0, and Me being a metal.

The considerable improvement in capability of the tools and components in comparison with the state of the art is, in accordance with the invention, thus achieved by SiB-coatings.

According to the invention, it is therefore proposed to minimize, as the case me be to eliminate the fraction of metallic components in the coating so that Si/B dominated coatings are used.

There is only little knowledge available due to the complex production of SiBx ceramics. The following information is available for SiB_6 volumetric materials: orthorombic lattice, hardness ca. 2600, modulus of elasticity 290 GPa, density 2,43 g/cm^3, thermal coefficient of expansion 4,6 *10^{-6}/ °C, thermal conductivity 9 W/mK, melting point 1950 °C. In particular the high oxidation resistance must be mentioned: stable in air up to 1550 °C.

Such a stability is not achieved by classical coating systems such as AlTiN, AlCrSiN and TiSiN.

These volumetric properties in respect of hardness and oxidation properties can similarly be found in coatings of the type SiBx, wherein the manufacture of these coatings has a certain industrial relevance.

The mechanism of oxidation protection of the SiBx-coatings is based upon the development of a double-layer of the type SiO/BO. The developing outer Si-enriched coating prevents the diffusion of oxygen into the coating.

Consequently, according to the invention, the new class of coating materials comprising SiBx, in particular the new class of coating materials comprising SiBCN is proposed to use them for the coating of tools.

Thereby, it turned surprisingly out that a coating on the basis of SiB- or SiBCN-compositions in combination with known classical hard coating results also in noticeably improved coating properties.

Depending on the demands required by the substrates or tools to be coated, it can be particular advantageous to dope the coatings with oxygen, to come for example to SiBNCO-coatings, which, among other things, reduce the diffusion of oxygen by pre-oxidation as well as by refining of the structure of the coatings, and strongly increase the oxidation resistance even at high temperatures.

In addition, the doping with oxygen leads to a occupancy of the grain boundaries with oxygen so that at least in case of a partial development of the above mentioned double-layer systems, as well as of other double-layer systems, the tendency to structural transitions within in the coatings, having frequently more or less open pores, is reduced, because by doping with oxygen a pre-oxidation is initiated.

According to the present invention, for the building of the coatings in accordance with the invention, it is decisive that the coatings comprise at least

the two elements Si and B, in particular for the development of the protecting double-layer. That is, the coating system in accordance with the invention includes at least a hard layer of the composition $Si_aB_bMe_cN_uC_vO_w$ with a,b > 0 and 33at% > c ≥ 0 and u,v,w ≥ 0,wherein Me is a metal, in particular for example a metal being used for the production of the target such as Al in case of SiC or which metal can be a selective integrated metallic element.

The layers of the layer arrangement in accordance with the invention can be preferably deposited onto a suitable metallic intermediate layer, but onto a Si, SiC intermediate layer, as well as directly onto metallic or ceramic tool materials, or, preferably, onto tool materials being coated with hard layers.

Preferably, but not necessary, the layers of a layer arrangement in accordance with the invention are largely in an amorphous state, wherein in a special embodiment a development of nano-crystalline regions inside the layers is present.

The thickness of the layers is in the range between ca. 5 nm – 50 000 nm, especially between 10 nm and 2500 nm, preferably between (100 – 500) nm and can comprise e.g. Al-base-hard-layers in form of a base coating.

The metallic component Me of the layer arrangement according to the invention is at least one metal of the group Al, Cr, Mo, W, V,Nb, Ta, Ti, Zr, HF, Mn, Fe; Co; Ni, Li, Be, Mg, Sc, Y, La, Ce, Nd, Sm.

Regarding a very preferred embodiment, on the surface of the substrate is at least one connecting layer, preferably a connecting layer provided, having the composition $Me_xE_yN_z$, with x,y ≥ 0 and z > 0, wherein Me is at least one metal of the group consisting of Al, Cr, Mo, W, V,Nb, Ta, Ti, Zr, HF, Mn, Fe; Co; Ni, Li, Be, Mg, Sc, Y, La, Ce, Nd, Sm and E being an element of the group consisting of Si, B, C, O.

For special applications, a special layer arrangement in accordance with the invention can also comprise a first hard layer having the composition $Si_aB_bMe_cN_uC_vO_w$, in particular a first hard layer having the composition

$Si_aB_bMe_cC_vN_u$, in particular a first hard layer having the composition $Si_aB_bC_vN_u$.

