Layer System with at least one Mixed Crystal Layer of a Polyoxide

This invention relates to a PVD layer system for the coating of workpieces, as specified in the characterizing clause of Claim 1, and to a method for producing a corresponding coating system as specified in the characterizing clauses of Claims 21 and 26. The invention further relates to workpieces coated with a layer system according to the invention and having the characterizing features specified in Claim 42

Prior Art

EP 0513862 and US 5,310,607 (Balzers) describe an $(Al,Cr)_2O_3$ hard-metal layer, a tool coated with it and a process for producing that layer whereby, from a crucible serving as the anode for a low voltage arc (LVA) discharge, Al and Cr powder are jointly vaporized and tools are coated in an Ar/O_2 atmosphere at about 500°C. That layer exhibits intrinsic compressive stress and consists essentially of mixed crystals with a Cr content in excess of 5%, its thermodynamic stability enhanced by a high aluminum content, its abrasion resistance enhanced by an increased chromium content. While on the basis of a purported 202 line the layer is referred to as a modified α-aluminum oxide (corundum) with a shift reflecting the chromium content, all other corundum lines are missing in the analyses performed. Their described advantages notwithstanding, these layers have failed to establish themselves as an industrial standard since due to their insulating properties their production by the stated LVA process causes process-related problems in continuous operation.

The three documents mentioned below describe ways to circumvent these process-related problems by the deposition of an at least adequately conductive layer of a ternary nitride followed by an oxidation step. All three documents, however, aim at providing an oxide layer or dispersion in a corundum structure to serve as a base for the epitaxial growth of an α-aluminum oxide layer. The latter is produced by an unbalanced magnetron sputter (UBMS) process in an Ar/O_2 atmosphere with extensive process monitoring, using a plasma emission monitor (PEM), in order to keep the Al sputtering targets in a transitional range between a contaminated, i.e. oxidic, and a metallic surface.

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US 6,767,627 and JP No. 2002-53946 (Kobe) describe a layer system and a method for producing an α-aluminum oxide containing layer system. As a first step, by way of example, a TiAlN and an AlCrN hard layer are applied, followed by the oxidation of at least the surface of the AlCrN hard layer, the result being a corundum-like lattice structure, with a lattice constant of between 0.4779 and 0.5 nm, as an intermediate layer on which the α-aluminum oxide layer (a = 0.47587 nm) is deposited. The authors claim to be able even at temperatures between 300 and 500°C to produce layers of a corundum structure by employing an AIP process with a subsequent oxidation step, followed by the UBMS of aluminum oxide. Also, as an alternative, they describe aluminum oxide layers deposited on Cr_2O_3, $(Al,Cr)_2O_3$, and $(Fe,Cr)_2O_3$ intermediate layers which also were produced by UBMS in an Al/O_2 atmosphere. In addition, making reference to JP5-206326, the authors mention the inadequate suitability of $(Al,Cr)_2O_3$ layers for the processing of steels due to the reaction of chromium on the surface of the layer with the iron of the material being treated.

In contrast thereto, inventors of the same applicant acknowledge in the more recent US 2005 005 8850 (Kobe) that these techniques do in fact require temperatures of 650°C to 800°C since no oxidation takes place if the temperature is too low. Yet they only describe examples at temperatures of 700° and 750°C and lay claim to a method whereby at least the oxidation step or the deposition of the aluminum oxide film takes place at a temperature of 700°C and above. Preferably, they say, both process steps are carried out at the same temperature. The inventors further describe the additional application of a preferably Ti-containing diffusion barrier such as TiN, TiC, TiCN, among others, in order to prevent the harmful diffusion of the oxygen through the oxide layer into the substrate, which would occur at these high temperatures.

WO 2004 097 062 (Kobe) as well sees a need for improvement on the invention described in JP No. 2002-53946. The starting point in this case is an attempt whereby, as in JP No 2002-53946, CrN is oxidized at 750°C whereupon, at the same temperature, aluminum oxide is deposited by a PEM-monitored sputter process in an Ar/O_2 atmosphere. While this does result in crystalline layers, these become increasingly coarse-grained and thus excessively rough with the progressive augmentation of the layer thickness. WO 2004 097 062 tries to solve that problem with a method whereby the growth of the aluminum oxide crystals is interrupted either at periodic intervals by thin oxide layers of different metal oxides which also grow with a corundum structure, such as

Cr_2O_3, Fe_2O_3 $(AlCr)_2O_3$, $(AlFe)_2O_3$, or at least by the periodic dispersion of such oxides. The layer regions encompassing those other metal oxides are supposed to be held at less than 10 and preferably even less then 2%. It would appear, however, that the long coating times involved in producing these layers, about 5 hours for 2 µm, are hardly practical for industrial processes.

A publication by Ashenford [Surface and Coatings Technology 116-119 (1999), 699-704] describes the growing of aluminum oxide of a corundum structure and chromium oxide of an eskolaite structure in a temperature range between 300°C and 500°C. The eskolaite structure of the chromium oxide is similar to the corundum structure of the aluminum oxide, albeit with somewhat modified lattice parameters. The objective of the tests, performed with an MBE system in the UHV range, was to use chromium oxide of a corundum structure as a crystallization base for growing the corundum high temperature phase of the aluminum oxide. In the process the oxygen is excited by the plasma, the metals are vaporized separately by elemental sources so disposed that the material flows reach the substrate at the same time. In the temperature range explored, between 300 and 500°C, steel substrates permitted the deposition of amorphous aluminum oxide only, whereas, largely independent of the pretreatment of the steel substrates, chromium oxide grows as a polycrystalline layer with an eskolaite structure. Still, it was not possible to produce a pure α-aluminum oxide even on eskolaite layers since in that temperature range, at an aluminum concentration of 35 at% and up, the crystalline structure flips into amorphous aluminum oxide within just e few atom layers. The practical results were then confirmed by simulated calculations using a semi-empirical model, predicting a destabilization of the α-aluminum oxide by oxygen defects in favor of a x-modification.

EP 0 744 473 B1 describes a sputter process which for substrate temperatures below 700°C provides a layer that consists of an α- and γ-phase of the aluminum oxide and is completely crystalline but exhibits high compressive stress of at least 1 GPa. The intermediate layers between the tool and the aluminum oxide layer are said to be metal compounds with O, N and C.

To summarize, it can be said that, in terms of producing oxides with a corundum structure using PVD processes, prior art has for more than 10 years endeavored to come up with α-aluminum oxide layers that can match the layer long successfully obtained with CVD but without the

drawbacks inherent in the CVD process. The techniques applied, however, are so complex, error-prone and cumbersome that to this day there has only been one manufacturer that offers an amorphous aluminum oxide layer but still no crystalline and especially no α-aluminum oxide layers for tool-coating purposes. For similar reasons there are still no other pure oxide layers available, in particular thick oxide layers, even though it is evident from the available gamut of oxynitrides, oxycarbonitrides, etc. that in the tool market there is a great demand for thermochemically resistant coatings

Definitions

The term **thermally stable**, for the purpose of this invention, defines layers which, exposed to air within a temperature range from room temperature to at least 900°C, preferably 1000°C and especially 1100°C, reveal no changes in their crystal structure, hence no significant changes in their x-ray diffraction pattern and thus in their lattice parameters. Layers of this type, if they exhibit a corresponding basic hardness of at least 1500 HV but preferably at least 1800 HV, are of particular interest for tools exposed to high thermal stress, since no phase conversion processes are to be expected during the machining cycle, and because they offer clearly superior thermal hardness compared to other layers.

The term **stress-free** refers to layers which in test procedures, described in more detail below, have exhibited minor if any compressive or tensile stress. Consequently, a shift for instance of the interplanar spacing or the lattice constant of $(AlCr)_2O_3$ layers, established through a linear interpolation between the lattice constants of the binary compounds α-Al_2O_3 and α-Cr_2O_3, will provide a direct indication of the Al and, respectively, Cr content of the layer (Vegard's Law). This is in contrast to the PVD methods described for instance in EP 0513662 and EP 0744473. The layers discussed in these documents, grown with mechanical bias due to the inclusion of inert-gas atoms, direct-current bias or for other reasons exhibit high intrinsic compressive stress in excess of one GPa, which in the case of thicker layers often leads to spalling.

By comparison, CVD layers are usually subject to tensile stress as a result of the different thermal expansion coefficients of the layer and the base material during the cooling-off of the high deposition temperatures that are typical of the process. For example, according to US 2004202877 the deposition of α-Al_2O_3 requires temperatures of between 950 and 1050°C. Apart from the

additional problem of an unavoidable concentration of undesirable decomposition products (such as halogens) from the deposition process, this constitutes the main drawback of the CVD coating process, since such stress leads to fissuration, for instance ridge cracks, making these layers less than suitable for machining processes such as jump cutting.

