

Dual phase TiAlSiBN coating for cutting applications

The present patent application relates to a new TiAlSiBN coating exhibiting enhanced performance, being in particular advantageous for tools used in cutting operations, i.e. being in particular suitable for cutting applications.

This patent application claims the benefits of the German patent application No. 10 2023 002 527.5, filed on June 21, 2023, the entire contents of which are hereby expressly incorporated by reference.

Coating systems comprising TiAlN and/or TiSiN layers (e.g. $Ti_{1-x}Al_xN$ / $Ti_ySi_{1-y}N$ coating systems) are well-known coating systems for hard machining as they provide a good protection against harsh cutting conditions, e.g., against high thermal loads, oxidation, and abrasion.

In particular the use of a coating system comprising a TiAlN layer as supporting layer and a TiSiN layer as top layer has shown to be successful mainly due to:

- i. high thermal stability as well as oxidation and abrasion resistance of the TiSiN top layer,
- ii. high hardness and toughness of the TiAlN supporting layer, providing at the same time good adhesion to the substrate.

However, in such coating systems was also observed that the TiAlN supporting layer has a coarser morphology compared to the TiSiN top layer and it can lead to cohesive failure.

Furthermore, it was observed that when the temperature rises during a cutting process and the coating system is subjected to the resultant increased temperature, it causes decomposition of thermodynamically metastable cubic TiAlN into cubic TiN and wurtzite AlN. This phase transformation is undesirable because it can result in an undesirable drop of hardness and elastic modulus, and in volume change up to 20 % per mole. This was also confirmed in the cutting tests described by Hörling et al in the scientific paper "Mechanical properties and machining performance of $Ti_{1-x}Al_xN$ -coated

cutting tools” published in Surface and Coatings Technology, Volume 191, Issues 2–3, 21 February 2005, pages 384-392.

The inventors intended to mitigate the adverse effects of the above-mentioned phase decomposition by using a dual phase TiAlN layer (TiAlN layer exhibiting both cubic and wurtzite phases, preferably predominately wurtzite phase) instead of a fully cubic phase TiAlN layer (TiAlN layer exhibiting only cubic phase).

However, the dual phase TiAlN layer exhibited undesirable mechanical properties and inferior adhesion to substrate (in particular in cases of using typical cutting tool substrates made of hard materials such as cemented carbide, cubic boron nitride (cBN), cermets and similars) in comparison with a fully cubic phase TiAlN layer.

Problem to be solved

The decomposition of the $Ti_{1-x}Al_xN$ bottom layer in $Ti_{1-x}Al_xN / Ti_ySi_{1-y}N$ coating systems at elevated temperatures (temperatures higher than 500 °C) causes cracking in the $Ti_{1-x}Al_xN$ bottom layer and consequently failure of the $Ti_{1-x}Al_xN / Ti_ySi_{1-y}N$ coating system.

In addition, the coarser morphology of the $Ti_{1-x}Al_xN$ bottom layer compared to the $Ti_ySi_{1-y}N$ top-layer causes cohesive failure at the interface between the $Ti_{1-x}Al_xN$ bottom layer and the $Ti_ySi_{1-y}N$ top-layer.

Objective of the present invention

The main objective of the present invention is to provide a new coating that is able to provide better performance, in particular in cutting applications, in comparison to known coatings comprising TiAlN and/or TiSiN layers, especially when using cutting tool substrates made of hard materials such as cemented carbide, cubic boron nitride (cBN), cermets and similars.

A further objective of the present invention is to mitigate the above-mentioned problem observed in coating systems comprising a TiAlN support layer and a TiSiN top layer,

without incurring in deterioration of mechanical coating properties and worsening of adhesion of the coating system to the substrate.

Solution according to the present invention

The above-mentioned objectives were attained according to the present invention by providing a new dual phase TiAlSiBN coating according to claim 1.

The inventive TiAlSiBN coating (see schematic drawing of coating 100 in Fig. 1 - in the context of the present invention the inventive TiAlSiBN coating is also called new dual phase TiAlSiBN coating or simply dual phase TiAlSiBN coating) is a coating comprising at least three layers, wherein the first of the at least three layers is a first layer acting as adhesion layer (see coating section 5 in Fig. 1), exhibiting mainly crystalline cubic phase and comprising Ti and N, the second of the at least three layers is a second layer acting as support layer (see coating section 10 in Fig. 1), exhibiting mainly crystalline hexagonal wurtzite phase and comprising Ti, Al, N and additionally B and/or Si, and the third of the at least three layers is a third layer acting as functional layer (see coating section 50 in Fig. 1), exhibiting mainly crystalline cubic phase and comprising Ti, Si and N.

The crystalline hexagonal wurtzite phase in the TiAlSiBN coating 100 comprises Al and N.

The term “acting as adhesion layer” refers in particular to improving adhesion between the TiAlSiBN coating 100 and the substrate surface on which the TiAlSiBN coating 100 is deposited. The first section 5 comprises one or more adhesion layers and should be deposited as closest to the surface of the substrate 1 as possible, preferably directly on the substrate surface.

The term “acting as support layer”, refers in particular to improving cohesion and mechanical properties within the TiAlSiBN coating 100, in this manner providing support to the functional layer deposited above it. The second section 10 may comprise one or more support layers and should be deposited as closest to the first section 5 as possible, preferably directly on the outermost surface of the first section 5.

In the context of the present invention the functional layers may also be referred to as top layers, so that the third section 50 may be formed of one or more top layers. Preferably the outermost layer of the third section 50 in the TiAlSiBN coating 100 is the outermost surface of the coated substrate surface.

Optionally between the substrate surface and the first section 5 of the TiAlSiBN coating 100 there is one or more layers for example metallic layers or metal nitride layers (not shown in Fig. 1) used for modifying the properties of the substrate surface before beginning deposition of TiAlSiBN coating 100.

