

The invention concerns a coated workpiece as set forth in the classifying portion of claim 1, a process for the production thereof as set forth in the classifying portion of claim 12, and an apparatus for carrying out the process as set forth in the classifying portion of claim 20. Preferred
5 embodiments of the invention are claimed in the corresponding appendant claims 2 to 11, 13 to 19 and 21.

A reactive PVD coating process of that kind and a workpiece coated in accordance with that process in order to increase the hardness and
10 toughness thereof are known from EP-A-0 191 554; workpieces of that kind are used for example as cutting tools. The known coating operation is performed by means of a PVD process at temperatures between 200 and 700°C. Up to four discrete layers of titanium carbide, titanium nitride and
15 titanium carbonitride are applied, wherein a titanium nitride layer is always applied directly over the surface to be coated.

A further reactive PVD coating process of the general kind set forth is known from EP-A-0 306 612. This involves a magnetic field-assisted cathode sputtering process combined with an electric arc discharge process, with
20 which compact dense layers are produced on tools, while avoiding a columnar structure in the coating. The workpieces to be coated are alternately exposed in rapid succession to a metal-vaporising arc discharge electrode and a sputtering source, wherein the deposit of metal vapour, for the layers in question, is due in respect of more than 95 out of 100 parts to
25 the magnetic field-assisted cathode sputtering effect. In that procedure the period for a cathode sputtering coating is so short that during each respective individual period, the partial layer thickness deposited cannot be more than 30 nanometres. In order to produce a uniform coating effect on all tools arranged on a turntable, the tools are simultaneously
30 displaced in a continuous or intermittent rotary movement about their vertical axis. The homogeneity to be achieved in the coating is checked by means of a scanning electron microscope.

A further hard metal cutting tool coating which is not of the same general
35 kind as the present invention is known from EP-A-0 302 984. In that case, coating is effected by a CVD process (chemical vapour deposition) in contrast to the above-mentioned reactive PVD coating process. In contrast to the homogenous distribution of material in the coating of EP-A-0 306 612, the aim here is the formation of islands formed by precipitations or
40 deposits of oxides and/or nitrides and/or carbides in the layers in order to obtain good wear resistance for the coated tool.

The invention as characterised in the claims solves the problem of providing a coated workpiece, as well as a process for the production of
45 the coated workpiece, in which the applied layers adhere firmly to the workpiece surface and exhibit a high level of toughness.

Claims 2 to 13 describe preferred embodiments of the workpiece coated in accordance with the invention and claims 15 to 21 described preferred
50 embodiments of the process according to the invention.

An embodiment of the process according to the invention and the workpiece

coated in accordance with the invention are described in greater detail with reference to drawings in which:

- 5 Figure 1 is a diagrammatic view of a vapour deposition installation,
- Figures 2a-f show the variation in respect of time of various parameters during the operation of applying layers to the workpieces, and
- 10 Figures 3a-c show percentage proportions of the vapour-deposited materials relative to the layer thickness.

Figure 1 shows an example of a vapour deposition installation for carrying out the process according to the invention for producing coated workpieces 2. The apparatus has a vacuum chamber 1 with an evacuation connection 3 and a thermionic cathode chamber 5 with a thermionic cathode 6 which is connected to the vacuum chamber 1 by way of an opening 7. The thermionic cathode 6 is supplied by a current supply unit 9. Disposed approximately over the centre of the bottom 10 of the vacuum chamber 1 is a coolable crucible 11 which is displaceable in respect of height and in which titanium 13 is converted into the gaseous state by vaporisation. The crucible 11 is shown in broken lines in Figure 1 as being moved away from its lowermost position by a distance d. Displacement is effected by way of a motion device 14 which is displaceable in respect of height; it comprises three cylinders which are displaceable one into the other with a spindle guide means. Provided in the vacuum chamber 1 are twelve carriers 15 which are rotatable about the longitudinal axis, two of the carriers being shown; the workpieces 2 to be coated are held on the carriers 15, on respective holders 17. The thermionic cathode chamber 5 also has a coolant passage 19 in order to cool the wall thereof during operation. Respective gas feed conduits 21 and 22 open into the thermionic cathode chamber 5 and the vacuum chamber 1, the gas feed conduit 22 being divided in the vacuum chamber 1 into a plurality of branches of 24a, 24b of which two are shown and which are provided with openings 23 in order to provide for distribution which is as uniform as possible of the gas or gas mixture introduced through the gas feed conduit 22, within the vacuum chamber 1. Two diagrammatically illustrated magnetic coils 25 are disposed beneath the bottom 10 and above a cover portion 26 of the vacuum chamber 1 in rotationally symmetrical relationship with the crucible 11 to produce an approximately parallel vertical magnetic field.