The term **polyoxides** refers to compounds of at least two or more metals with an oxide. It also refers to the oxides of one or more metals which additionally contain one or several semiconductor elements such as B or Si. Examples of such oxides include the cubic double or polyoxides of aluminum, known as spinels. This present invention, however, relates to oxides with a corundum-type isomorphous α-aluminum oxide structure composed of $(Me1_{1-x}\ Me2_x)_2O_3$, where Mel and Me2 each contain at least one of the elements Al, Cr, Fe, Li, Mg, Mn, Ti, Sb or V and where the Mel elements differ from the Me2 elements.

Measuring Methodology

To permit a better comparison, the following will briefly discuss individual methods and equipment used in determining specific layer characteristics.

X-ray Diffraction Analyses

For the analysis of the XRD spectra and the lattice constants calculated on the basis of the latter, the equipment employed was a D8 X-ray diffractometer by Bruker-AXS, with a Goebel mirror, a Soller slit and an energy-dispersive detector.

The simple θ-2θ measurement was performed in a Bragg-Brentano geometry with Cu-kα radiation, no grazing incidence.

Angular range: 20 to 90°, with rotating substrate.

Test duration: With a dwell time of 4 s per 0.01° the test duration was 7 h 46 min (for 70°).

Measuring the Intrinsic Stress of the Layers

One method applied to measure the intrinsic stress of the layers was the Stoney bending strip method using hard metal sticks (L=2r=20mm, D_s=0.5 mm, E_s=210 GPa, v_s=0.29) and calculating the intrinsic stress with the following formula:

$$\sigma = \frac{E_s * D_s^2}{3*L^2 * d_f} * f$$

where E_s ... Young Module of the substrate, D_s ... total thickness of the substrate, d_f ... layer thickness, f ... deflection, and f ... free bar length.

Another method applied was the bending disk method, with the intrinsic stress calculated with the following formula:

$$\sigma = \frac{E_s}{(1 - v_s)} * \frac{D_s^2 * 8}{6 * L^2 *} * \frac{f}{d_f}$$

where L=2r=20mm, D_s=0.5 mm, E_s=210 GPa, v_s=0.29.

Moreover, the deviation, determined by x-ray diffractometry, of the measuring points of a polyoxide from the straight line determined by applying Vegard's Law provides an indication of the intrinsic stress patterns in a composite layer system.

Overview

It is the objective of this invention to offer improvements over the drawbacks of prior art, described in detail above, and to provide a layer system that lends itself well to high-temperature applications and contains at least one thermally stable oxidic layer, as well as workpieces, in particular tools and components, protected by said layer system. Another objective consists of a method for producing the layer system in such fashion that a simple and reliably reproducible coating of workpieces and an adjustment of the properties of the layer system to varying applications is possible.

This objective is achieved with a PVD layer system for the coating of workpieces, comprising at least one mixed-crystal layer of a polyoxide having the following composition:

$$(Me1_{1-x}Me2_x)_2O_3$$

where Mel and Me2 each include at least one of the elements Al, Cr, Fe, Li, Mg, Mn, Nb, Ti, Sb or V, with the elements of Me1 differing from those of Me2 and the crystal lattice of the mixed-crystal layer having a corundum structure which in a spectrum of the mixed-crystal layer, measured by x-ray diffractometry or electron diffraction, is characterized by at least three, preferably four and especially five lines associated with the corundum structure. Especially well suited are layer systems in which Mel is aluminum and Me2 consists of at least one of the elements Cr, Fe, Li, Mg, Mn, Nb, Ti, Sb or V while $0.2 \leq x \leq 0.98$, preferably $0.3 \leq x \leq 0.95$. In this case, particular significance is attributed to aluminum as the element enhancing oxidation resistance as well as high-temperature hardness. Too high an aluminum content, however, has been found to pose a problem especially in producing the layers since, particularly at low coating temperatures, these layers form progressively smaller crystallites with a correspondingly diminished reflection intensity in the x-ray diffractogram.

For growing the layer in as undisturbed and stress-free a manner as possible, the concentration of halogens and inert gas in the mixed-crystal layer should in any event be less than 2%. This can be achieved by operating the sources with a process gas that consists of a minimum of 80%, preferably 90% and ideally even 100% of oxygen. The inert gas content in the mixed-crystal layer can then be limited to a maximum or 0.1 at%, preferably a maximum of 0.05 at% and/or the halogen content can be limited to a maximum of 0.5 at% and preferably to a maximum of 0.1 at%, or, in a best-case scenario, the mixed-crystal layer can preferably be produced essentially free of any inert gas and halogens.

The mixed-crystal layer can be built up in different ways. For example, the layer can be produced as a single or a multi-stratum layer from at least two different, alternatingly deposited polyoxides. Alternatively, a polyoxide can be deposited in an alternating sequence with another oxide. Polyoxides that have been found to be particularly resistant to high temperatures are those produced by arc vaporization or sputtering of aluminum/chromium and aluminum/vanadium alloys. Other oxides with good high-temperature resistance characteristics and suitable for alternating coating with polyoxides include HfO_2, Ta_2O_5, TiO_2, ZrO_2, and γ-Al_2O_3, but especially oxides with a corundum structure such as Cr_2O_3, V_2O_3, Fe_2O_3, $FeTiO_3$,Ti_2O_3, $MgTiO_2$ and, of course, especially α-Al_2O_3.

In generating the layer system it was found to be desirable to minimize any stress in the mixed-crystal layer so as to permit the deposition even of thick layers that are needed especially for high-speed lathe work on metals. If the layer system is to feature additional characteristics such as a specific intrinsic stress pattern for the machining of hardened steels, particular antifriction qualities for improved chip removal or for use on sliding elements, enhanced adhesion to different substrates, or the like, such properties can be attained for instance by selecting appropriate intermediate layers between the substrate and the mixed-crystal layer, consisting of at least one bonding and/or hard-metal layer, or by providing the mixed-crystal layer with one or several cover layers.

The hard-metal layer or cover layer preferably contains at least one of the metals of subgroups IV, V and VI of the periodic system, or Al, Si, Fe, Co, Ni, Co, Y, La or of such metal compounds of these elements with N, C, O, B, or mixtures thereof, compounds with N or CN being preferred. Compounds found to be particularly suitable for the hard-metal layer include TiN, TiCN, AlTiN, AlTiCN, AlCrN and AlCrCN, while the compounds that are especially suitable for the cover layer include AlCrN, AlCrCN, Cr_2O_3 or Al_2O_3, and in particular γ-Al_2O_3 or α-Al_2O_3. Much like the mixed-crystal layer, the intermediate and/or the hard-metal layer may comprise several strata. The layer system may also be built up as a multilayer structure with an alternating intermediate and mixed-crystal layer or alternating cover layer and mixed-crystal layer.

The mixed crystals with a corundum structure can be produced employing arc processes without or with a specially configured, small vertical magnetic field, by pulse-superposed arc processes, as well as by general methods such as arc or sputter processes where high-current pulses are fed to the material sources such as arc vaporizers or sputter sources or are superimposed on the DC base mode. This permits operation in the contaminated state, or alloying on the target, as long as certain prerequisites, explained in more detail below, are observed.

In connection with the arc processes employed for producing the layer system according to the invention and in particular for producing the oxidic mixed-crystal layer, please refer to the following patent applications by the same claimant which in terms of the methodology represent

the latest state of the art: WO 2006099758, WO 2006/099760 as well as CH 01166/06. All of the processes were implemented using a Balzers RCS coating system.

To produce mixed crystals with a corundum structure it is important that in each process the target is an alloy target, because otherwise, as explained below, it will not be possible at deposition temperatures below 650°C to deposit an oxidic mixed-crystal layer with a corundum structure. In the interest of an as simple as possible reproducible process, the process parameters should be selected so that the metal composition of the mixed-crystal layer, scaled to the total metal content, will not differ for the respective constituent metals by more than 10%, preferably 5% and especially 3% from the concentrations in the metal composition of the target. This is attainable for instance by observing the parameters indicated in the experiment examples, by selecting a rather low substrate bias of perhaps less than 100 V so as to prevent dissociation by an edge effect etc. Those skilled in the art can adjust and vary these parameters depending on the alloying system, for instance if there is a need to achieve a very high compressive stress.

Arc processes in which no magnetic field is applied to the target surface, or only a small external magnetic field extending in a direction essentially perpendicular to the target surface, are generally suitable for producing polyoxides according to this invention. If a magnetic field with a vertical component B_z is applied, it will be desirable to set the radial or surface-parallel component B_r over most but at least not less then 70% and preferably 90% of the target surface at a value smaller than B_z. The vertical component B_z is set between 3 and 50 Gauss but preferably between 5 and 25 Gauss. This type of magnetic field can be generated for instance by means of a magnet system consisting of at least one axially polarized coil whose geometry fairly matches the target circumference. The coil plane may be positioned at the level of the target surface or preferably behind and parallel to the latter. The processes described below, employing pulsed sources, lend themselves well to arc processes using sources that have such weak magnetic fields or even no magnetic field.