Optionally atop the third section 50 of the TiAlSiBN coating 100 there is one or more layers for example decorative layers or run-in layers (not shown in Fig. 1) used for modifying the outermost surface of TiAlSiBN coating 100.

In any case the sum of the thicknesses of the above-mentioned optional layers preferably should not be higher than the sum of the thicknesses of the first section 5, second section 10 and third section 50 forming the TiAlSiBN coating 100, more preferably not higher than 50% of the sum of the thicknesses of the first section 5, second section 10 and third section 50, still more preferably not higher than 30% of the sum of the thicknesses of the first section 5, second section 10 and third section 50.

In a preferred embodiment the new dual phase TiAlSiBN coating according to the present invention comprises three different sections along its coating thickness, each section comprising at least one layer, in this manner the inventive dual phase TiAlSiBN coating comprising at least three layers: at least one adhesion layer comprised in the first section 5, at least one support layer comprised in the second section 10 (in the context of the present description the support layer or layers are also referred to as bottom layer or layers) and at least one functional layer comprised in the third section 50 (in the context of the present description the functional layer or layers are also referred to as top layer or layers).

The first section provided to improve adhesion of the TiAlSiBN coating to the substrate surface.

The second section provided to improve cohesiveness within the TiAlSiBN coating while providing high hardness and toughness and good support to the third section.

The third section provided to attain high thermal stability as well as oxidation and abrasion resistance.

The first section is formed by at least one adhesion layer (e.g. one or more adhesion layers), the second section is formed by at least one support layer (e.g. one or more support layers) and the third section is formed by at least one top layer (e.g. one or more top layers), wherein:

- said at least one adhesion layer, preferably the whole first section:
 - o exhibiting fully crystalline cubic phase (hereafter abbreviated as “cub”), in particular face centered cubic phase (usually abbreviated as fcc phase), or exhibiting a mixture of crystalline phases comprising crystalline cubic phase and crystalline hexagonal wurtzite phase (hereafter abbreviated as “hex” or “wur”), wherein if a mixture of crystalline phases, exhibiting mainly cubic phase, which can be detected for example by using transmission electron microscopy analysis (TEM) (see for example Fig. 3, and
 - o comprising titanium (Ti) and nitrogen (N), optionally, additionally comprising at least one of aluminum (Al), boron (B) and silicon (Si), preferably aluminum (Al) and boron (B);
- said at least one bottom layer, preferably the whole second section:
 - o exhibiting fully crystalline hexagonal wurtzite phase, or exhibiting a mixture of crystalline phases comprising crystalline cubic phase and crystalline hexagonal wurtzite phase, wherein if a mixture of crystalline phases, exhibiting mainly wurtzite phase, which can be detected for example by using transmission electron microscopy analysis (TEM) (see for example Fig. 3), and
 - o comprising titanium (Ti), aluminum (Al) and nitrogen (N), and additionally comprising at least one of boron (B) and silicon (Si), preferably boron (B);
- said at least one top layer, preferably the whole third section:
 - o exhibiting fully crystalline cubic phase, in particular fcc phase, or exhibiting a mixture of crystalline phases comprising crystalline cubic

phase and crystalline hexagonal wurtzite phase, wherein if a mixture of crystalline phases, exhibiting mainly cubic phase, which can be detected for example by using transmission electron microscopy analysis (TEM) (it is not shown in Fig. 3), and

- comprising titanium (Ti), silicon (Si) and nitrogen (N);

If each coating section 5, 10 and 50 respectively (hence respectively the at least one adhesion layer, the at least one bottom layer, and the at least one top layer) is deposited separately on a substrate surface, and analyzed by using X-ray diffraction (XRD) analysis, the ratio between cubic phase and wurtzite phase:

- in the adhesion layer may be preferably greater than 0.3, thus: $\text{cub/wur} \geq 0.3$, in the bottom layer may be preferably in a range between 0.01 and 0.3, thus: $0.01 < \text{cub/wur} < 0.3$,
- in the top layer may be preferably greater than 1, thus: $\text{cub/wur} > 1$, more preferably said at least one top layer may exhibit fully crystalline cubic phase.

above-mentioned ratio between cubic phase and wurtzite phase corresponds to the peak intensity ratio of (200)cubic/(110)wurtzite ratio.

The term peak intensity in this context is used in particular to refer to the net height of the corresponding peak (measure using known X-ray diffraction analysis software EVA).

The measurements made for the definition of the above-mentioned ranges of values regarding ratios between cubic phase and wurtzite phase, where obtained by using XRD techniques, wherein the cubic peak (200) is located at two-theta angles 40-44° and wurtzite peak (110) is located at two-theta angles 49-60°, and where X-ray diffraction (also abbreviated as XRD) is taken using theta-2theta (θ -2 θ) configuration in X-ray diffractometer from Bruker and Copper x-ray tube with a wavelength of 1.5406 Å (see for example Fig. 4).

Likewise, if each coating section 5, 10 and 50 respectively (hence respectively the at least one adhesion layer, the at least one bottom layer, and the at least one top layer) is deposited separately on a substrate surface, and analyzed by using commonly

known nanoindentation techniques, the modulus of elasticity (Young's modulus, hereafter abbreviated E):

- in the adhesion layer may be preferably in a range between 300 GPa and 480 GPa, more exactly: $300 \pm 15 \text{ GPa} \leq E < 480 \pm 15 \text{ GPa}$,
- in the bottom layer may be preferably in a range between 250 GPa and 360 GPa, more exactly: $250 \pm 15 \text{ GPa} \leq E < 360 \pm 15 \text{ GPa}$,

Preferably E of the adhesion layer is higher than E of the bottom layer.

Preferably the bottom layer exhibits a predominantly wurtzite phase characterized by a XRD peak intensity ratio of (200)cubic / (110)wurtzite is in a range from 0.01 to a value lower than 0.3, and a Young's modulus E between 250 GPa and 360 GPa, given measurements error of $\pm 15 \text{ GPa}$, and wherein the above mentioned cubic peak (200) is located at two-theta angles 40-44°, while the above mentioned wurtzite peak (110) is located at two-theta angles 49-60°.