To produce the coated workpieces 2 they are fixed to the holders 17 of the carriers 15 and titanium 13 is placed in the crucible 11. In a first process step the vacuum chamber 1 is closed and evacuated and the inert gas argon is introduced by way of the gas feed conduit 21 until a partial pressure of 200mPa is reached. For heating up and ion etching of the workpiece surfaces, a low-voltage arc burns in the argon atmosphere from the thermionic cathode 6 to the surfaces of the workpieces 2. The carriers rotate at a rate of about one revolution in five seconds for uniform heating and cleaning of the workpieces 2 arranged around the carriers 15.

The progress in respect of time of the individual process steps for producing the coating after the cleaning and heating procedure is shown in Figure 2. The layers which are produced during each one of the respective

process steps, namely an underneath layer A, an interface layer B, a first sub-layer C of a solid-solution layer and a second sub-layer D of the solid-solution layer which forms the uppermost layer of the coating are shown on the abscissa. Figure 2a shows the current variation in respect of time I_{arc} of the current strength of the low-voltage arc, Figure 2b shows the variation in respect of the negative bias voltage U_{sub} at the workpieces 2, Figure 2c shows the spacing d of the crucible 11 from the lowermost position thereof to the bottom 10 of the vacuum chamber 1, Figure 2d shows the gas flow of the argon Ar into the vacuum chamber 1 through the gas feed conduit 21, Figure 2e shows the gas flow of acetylene C_2H_2 through the gas inlet 22 and Figure 2f shows the gas flow of nitrogen N_2 .

Subsequent to the operations for heating and cleaning the surfaces of the workpieces 2, in a subsequent process step a titanium underneath layer A of approximately 1000 Å is applied directly to the surfaces of the workpieces 2.

The materials deposited throughout the entire process on the surface of the workpieces 2 are shown in Figure 3 in terms of their percentage composition at the spacing a from the original surface of the workpiece. Figure 3a shows the titanium nitride content TiN, Figure 3b shows the titanium carbide content TiC and Figure 3c shows the content of pure titanium Ti.

For applying the pure titanium layer A see Figure 3c and Figure 2, the low-voltage arc 27 burns from the thermionic cathode 6 to the crucible 11 with a current (Figure 2a) of approximately 80A; the workpieces 2 are at a potential (Figure 2b) of about -100V relative to the crucible 11. The vaporising titanium Ti is ionised in the gas discharge and attracted by the surfaces of the workpieces 2. In order to achieve a uniform titanium layer the crucible 11 is moved in the direction towards the thermionic cathode 6 away from the bottom 10 of the vacuum chamber 1 to a maximum spacing d_{max} past the workpieces 2 fixed to the carriers 15 (see Figure 2c). The time for producing that titanium underneath layer A is so great that the surfaces of the rotating workpieces 2 face the crucible 11 a number of times.

When the titanium underneath layer has been produced by vapour deposition in a thickness of approximately 1000 Å, nitrogen N_2 (Figure 2f) is introduced through the gas inlet 22 in a subsequent process step while the low-voltage arc 27 is burning, a nitrogen partial pressure of 50 mPa being set in order to have available a sufficient supply of nitrogen atoms and ions for a complete reaction with the vaporised titanium Ti, vaporisation being increased by increasing the current (Figure 2a) of the low-voltage arc 27 to about 200A. The nitrogen N_2 is uniformly distributed in the vacuum chamber 1 through the branches 24a, 24b etc. and with the titanium vapour Ti forms titanium nitride TiN which is deposited on the surfaces of the workpieces 2. A current of approximately 20 A flows from the workpieces 2 after a reduction in the negative bias voltage (Figure 2b) to -50V. During this process step also the workpieces 2 rotate. The crucible 11 (Figure 2c) is moved from its uppermost position downwardly towards the bottom 10 and towards the end of this step in the process it is moved once again upwardly and downwardly again in order to produce a uniform coating with titanium nitride TiN.