The following pulse source processes for producing in particular thermally stable mixed-crystal layers of polyoxides with a corundum-type crystal lattice involve the simultaneous feeding of at least one arc source with a direct current and a pulsed or alternating current. A first electrode of an

arc or sputter source, in the form of an alloy target, and a second electrode serve to deposit a layer on the workpiece, the source simultaneously being fed a direct current or DC voltage as well as a pulsed or alternating current or a pulsed or alternating AC voltage. The composition of the alloy target is essentially the same as that of the mixed-crystal layer. The preferred pulse frequency is in a range from 1 kHz to 200 kHz. The pulse current supply may also be operated at some other pulse-width ratio or with pulse separations.

The second electrode may be either separated from the arc source or constitute the anode of the arc source, with the first and the second electrodes connected to and powered by a single pulse current supply. If the second electrode does not serve as the anode of the arc source, the arc source can be connected to and operated with one of the following material sources via the pulse current supply:

- Another arc vaporizing source that is itself connected to a DC power supply;
- A cathode of a sputter source, in particular a magnetron source, also connected to a power supply, especially to a DC power supply;
- A vaporizing crucible that doubles as the anode of a low voltage arc vaporizer.

The DC power supply delivers a base current in a manner whereby the plasma discharge is maintained essentially without interruption at least at the arc vaporizer sources but preferably at all sources.
It is desirable to decouple the DC power supply and the pulse current supply by means of an electric decoupling filter that preferably contains at least one blocking diode. The coating process can take place at temperatures below 650°C and preferably below 550°C.

In this case the polyoxide layers grow with a corundum-like structure in spite of the relatively low coating temperature and the bonding or intermediate layer that may be positioned underneath them perhaps as a cubic metal nitride or carbonitride layer, which is surprising given the fact that in earlier experiments in which layers were produced through simultaneous vapor deposition on workpieces using elemental aluminum and chromium targets in an oxygen atmosphere only

amorphous layers such as $(Al_{1-x}Cr_x)_2O_3$ were attainable. This was even the case when the coating range of the sources was set in overlapping fashion. Only when alloy targets are used is it possible, already at relatively low process temperatures, to deposit polyoxides with a crystalline and especially corundum structure. It is also necessary to ensure that enough oxygen is available at the target, which is why a high oxygen content of at least 80% and preferably 90% is selected for the process gas or, as in the following Example #1), only oxygen is used as the process gas. During the arc process the target surface is immediately coated with a thin, nonconductive layer. In the opinion of the inventors, the growth of a crystalline layer and especially one with a corundum structure, which used to be possible at much higher temperatures only, at a lower temperature can be attributed to the formation of polyoxides on the target surface which evaporate during the process, initially form growth nuclei on the workpiece and ultimately participate in the build-up of the layer. There are several reasons pointing to this growth mechanism. For one, the temperatures generated on the target surface by the arc are within the melting point of the alloy, which in the presence of a sufficiently high oxygen concentration establishes a good basis for the formation of high-temperature-stable corundum-like polyoxide structures. For another, as mentioned above, the simultaneous vaporization of elemental aluminum and chromium targets failed to produce mixed crystals. Similar results were obtained with oxide layers produced by a sputter process. For example, in experiments analogous to those per US 6,767,627 the inventors authoring this patent application produced aluminum oxide and aluminum-chromium oxide layers in a temperature range between 400 and 650°C by sputtering, although crystalline aluminum oxide or aluminum-chromium oxide layers having a corundum structure could not be established. Nor were attempts using alloy targets successful, which may be due to the absence in a typical sputter process of a thermal excitation on the substrate surface, and to the fact that the target surface does not sputter compounds but atoms only.

While at this juncture there is no factual proof, for instance by a spectrographic analysis, of such a formation mechanism, and while other mechanisms are perhaps a factor in this, it can nevertheless be stated that this present invention makes it possible for the first time to produce polyoxides with a distinctly verified corundum lattice structure at a coating temperature of between 450 and 600°C.

To further increase the thermal excitation on the target surface, individual experiments were

conducted with uncooled or with heated targets, vaporizing material in an oxygen atmosphere on the nearly red-hot target surface. Even layers produced in that fashion exhibit a corundum-like lattice. At the same time, the rising discharge voltages in these processes point to an increased plasma impedance which is attributable to the increased electron emission of glowing surfaces in combination with an elevated vapor pressure of the target material, further intensified by the pulsation of the source current.

Another way to produce oxide layers according to this invention is through the operation of a high-power discharge with at least one source. This is attainable for instance by operating the pulse current source or pulse voltage supply with pulse slopes that are generated at least in the range from 0.02 V/ns to 2.0 V/ns, preferably in the range from 0.1 V/ns to 1.0 V/ns. The currents applied are at a level of at least 20 A but preferably equal to or greater than 60 A, with voltages between 60 and 800 V, preferably between 100 and 400 V above or in addition to the voltage and current of the simultaneous DC discharge. These voltage spike pulses can be generated for instance by means of one or several capacitor cascades which, apart from a few other advantages, also makes it possible to alleviate the load on the basic power supply. Preferably, however, the pulse generator is connected between two simultaneously DC-powered arc sources. Surprisingly, by applying the spike impulses in the arc process, it is possible to increase the voltage at the source over several μs as a function of the magnitude of the voltage signal applied, whereas pulses with a flatter slope will result in an increased source current, as would be expected.

Initial experiments have shown that with these high-current discharges it is also possible to produce from sputter sources with alloy targets oxidic polyoxides with corundum, eskolaite or comparable hexagonal crystal structures, which can presumably be ascribed to the increased energy density on the target surface and the concomitant large temperature increase, so that here as well the use of uncooled or heated targets, described above, could prove beneficial. For processes of that nature the high-power discharge exhibits similar characteristics for both high-power arcing and high-power sputtering, corresponding to the anomalous glow discharge pattern known from Townsend's current-voltage diagram. The convergence on that range occurs from mutually opposite sides, one being the arc discharge of the arc technique (low voltage, high current), the other being the glow discharge of the sputter process (medium voltage, low current).

Approaching the stage of an anomalous glow discharge from the high-current side, i.e. the "arc side", will in any event require measures aimed at increasing the impedance of the plasma or of the target surface (see above). As stated, this can be accomplished by the superposition of spike pulses, by heating the target surface or by a combination of these measures.

Another way to increase the plasma impedance is to pulse the magnetic field of the source. This can be accomplished by means of the pulse current of the source which, either entirely or as a partial current, is passed through a magnetic system composed of an axially polarized coil as described above. In this case, in adaptation to the high current peaks, cooled coils with a small number of turns (1 to 5) can be used if necessary.

From the above explanations and the experiments described below it will be evident that layer systems according to this invention are in general superbly suited to tool applications. These layer systems can thus be advantageously applied on such tools as milling cutters, drills, gear cutting tools, interchangeable cutting inserts, cut-off tools and broaches made of different metals such as cold work steel and hot forming tool steel, HSS steel as well as sintered materials such as powder metallurgical (PM) steel, hard metal (HM), cermets, cubic boronitride (CBN), silicon hard (SiC) and silicon nitride (SiN). They lend themselves particularly well, however, to tool applications involving high machining temperatures or cutting speeds as for instance in lathe work, high-speed milling and the like which, apart from abrasion resistance, are subject to highly demanding requirements in terms of thermochemical stability of the hard-metal layer. Nowadays, these tools use primarily CVD-coated interchangeable inserts, often with coatings between 10 and 40 µm thick. In view of their above-described properties, the layers according to the invention constitute a preferred application for coated interchangeable inserts, with particular emphasis on interchangeable inserts made of PM steel, hard metal, cermet, CBN, SiC, SiN sintered metals, or interchangeable inserts precoated with a polycrystalline diamond layer.

While the emphasis of the work performed in connection with this invention was primarily focused on the development of protective layers for metal-cutting tools, it is of course possible to use these layers to advantage in other fields as well. For example, they can be assumed to be quite

suitable for tools used in various hot-forming processes, for instance in the precision forging and swaging or die-casting of metals and alloys. Given their high chemical resistance these layers can also be used on tools for plastics processing such as injection and compression molding equipment for producing preformed components.

Other application possibilities exist in the realm of parts and components coating, for instance of heat-exposed components of combustion engines, including fuel injection nozzles, piston rings, tappets, turbine blades and similarly stress-exposed parts. In these cases as well, much like those discussed above and at least in areas exposed to wear, the following base materials can be employed: Cold work steel, HSS steel, PM steel, HM, cermet or CBN-sintered metals.

Even for thermally stable sensor layers, layers can be deposited by the method according to the invention, such as piezoelectric and ferroelectric materials and all the way to quaternary superconductive oxide layers. It will be understood that these layers are not limited to any particular substrate structure and that in this context their application is indicated especially in connection with silicon-based MEMS.