Preferably the adhesion layer exhibits a predominately cubic phase characterized by a XRD peak intensity ratio of (200)cubic / (110)wurtzite that is equal to or higher than 0.3, and a Young's modulus E between 300 GPa and 450 GPa, given measurements error of $\pm 15 \text{ GPa}$, and wherein the above mentioned cubic peak (200) is located at two-theta angles 40-44°, while the above mentioned wurtzite peak (110) is located at two-theta angles 49-60°.

The above-mentioned ranges of values regarding hardness and elasticity modulus were defined according to measurements conducted by using standard nanoindentation techniques as standard used for PVD coating films having thicknesses in the ranges mentioned in the present description.

Figure 5 shows the variation of the Elastic Modulus measured on a sample in which the substrate 1 is coated with a TiAlSiBN coating 100 according to the present invention, in which an adhesion layer forming the first section 5, a support layer forming the second section 10 and a functional layer as top layer forming the third section 50 (and as outermost layer of the TiAlSiBN coating 100).

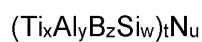
For the measurements of the Elastic Modulus the commonly known nanoindentation techniques and parameters listed in Table 1 were used:

Table 1:

Nanohardenss measurement method	Max Force (mN)	Indentation depth (set value) (um)	indenter
UNAT from asmec	10	0.1	Modified Berkovich
FT-I04 from FEMTO Tools	10	0.1	Modified Berkovich
FISCHERSCOPE from Fischer	10	0.1	Modified Berkovich

Before the Elastic Modulus measurements the surface of the coated sample was subjected to a Calotte Grinding process in known manner for discovering each one of the layers in order to make the Elastic Modulus measurements.

According to a further preferred embodiment of the present invention, the chemical element composition in atomic concentration of the at least one adhesion layer, preferably of the whole first section, is given by the formula:



where:

$$x+y+z+w = 1, \text{ and}$$

$$0 \leq y/x \leq 0.21 \text{ or } y/(x+y) < 0.67, \text{ and}$$

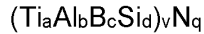
$$0 \leq z+w \leq 0.25, \text{ preferably } 0 \leq z+w \leq 0.10, \text{ more preferably } 0 < z+w \leq 0.05, \text{ and}$$

$$0 \leq z \leq 0.10, \text{ preferably } 0 \leq z \leq 0.05, \text{ more preferably } 0.01 \leq z < 0.05 \text{ and}$$

$$0 \leq w \leq 0.25, \text{ preferably } 0 \leq w \leq 0.10, \text{ and}$$

$$0.75 \leq t/u \leq 1.25, \text{ preferably } 0.85 \leq t/u \leq 1.15.$$

According to a further preferred embodiment of the present invention, the chemical element composition in atomic concentration of the at least one bottom layer, preferably of the whole second section, is given by the formula:



where:

$a+b+c+d = 1$, and

$0 \leq b/a \leq 2.1$ and/or $0 \leq b/(a+b) < 0.67$, preferably $1 \leq b/a \leq 2.1$, and

$0 \leq c+d \leq 0.25$, preferably $0 \leq c+d \leq 0.10$, more preferably $0 < c+d \leq 0.05$, and

$0 \leq c \leq 0.05$, preferably $0.01 \leq c < 0.05$, more preferably $0.01 \leq c \leq 0.04$, and

$0 \leq d \leq 0.25$, preferably $0 \leq d \leq 0.10$, and

$0.75 \leq v/q \leq 1.25$, preferably $0.85 \leq v/u \leq 1.15$.

According to a further preferred embodiment of the present invention, the chemical element composition in atomic concentration of the at least one top layer, preferably of the whole third section, is given by the formula:



where:

$e+f = 1$, and

$0.5 \leq f \leq 0.35$, preferably $0.5 \leq f \leq 0.25$, and

$0.75 \leq r/p \leq 1.25$, preferably $0.85 \leq r/p \leq 1.15$.

In order to explain the invention in more detail some Figures (see Fig.1 to Fig. 4), Examples and Results will be used and described below. This information should be however understood as details of preferred variants of the present invention and showcases and not as a limitation of the present invention.

Figure captions:

Figure 1: Schematic drawing of a dual phase TiAlSiBN coating according to the present invention

Figure 2: Wear evolution comparison between non-inventive and inventive variants together with cutting parameters.

Figure 3: TEM selected area diffraction patterns confirming adapted TiAlBN adhesion layer in one of the preferred variants of the inventive coatings.

Figure 4: XRD comparison of non-inventive and inventive coatings.

Figure 5: Elastic Modulus variation along the thickness of the inventive TiAlSiBN coating 100.

Figure 1 schematically shows a coated product 200, which is coated with a preferred embodiment of a dual phase TiAlSiBN coating 100 according to the present invention, wherein the first section 5 of the TiAlSiBN coating 100 (for example formed of or comprising one adhesion layer with chemical element composition $(\text{Ti}_x\text{Al}_y\text{B}_z\text{Si}_w)_t\text{N}_u$), directly deposited on a surface of a substrate 1, the second section 10 (for example formed of or comprising one bottom layer with chemical element composition $(\text{Al}_a\text{Ti}_b\text{Si}_c\text{B}_d)_e\text{N}_q$), directly deposited on the first section 5, the third section 50 (for example formed of or comprising one top layer with chemical element composition $(\text{Ti}_e\text{Si}_f)_g\text{N}_h$) directly deposited on the second section 10.