In a special embodiment an AlTi-hard layer is provided, for example as a first hard layer and or as an other hard layer having the composition $(Al_{1-\alpha-\beta\square}Ti_\alpha X_\beta)(N_{1-\gamma}C_\gamma O_\delta B_\varepsilon)$, with $0.2 < \alpha < 0.6$, $0 \leq \beta < 0.2$ and $\alpha+\beta > 0.01$ and $0 \leq \gamma < 0.5$, $0 \leq \delta < 0.5$, $0 \leq \varepsilon < 0.5$ and $\gamma+\delta+\varepsilon > 0.01$, wherein X is an element of the group consisting of Zr, V, Cr, Nb, Ta; W; Mo; Hf, Mg Si, Y.

The layers on the basis of SiB are deposited in an atomic composition of Si:B in the range of 9 to 0.1, wherein a crossfire of compositions within a gradient-mixed layer as well in form of multi layers can be developed. Boron-enriched layers are preferably deposited, that is the concentration of Si is smaller than the concentration of boron. In particular, the composition with six boron atoms per Si atom is interesting, because very stable SiB6-structures can be at least locally established inside the layers.

The addition of N,C, O leads to the development of a crossfire of bonding states in the layers, e.g. B-N, B-C, Si-N ,Si-C, Si-O, B-O bonds appear, which, however, are difficult to be quantified. The covalent fraction of bonds (e.g. SiN and BC) lead to a high hardness. The structural mechanism and the bonding mechanism of these complex coatings is up to now only insufficient understood to make predictions on the complex layer properties.

In a preferred embodiment, the atomic composition of the layers should consist of about equal fractions of Si and boron and N or should consist of a composition comprising N, C, O. But a surplus-stöchiometric composition with respect to the contents of N and C relating to SiB is also possible, which is , however, difficult to produce. For example, a layer composition could make sense comprising approximately equal fractions of Si, B and C and a N-fraction with is about three times the Si-fraction according to the volumetric ceramic.

At least locally, the above described preferred compositions can develop very stable compositions - in form of $Si_3B_3N_7$ or $SiBN_3C$. Unlike the ceramics of this

type, the PVD-layers are, by nature, layers having PVD specific structures such as growth-defects, growth-structures as well as residual stress to due growing processes.

The oxygen content within the layers is limited to less than 50%, and is preferably about 10 at% in relation to the whole composition, because the fraction of ionic bonds, leading as a rule to a brittle material behavior, should be limited.

It makes sense to set up also the fractions of metal in the layers to less than 50 at%, wherein the metal fraction is mostly limited to 10 at% at a maximum, except for the intermediate layers. These fractions act as bond-bridges to the a lower hard layer, as the case may be, are from the target bonding agent.

The hardness of the coating are thereby between 1000 to 5000 Vickers, preferably between 2000 and 3500 Vickers. The selection of the capable coating is based on the respective tribological properties. For example in case of various micro tools, the friction is a crucial point to avoid overheating, so that friction reducing boron oxide is desirable, wherein a hardness of the coating about 1000 Vickers can make sense already. The crucial point is a tribological segregation-coating. Under the influence of humidity, boron oxid transforms to boron-acid, leading to low friction values.

However, in case of spherical cutters in direct contact to Ti-alloys, a high level of hardness should be adjusted.

Not only, but also to improve the adhesion properties on the substrate, e.g. in case of a strong stressed tool, between the substrate and the hard layer and / or between the connecting layer and the hard layer and / or between the first hard layer and the hard layer, an intermediate layer comprising the elements Si and / or C is provided.

Furthermore, it is possible that in another embodiment between the substrate and the hard layer and / or between the connecting layer and the first hard layer and / or between the first hard layer and the hard layer a gradient-mixed

layer is provided, comprising the elements Si and / or C of the intermediate layer and having the composition $Si_aB_bMe_cN_uC_vO_w$, in particular $Si_aB_bMe_cC_vN_u$, and in more particular $Si_aB_bC_vN_u$ of the first hard layer. The composition of the gradient-mixed layer is changing more or less continuously starting with the composition of a first layer, the gradient-mixed layer being in contact with, towards a composition of a second layer, which is in contact with the gradient-mixed layer, too, so that the first layer and the second layer, which may have different chemical or physical properties, such as different lattice structures, crystalinity, thermal coefficient of expansion, etc, can be optimal adapted to each other.