Examples and Figures

The following explains this invention solely with the aid of examples and with reference to the exemplary figures which illustrate the following:

Fig. 1 X-ray spectra of $(Al_{1-x}Cr_x)_2O_3$ layers;
Fig. 2 Lattice parameters of $(Al_{1-x}Cr_x)_2O_3$ layers;
Fig. 3 Temperature pattern of the lattice parameters;
Fig 4 Oxidation pattern of a TiAlN layer;
Fig. 5 Oxidation pattern of a TiCN layer;
Fig. 6 Oxidation pattern of a TiCN / $(Al_{1-x}Cr_x)_2O_3$ layer;
Fig. 7 Detail of a $(Al_{1-x}Cr_x)_2O_3$ layer.

The example per test #1), described below in more detail, covers a complete coating cycle according to the invention, employing a weak, essentially vertical magnetic field in the area of the target surface.

The workpieces were placed in appropriately provided double- or triple-rotatable holders, the holders were positioned in the vacuum processing chamber, whereupon the vacuum chamber was pumped down to a pressure of about 10^{-4} mbar.

For generating the process temperature, supported by radiation heaters, a low voltage arc (LVA) plasma was ignited between a baffle-separated cathode chamber housing a hot cathode and the anodic workpieces in an argon-hydrogen atmosphere.

The following heating parameters were selected:

Discharge current (LVA)	250 A
Argon flow	50 sccm

Hydrogen flow	300 sccm
Process pressure	$1.4x10^{-2}$ mbar
Substrate temperature	approx. 550°C
Process duration	45 min

Those skilled in the art will be familiar with possible alternatives. As a matter of preference the substrate was connected as the anode for the low voltage arc and in addition preferably pulsed in unipolar or bipolar fashion.

As the next process step, the etching was initiated by activating the low voltage arc between the filament end the auxiliary anode. Here as well, a DC-, pulsed DC- or AC-operated MF or RF power supply can be connected between the workpieces and ground. By preference, however, a negative bias voltage was applied to the workpieces.

The following etching parameters were selected:

Argon flow	60 sccm
Process pressure	$2.4x10^{-3}$ mbar
Discharge current LVA	150 A
Substrate temperature	approx. 500°C
Process duration	45 min
Bias	200-250 V

The next process step consisted in the coating of the substrate with an AlCrO layer and a TiAlN intermediate layer. If higher ionization is needed, all coating processes can be assisted by means of the low voltage arc plasma.

For the deposition of the TiAlN intermediate layer the following parameters were selected:

Argon flow	0 sccm (no argon added)
Nitrogen flow	Pressure-regulated to 3 Pa

Process pressure	$3x10^{-2}$ mbar
DC source current TiAl	200 A
Coil current of the source magnetic field (MAG 6)	1 A
DC substrate bias	U = -40 V
Substrate temperature	approx. 550°C
Process duration	120 min

For the transition of about 15 min to the actual functional layer, the AlCr arc sources with a DC source current of 200 A were added, with the positive pole of the DC source connected to the annular anode of the source and to ground. During that step a DC substrate bias of -40 V was applied to the substrate. 5 minutes after activation of the AlCr(50/50) targets the oxygen inflow was started and was then ramped up within 10 min from 50 to 1000 sccm. At the same time the TiAl(50/50) targets were switched off and the N_2 was reduced back to approx. 100 sccm. Just before the introduction of oxygen the substrate bias was switched from DC to bipolar pulses and increased to U = -60 V. That completed the intermediate layer and the transition to the functional layer. The targets were powder-metallurgically produced targets. Alternatively, melt-metallurgical targets may be used as well. To reduce spattering, monophase targets as described in DE 19522331 may be used.

The coating of the substrate with the actual functional layer took place in pure oxygen. Since aluminum oxide constitutes an insulating layer, either a pulsed or an AC bias supply was used.

The key functional-layer parameters were selected as follows:

Oxygen flow	1000 sccm
Process pressure	$2.6x10^{-2}$ mbar
DC source current, AlCr	200 A
Coil current of the source magnetic field (MAG 6)	0.5 A, which generated on the target surface a weak, essentially vertical field of approx. 2 mT (20 Gs).

Substrate bias	U = 60 V (bipolar, 36 µs negative, 4 µs positive)
Substrate temperature	approx. 550°C
Process duration	60 to 120 min

The process described yielded well-bonded, hard layers. Comparison tests of the layer on lathe-work and milling tools revealed an edge life significantly improved over traditional TiAlN layers, although the surface roughness was clearly higher than the roughness values of optimized pure TiAlN layers.

The experiment examples #2 to #22 shown in Table 1 refer to simple layer systems according to the invention, each consisting of a double oxide layer of the $(Al_{1-x}Cr_x)_2O_3$ type produced at a coating temperature of between 450 and 600°C. The remaining parameters were identical to the parameters described above for producing the functional layer. The stoichiometric component of the layer composition was measured by Rutherford backscattering spectrometry (RBS). The largest deviation from the target alloy composition shown in column 2 was encountered in experiments #10 to #12, with a deviation of 3.5 percentage points at a 70/30 Al/Cr ratio. The metal components of the layer are scaled to the total metal content of the oxide. In terms of the stoichiometry of the oxygen, however, there were somewhat greater deviations of up to over 8%. All layers nevertheless exhibited a clearly corundum-like lattice structure. Preferably, therefore, layers produced according to the invention should have an oxygen-related stoichiometry shortage of 0 to 10% since even with an oxygen deficit of as much as 15% the desired lattice structure will be obtained.

Fig. 1 A to C show typical corundum structures of $(Al_{1-x}Cr_x)_2O_3$ layers produced at 550°C in accordance with the invention, with targets of varying alloys as indicated in experiments #18 (Al/Cr=25/75), #14 (50/50) and #3 (70/30). The measurements and analyses were obtained by x-ray diffractometry with the parameter selections described in more detail under Measuring Methodology, above. In the illustration any correction for background noise was dispensed with. Lattice parameters can be determined by other means as well, such as electron diffraction spectrometry. Due to the decreasing layer thickness from Fig. 1A to 1C, from 3.1 to 1.5 µm, there is a strong increase of the unmarked substrate lines relative to the marked layer lines of the

corundum structure. But even in spectrum C, the linear presentation of the Y-axis notwithstanding, 7 lines can still be clearly associated with the corundum lattice. The remaining lines belong to the base hard-metal material (WC/Co alloy). Of course, for an unambiguous association of the crystal lattice and the determination of the lattice constants, at least 3 and preferably 4 to 5 lines should be clearly identifiable.

The crystal structure of the layers is compact-grained, in large measure with an average crystallite size of less than 0.2 µm. Only in cases of large chromium content and at coating temperatures of 650°C were crystallite sizes found to be between 0.1 and 0.2 µm.

For the experiments #2 to #22, Fig. 2 shows the lattice constants a (solid line) and c (dashed line) of the $(Al_{1-x}Cr_x)_2O_3$ crystal lattice plotted above the stoichiometric chromium content and comparing them with the dotted straight lines determined by three values DB1 to DB3 from the ICDD (International Center for Diffraction Data), applying Vegard's Law. Over the entire concentration range the maximum deviation from the ideal Vegard's straight line is 0.7 to 0.8%. Measurements taken on other polyoxide layers showed similar results, with deviations for the parameters indicated amounting to a maximum of 1%. This suggests very low intrinsic stress in the mixed-crystal layer, which is why, in contrast to many other PVD layers, it is possible to deposit these layers with a greater layer thickness for instance between 10 and 30 µm, in some cases even up to 40 µm, with good bonding qualities. Larger stress patterns in the layer were obtained only by applying greater substrate voltages (>150) and/or by using an Ar/O_2, mixture of the process gas with a high Ar component. Since for many applications it is especially the multilayer systems, described in more detail below, that are well suited, it is possible within a wide range to adjust, where necessary, the layer stress values by selecting perhaps a multistratum intermediate layer and/or cover layer between the workpiece and the mixed-crystal layer. For example, this allows for the selection of higher intrinsic compressive stress values to increase the hardness of the layer for hard-metal machining processes. For industrial applications involving a high level of abrasive wear, thick layer systems with layers more than 10 or 20 µm thick can be produced economically, with the mixed-crystal layer preferably having a thickness of more than 5 and especially more than 8 µm.

Parallel tests were performed on mixed-crystal layers 2 μm thick, employing the methods described above (Stoney's bending strip method and the bending disk method). The layer stress values measured ranged from stress-free to minor compressive and tensile stress values less than or equal to 0.5 GPa. However, thicker PVD layers can still be deposited with layers exhibiting a somewhat higher layer stress of about 0.8 GPa. Another possibility consists in a sequence of thin layers (≤ 1 μm) deposited with alternating tensile and compressive stress, constituting a multilayer system.