After an interface layer B of titanium nitride TiN of a thickness of about

one micrometre has been applied by vapour deposition (the thickness can be altered according to the respective purpose of use of the workpieces 2), acetylene C_2H_2 , as a gas which gives off carbon, as shown in Figure 2e, is introduced through the gas inlet 22 together with the nitrogen N_2 in a further step in the process, and uniformly distributed in the vacuum chamber 1 by way of the branches 24a, 24b etc. The nitrogen component N_2 is reduced to the extent that the proportion of acetylene C_2H_2 in the vacuum chamber 1 increases; see Figures 2e and 2f. Due to the gas discharge, the acetylene C_2H_2 is divided up and the carbon which is given off is ionised. Both the ionised carbon and the ionised nitrogen combine with the titanium vapour Ti to form titanium nitride TiN and titanium carbide TiC respectively. The feed flow of acetylene is increased in such a way and the feed flow of nitrogen is reduced in such a way until 70% nitrogen N_2 and 30% acetylene C_2H_2 are contained in the vacuum chamber 1. The feed flow of argon continues (see Figure 2d). During the increase in the acetylene feed flow the crucible 11 (see Figure 2c) is moved to and fro twice. During the to and fro movement, this produces a solid- solution layer, the sub-layer C, of a layer thickness of about two micrometres, consisting of titanium carbide TiC and titanium nitride TiN. Depending on the respective purpose of use of the workpieces 2 the layer thickness is preferably from 1.2 to 2 times the thickness of the interface layer B.

After the acetylene feed flow has reached 30% of the nitrogen feed flow, in a further process step a sub-layer D which is about one micrometre thick (thinner sub-layer D of the solid-solution layer) is formed with that constant nitrogen-acetylene ratio. Depending on the respective purpose of use of the workpieces 2 the thickness of that layer is between a fifth of the preceding layer C and half thereof.

Surprisingly, the carbon inclusions in the applied layers C and D, which adversely affect adhesion and toughness, substantially disappeared due to the above-discussed rotary movement of the workpieces 2 and the upward and downward movement of the crucible 11. In addition, on the basis of thin microsections on coated workpieces 2, it was possible to detect that superimposed on a steady increase in the titanium carbide content of the applied layer C are fluctuations in concentration k of titanium carbide TiC to titanium nitride TiN which coincide with the movements of the crucible 11. Superimposed on those fluctuations were further fluctuations in concentration s which correlate with the rotary movement of the carriers 15.

Figure 3 shows the variation in concentration of pure titanium Ti (Figure 3a), titanium nitride TiN (Figure 3b) and titanium carbide TiC (Figure 3c), corresponding to a microsection. The fluctuations with a low amplitude s and a short period in the thickness regions C and D (see also Figure 2) are due to the rotary movement of the workpieces 2 on the carriers 15. The two fluctuations of large amplitude k and long period in the region C and the one fluctuation in the region D are to be attributed to the two upward and downward movements of the crucible 11 during the operation for vapour deposition of the layer in the region C and the one upward and downward movement in the region D.

The broken straight lines g_1 and g_2 in Figure 3a and j_1 and j_2 in Figure 3b specify the percentage of titanium carbide TiC and titanium nitride content TiN respectively in the vapour-deposited layer if there had been no

movements of the crucible and no movements of the workpieces. The configurations of the straight lines m_1 to m_4 in respect of titanium nitride TiN and n_1 to n_4 in respect of titanium carbide TiC give the variation in the percentage titanium nitride content TiN and titanium carbide content TiC respectively in a vapour-deposited layer if the workpieces 2 had not been rotated about carriers 15. The indices used coincide with the indices in respect of the movement o of the crucible 11 in Figure 2c. The curves shown in Figure 3 apply in relation to workpieces 2 in the vicinity of the bottom 10. For workpieces 2 in the vicinity of the cover portion 26 the straight line m_1 is tilted upwardly symmetrically relative to the straight line g_1 and the straight line n_1 is tilted downwardly symmetrically relative to the straight line j_1 . A similar situation applies for the straight lines m_2 and n_2 . The straight line m_3 is then above the straight lines g_1 and g_2 respectively and the straight line n_3 is below the straight lines j_1 and j_2 respectively.