Particularly advantageous is a oxygen hard layer provided, having the composition $Si_aB_bMeN_uC_vO_w$, in particular having the composition $Si_aB_bN_uC_vO_w$ and which oxygen hard layer is in more particular provided as a protective hard layer. This protective hard layer can for example, but not only, prevent oxygen from diffusion into the layer, or at least minimize such oxygen diffusion, and can, thus, increase among other things the oxidation resistance. Moreover, the protective hard layer may protect the layer arrangement against influences from the environment, and can provide the layer arrangement with special chemical, thermal and mechanical properties, so that the layer arrangement is very good protected against e.g. high temperatures by the protective hard layer, and or may provide the layer arrangement with particularly advantageous mechanical properties, or the layer arrangement will show good tribological properties.

The thickness of the connecting layer and / or of the intermediate layer and / or of the hard layer and / or of the first hard layer and / or of the gradient-mixed layer and / or of the oxygen hard layer and / or of the protective layer is between 5 nm and 50000 nm, especially between 10 nm und 5000 nm, in particular ca. 50 nm – 5 000 nm, prefarably between 100 nm– 500nm, and in more particular between 80 nm und 600 nm.

The thickness of the connecting layer is preferably between 100 nm and 50 000 nm, in particular between 100 nm and 3000 nm, the thickness of the first hard coating is between 100 nm and 3000 nm, preferably between 400 nm

and 600 nm, the thickness of of the intermediate layer and / or of the gradient-mixed layer is between 20 nm and 500 nm, preferably between 50 nm and 120 nm and a thickness of the oxygen hard layer is between 10 nm and 100 nm, preferably between 40 nm and 60 nm.

It is understood that, depending on the special application, the above described embodiments according to the invention can be combined in every suitable manner and that in particular the examplarily described sequences of layers, can be as well realized in other sequences and it is possible, that in a special embodiment of a layer arrangement in accordance with the invention, one or more of the described layers may be not present, or that in an other embodiment, one and the same layer arrangement may comprise a specific type of layer several times.

As above described in great detail, the invention is furthermore related to a coating method for depositing a layer arrangement onto a surface of a substrate, in particular onto the surface of a tool, in a process chamber of a coating apparatus. The coating apparatus comprises a RF-coating source having a RF-magnetron and / or a DC-coating source, in particular a DC-magnetron or a vacuum arc-evaporator, wherein the RF-coating source and / or the DC-coating source can be closed by a shutter, and wherein means are provided so that a process gas can be supplied into the process chamber. The method according to the invention includes the following steps: placing the substrate into the process chamber; heating the substrate to an ion-cleaning temperature; ion-cleaning the substrate at the ion-cleaning temperature; deposition of a layer arrangement having the composition $Si_aB_bMe_cN_uC_vO_w$ with $a,b > 0$ and $33\ at\% > c \geq 0$ and $u,v,w \geq 0$, wherein Me is a metal, using the RF-coating source and / or the DC-coating source.

In particular is $25\ at\% > c \geq 0$, in more particular $10\ at\% > c \geq 0$.

In a special case is $a+b+c = 100\%$, what can stand for, that a layer of a layer arrangement in accordance with the invention, may contain, for example, only Si, B and a metal.

In an other embodiment the equation a+b+c = 100% can stand for, that a method of counting for determining the fraction of the elements being included in the composition $Si_aB_bMe_cN_uC_vO_w$ has been chosen, which method of counting is carried out in such a manner, that the two sums (a+b+c) and (u+v+w) will each equal to 100% separately, wherein it is possible that the elements N and / or C and or / O may not be present, as above already mentioned. An example for the aforementioned method of counting to indicate a composition, is $Si_{0.3}B_{0.6}Cr_{0.1}N_{0.2}\ C_{0.5}O_{0.3}$. That is, the indication of the composition is given in such a way that Si, B and Me (in this case Cr) equal to 100% and the second group of elements N, C, O add to 100% likewise.

Regarding an embodiment which is very important in practice, the coating method comprises the following steps: placing the substrate into the process chamber; heating the substrate to the ion-cleaning temperature; ion-cleaning of the substrate at the ion-cleaning temperature and feeding a bias constant-voltage and / or a RF-voltage to the substrate to achieve an ion-cleaning; opening the shutter of the DC-coating source and / or the shutter of a first RF-coating source; deposition of a connecting layer onto the surface of the substrate, in particular a connecting layer having the composition $Me_xE_yN_z$, with $x,y \geq 0$ und $z > 0$, wherein Me is at least a metal of the group consisting of Al, Cr, Mo, W, V,Nb, Ta, Ti, Zr, HF, Mn, Fe; Co; Ni, Li, Be, Mg, Sc, Y, La, Ce, Nd, Sm, and E being an element of the group consisting of Si, B, C, O; deactivating the DC-coating source and / or the first RF-coating source, opening a shutter of a second RF-coating source and putting said second RF-coating source into operation; deposition of an intermediate layer comprising the elements Si and / or C by using the second RF-coating source; opening a shutter of a third RF-coating source, putting said third RF-coating source into operation and depositing in parallel with the second RF-coating source $Si_aB_bMe_cN_uC_vO_w$, in particular $Si_aB_bMe_cC_vN_u$, in more particular $Si_aB_bC_vN_u$ according to the first hard layer by means of the second RF-coating source in order to deposit a gradient-mixed layer; deactivating the second RF-coating