As shown in Table 2, experiment #2, the temperature and oxidation resistance of the corundum structure of the deposited $(Al_{1-x}Cr_x)_2O_3$ layers was tested by heating coated hard metal test objects with an elevated Co content to a temperature of 1000° and 1100°C over a period of 50 minutes, then holding them there for 30 minutes and finally cooling them to 300°C over a time span of 50 minutes. Once cooled to room temperature, the lattice constants were reevaluated. According to the phase diagram [W. Sitte, Mater.Sci.Monogr., 28A, React. Solids 451-456, 1985] referred to in Phase Equilibria Diagrams Volume XII Oxides published by the American Ceramic Society, there is a miscibility gap in the range between about 5 and 70% aluminum, i.e. $(Al_{0.05-0.7}Cr_{x0.95-0.30})_2O_3$ for temperatures up to about 1150°C, which would predict a segregation of the $(Al_{1-x}Cr_x)_2O_3$ mixed crystal into Al_2O_3 and Cr_2O_3 and an $(Al_{1-x}Cr_x)_2O_3$ mixed crystal of some other composition. From that diagram it is also evident that with the process according to this invention it is possible to shift the thermodynamic formation temperature for $(Al_{1-x}Cr_x)_2O_3$ mixed-crystal layers from 1200°C to between 450° and 600°C. Surprisingly it was also found that the mixed-crystal layers produced by this method according to the invention experience only minimal changes in their lattice constants as a result of the glow process and that there is no segregation into their binary components. The maximum deviation, shown in Fig. 3, of the value of the lattice parameters a and of the red hot sample, measured after the coating process at room temperature, is about 0.064% while the maximum deviation of value c is 0.34%. For various other polyoxides as well, the measurements revealed an extraordinary thermal stability of the layer with a minor deviation of the lattice constants by 1 to 2% at the most.

Fig. 4 and 5 show the results of oxidation experiments on known layer systems based on an REM fracture pattern of a TiAlN and a TiCN layer, heated to 900°C as described above and then glowed

at that temperature for 30 minutes in an oxygen atmosphere. In a range of over 200 nm the TiAlN layer reveals a distinct alteration of its surface structure. An outer layer, consisting essentially of aluminum oxide and having a thickness of between 130 and 140 nm, is followed by a porous aluminum-depleted layer with a thickness of between 154 and 182 nm. Much poorer yet is the oxidation pattern of the TiCN layer in Fig. 5 which, subjected to the same treatment, has oxidized right down to the base material and reveals an incipient layer separation on the right side in the illustration. The layer is coarse-grained and no longer features the columnar structure of the original TiCN layer.

Fig. 6 and Fig. 7 show the results of identical oxidation experiments on a TiCN layer protected by an $(Al_{0.7}Cr_{0.3})_2O_3$ layer, about 1 µm thick, according to this invention. Fig. 6 is a 50,000 x magnification of the layer composite. The known columnar structure of the TiCN layer and the slightly finer-grown crystalline $(Al_{0.7}Cr_{0.3})_2O_3$ layer are clearly recognizable. The crystallite size of the aluminum/chromium oxide layer can be further refined by using targets with a higher Al content. Fig. 7 is a 150,000 x magnification of the layer composite, with the TiCN layer still visible only at the bottom edge of the image. Compared to the layers in Fig. 4 and Fig. 5 the reaction zone of the $(Al_{0.5}Cr_{0.5})_2O_3$ layer with a height H2 of maximally 32 nm is substantially narrower, having a dense structure without detectable pores. A series of comparison experiments with different mixed-crystal layers according to the invention revealed that, unlike other, prior-art, oxide layers, they protect the intermediate layers underneath, thus giving the entire layer system excellent thermal and oxidation resistance. It is generally possible to use for this purpose all inventive mixed-crystal layers which in the oxidation test described do not form reaction zones larger than 100 nm. The preferred mixed-crystal layers are those with reaction zones between 0 and 50 nm.

The hardness values of the $(Al_{0.5}Cr_{0.5})_2O_3$ layers were determined to be about 2000 HV_{50}. Measurements performed on other polyoxides such as $(Al_{0.5}Ti_{0.3}Cr_{0.2})_2O_3$, or $(Al_{0.6}Ti_{0.4})_2O_3$, $(V_{0.5}Cr_{0.5})_2O_3$, $(Al_{0.2}Cr_{0.8})_2O_3$, on their part yielded values between 1200 and 2500 KV.

Tables 3 to 6 list additional multilayer implementations of the layer system according to the invention. Process parameters for producing AlCrO and AlCrON mixed-crystal layers on a 4-source coating system (RCS) are shown in Table 7 while corresponding process parameters for

producing individual strata for various support layers are shown in Table 8.

The experiments #23 to #60 in Tables 3 and 4 refer to layer systems in which the oxidic mixed-crystal layer is of a corundum structure throughout and is mostly formed as a monolayer. Only in experiments #25, #29 and #31 in the mixed-crystal layer formed from two consecutive individual strata of different chemical compositions. In experiment #29 the only difference between the mixed-crystal layers is their different Al/Cr ratio.

The experiments #61 to #107 in Tables 5 and 7 refer to layer systems in which the mixed-crystal layer is composed of 5 to as many as 100 very thin layers measuring between 50 nm and 1 μm. In these cases, there may be alternating oxidic mixed-crystal layers of a corundum structure with different chemical compositions and corresponding mixed-crystal layers with different layer systems.

In comparison experiments on various turning and milling tools, the layers used in experiments #23, #24 and #61 to #82 proved clearly superior in turning and milling applications over conventional layer systems such as TiAlN, TiN/TiAlN and AlCrN. Even when compared to CVD layers, tool edge life improvements were achieved in milling and in some turning applications.

Although, as stated above, analyses and tests have already been conducted on a substantial number of different layer systems, those skilled in the art will use conventional measures, where necessary, to adapt certain characteristics of the invention's layer system to specific requirements. For example, one may consider adding further elements to individual or all layers of the system but in particular to the mixed-crystal layer. Elements known to improve for instance the heat resistance at least of nitridic layers include Zr, Y, La or Ce.

Table 1.

Exp. No.	Target [Al/Cr]	Depos'n Temp. [°C]	Glow Temp [°C]	Stoichiometric Component			Cr / (Cr+ Al)	Lattice Constants			d [µm]
				Cr	Al	O		a	c	c/a	
DB1-	Al_2O_3			0.00	2.00	3.00	0.00	4.75870	12.99290	2.7303	
DB2-	90/10			0.20	1.80	3.00	0.10	4.78550	13.05900	2.7289	
2	70/30	560°	-	0.59	1.41	3	0.30	4.85234	13.26296	2.7333	
3	70/30	550°	-	0.60	1.40	2.80	0.30	4.85610	13.24587	2.7277	1.5
4	70/30	600°	-	0.61	1.39	3.00	0.31	4.84603	13.23092	2.7303	3.3
5	70/30	550°	-	0.62	1.38	2.75	0.31	4.85610	13.24587	2.7277	3.0
6	70/30	550°	-	0.64	1.36	3.1	0.32	4.85610	13.24587	2.7277	3.1
7	70/30	550°	-	0.63	1.37	2.90	0.32	4.85612	13.23089	2.7246	2.9
8	70/30	550°	-	0.67	1.33	2.8	0.34	4.88443	13.15461	2.6932	2.7
9	70/30	550°	-	0.68	1.32	2.95	0.34	4.86815	13.15461	2.7022	
10	70/30	650°	-	0.67	1.33	3	0.34	4.85610	13.24567	2.7277	1.9
11	70/30	650°	-	0.67	1.33	2.95	0.34	4.84804	13.23103	2.7292	2.5
12	70/30	550°	-	0.67	1.33	2.85	0.34	4.83993	13.24192	2.7360	2.5
13	50/50	500°	-	1.01	0.99	2.80	0.51	4.89218	13.32858	2.7245	4.1
14	50/50	550°	-	1.04	0.96	2.95	0.52	4.88403	13.31746	2.7267	1.9
15	50/50	600°	-	1.06	0.94	2.95	0.53	4.87996	13.33965	2.7336	3.5
16	25/75	600°	-	1.52	0.48	2.85	0.76	4.92028	13.44988	2.7336	
17	25/75	500°	-	1.54	0.46	2.8	0.77	4.92464	13.43581	2.7283	4.5
18	25/75	550°	-	1.53	0.47	2.8	0.77	4.92053	13.44655	2.7327	3.1
19	1/100	550°	-	2.00	0.00	2.80	1.00	4.95876	13.58287	2.7392	
21	1/100	450°	-	2.00	0.00	2.85	1.00	4.97116	13.58280	2.7323	2.0
22	1/100	500°	-	2.00	0.00	2.75	1.00	4.97116	13.59412	2.7346	1.7
DB3-	Cr_2O_3			2.00	0.00	3.00	1.00	4.95876	13.59420	2.7415	

Table 2.

Exp. No.	Target [Al/Cr]	Depos'n Temp. [°C]	Glow Temp [°C]					Lattice Constants		
								a	C	c/a
2	70/30	550°	RT	-	-	-	-	4.85030	13.24484	2.7307
2	70/30	550°	1000°	-	-	-	-	4.85339	13.22837	2.7256
2	70/30	550°	1100°	-	-	-	-	4.84727	13.20028	2.7232

Test objects: Hard metal

Table 3.