As is already known from EP-A-0 191 554, workpieces which are coated only with titanium nitride TiN are less resistant to free-surface wear, because of their lower level of hardness, than workpieces which are coated only with titanium carbide TiC. However, a workpiece which is coated only with titanium carbide TiC has a higher degree of scouring or erosion wear, because of the lower level of chemical resistance. The attempt was made in EP-A-0 191 554 to combine the two advantages by applying a titanium carbide layer TiC or a titanium carbonitride layer TiCN to a titanium nitride layer TiN.

It has now been found that the coating produced in accordance with the process of the invention, in which there are no longer any individual discrete layers, but only layers whose incorporation ratio continuously fluctuates over the layer thickness, have significantly better adhesion to the workpiece and the workpieces have a significantly higher level of toughness than those coated with the known process.

In long-duration tests, it was possible to cut 7000 screwthreads with an M8 uncoated screw tap, 25000 screwthreads were cut with a screw tap coated with TiN and 75000 threads were cut with a screw tap with a coating according to the invention. In the case of a stamping hole punch, material 1.0334, 20000 stampings were obtained with uncoated material, 62000 with material coated with TiN, and 140000 with the material coated in accordance with the invention.

The fluctuations in concentration within the coating can be explained with a high degree of probability on the basis of the differences in affinity of ionised carbon and nitrogen in relation to titanium vapour. As long as there is only nitrogen, it combines with the titanium. If there is ionised carbon, it preferably combines with the titanium, that is to say the area immediately around the crucible 11 is depleted of carbon as it has combined with the titanium. The smaller therefore the spacing of a workpiece surface from the crucible 11, the more titanium nitride TiN is deposited on the surface thereof.

Instead of using acetylene C_2H_2 as a gas which gives off carbon, it is possible to use ethylene C_2H_4 or other gases which give off carbon.

Instead of the two fluctuations in the first sub-layer C of the solid-

5 solution layer, it is also possible to produce more fluctuations, by virtue of a greater number of crucible movements; preferably, one to five fluctuations are produced for each two micrometres. The rotary movement of the workpieces 2 about the carriers 15 can also be varied in the range of from 5 to 100 periods per crucible cycle.

Instead of converting the titanium 13 in the crucible 11 into the gaseous state with a low-voltage arc, it is also possible to effect cathode sputtering, plasma-assisted vaporisation or cathodic arc vaporisation.



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CLAIMS

1. A coated workpiece (2) with a firmly adhering, tough solid-solution coating (C, D) which is applied by a reactive physical coating process and which comprises titanium nitride and titanium carbide whose concentration ratio relative to each other, at least in a predominant solid-solution coating sub-region (C), continuously increases and decreases with a periodic component of change (k) in the direction of the surface normal.

2. A coated workpiece (2) according to claim 1 characterised in that the solid-solution coating (C, D) is arranged on an interface layer region (B) which contains only titanium nitride or titanium carbide, that the pattern of concentration in respect of titanium nitride and titanium carbide respectively is constant between the interface region (B) and the solid-solution coating (C, D) and that the solid-solution coating (C, D) is preferably 1.2 to 2 times as thick as the interface region (B).

3. A coated workpiece (2) according to claim 2 characterised in that the solid-solution coating (C, D) comprises a first solid-solution coating sub-region (C), which is towards the workpiece (2), with a continuously changing concentration ratio, and a second thinner solid-solution coating sub-region (D), which is remote from the workpiece, with an at least approximately constant concentration ratio, wherein the concentration ratio of the first sub-region (C) continuously merges into that of the second sub-region (D) and the first sub-region (C) is 2 to 5 times as thick as the second (D).

4. A coated workpiece (2) according to one of claims 1 to 3 characterised in that superimposed on the periodic component of change (k) of the concentration ratio in the first solid-solution coating sub-



range (C, D) is a second component of change (m, n) which increases or decreases in the manner of a straight line in the direction of the surface normal.

5. A coated workpiece (2) according to one of claims 1 to 4 characterised in that the concentration ratio, periodically fluctuating in the direction of the surface normal, increases or decreases with preferably 1 to 5 fluctuations per approximately two micrometres of layer thickness.