source and depositing a first hard layer having the composition $Si_aB_bMe_cN_uC_vO_w$, in particular $Si_aB_bMe_cC_vN_u$, in more particular $Si_aB_bC_vN_u$ and keeping the third coating source in operation until a presetted thickness of the first hard layer is deposited; feeding a reactive gas, especially oxygen, nitrogen, or a carbon containing gas, into the process chamber and depositing an oxygen hard layer having the composition $Si_aB_bMe_cN_uC_vO_w$.

In a particular preferred embodiment, the DC-coating source and or the RF-coating source is a sputter source and / or an arc evaporation source.

According to the invention, the coating method itself can be a coating process being carried out by means of a PVD-method, in particular a RF-sputter method and / or a DC-sputter method and / or a CVD-method, especially a PE-CVD method and / or a Laser-CVD method and / or an ion implantation method and or a laser-ablation method and / or an arc evaporation method, especially a cathodic and / or an anodic arc evaporation method.

Preferably, but not necessarily, the coating, which is deposited in direct contact with the surface of the substrate, e.g. which is deposited onto the surface of a tool, is deposited by means of an arc evaporation method, e.g. by anodic and / or cathodic arc evapoartion.

In a special embodiment of a coating method in accordance with the invention, after the ion-cleaning of the substrate and before depositing the hard coating, a connecting layer, in particular a connecting layer having the composition $Al_xCr_yN_z$, with $x,y,z \geq 0$, is deposited onto the surface of the substrate, preferably by means of a DC-coating source.

Regarding an other embodiment, between a first hard coating having the composition $Si_aB_bMeC_vN_u$, in particular $Si_aB_bC_vN_u$ and the substrate and / or between the connecting layer and the first hard coating an intermediate layer is deposited comprising the elements Si and / or C.

Regarding a further embodiment, a gradient-mixed layer is deposited between the substrate and the hard coating and or between the connecting layer and the first hard coating, which gradient-mixed layer comprises the elements Si and C of the intermediate layer and comprising the composition $Si_aB_bMeC_vN_u$, in particular $Si_aB_bC_vN_u$ of the first hard coating.

Thereby, in an other embodiment of the invention which is very important in practice, a oxygen hard coating having the composition $Si_aB_bMeN_uC_vO_w$, in particular an oxygen hard coating having the composition $Si_aB_bN_uC_vO_w$ can be deposited on the substrate as a protective hard layer, onto the connecting layer and / or onto the first hard layer and / or onto the intermediate layer and / or onto a oxygen hard layer.

Regarding a very special embodiment, a metallic intermediate layer, e.g. a chromium, an aluminum or an other metallic intermediate layer can be provided to improve a connection between two layers, wherein said intermediate layer can be provided between the substrate and the connecting layer and / or between the connecting layer and the intermediate layer and / or between the intermediate layer and the hard coating and / or between the hard coating and the protective hard layer and / or between two other layers of the layer arrangement in accordance with the invention, wherein such a metallic intermediate layer can contribute to reduce residual stress in or between to successive layers.

The ion-cleaning temperature of a coating method in accordance with the invention is, preferably, between 100 °C and 1000 °C, in particular between 250 °C and 800 °C and the ion cleaning is preferably, but not necessarily, carried out by applying a pulsed bias voltage to the substrate. During the building of the intermediate layer and / or the gradient-mixed layer, an electric RF-voltage can be applied to the substrate, too.

It is understood that the above discussed embodiments of methods according to the invention are only examplarily and that, in special cases, the described methods can be combined in every suitable manner.

Furthermore, the invention is related to a substrate, in particular to a tool having a layer arrangement according to the invention and or which layer arrangement is deposited with a coating method according to the present invention.

Among other things, the tool can be a cutting tool, especially a drill, a milling cutter, a tool for a turning lathe, or a plane, a conversion tool or a micro tool, in particular a conversion micro tool, a micro-indexable insert, a micro-milling cutter or an other tool or an other micro tool or a plastic tool.