According to one more further preferred embodiment of the present invention, at least one adhesion layer in the first section 5, preferably the whole section 5 (i.e. all adhesion layers in the section 5) having chemical element composition in atomic percentage (without consideration of contaminant elements, i.e. unavoidable impurities which should be less than 2 at.% of the sum of all elements present) given by the formula $(\text{Al}_a\text{Ti}_b\text{Si}_c\text{B}_d)_e\text{N}_q$, with $a+b+c+d=1$, $0.75 \leq c/d \leq 1.15$, $0.425 \leq a \leq 0.76$, $0.17 \leq b \leq 0.425$, $0.002 \leq q \leq 0.05$, preferably $0.003 \leq q \leq 0.050$, more preferably $0.003 \leq q \leq 0.045$ or $0.003 \leq q \leq 0.040$, measured by using standard ToF-ERDA (Time-of-flight Elastic Recoil Detection Analysis) or ERDA (Elastic Recoil Detection Analysis) and SIMS (Secondary Ion Mass Spectrometry) techniques as standard used for PVD coating films having thicknesses in the ranges mentioned in the present description and comprising elements as mentioned in the present description.

According to one more further preferred embodiment of the present invention, at least one adhesion layer in the first section 5, preferably the whole first section 5 (i.e. all adhesion layers in the section 5) having chemical element composition in atomic percentage (without consideration of contaminant elements, i.e. unavoidable impurities which should be less than 2 at.% of the sum of all elements present) given by the formula $(\text{Al}_a\text{Ti}_b\text{Si}_c\text{B}_d)_e\text{N}_q$, with $a+b+c+d=1$, $0.75 \leq c/d \leq 1.15$, $0.425 \leq a \leq 0.76$,

$0.17 \leq b_i \leq 0.425$, $0.002 \leq q_i \leq 0.05$, preferably $0.003 \leq q_i \leq 0.050$, more preferably $0.003 \leq q_i \leq 0.045$ or $0.003 \leq q_i \leq 0.040$, measured by using ERDA and SIMS techniques.

More preferably also (as well as in the first section 5 in the embodiment described directly above) at least one bottom layer in the second section 10, preferably the whole second section 10 (i.e. all bottom layers in the section 10) having chemical element composition in atomic percentage (without consideration of contaminant elements, i.e. unavoidable impurities which should be less than 2 at.% of the sum of all elements present) given by the formula $(Al_{a_i}Ti_{b_i}B_{q_i})_{c_i}N_{d_i}$, with $a_i + b_i + q_i = 1$, $0.75 \leq c_i/d_i \leq 1.15$, $0.425 \leq a_i \leq 0.76$, $0.17 \leq b_i \leq 0.425$, $0.002 \leq q_i \leq 0.05$, preferably $0.003 \leq q_i \leq 0.050$, more preferably $0.003 \leq q_i \leq 0.045$ or $0.003 \leq q_i \leq 0.040$, measured by using ERDA and SIMS techniques.

In the context of the present description and especially hereafter, for facilitating descriptions of embodiments and explanations, the term:

- “the adhesion layer” is also used for referring to the whole first section 5 of the TiAlSiBN coating 100, and
- “the bottom layer” is also used for referring to the whole second section 10 of the TiAlSiBN coating 100, and
- “the top layer” is also used for referring to the whole third section 50 of the TiAlSiBN coating 100.

The chemical element composition of the adhesion layer in atomic percentage ($Comp_{Bottom_1stPort}$) and the chemical element composition of the bottom layer in atomic percentage ($Comp_{Bottom_lastPort}$) being similar or equal, i.e. $0.9 \leq Comp_{Bottom_1stPort} / Comp_{Bottom_lastPort} \leq 1.11$.

Preferably the chemical element composition along the thickness of the bottom layer remains constant or vary in a proportion less than 10% under consideration of the values in the last portion 10f of the bottom layer 10, more preferably less than 5%.

According to one more further preferred embodiment of the present invention, the top layer has chemical element composition in atomic percentage (without consideration of contaminant elements, i.e. unavoidable impurities which should be less than 2 at.%)

of the sum of all elements present) given by the formula $(\text{Ti}_e\text{Si}_f)_g\text{N}_h$, with $e+f=1$, $0.75 \leq g/h \leq 1.15$, $0.6 \leq e \leq 0.95$, $0.05 \leq f \leq 0.4$.

According to a further preferred embodiment of the present invention, an adhesion layer 5 (see Figures 3 and 4) is deposited between the bottom layer 10 and the surface of the substrate 1 being coated (hereafter also called substrate surface being coated or simply substrate surface) with the dual phase TiAlBSiN coating, wherein the adhesion layer 5 exhibiting predominantly face centered cubic phase. The adhesion layer 5 being preferably a TiAlN layer or a TiAlBN layer, when the bottom layer is a TiAlBN layer.

The surface of the coating system exhibits preferably an average roughness Ra lower than 0.05 μm .

The coating exhibiting improved wear resistance, in particular in cutting operations when applied to cutting tools.

By doping the bottom layer of TiAlN with boron (B) a dual phase microstructure (of TiAlBN) was produced, which lead to improved mechanical properties as well as refined feather-like morphology similar to TiSiN.

Examples

In order to show the impressive improvement attained by using the present inventive coatings for cutting applications three inventive examples and two non-inventive examples will be explained below in more detail:

All coatings in the examples were deposited by using High Power Impulse Magnetron Sputtering (HiPIMS) techniques. However, the use of this method should not be understood as a limitation of the possible methods that can be used for producing the present inventive coatings. Any Physical Vapor Deposition (PVD) techniques can be able for producing the inventive coatings according to the present invention.

Deposition of T1 (non-inventive example):

The T1-coating consists of a bottom layer of TiAlN and a top layer of TiSiN. Both the TiAlN and the TiSiN exhibiting phase centered cubic phase.

The TiAlN bottom layer was deposited in known manner by using TiAl-targets having a ratio of content of Ti and Al in atomic percent of Ti/Al = 40/60. The TiAl-targets were sputtered (via HiPIMS) in a reactive atmosphere containing argon as inert gas and nitrogen as reactive gas. A negative bias voltage of -50 V was applied to the substrate during deposition of the TiAlN bottom layer.