6. A coated workpiece (2) according to one of claims 1 to 5 characterised in that superimposed on the periodic first component of change (k) of the concentration ratio is a periodic third component of change (s) of the concentration ratio with a shorter spatial period and a lower fluctuation in concentration ratio at 5 to 100 fluctuations in respect of the third component of change (s) per fluctuation in respect of the first component of change (k).

7. A coated workpiece (2) according to one of claims 2 to 6 characterised in that the interface layer region (B) lies on a base layer (A) which is preferably 0.01 to 0.5 μm in thickness.

8. A coated workpiece (2) according to one of claims 1 to 7 characterised in that the interface layer region (B) comprises titanium nitride.

9. A coated workpiece (2) according to one of claims 1 to 8 characterised in that the base layer (A) comprises titanium.

10. A coated workpiece (2) according to one of claims 3 to 9 characterised in that the second sub-layer region (D) comprises a solid solution with approximately 30% titanium carbide and 70% titanium nitride.



11. A coated workpiece (2) according to one of claims 1 to 10 characterised in that it is in the form of a cutting or shaping tool.

12. A reactive PVD coating process for the production of the coated workpiece (2) according to one of claims 1 to 11 wherein a metal which is converted into the gaseous state by means of a vapour source (11) in a vacuum chamber (1) is deposited on a surface of a moved workpiece (2), with chemical reaction with a gaseous reactant introduced into the vacuum chamber (1), characterised in that as the reactants a first gas is introduced at a continuously reduced feed flow and a second gas is introduced at a continuously increased feed flow, for the formation of a first and a second compound respectively, and the workpiece (2) is relatively so moved in relation to the vapour source (11) that the spacing thereof and/or the orientation thereof with respect to the vapour source (11) periodically alters at such a speed that deposited on the workpiece (1) is a solid-solution coating with said compounds whose concentration ratio relative to each other is made up only in the direction of the surface normal from superimposition of the periodic changes in concentration corresponding to the changes in spacing and the change in concentration corresponding to the change in feed flow.

13. A process according to claim 12 wherein the metal (13) is vaporised from a vapour source (11) by means of an arc vaporisation operation, in particular a low-voltage arc vaporisation operation.

14. A process according to claim 12 or claim 13 characterised in that the vapour source (11) is periodically moved along the workpiece surface to be coated in such a way that the concentration ratio of said compounds of the solid-solution coating sub-region (C) which is formed on the surface changes along the direction of movement.



15. A process according to claims 12 and 14 or 13 and 14 characterised in that the vapour source (11) is moved at a lower speed than the workpiece (2).

16. A process according to one of claims 12 to 15 characterised in that in a first process step during transformation of the metal (13) into the gaseous state only the first gas is let into the vacuum chamber (1) in order to form directly on the surface of the workpiece (2) an interface layer region (B) which does not contain any chemical compound with the second gas, and then in a second process step the second gas is introduced with a reduction in the feed flow of the first gas.

17. A process according to one of claims 12 to 16 for the production of the coated workpiece (2) according to claim 3 characterised in that in a first process step during transformation of the metal (13) into the gaseous state only the first gas is let into the vacuum chamber (1) in order to form directly on the workpiece (2) an interface layer region (B) which does not contain any chemical compound with the second gas, and then in a second process step to form the first solid-solution coating sub-region (C) the second gas is introduced with a reduction in the feed flow of the first gas and in a third process step the feed flow of the first and second gases is kept approximately constantly at the last-set value in the second process step for forming the second solid-solution coating sub-region (D).

18. A process according to one of claims 12 to 17 characterised in that the first gas used is nitrogen and the second gas used is a gas which gives off carbon and the metal to be vaporised is titanium.



19. A process according to claims 17 and 18 characterised in that the last lowest feed flow value for the first gas and the last greatest feed flow value for the second gas are so set that a $\text{TiC}_{0.3}\text{N}_{0.7}$ -solid solution is produced as the second solid-solution coating sub-region(D).

20. Apparatus for carrying out a reactive PVD coating process according to one of claims 12 to 19 having a vacuum chamber (1), an inlet unit (21, 22) for gaseous reactants, a movable holder (17) for the workpieces (2) to be coated, and a vapour source (11) which is arranged in the vacuum chamber (1) and which is movable by means of a motion device (14).

21. Apparatus according to claim 20 characterised in that the holder (17) is rotatable.