It is understood that the layer arrangement in accordance with the invention, can be particular advantageously be deposited onto a wearing part, in particular a wearing part for an air- or land-based turbine, for an engine, especially for a combustion engine, in particular a gasket, a gearwheel, a piton or onto an other wearing part.

In the following, the invention is described with reference to the schematic drawing. There are shown:

Fig. 1 a layer arrangement in accordance with the invention;

Fig. 2 a coating apparatus for carrying out the method according to the invention.

In Fig. 1 a layer arrangement in accordance with the invention is schematically displayed, which layer arrangement is designated overall in the following by the reference numeral 1.

Onto the substrate 3, which can be e.g. a cutting tool 3, a connecting layer 4 is deposited. In the present embodiment, the connecting layer 4 is a connecting layer 4 having the composition $Me_xE_yN_z$, with $x,y \geq 0$ and $z > 0$, wherein Me is at least one metal of the group consisting of Al, Cr, Mo, W, Sc, Y, La, Ti, Zr, Hf, V, Nb, Ta, Mn, Tc, Re, Fe, Co Ni, Li, Ce and E is an element of the group consisting of Si, B, C, O. Especially, the connecting layer 4 is an AlCrN-layer having a thickness of about 2500 nm.

A SiC intermediate layer 7 is deposited onto the connecting layer 4, which intermediate layer 7 has e.g. a thickness of about 100 nm and following the intermediate layer 7 a first hard coating 5 is provided, which has in the present example a thickness of about 500 nm. The first hard coating 5 is a $Si_aB_bMe_cN_uC_vO_w$ hard coating 5, in particular a first hard coating 5 having the composition $Si_aB_bMe_cC_vN_u$, in particular a hard coating 5 having the composition $Si_aB_bC_vN_u$, with a,b > 0 and 33 at% > c ≥0 and u,v,w ≥ 0, and wherein Me is a metal. The first hard coating 5 of the special embodiment displayed in Fig. 1, is e.g. a SiBCN hard coating 5.

In a special embodiment according to a layer arrangement as displayed in Fig. 1, the connecting layer 4 may have a thickmness between 20nm – 50000nm, the intermediate layer may have a tickness between 10nm – 1000nm, the hard coating a thickness between 100nm – 5000nm and the protective hard layer may have a thickness between 5nm und 500nm.

Preferably, the connecting layer has a thickness between 100nm – 2500nm, the intermediate layer a thickness between 20nm – 500nm, the hard coating between 100nm – 2500nm and tthe protective hard layer a thickness between 10nm und 50nm.

The transition between the SiC intermediate layer 7 and the first hard coating 5 is realized via a gradient-mixed layer 8. The gradient-mixed layer 8 includes the elements Si and / or C of the intermediate layer 7 and includes the composition $Si_aB_bMe_cN_uC_vO_w$, in particular $Si_aB_bMe_cC_vN_u$, in more particular $Si_aB_bC_vN_u$ of the first hard layer 5, so that a more or less continuous transition form the composition of the intermediate layer 7 and the first hard coating 5, and vise versa, is assured.

As a top layer 10 an oxygen hard coating 9 having the composition $Si_aB_bMeN_uC_vO_w$, in particular having the composition $Si_aB_bN_uC_vO_w$ is provided, protecting the layer arrangement against the environment.

Thereby, in a special embodiment the protective hard layer 10, can also be developed as a hard layer 6.

Fig. 2 shows schematically the bodywork of a coating apparatus 11, which is very suitable for the coating method in accordance with the invention. The as such well know coatung apparatus 11 comprises a process chamber 12, in which process chamber 12 of the special coating apparatus 11 according Fig.2, three different coating sources are provided, namely the two RF-coating sources 1300 and 1310, which are provided as displayed at the right process chamber wall and the left process chamber wall, respectively, and the DC-coating source 13, 1320, which is provided at a rear-plane of the process chamber 12. All coating sources 1300, 1310, 1320 include a shutter 131, which allows to shield each coating source 1300, 1310, 1320 seperately and independently from each other, so that e.g. a respective coating source can be deactivated, without the need to deactivate the coating source as such.

For feeding a process gas, e.g. the sputter gas argon or the reactive gas N_2, O_2, C_2H_2 or for feeding another gas into the process chamber 12, means 15 are provided, which is in the present example an inlet pipe 15 which can be shut. In the process chamber 12, the substrate 3 to be coated is provided at a not shown carrier and is connected to a voltage source to be provided with a bias constant-voltage 16 or a RF-voltage 16.