The TiAlN bottom layer was deposited directly on the substrate.

The TiSiN top layer was deposited in known manner atop the TiAlN bottom layer by using TiSi-targets having a ratio of content of Ti and Si in atomic percent of Ti/Si = 75/25. The TiSi-targets were sputtered (via HiPIMS) in a reactive atmosphere containing argon as inert gas and nitrogen as reactive gas. A negative bias voltage of -70 V was applied to the substrate during deposition of the TiSiN top layer.

Deposition of T2 (inventive example):

The T2-coating consists of an adhesion layer of TiAlBN, a bottom layer of TiAlBN and a top layer of TiSiN. The adhesion layer of TiAlBN exhibiting face centered cubic phase, and the bottom layer of TiAlBN exhibiting hexagonal wurtzite phase. The TiSiN top layer exhibiting face centered cubic phase.

The TiAlBN adhesion layer and bottom layer was deposited by using TiAlB-targets having a content of Ti, Al and B in atomic percent of Ti=32, Al=63, B=5. The TiAlB-targets were sputtered (via HiPIMS) in a reactive atmosphere containing argon as inert gas and nitrogen as reactive gas. A negative bias voltage of -100 V was applied to the substrate during deposition of the TiAlBN bottom layer. The difference for the deposition of the adhesion layer of TiAlBN with cubic phase and the bottom layer with wurtzite phase was attained by setting a different total pressure during deposition of the TiAlBN adhesion layer and bottom layer. The total pressure used during the deposition of the TiAlBN adhesion layer was lower (in a range from 0.1 Pa to 0.5 Pa)

than the total pressure used during deposition of the TiAlBN bottom layer (in a range from more than 0.5 Pa to 0.9 Pa).

The TiAlBN adhesion layer was deposited directly on the substrate.

The TiSiN top layer was deposited in the same manner that the TiSiN top layer in example T1 with the solely difference that the negative bias voltage applied to the substrate during deposition of the TiSiN top layer was of -50 V.

Deposition of T3 (inventive example):

The T3-coating consists of an adhesion layer of TiAlBN, a bottom layer of TiAlBN and a top layer of TiSiN. The TiAlBN adhesion layer exhibiting face centered cubic phase, and the TiAlBN bottom layer exhibiting hexagonal wurtzite phase. The TiSiN top layer exhibiting face centered cubic phase.

The TiAlBN adhesion layer and the TiAlBN bottom layer were deposited by using TiAlB-targets having a content of Ti, Al and B in atomic percent of Ti=32, Al=63, B=5. The TiAlB-targets were sputtered (via HiPIMS) in a reactive atmosphere containing argon as inert gas and nitrogen as reactive gas. The difference in the phase of TiAlBN adhesion layer and the phase in the TiAlBN bottom layer was attained by setting different pressures and bias voltages during deposition of the TiAlBN bottom layer. The total pressure used during the deposition of the adhesion layer was lower than the total pressure used during deposition of the bottom layer in a similar manner as in T2, and for T3 the negative bias voltage applied to the substrate during the deposition of the adhesion layer was of -50 V while during deposition of the bottom layer was of -100 V.

The TiAlBN adhesion layer was deposited directly on the substrate.

The TiSiN top layer was deposited exactly in the same manner that the TiSiN top layer in example T2.

Deposition of T4 (inventive example):

The T4-coating consists of a bottom layer of TiAlBN, a top layer of TiSiN and an adhesion layer of TiAlN. The TiAlBN bottom layer exhibiting hexagonal wurtzite phase. The TiSiN top layer and the TiAlN adhesion layer exhibiting face centered cubic phase.

The TiAlBN bottom layer was deposited by using TiAlB-targets having a content of Ti, Al and B in atomic percent of Ti=32, Al=63, B=5. The TiAlB-targets were sputtered (via HiPIMS) in a reactive atmosphere containing argon as inert gas and nitrogen as reactive gas. No different portions of the TiAlBN bottom layer were produced. During deposition of the of the TiAlBN bottom layer a negative bias voltage of -100 V was applied to the substrate.

The TiAlBN bottom layer was not deposited directly on the substrate but an adhesion layer of TiAlN exhibiting face centered cubic phase was deposited between the substrate and the TiAlBN bottom layer. The coating deposition of the adhesion layer was carried out in known manner under same conditions as described in example T1 for the TiAlN bottom layer.

The TiSiN top layer was deposited exactly in the same manner that the TiSiN top layer in example T2 and T3.

Deposition of T5 (non-inventive example):

The only difference between T4 and T5 is that T5 does not comprise an adhesion layer but the TiAlBN bottom layer exhibiting hexagonal wurtzite phase was deposited directly on the substrate. Apart from that the deposition of T5 was conducted in the same manner that the deposition of T4.

In general the inventive coatings according to the present invention are deposited comprising at least one adhesion layer exhibiting face centered cubic phase, one bottom layer of TiAlBN or TiAlBSiN or TiAlSiN exhibiting hexagonal wurtzite phase, a top layer of TiSiN exhibiting face centered cubic phase and an adhesion layer of TiN or TiAlN or TiAlBN or TiAlBSiN or TiAlSiN exhibiting face centered cubic phase.

The inventors found that it is possible to gain an increase of more than 50% in the tool life in comparison with coating of the state of the art by using tools coated according to the present invention and the coated tools were tested in milling of hard materials.

The coatings described in the examples mentioned above were investigated and tested in more detail. The Figures 2 to 4 will be used for describing the invention in this regard in more detail but should not be understood as a limitation of the invention.