	Intermediate Layer				Mixed-Crystal Layer Monolayer				Cover Layer			
	Bonding Layer		Hard Metal Layer		Corundum Structure		Other Oxide Layer		DS1		DS2	
Exp. No.	[(Me1Me2)X]	d [µm]	[(Me1Me2)X]	d [µm]	[(Me1Me2)X]	d [µm]	[(Me1Me2)X]	D [µm]	[(Me1Me2)X]	d [µm]	[(Me1Me2)X]	d [µm]
23	TiN	0.2	TiAlN	3.0	$(Al_{.5}Cr_{.5})_2O_3$	3.0	wo		wo		wo	
24	wo		TiAlN	3.0	$(Al_{.5}Cr_{.5})_2O_3$	3.0	wo		wo		wo	
25	TiN	0.3	TiAlN	4.0	$(Al_{.5}Cr_{.5})_2O_3$	2.0	$(Al_{.7}Cr_{.3})_2O_3$	1.0				
26	TiN	0.4	TiCN	6.0	$(Al_{.65}Cr_{.35})_2O_3$	5.0						
27	TiN	8.0			$(Al_{.65}Cr_{.35})_2O_3$	8.0						
28			TiCN	8.0	$(Al_{.7}Cr_{.3})_2O_3$	6.0						
29	TiN	0.5	TiAlN	3.0	$(Al_{.7}Cr_{.3})_2O_3$	3.0	(Al, Cr, $Zr)_2O_{3+z}$		ZrO_2	1.0	ZrN	0.5
30	TiN	0.3	TiC	4.0	$(Al_{.7}Cr_{.3})_2O_3$	2.0						
31	TiN	0.4	TiAlN	2.0	$(Al_{.7}Fe_{.3})_2O_3$	4.0	$(Al, Cr)_2O_3$	2.0	AlCrN	0.5		
32	TiN				$(Al_{.6}Fe_{.4})_2O_3$	5.0			AlCrN	2.0		
33	TiN		TiCN	8.0	$(Al_{.6}Fe_{.4})_2O_3$	4.0						
34			TiCN	8.0	$(Al_{.1}Fe_{.9})_2O_3$	4.0						
35	wo		TiAlN	3.0	$(Al_{.1}Fe_{.9})_2O_3$	5.0						
36	wo		wo		$(Al_{.5}Fe_{.5})_2O_3$	8.0						
37	wo		wo		$(Al_{.5}Fe_{.5})_2O_3$	8.0			AlCrN	3.0		
38	TiN	0.3	wo		$(Al_{.5}V_{.5})_2O_3$	5.0					TiN	0.3
39	VN	0.4	VCN	4.0	$(Al_{.5}V_{.5})_2O_3$	6.0			AlVN	1.0		
40	VN	0.4			Cr_2O_3	10.0			AlVN	1.0		
41	CrN	0.5	CrC	4.0	Cr_2O_3	3.0			CrN	2.0		
42	CrN	0.5	CrCN	6.0	Cr_2O_3	4.0			CrN	1.0		
43	CrN	0.5	wo		Cr_2O_3	4.0			CrN	2.0		
44	CrN	0.5	wo		Cr_2O_3	5.0						
45	AlCrN	0.3	wo		$(Al_{.7}Cr_{.3})_2O_3$	4.0			AlCrN	1.0		

Table 4.

	Intermediate Layer				Mixed-Crystal Layer Monolayer				Cover Layer			
	Bonding Layer		Hard Metal Layer		Corundum Structure		Other Oxide Layer		DS1		DS2	
Exp. No.	[(Me1Me2)X]	d [µm]	[(Me1Me2)X]	d [µm]	[(Me1Me2)X]	d [µm]	[(Me1Me2)X]	D [µm]	[(Me1Me2)X]	d [µm]	[(Me1Me2)X]	d [µm]
46	CrN	0.3	AlCrON	5.0	$(Al_{.02}Cr_{.98})_2O_3$	3.0			wo		wo	
47	CrN	0.5	AlCrN	3.0	$(Al_{.05}Cr_{.95})_2O_3$	3.0			$(Al_{.7}Cr_{.3})_2O_3$	1.0	CrN	2.0
48	AlCrN	0.5	AlCrON	5.0	$(Al_{.05}Cr_{.95})_2O_3$	3.0						
49	TiN	0.8	TiAlN	4.0	$(Al_{.5}Ti_{.5})_2O_3$	4.0			TiN	1.0		
50	wo		TiAlN	6.0	$(Al_{.5}Ti_{.5})_2O_3$	2.0						
51	TiN	0.3	TiCN	8.0	$(Al_{.7}Ti_{.3})_2O_3$	4.0						
52	wo		TiAlN	3.0	$(Al, Mg, Ti)_2O_3$	3.0						
53	TiN	0.5	AlMgTiN	6.0	$(Al, Mg, Ti)_2O_3$	4.0						
54	TiN	5.0			$(Al, Mg, Ti)_2O_3$	3.0			TiN	2.0		
55	TiN	0.3	(Al, Mg,Ti)ON	5.0	$(Al, Mg, Ti)_2O_3$	2.0						
56	AlCrN	0.2	(Al, Mg, Ti)ON	1.0	$(Al, Mg, Ti)_2O_3$	6.0						
57	TiN	1.0			$(Al, Fe, Ti)_2O_3$	5.0			TiN	0.5		
58	TiN	1.0	TiCN	6.0	$(Al, Fe, Ti)_2O_3$	2.0			TiN	1.0		
59	TiN	1.0	TiAlN	4.0	$(Al, Fe, Ti)_2O_3$	4.0						
60			TiCN	4.0	$(Al, Fe, Ti)_2O_3$	2.0						

Table 5

	Intermediate Layer				Mixed-Crystal Layer as Multi-layer				Cover Layer				
	Bonding Layer		Hard Metal Layer		Corundum Structure		Other Multi-layer		No.MLs	DS1		DS2	
Exp. No.	[(Me1Me2)X]	d [µm]	[(Me1Me2)X]	d [µm]	[(Me1Me2)X]	d [µm]	[(Me1Me2)X]	d [µm]		[(Me1Me2)X]	d [µm]	[(Me1Me2)X]	d [µm]
61	TiN	0.2	TiAlN	3.0	$(Al_{.65}Cr_{.35})_2O_3$	0.100	AlCrN	0.100	50.0	AlCrN	0.5		
62	wo		TiAlN	2.0	$(Al_{.65}Cr_{.35})_2O_3$	0.500	AlCrN	0.500	10.0				
63	TiN	0.3	TiAlN	3.0	$(Al_{.65}Cr_{.35})_2O_3$	0.100	AlCrN	0.050	100.0	AlCrN	0.2		
64	TiN	0.3	TiAlN	4.0	$(Al_{.65}Cr_{.35})_2O_3$	0.050	AlCrN	0.050	100.0				
65	TiN	0.3	TiAlN	3.0	$(Al_{.65}Cr_{.35})_2O_3$	0.100	ZrO_2	0.300	10.0	ZrN	1.0		
66	TiN	0.3	TiAlN	6.0	$(Al_{.65}Cr_{.35})_2O_3$	0.200	Ta_2O_5	0.100	30.0	TaN	0.5		
67	TiN	0.3	TiAlN	3.0	$(Al_{.65}Cr_{.35})_2O_3$	0.200	Nb_2O_5	0.500	10.0	NbN	1.0		
68	TiN	0.3	TiAlN	4.0	$(Al_{.65}Cr_{.35})_2O_3$	0.200	V_2O_3	0.100	50.0				
69	TiN	0.3	TiAlN	3.0	$(Al_{.65}Cr_{.35})_2O_3$	0.200	$(Al_{.8}Cr_{.2})_2O_3$	0.050	30.0	AlCrN	0.2		
70	TiN	0.3	TiAlN	2.0	$(Al_{.65}Cr_{.35})_2O_3$	0.200	$(Al, V)_2O_3$	0.050	30.0	AlVN	0.2		
71	TiN	0.3	TiAlN	2.0	$(Al_{.5}Cr_{.5})_2O_3$	0.100	TiAlN	0.100	50.0				
72	TiN	0.2	TiCN	6.0	$(Al_{.5}Cr_{.5})_2O_3$	0.100	0.100	0.100	50.0	AlCrN	0.5		
73	wo		TiCN	3.0	$((Al_{.5}Cr_{.5})_2O_3$	0.500	AlCrN	0.500	10.0				
74	TiN	0.3	TiCN	12.0	$(Al_{.6}Cr_{.6})_2O_3$	0.100	AlCrN	0.050	100.0	AlCrN	0.2		
75	TiN	0.3	TiCN	8.0	$(Al_{.5}Cr_{.5})_2O_3$	0.050	AlCrN	0.500	100.0				
76	TiN	0.3	TiCN	4.0	$(Al_{.5}Cr_{.5})_2O_3$	0.100	ZrO_2	0.300	10.0	ZrN	1.0		
77	TiN	0.3	TiCN	3.0	$(Al_{.5}Cr_{.5})_2O_3$	0.200	Ta_2O_5	0.100	30.0	TaN	0.5		
78	TiN	0.3	TiCN	6.0	$(Al_{.4}Cr_{.6})_2O_3$	0.200	Nb_2O_5	0.500	10.0	NbN	1.0		
79	TiN	0.3	TiCN	3.0	$(Al_{.4}Cr_{.6})_2O_3$	0.200	V_2O_3	0.100	50.0				
80	TiN	0.3	TiCN	2.0	$(Al_{.4}Cr_{.6})_2O_3$	0.200	$(Al, Cr)_2O_3$	0.050	30.0	AlCrN	0.2		
81	TiN	0.3	TiCN	3.0	$(Al_{.4}Cr_{.6})_2O_3$	0.200	$(Al, Zr)_2O_3$	0.050	30.0	AlZrN	0.2		
82	TiN	0.3	TiC	4.0	$(Al_{.4}Cr_{.6})_2O_3$	0.100	AlCrN	0.050	100.0	TiN	0.2		
83	TiN	0.5	TiAlN	3.0	$(Al_{.4}Cr_{.6})_2O_3$	0.300	$(Al, Zr, Cr)_2O_{3+x}$	0.300		ZrN	1.0	ZrN	0.5
84	TiN	0.4	TiAlN	2.0	$(Al_{.7}Cr_{.3})_2O_3$	0.200	$(Al, Cr)_2O_3$	0.200	10.0	AlCrN	0.5		
85	TiN	0.3	wo		$(Al_{.6}V_{.4})_2O_3$	0.200	AlVN	0.100				TiN	0.3
86	VN	0.4	VCN	4.0	$(Al_6V_4)_2O_3$	0.200	$(Al, Cr,)_2O_3$	0.100					