In order to explain the mode of operation of the coating apparatus 11 in the course of the execution of a coating method in accordance with the invention, in the following a coating process is examplarily described for the coating of a tool 3, which process is in practise of great importance.

After the tool 3 has been placed in the process chamber 12, the tool is heated, preferably at 250 °C . 800 °C while the shutter 131 are shut. Then, an ion cleaning of the tool 3 is performed by applying a pulsed bias voltage 16 (AAFP asymmetric alternating field pulsing). In a successional first coating process the shutter 131 of the DC-coating source 13, 1320 is opened to deposit e.g. a AlCrN-connecting layer 4. The deposition of the connecting layer 4 can be performed by a DC sputter process or by a DC-arc evaporation process. During the deposition a bias voltage 16, preferably a negative bias voltage 16 of about 10 - 400 V is applied to the tool 3, wherein a polarity changing pulsed bias voltage 16 (AAFP) can also be used.

The frequencies are e.g. in the range of 0.1 to 300 KHz, the positive bias voltage is in particular in the range of 3 to 100 V. The pulse / pause ratio can be in the range of 0.1 to 0,95.

During the deposition of the connecting layer 4 the RF-magnetron 1310 is activated, wherein the respective shutter 131 is still closed.

Following, the shutter 131 is opened and in dependence of the desired intermediate layer 7, an operation of the DC-magnetron 13, 1320 in parallel with the RF-magnetron 1310 is performed. In order to adjust a gradient the power of the magnetrons can be suitable changed.

Following, the shutter 1303 of the DC-coating source 1320 is closed and the DC-coating source is deactivated for the coating process.

Preferably a RF-voltage is now applied to the substrate 3.

The RF-coating source 1310 is used for the deposition of a SiCx intermediate layer 7 and comprises a Si-target or a SiC-target.

During the deposition of the intermediate layer 7, the second RF-magnetron 1300 is activated while the respective shutter 131 is still closed.

After having reached the desired thickness of the layer, in an additional step the shutter 131 of the coating source 1300 is now opened.

Depending on the desired intermediate layer 7 as a gradient-mixed layer, the first RF-magnetron 1310 and the RF-Magnetron 1300 are operated in parallel. In order to adjust the gradient the power of the magnetrons can be suitable changed.

Then the shutter 131 of the RF-magnetron 1310 is closed and thus disabled for the coating process.

A SiBNC-layer as a first hard coating 5 is deposited by the RF-coating source 1300. That is, the RF coating source 1300 includes in the present example a target comprising at least the elements SiB, preferably a composition of BN and SiC.

The operation of the SiBNC-coating source 1300 is kept on in order to deposit a SiBNC-layer as a first hard layer 5 onto the gradient-mixed layer 8. In a following step, a process gas, e.g. of oxygen is supplied into the process chamber 12 through the inlet pipe 15, preferably oxygen is supplied in order to deposit a SiBNCO-layer as a oxygen hard layer 9, which acts as a protective hard layer 10, wherein the coating process in accordance with the invention is e.g. performed in such away that the fraction of oxygen in the oxygen hard layer in the direction opposite to the surface of substrate, that is taht the fraction of oxygen in direction to the outside is increasing.

Preferably, according to the method in accordance with the invention, the substrate to be coated can heated up to a temperature of about 300 - 800 °C. Following, after having reached a common starting pressure (ca. 0.01 Pa) an ion cleaning, e.g. by means of the AEGD-process is performed. The AEGD-process is well known to the person skilled in the art and, thus, there is no need to discuss this process in greater detail. For the deposition of the layers, in particular for the deposition of the connecting layer, a DC-Magnetron or a vacuum arc evaporation source including a suitable cathode material is used.

It is understood that in the process chamber 12 only one but also three or more RF-coating sources or more than one DC-coating sources 13 can be provided, depending on the special application and depending on the desired composition of the layers.

Consequently, the above examplarily described methods in accordance with the invention, can also be performed using three RF-coating sources 13, even if there are special requirements to the layers to be coated or to the their chemical composition.

Example 1:

Placing hard metal micro tool at the carrier.

1) Heating up the tool to 500 °C.

2) Ion cleaning ca. 30 min at 200V pulsed bias voltage, positive voltage 30V, (20Khz),pulse/pause 4, within the AEGD-process.

3) Deposition of a Al70Cr30-Schicht using DC-Sputtern, TARGET POWER 5 W/cm2 , bias voltage 50 V.

4) Reactive layer deposition of AlCrN by supplying N (nitrogen).

5) Metallic intermediate layer according to item 3.

6) Activating the RF-target, mixing ratio of the atomic composition Si:B being 1:6.