Figure 2 shows comparison of wear evolution comparison between non-inventive coatings (e.g. a dual layer coating of TiAlN and TiSiN) and inventive coatings (e.g. inventive variants comprising AlTiBN and TiSiN layers), as well as respective cutting parameters. Corresponding tools (in this case WC-C- ballnose endmills) were coated with non-inventive and inventive coatings (T1 to T5) as described above and afterwards used for machining of hardened steel. T5 shows that the using an AlTiBN bottom layer and a TiSiN top layer, without an (adapted) adhesion layer, that is at least mainly (i.e. predominantly) cubic as mentioned above (e.g. an adhesion layer of cubic TiAlN) does not result in the big advantages over state-of-the-art coating that are attained by using the inventive coatings, which comprise an adhesion layer, a bottom layer and a top layer as described in the present description.

Figure 3 shows TEM selected area diffraction patterns that confirm the formation of the adapted TiAlBN adhesion layer, which exhibits predominantly cubic phase, while the TiAlBN bottom layer exhibits predominantly wurtzite phase according to the present invention. Fig. 3 also shows that the bottom TiAlBN has a feather-like microstructure similar to TiSiN top layer according to a preferred embodiment of the present invention, which has shown to prevent cohesive failure. Thus, the confirmation of mainly cubic adapted TiAlBN adhesion layer is provided by TEM study presented in Figure 3.

Figure 4 shows a XRD comparison of non-inventive coatings (in particular an state-of-the-art cubic TiAlN/TiSiN coating) with inventive coatings prepared according to different preferred embodiments of the present invention, comprising a TiAlBN bottom layer and a TiSiN top layer.

The inventors proved that the predominately wurtzite bottom layer, in the inventive examples described above, predominantly wurtzite TiAlBN bottom layer, as can be

seen in XRD in Fig. 4, resulted in an outstanding advantage in comparison with the coatings known from the state of the art. In addition, the fact that this predominantly wurtzite bottom layer (in the examples predominantly wurtzite TiAlBN bottom layer) has a feather-like microstructure similarly to TiSiN further has the advantage that it provides a great morphological integrity in order to prevent cohesive failure at the interface between the bottom layer (in the above-described examples TiAlBN bottom layer) and the TiSiN top layer.

Concretely the present invention is in particular about:

A TiAlBSiN coating deposited on a surface of a substrate 1, the coating 100 comprising three different sections along its coating thickness, a first section 5 deposited directly atop said surface of the substrate 1, formed by at least one adhesion layer, a second section 10 deposited directly atop said first section 5, formed by at least one support layer, and a third section 50 deposited directly atop said second section 10, formed by at least one top layer, wherein:

- said at least one adhesion layer:
 - exhibiting fully crystalline cubic phase, or exhibiting a mixture of crystalline phases comprising crystalline cubic phase, and crystalline hexagonal wurtzite phase, wherein if a mixture of crystalline phases, exhibiting mainly cubic phase, and
 - comprising titanium and nitrogen; and
- said at least one support layer:
 - exhibiting fully hexagonal wurtzite phase, or exhibiting a mixture of crystalline phases comprising crystalline cubic phase and crystalline hexagonal wurtzite phase, wherein if a mixture of crystalline phases, exhibiting mainly wurtzite phase, and
 - comprising titanium, aluminum, nitrogen, and at least one of boron and silicon; and
- said at least one top layer:
 - exhibiting fully crystalline cubic phase, or exhibiting a mixture of crystalline phases comprising crystalline cubic phase and crystalline

hexagonal wurtzite phase, wherein if a mixture of crystalline phases, exhibiting mainly cubic phase, and

- comprising titanium, silicon and nitrogen.

The crystalline hexagonal wurtzite phase in the TiAlSiBN coating 100 comprises Al and N.

Preferably, the thicknesses th_5 , th_{10} and th_{50} , of the respective first coating section, second coating section, and third coating section in the TiAlBSiN coating may fulfill following equations with th_5 , th_{10} and th_{50} in micrometers or nanometers:

- $2 \leq th_5 \times 100 / (th_5 + th_{10} + th_{50}) \leq 60$, and
- $15 \leq th_{510} \times 100 / (th_5 + th_{10} + th_{50}) \leq 60$, and
- $20 \leq th_{50} \times 100 / (th_5 + th_{10} + th_{50}) \leq 60$.

Moreover, the thicknesses th_5 , th_{10} and th_{50} , of the respective first coating section, second coating section, and third coating section in the TiAlBSiN coating may fulfill following equations with th_5 , th_{10} and th_{50} in micrometers or nanometers:

- $0.3 \mu m \leq th_5 + th_{10} + th_{50} \leq 40 \mu m$, and
- $0.33 \leq th_{10} / th_{50} \leq 3$, and/or
- $0.67 \leq (th_{10} + th_{50}) / th_5 \leq 49$.

According to a preferred embodiment of the present invention the TiAlBSiN coating exhibits:

- ratio between cubic phase “cub”, and wurtzite phase “wur”, in said at least one adhesion layer being greater than 0.3, thus: $cub/wur \geq 0.3$; and
- ratio between cubic phase and wurtzite phase in said at least one support layer being in a range between 0.01 and 0.3, thus: $0.01 < cub/wur < 0.3$; and
- ratio between cubic phase “cub” and wurtzite phase “wur”, in said at least one top layer being greater than 1, thus: “cub” / “wur” > 1, or said at least one top layer exhibiting fully crystalline cubic phase;

wherein the ratio between cubic phase and wurtzite phase corresponds to the peak intensity ratio of (200)cubic/(110)wurtzite ratio.

The TiAlBSiN coating preferably exhibiting:

- said at least one adhesion layer composed of:
 - titanium, aluminum, nitrogen, at least one of aluminum, boron and silicon, and less than 1.5 at.% unavoidable impurities, or
 - titanium, aluminum, boron and nitrogen and less than 1.5 at.% unavoidable impurities; and
- said at least one support layer composed of:
 - titanium, aluminum, nitrogen, at least one of boron and silicon, and less than 1.5 at.% unavoidable impurities, or
 - titanium, aluminum, boron and nitrogen and less than 1.5 at.% unavoidable impurities; and
- said at least one top layer composed of:
 - titanium, silicon, nitrogen, and less than 1.5 at.% unavoidable impurities.