Table 6

	Intermediate Layer				Mixed-Crystal Layer as Multi-layer				Cover Layer				
	Bonding Layer		Hard Metal Layer		Corundum Structure		Other Multi-layer		No.MLs	DS1		DS2	
Exp. Nr.	[(Me1Me2)X]	d [µm]	[(Me1Me2)X]	d [µm]	[(Me1Me2)X]	d [µm]	[(Me1Me2)X]	D [µm]		[(Me1Me2)X]	d [µm]	[(Me1Me2)X]	d [µm]
87	CrN	0.5	CrC	4.0	Cr_2O_3	0.200	CrN	0.300	5.0	CrN	2.0		
88	CrN	0.5	CrCN	6.0	Cr_2O_3	0.200	$(Al_{.65}Cr_{.35})_2O_3$	0.100	10.0	CrN	1.0		
89	CrN	0.5	wo		Cr_2O_3	1.000	$(Al_{.65}Cr_{.35})_2O_3$	0.500	5.0				
90	CrN	0.5	wo		Cr_2O_3	0.050	$(Al_{.65}Cr_{.35})_2O_3$	0.050	200.0				
91	CrN	0.5	wo		Cr_2O_3	0.050	CrN	0.050	100.0				
92	AlCrN	0.3	wo		$(Al_{.65}Cr_{.35})_2O_3$	0.100	CrN	0.400	8.0	AlCrN	1.0		
93	CrN	0.3	AlCrON	5.0	$(Al_{.5}Cr_{.5})_2O_3$	0.200	$(Al_{.7}Cr_{.3})_2O_3$	0.100	10.0				
94	CrN	0.5	AlCrN	3.0	$(Al_{.5}Cr_{.5})_2O_3$	1.000	$(Al_{.7}Cr_{.3})_2O_3$	0.500	5.0	CrN	0.5	CrN	2.0
95	AlCrN	0.5	AlCrON	5.0	$(Al_{.5}Cr_{.5})_2O_3$	0.050	$(Al_{.7}Cr_{.3})_2O_3$	0.050	200.0				
96	TiN	0.8	TiAlN	4.0	$(Al_{.5}Ti_{.5})_2O_3$	0.100	TiAlN	0.200	30.0	TiN	1.0		
97	wo		TiAlN	6.0	$(Al_{.1}Ti_{.9})_2O_3$	0.050	TiAlN	0.300	10.0				
98	TiN	0.3	TiCN	8.0	$(Al_{.1}Ti_{.9})_2O_3$	0.200	$(Al_{.7}Cr_{.3})_2O_3$	0.100	20.0				
99	wo		TiAlN	3.0	(Al, Mg, Ti)$_2O_3$	0.100	0.100	0.100	40.0				
100	TiN	0.5	AlMgTiN	6.0	(Al, Mg, Ti)$_2O_3$	0.500	AlCrN	0.500	12.0				
101	TiN	5.0			(Al, Mg, Ti)$_2O_3$	0.100	AlCrN	0.050	50.0				
102	TiN	0.3	(Al, Mg, Ti)ON	5.0	(Al, Mg, Ti)$_2O_3$	0.050	AlCrN	0.050	30.0				
103	AlCrN	0.2	(Al, Mg, Ti)ON	1.0	(Al, Mg, Ti)$_2O_3$	0.100	$(Al_{.65}Cr_{.35})_2O_3$	0.300	15.0				
104	TiN	1.0			(Al, Fe, Ti)$_2O_3$	0.200	Nb_2O_5	0.500	20.0	TiN	0.5		
105	TiN	1.0	TiCN	6.0	(Al, Fe, Ti)$_2O_3$	0.200	V_2O_3	0.100	20.0	TiN	1.0		
106	TiN	1.0	TiAlN	4.0	(Al, Fe, Ti)$_2O_3$	0.200	$(Al_{.65}Cr_{.35})_2O_3$	0.100	10.0				
107			TiCN	4.0	(Al, Fe, Ti)$_2O_3$	0.200	(Al, Me)$_2O_3$	0.050	15.0				

Table 7.

Material	I-Source 1	I-S. 2	I-S. 3	I-S. 4	U-bias bp	O2	N2	p	T
	[A]	[A]	[A]	[A]	[V]	[sccm]	[sccm]	[Pa]	[°C]
AlCrO	--	200	--	200	-60	1000	--	2.6	550° C
AlCrO-AlCrN Multilayer	--	200	--	200	-60	1000	1000	2.6	550° C

Coil current of the source magnetic system 0.5 to 1 A

Table 8.

Material	I-Source 1	I-S. 2	I-S. 3	I-S. 4	U-bias DC	Ar	C2H2	N2	p	T
	[A]	[A]	[A]	[A]	[V]	[sccm]	[sccm]	[sccm]	[Pa]	[°C]
TiAlN	200	--	200	--	-40		--	Pressure regulated	3	550° C
TiN	180	--	180	--	-100		--	Pressure regulated	0.8	550° C
TiCN	190	--	190	--	-100	420	15-125	500-150	2.5 - 2.0	550° C
AlCrN	200	--	200	--	-100	--		1000	2.6	550° C
AlMeN	140	--	140	--	-80	--		800	0.8	500° C
AlMeCN	220	--	220	--	-120	300	10-150	Pressure regulated	2.5	600° C

Coil current of the source magnetic system 0.1 to 2 A

Patent Claims

1. PVD layer system for the coating of workpieces, comprising at least one mixed-crystal layer of a polyoxide of the following composition:

$$(Me1_{1-x}Me2_x)_2O_3$$

where Me1 and Me2 each represent at least one of the elements Al, Cr, Fe, Li, Mg, Mn, Nb, Ti, Sb or V and the elements of Me1 and Me2 differ from one another,
characterized in that the crystal lattice of the mixed-crystal layer exhibits a corundum structure which in a spectrum of the mixed crystal layer analyzed by x-ray diffractometry is characterized by at least three, preferably four and especially five of the lines associated with the corundum structure.

2. Layer system as in Claim 1, **characterized in that** the corundum structure of the mixed-crystal layer is so thermally stable that even after 30 minutes of heating in air at a temperature of at least 1000°C or at least 1100°C the lattice parameter(s) *a* and/or *c* of the mixed-crystal layer will not shift by more than a maximum of 2% or preferably a maximum of 1%.

3. Layer system as in one of the preceding claims, **characterized in that** the mixed-crystal layer has a stoichiometric or substoichiometric oxygen content.

4. Layer system as in Claim 3, **characterized in that** the oxygen content remains 0 to 15 percentage points and preferably 0 to 10 percentage points below the stoichiometric composition of the compound.

5. Layer system as in one of the preceding claims, **characterized in that** the mixed-crystal layer is compact-grained with an average crystallite size of less than 0.2 µm, preferably less than 0.1 µm.

6. Layer system as in one of the preceding claims, **characterized in that** Me1 is comprised of Al and Me2 of at least one of the elements Cr, Fe, Li, Mg, Mn, Nb, Ti, Sb or V and is $02 \leq x \leq 0.98$, preferably $0.3 \leq x \leq 0.95$.

7. Layer system as in one of the preceding claims, **characterized in that** the content of inert gas and halogens in the mixed-crystal layer is less than 2 at% each.