7) Addition of N O (nitrogen, oxygen) in order to deposit a protective hard layer.

Example 2:

1) Heating up the tools to 500 °C.

2) Ion cleaning ca. 30 min at 200V pulsed bias voltage, positive voltage 30V, (20Khz),pulse/pause 4, in the course of the AEGD-process.

3) Deposition of a TiAlSiN-coating by means of a vacuum arc evaporation source.

4) Switching on the RF-target having a target including a molar mixing of BN plus SiC in a ratio 1:1.

5) Addition of nitrogen and acetylene.

6) Addition of oxygen.

Example 3:

1) Heating up the tool to 500 °C.

2) Ion cleaning ca. 30 min at 200V pulsed bias voltage, positive voltage 30V, (20Khz),Puls/Pause 4, in the course of the AEGD-process.

3) RF-sputtern of SiC.

4) Addition of N (nitrogen).

5) Activating the RF-target according to example 2, item 4).

6) Deactivating of the SiC target.

Common pressures for sputtering are typically in the range of 0.1 bis 5 Pa.

Regarding the arc evaporation coating technique (arc-coating), typical discharge currents are between 30 - 200 A. Common diameter of arc-cathode is for example 100 mm. Typical pressures for arc coating are e.g. in the range between 1Pa to 10 Pa.

Patent Claims

1. Layer arrangement for the formation of a coating on a surface (2) of a substrate (3), in particular on the surface (2) of a tool (3), characterized in, that the layer arrangement comprises at least one hard layer (4, 5, 6, 7, 8) having the composition $Si_aB_bMe_cN_uC_vO_w$ with a,b > 0 and 33 at% > c ≥0, preferably 25 at% > c ≥0, in particular 10 at% > c ≥0 and u,v,w ≥ 0, and Me being a metal.

2. Layer arrangement in accordance with claim 1, wherein Me is at least one metal of the group consisting of Al, Cr, Mo, W, V,Nb, Ta, Ti, Zr, HF, Mn, Fe, Co, Ni, Li, Be, Mg, Sc, Y, La, Ce, Nd, Sm.

3. Layer arrangement in accordance with claim 1 or 2, wherein on the surface (2) of the substrate (3) at least one connecting layer (4), preferably a connecting layer (4) having the composition $Me_xE_yN_z$, with x > 0, y ≥ 0 and z > 0 wherein Me is at least one metal of the group consisting of Al, Cr, Mo, W, V,Nb, Ta, Ti, Zr, HF, Mn, Fe, Co, Ni, Li, Be, Mg, Sc, Y, La, Ce, Nd, Sm and E being an element of the group consisting of Si, B, C, O.

4. Layer arrangement in accordance with anyone of the preceding claims, wherein a first hard layer (5) is provided having the composition $Si_aB_bMe_cN_uC_vO_w$, in particular a first hard layer (5) having the composition $Si_aB_bMe_cC_vN_u$, and in more particular a first hard layer (5) having the composition $Si_aB_bC_vN_u$.

5. Layer arrangement in accordance with anyone of the preceding claims, wherein between the substrate (3) and the hard layer (4, 5, 6) and / or between the connecting layer (4) and the hard layer (5, 6) and / or between the first hard layer (5) and the hard layer (6) an intermediate layer (7) comprising the elements Si and / or C is provided.

6. Layer arrangement in accordance with anyone of the preceding claims,, wherein between the substrate (3) and the hard layer (4, 5, 6) and / or between the connecting layer (4) and the first hard layer (5) and / or the first

hard layer (5) and the hard layer (6) a gradient-mixed layer (8) is provided, comprising the elements Si and / or C of the intermediate layer (7) and having the composition $Si_aB_bMe_cN_uC_vO_w$, in particular $Si_aB_bMe_cC_vN_u$, and in more particular $Si_aB_bC_vN_u$ of the first hard layer (5).

7. Layer arrangement in accordance with anyone of the preceding claims, wherein a oxygen hard layer (9) is provided, having the composition $Si_aB_bMeN_uC_vO_w$, in particular having the composition $Si_aB_bN_uC_vO_w$ and which oxygen hard layer (9) is in more particular provided as a protective hard layer (10).

8. Layer arrangement in accordance with anyone of the preceding claims, wherein the thickness of the connecting layer (4) and / or of the intermediate layer (7) and/ or of the hard layer (4, 5, 6, 7, 8) and / or of the first hard layer (5) and / or of the gradient mixed layer (8) and / or of the oxygen hard layer (9) and / or of the protective layer (10) is between 5 nm and 50000 nm, especially between 10 nm and 5000 nm, in particular between 80 nm und 600 nm.