Additionally, the TiAlBSiN coating may be formed that:

- the at least one adhesion layer is a layer mainly comprising or consisting of TiN or TiAlN or TiAlBN or TiAlSiN or TiAlBSiN, and/or
- the at least one support layer is a layer mainly comprising or consisting of TiAlBN or TiAlSiN or TiAlBSiN, and/or
- the at least one functional layer is a layer mainly comprising or consisting of TiSiN.

According to a preferred embodiment the TiAlBSiN coating is formed in that

- the elasticity modulus varies along the thickness of the TiAlBSiN coating (100) in such a manner that the lowest value E_{lowest} of elasticity modulus along the three costing sections (5), (10) and (50) is detected at a point within the second coating section (10) and/or beginning of section 50 (since thickness of section 50 right above section 10 is not enough for measuemtns, the E of section 10 influences the measurements-this is applies to the interfaces of all sections).

More preferably the TiAlBSiN coating also exhibiting:

- said at least one adhesion layer has an elasticity modulus " E_{AL} " in a range from 300 GPa to 480 GPa, thus: $300 \text{ GPa} \pm 15 \text{ GPa} \leq E_{AL} < 480 \text{ GPa} \pm 15 \text{ GPa}$; and
- said at least one support layer has an elasticity modulus " E_{SL} " in a range from 250 GPa to 360 GPa, thus: $250 \text{ GPa} \pm 15 \text{ GPa} \leq E_{SL} < 360 \text{ GPa} \pm 15 \text{ GPa}$; and
- the elasticity modulus of the at least one adhesion layer is greater than the elasticity modulus of the at least one support layer, thus: $E_{AL} > E_{SL}$.

Said at least one support layer preferably exhibiting feather-like growth and more preferably also said at least one top layer exhibiting feather-like growth.

Said at least one adhesion layer exhibiting preferably fine-grained or columnar growth.

According to a preferred embodiment the TiAlBSiN coating the adhesion layer is a TiAlBN adhesion layer and exhibits fine-grained growth. In such a case preferably the bottom layer is also a TiAlBN layer but exhibiting feather-like growth and the top layer is preferably a TiSiN layer but exhibiting feather-like growth.

Preferably said at least one adhesion layer and said at least one support layer have the same chemical element composition or is formed comprising the same chemical elements, wherein if the chemical element composition is not the same, then the difference in the atomic concentration of each chemical element is less than 10 at.% or even less than 5 at.%.

The TiAlBSiN coating 100 according to the present invention comprises preferably along its whole thickness the chemical element Ti.

The TiAlBSiN coating 100 according to the present invention preferably consists of the three sections: the first section 5, the second section 10 and the third section 50.

Claims

- 1. A TiAlBSiN coating deposited on a surface of a substrate (1), the coating (100) comprising three different coating sections along its coating thickness, a first section (5), a second section (10) and a third section (50), said first section (5) deposited closer to said surface of the substrate (1) than the second and third sections, said second section (10) deposited directly on the outermost surface of said first section (5), and a third section (50) deposited directly on the outermost surface of said second section (10), characterized in that:
 - o said first section (5) formed of one or more layers, in any case formed by at least one adhesion layer, wherein:
 - the first section (5) exhibiting fully crystalline cubic phase, or exhibiting a mixture of crystalline phases comprising crystalline cubic phase, and crystalline hexagonal wurtzite phase, wherein if a mixture of crystalline phases, exhibiting mainly cubic phase, and
 - the at least one adhesion layer comprising titanium and nitrogen; and
 - o said second section (10) formed of one or more layers, in any case formed by at least one support layer, wherein:
 - the second section (10) exhibiting fully crystalline hexagonal wurtzite phase, or exhibiting a mixture of crystalline phases comprising crystalline cubic phase and crystalline hexagonal wurtzite phase, wherein if a mixture of crystalline phases, exhibiting mainly wurtzite phase, and
 - the at least one support layer being comprising titanium, aluminum, nitrogen, and at least one chemical element selected from boron and silicon; and
 - o said third section (50) formed of one or more layers, in any case formed by at least one functional layer, wherein:
 - the third section (50) exhibiting fully crystalline cubic phase, or exhibiting a mixture of crystalline phases comprising crystalline cubic phase and crystalline hexagonal wurtzite phase, wherein if a mixture of crystalline phases, exhibiting mainly cubic phase, and

- the at least one functional layer comprising titanium, silicon and nitrogen,

and wherein the crystalline hexagonal wurtzite phase in the TiAlBSiN coating (100) comprises Al and N for example in the form of AlN.

2. The TiAlBSiN coating (100) according to claim 1, characterized in that the thicknesses th_5 , th_{10} and th_{50} , of the respective first coating section (5), second coating section (10), and third coating section (50) in the TiAlBSiN coating (100), fulfill following equations with th_5 , th_{10} and th_{50} in micrometers or nanometers:

- $2 \leq th_5 \times 100 / (th_5 + th_{10} + th_{50}) \leq 60$, and
- $15 \leq th_{510} \times 100 / (th_5 + th_{10} + th_{50}) \leq 60$, and
- $20 \leq th_{50} \times 100 / (th_5 + th_{10} + th_{50}) \leq 60$.

3. The TiAlBSiN coating (100) according to claim 1 or 2, characterized in that:

- $0.3 \mu m \leq th_5 + th_{10} + th_{50} \leq 40 \mu m$, and
- $0.33 \leq th_{10} / th_{50} \leq 3$, and/or
- $0.67 \leq (th_{10} + th_{50}) / th_5 \leq 49$.