8. Layer system as in Claim 7, **characterized in that** the inert gas content in the mixed-crystal layer does not exceed a maximum of 0.1 at% or preferably a maximum of 0.05 at% and/or the halogen content does not exceed a maximum of 0.5 at% or preferably a maximum of 0.1 at% or that, preferably, the mixed-crystal layer contains essentially no inert gas and/or halogen.

9. Layer system as in Claim 1, **characterized in that** the layer stress of the mixed-crystal layer is so minor that the deviation of the lattice parameters of the polyoxides from the value determined by Vegard's Law is less than or equal to 1%, preferably less than or equal to 0.8%.

10. Layer system as in one of the preceding claims, **characterized in that** the layer stress measured on a mixed-crystal layer 2 μm thick represents a compressive or tensile stress with a value of less than ± 0.8 GPa, preferably less than ±0.5 GPa.

11. Layer system as in one of the preceding claims, **characterized in that** the mixed-crystal layer comprises a multi-stratum layer consisting of at least two different, alternatingly deposited polyoxides.

12. Layer system as in one of the preceding claims, **characterized in that** the mixed-crystal layer comprises a multi-stratum layer consisting of at least one polyoxide and an additional oxide in an alternating sequence.

13. Layer system as in one of the preceding claims, **characterized in that** the polyoxide is a double oxide, in particular $(AlCr)_2O_3$ or $(AlV)_2O_3$.

14. Layer system as in Claim 13, **characterized in that** the additional oxide is HfO_2, Ta_2O_5, TiO_2, ZrO_2, γ-Al_2O_3, but in particular an oxide having a corundum structure such as Cr_2O_3, V_2O_3, Fe_2O_3, $FeTiO_3$, $MgTiO_2$ or α-Al_2O_3.

15. Layer system as in one of the preceding claims, **characterized in that** in addition to the mixed-crystal layer at least one intermediate layer, in particular a bonding layer and/or a hard-metal layer, is positioned between the workpiece and the mixed-crystal layer and/or a cover layer is located on the mixed-crystal layer, and that these preferably contain one of the metals of subgroups IV, V and VI of the periodic system and/or Al, Si, Fe, Ni, Co, Y, La or a mixture thereof.

16. Layer system as in Claim 15, **characterized in that** the metals of the hard-metal layer and/or the cover layer are compounds with N, C, O, B or mixtures thereof, the compound with N or CN being preferred.

17. Layer system as in Claim 15 or 16, **characterized in that** the hard-metal layer comprises TiN, TiCN, AlTiN, AlTiCN, AlCrN or AlCrCN and the cover layer comprises AlCrN, AlCrCN, Cr_2O_3 or Al_2O_3, in particular γ-Al_2O_3 or α-Al_2O_3.

18. Layer system as in one of the Claims 15 to 17, **characterized in that** the intermediate layer and/or the hard-metal layer comprises a multi-stratum layer.

19. Layer system as in one of the Claims 15 to 18, **characterized in that** the intermediate layer and the mixed-crystal layer and/or the cover layer and the mixed-crystal layer are disposed in the form of an alternating multi-stratum layer.

20. Layer system as in one of the Claims 15 to 18, **characterized in that** the layer system has an overall layer thickness of more than 10 µm, preferably more than 20 µm.

21. Layer system as in one of the Claims 15 to 18, **characterized in that** the mixed-crystal layer has a thickness of more than 5 µm, preferably more than 8 µm.

22. Vacuum coating method for producing a mixed-crystal layer of a polyoxide on a workpiece, whereby an electric arc discharge takes place in an oxygenous process-gas atmosphere

between at least one anode and a target constituting the cathode of an arc source, **characterized in that** on the target surface only a small, if any, external magnetic field is generated essentially perpendicular to the target surface, comprising a vertical component B_Z and a smaller, essentially radial or surface-parallel component B_r in support of the vaporization process, the target being an alloy target whose composition essentially corresponds to that of the mixed-crystal layer that is deposited with a corundum structure.

23. Method as in Claim 22, **characterized in that** the composition of the metals in the mixed-crystal layer, scaled to the total metal content, does not differ for the respective constituent metals by more than 10, preferably not more than 5 and especially not more than 3 percent from the concentrations in the target composition.

24. Method as in Claims 22 and 23, **characterized in that** the vertical component B_Z on the target surface is set at between 3 and 50 but preferably between 5 and 25 Gauss.

25. Method as in one of the Claims 22 to 24, **characterized in that** for generating the small magnetic field, an excitation current is fed to a magnetic system consisting of at least one axially polarized coil and having a geometry similar to the circumference of the target.

26. Method as in one of the Claims 22 to 25, **characterized in that** the arc discharge or the at least one arc source is simultaneously fed both a direct current and a pulsed or alternating current.

27. Vacuum coating method for producing a mixed-crystal layer of a polyoxide on a workpiece, whereby in an oxygenous process-gas atmosphere a first arc- or sputter-source electrode, constituting the target, and a second electrode deposit a layer on the workpiece, said source being simultaneously fed a direct current or direct voltage as well as a pulsed or alternating current or a pulsed or alternating voltage, **characterized in that** the target is an alloy target whose composition essentially corresponds to that of the mixed-crystal layer and that the latter is deposited with a corundum structure.

28. Method as in Claim 27, **characterized in that** the composition of the metals in the

mixed-crystal layer, when scaled to the total metal content, does not differ for the respective constituent metals by more than 10 at%, preferably not more than 5 at% and especially not more than 3 at% from the concentrations in the target composition.

29. Method as in Claims 27 and 28, **characterized in that** the source is an arc source and that the second electrode is separated from the arc source or constitutes the anode of the arc source.

30. Method as in Claim 29, **characterized in that** both electrodes are connected to and powered by a single pulsed-current power supply.

31. Method as in Claim 30, **characterized in that** the second electrode serves as the cathode of another arc vaporizing source, the latter, too, being connected to and powered by a DC power supply.

32. Method as in Claim 30, **characterized in that** the second electrode serves as the cathode of a sputter source, in particular a magnetron source, the latter, too, being connected to and powered by a power supply, in particular a DC power supply.

33. Method as in Claim 30, **characterized in that** the second electrode is in the form of an evaporation crucible and serves as the anode of a low voltage arc evaporator.

34. Method as in one of the Claims 26 to 33, **characterized in that** the DC power supply and the pulsed current supply are decoupled by means of an electrical decoupling filter which preferably contains at least one blocking diode.

35. Method as in one of the Claims 26 to 34, **characterized in that** the DC power supply is operated with a base current in a manner whereby the plasma discharge at the sources, especially at the arc evaporation sources, is maintained in an essentially continuous mode.

36. Method as in one of the Claims 26 to 35, **characterized in that** the pulsed current or pulsed voltage power supply is operated with pulse edges whose pulse slopes are greater than 2.0 V/ns,

preferably at least in the range from 0.02 V/ns to 2.0 V/ns and preferably at least in the range from 0.1 V/ns to 1.0 V/ns, and a high-power discharge is created.

37. Method as in one of the Claims 26 to 35, **characterized in that** the pulsed current power supply is operated at a frequency in the range from 1 kHz to 200 kHz.

38. Method as in one of the Claims 26 to 36, **characterized in that** the pulsed current power supply is operated with a varying pulse-width ratio setting.

39. Method as in one of the Claims 26 to 37, **characterized in that** a pulsed magnetic field is applied to at least one arc source.

40. Method as in Claim 38, **characterized in that** the magnetic field is pulsed by the pulsed current or by part of the pulsed current of the arc source.

41. Method as in one of the Claims 22 to 39, **characterized in that** at least one arc source is either not cooled or is heated.

42. Method as in one of the Claims 22 to 40, **characterized in that** the sources are operated with a process gas that consists of at least 80%, preferably 90% and most desirably 100% oxygen.

43. Method as in one of the Claims 22 to 41, **characterized in that** the coating temperature is set below 650°C, preferably below 550°C.

44. A tool or component for use at high temperatures and/or subject to strong chemical exposure, **characterized in that** it is coated with a layer system described in one of the Claims 1 to 21.

45. A tool or component as in Claim 43, **characterized in that,** at least in the areas exposed to wear, the base material of the tool consists of tool steel, HSS, PM steel or HM, cermet or CBN sintered material and that, at least in the areas exposed to wear, the base material of the component consists of a cold work steel, HSS, PM steel or HM, cermet, SiC, SiN or CBN

sintered material or of polycrystalline diamond.

46. Tool as in Claim 43, **characterized in that** it is a cutting tool, especially an interchangeable cutting insert consisting of HSS, HM, cermet, CBN, SiN, SiC or a PM steel or that it is a diamond-coated interchangeable insert.

47. Tool as in Claim 43, **characterized in that** it is a non-cutting shaping tool, in particular a forging tool.

48. Tool as in Claim 43, **characterized in that** it is a die-casting tool.

49. Component as in Claim 43, **characterized in that** the component is a part of a combustion engine, in particular a fuel injection nozzle, a piston ring, a tappet, or a turbine blade.