9. Coating method for depositing a layer arrangement (1) in aacordance with anyone of the preceding claims onto a surface (2) of a substrate (3), in particular onto the surface (2) of a tool (3), wherein in a process chamber (12) of a coating apparatus (11) a RF-coating source (13), having a RF-magnetron and / or a DC-coating source (1320), in particular a DC-magnetron, is provided, wherein the RF-coating source (13) and / or the DC-coating source (1320) can be closed by a shutter (131), and wherein means (15) are provided, so that a process gas can be supplied into the process chamber (12), and said coating method comprising the following steps:

a.) placing the substrate (3) into the process chamber (12);

b.) heating the substrate (3) to a ion-cleaning temperature;

c.) ion-cleaning of the substrate (3) at the ion-cleaning temperature;

d.) deposition of a layer arrangement (1) having the composition $Si_aB_bMe_cN_uC_vO_w$ with a,b > 0 and 33 at% > c ≥0, preferably 25 at% > c ≥0, in particular 10 at% > c ≥0 and u,v,w ≥ 0, and Me being a metal, using the RF-coating source (13) and / or the DC-coating source (1320).

10. Coating method in accordance with claim 9 comprising the following steps:

a.) placing the substrate (3) into the process chamber (12);

b.) heating the substrate (3) to the ion-cleaning temperature;

c.) ion-cleaning of the substrate (3) at the ion-cleaning temperature and feeding a bias constant-voltage (16) and / or a RF-Voltage (16) to the substrate (3) to achieve an ion-cleaning;

d.) opening the shutter (1303) of the DC-coating source (1320) and / or the shutter (1301) of a first RF-coating source (1300);

e.) deposition of a connecting layer (4) onto the surface (2) of the substrate (3), in particular a connecting layer (4) having the composition $Me_xE_yN_z$, with x,y ≥ 0 and z > 0, wherein Me is at least a metal of the group consisting of Al, Cr, Mo, W, V,Nb, Ta, Ti, Zr, HF, Mn, Fe, Co, Ni, Li, Be, Mg, Sc, Y, La, Ce, Nd, Sm and E being an element of the group consisting of Si, B, C, O;

f.) deactivating the DC-coating source (1320) and / or eht first RF-coating source (1300), opening a shutter (1302) of a second RF-coating source (1310) and putting said second RF-coating source (1310) into operation;

g.) deposition of an intermediate layer (7) comprising the elements Si and / or C by using the second RF-coating source (1310);

h.) opening a shutter of a third RF-coating source, putting said third RF-coating source into operation and depositing in parallel with the second RF-

coating source (1310) $Si_aB_bMe_cN_uC_vO_w$, in particular $Si_aB_bMe_cC_vN_u$, in more particular $Si_aB_bC_vN_u$ according to the first hard layer (5) by means of the second RF-coating source (1310) in order to deposit a gradient-mixed layer (8);

i.) deactivating the second RF-coating source (1310) and depositing a first hard layer (5) having the composition $Si_aB_bMe_cN_uC_vO_w$, in particular $Si_aB_bMe_cC_vN_u$, in more particular $Si_aB_bC_vN_u$ and keeping the third-coating source in operation until a presetted thickness of the first hard layer (5) is deposited;

j.) feeding a reactive gas, especially oxygen, nitrogen, or a carbon containing gas, into the process chamber (12) and depositing an oxygen hard layer (9) having the composition $Si_aB_bMe_cN_uC_vO_w$.

11. Coating method in accordance with anyone of claims 9 or 10, wherein the DC-coating source (1320) and / or the RF-coating source (13) is a sputter-source and / or an arc evaporating source.

12. Substrate, in paricular a tool (3), having a layer arrangement (1) in accordance with anyone of claims 1 to 8 and being coted using a method in accordance with anyone of claims 9 to 11.

13. Tool in accordance with claim 12, wherein the tool (3) is a cutting tool (3), especially a drill (3), a milling cutter (3), a tool (3) for a turning lathe or a plane (3), a conversion tool (3) or a micro tool (3), in particular a micro-tool (3), a mirco-indexable insert (3), a micro-milling cutter (3) or an other tool(3) or a micro tool (3) or a plastic tool.

14. Substrate in accordance with claim 12,, wherein the substrate is a wearing part (3), in particular a wearing part (3) for an air- or land-based turbine, for an engine, especially for a combustion engine, in particular a gasket (3), a gearwheel (3), a piston (3) or an other wearing part (3).