4. The TiAlBSiN coating (100) according to at least one of the preceding claims 1 to 3, characterized in that:

- said at least one adhesion layer composed of:
 - titanium, aluminum, nitrogen, at least one of aluminum, boron and silicon, and less than 1.5 at.% unavoidable impurities, or
 - titanium, aluminum, boron and nitrogen and less than 1.5 at.% unavoidable impurities; and
- said at least one support layer composed of:
 - titanium, aluminum, nitrogen, at least one of boron and silicon, and less than 1.5 at.% unavoidable impurities, or
 - titanium, aluminum, boron and nitrogen and less than 1.5 at.% unavoidable impurities; and
- said at least one functional layer composed of:

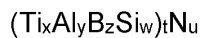
- titanium, silicon, nitrogen, and less than 1.5 at.% unavoidable impurities.

5. The TiAlBSiN coating (100) according to at least one of the preceding claims 1 to 4, characterized in that:

- the at least one adhesion layer is a layer mainly comprising or consisting of TiN or TiAlN or TiAlBN or TiAlSiN or TiAlBSiN, and/or
- the at least one support layer is a layer mainly comprising or consisting of TiAlBN or TiAlSiN or TiAlBSiN, and/or
- the at least one functional layer is a layer mainly comprising or consisting of TiSiN.

6. The TiAlBSiN coating (100) according to at least one of the preceding claims 1 to 5, characterized in that the chemical element composition in atomic concentration of:

- said at least one adhesion layer, preferably of the whole first section (5), is given by the formula:



where:

$$x+y+z+w = 1, \text{ and}$$

$$0 \leq y/x \leq 0.21 \text{ or } y/(x+y) < 0.67, \text{ and}$$

$$0 \leq z+w \leq 0.25, \text{ preferably } 0 \leq z+w \leq 0.10, \text{ more preferably } 0 < z+w \leq 0.05, \text{ and}$$

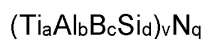
$$0 \leq z \leq 0.10, \text{ preferably } 0 \leq z \leq 0.05, \text{ more preferably } 0.01 \leq z < 0.05 \text{ and}$$

$$0 \leq w \leq 0.25, \text{ preferably } 0 \leq w \leq 0.10, \text{ and}$$

$$0.75 \leq t/u \leq 1.25, \text{ preferably } 0.85 \leq t/u \leq 1.15;$$

and/or

- said at least one bottom layer, preferably of the whole second section (10), is given by the formula:



where:

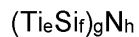
$$a+b+c+d = 1, \text{ and}$$

$$0 \leq b/a \leq 2.1 \text{ and/or } 0 \leq b/(a+b) < 0.67, \text{ preferably } 1 \leq b/a \leq 2.1, \text{ and}$$

$0 \leq c+d \leq 0.25$, preferably $0 \leq c+d \leq 0.10$, more preferably $0 < c+d \leq 0.05$, and
 $0 \leq c \leq 0.05$, preferably $0.01 \leq c < 0.05$, more preferably $0.01 \leq c \leq 0.04$, and
 $0 \leq d \leq 0.25$, preferably $0 \leq d \leq 0.10$, and
 $0.75 \leq v/q \leq 1.25$, preferably $0.85 \leq v/u \leq 1.15$;

and/or

- said at least one functional layer, preferably of the whole third section (50), is given by the formula:



where:

$e+f = 1$, and

$0.05 \leq f \leq 0.35$, preferably $0.05 \leq f \leq 0.25$, and

$0.75 \leq g/h \leq 1.25$, preferably $0.85 \leq g/h \leq 1.15$.

7. The TiAlBSiN coating (100) according to at least one of the preceding claims 1 to 6, characterized in that:

- the elasticity modulus varies along the thickness of the TiAlBSiN coating (100) in such a manner that the lowest value E_{lowest} of elasticity modulus along the three costing sections (5), (10) and (50) is detected at a point within the second coating section (10) and/or beginning of section 50 (since thickness of section 50 right above section 10 is not enough for measuemtns, the E of section 10 influences the measurements-this is applies to the interfaces of all sections).

8. The TiAlBSiN coating (100) according to claim 7, characterized in that:

the lowest value of elasticity modulus E_{lowest} detected in the second section (10) is in a range from 200 GPa to 360 GPa, preferably in a range from 250 GPa to 320 GPa, still more preferably in a range from 250 GPa to 360 GPa, thus:

- $200 \text{ GPa} \pm 15 \text{ GPa} \leq E_{\text{lowest}} \leq 360 \text{ GPa} \pm 15 \text{ GPa}$,
- preferably $250 \text{ GPa} \pm 15 \text{ GPa} \leq E_{\text{lowest}} \leq 320 \text{ GPa} \pm 15 \text{ GPa}$,
- more preferably $250 \text{ GPa} \pm 15 \text{ GPa} \leq E_{\text{lowest}} \leq 360 \text{ GPa} \pm 15 \text{ GPa}$.

9. The TiAlBSiN coating (100) according to at least one of the preceding claims 1 to 8, characterized in that:

- said at least one support layer exhibits feather-like growth.

10. The TiAlBSiN coating (100) according to at least one of the preceding claims 1 to 9, characterized in that:

- said at least one functional layer exhibits feather-like growth.

11. The TiAlBSiN coating (100) according to at least one of the preceding claims 1 to 10, characterized in that:

- said at least one adhesion layer exhibits fine-grained or columnar growth.

12. The TiAlBSiN coating (100) according to claim 11, characterized in that:

- the adhesion layer is a TiAlBN adhesion layer and exhibits fine-grained growth.

13. The TiAlBSiN coating (100) according to at least one of the preceding claims 1 to 12, characterized in that:

- said at least one adhesion layer and said at least one support layer have the same chemical element composition or is formed comprising the same chemical elements, wherein if the chemical element composition is not the same, then the difference in the atomic concentration of each chemical element is less than 10 at. %.

14. The TiAlBSiN coating (100) according to claim 13, characterized in that:

- the difference in the atomic concentration of each chemical element is less than 5 at. %.

15. The TiAlBSiN coating (100) according to at least one of the preceding claims 1 to 14, characterized in that:

the TiAlBSiN coating (100) comprises Ti along its whole coating thickness.