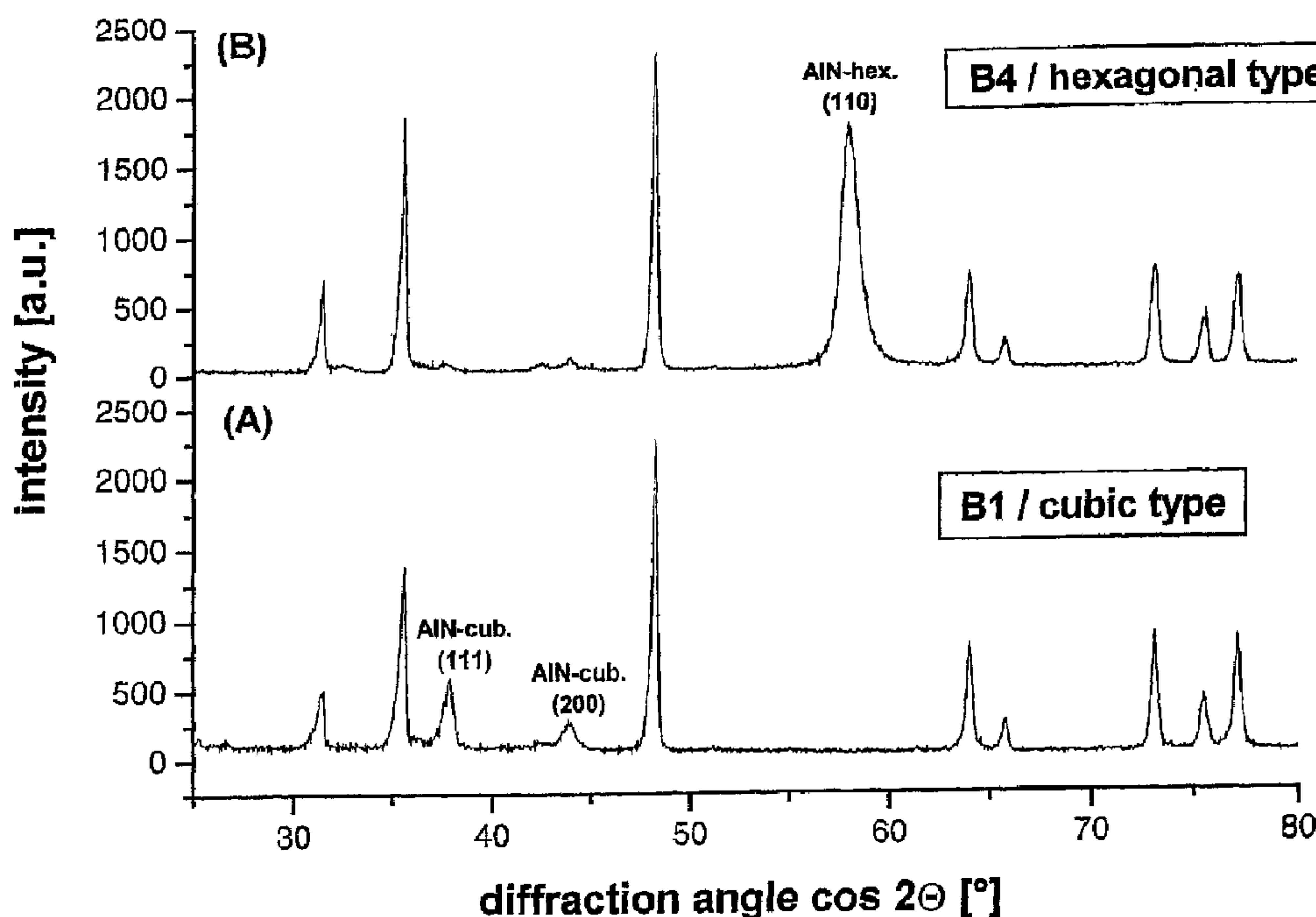




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PRODUCING THIS



X-Axis: diffraction angle cos (2 theta), unit: degrees

(57) Abrégé/Abstract:

Disclosed is a work piece with a layer system that contains at least one layer of composition $(Al_yCr_{1-y})N$, with a cubic structure, where $0.415 \leq y \leq 0.695$, the composition of the layer changing over the thickness of the layer continuously or incrementally, the work piece being a milling tool, a broaching cutter, a reamer, a turnover cutting plate for turning and milling, a molding tool, an injection- molding tool, a forming tool or a hot-forming tool. Also disclosed is a method for producing such a work piece or part.

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Abstract

Disclosed is a work piece with a layer system that contains at least one layer of composition $(Al_yCr_{1-y})N$, with a cubic structure, where $0.415 \leq y \leq 0.695$, the composition of the layer changing over the thickness of the layer continuously or incrementally, the work piece being a milling tool, a broaching cutter, a reamer, a turnover cutting plate for turning and milling, a molding tool, an injection-molding tool, a forming tool or a hot-forming tool. Also disclosed is a method for producing such a work piece or part.

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Work Piece with a Layer of Hard Material that Contains AlCr and a Method for Producing This

The technical domain to which the present invention relates includes work pieces that are covered with a layer system that contains at least one (Al_yCr_{1-y}) X layer as defined herein.

- 5 The present invention also relates to a PVD process for depositing an (Al_yCr_{1-y}) X layer on a work piece.

In particular, the present invention includes:

- work pieces that are coated with hard material and have one or a sequence of a number of different aluminum chromium nitride or aluminum carbon nitride layers;
- 10 - tools, in particular cutting and forming tools (drills, milling tools, turnover cutting plates, thread cutters, thread formers, hob milling cutters, stamps, matrices, drawing tools, etc.), and the use of these tools with AlCrN or AlCrCN layers;
- components, in particular components from the machine-building domain, such as gear wheels, pumps, barrel tappets, piston rings, injector needles, complete bearing sets or
- 15 individual parts thereof, and the use of these component parts with AlCrN or AlCrCN layers;
- a method for producing AlCrN or AlCrCN layers with a defined layer structure.

- One aspect of the invention relates to a PVD method for depositing at least one (Al_yCr_{1-y}) N layer on a work piece, with $0.415 \leq y \leq 0.695$, wherein the work piece is introduced into a
- 20 vacuum coating machinery with at least two compositionally different Al_zCr_{1-z} targets with $0.25 \leq z \leq 0.75$ and held at a pressure of 0.5 - 8 Pa during the addition of a reactive gas that comprises nitrogen, carbon, boron, or oxygen and the application of a substrate voltage between -3 to -150 V, applied as an arc or sputter source, such that the layer composition within at least one (Al_yCr_{1-y}) N layer changes continuously or incrementally across the
- 25 thickness of the layer.

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Another aspect of the invention relates to use of work piece with a layer system that contains at least one layer of composition $(Al_yCr_{1-y})N$, with a cubic structure, where $0.415 \leq y \leq 0.695$, the composition of the layer changing over the thickness of the layer continuously or incrementally, the work piece being a milling tool, a broaching cutter, a reamer, a turnover cutting plate for turning and milling, a molding tool, an injection-molding tool, a forming tool or a hot-forming tool, for machining a material.

Different AlCrN layers are known from the prior art. JP 09-041127 describes a wear-resistant layer of hard material of the following composition $(Al_{1-y}X_y)Z$, wherein $X = Cr, V$ or Mg , $Z = N, C, B, CN, BN$ or CBN and $0 < Y \leq 0.3$. This layer has been used advantageously to increase the useful life of turnover cutting plates.

In their paper "Multicomponent hard thin films...", "Thin films (Proc. 4th Int. Sympos. Trends and New Applications of Thin Films 1993) DGM Info.gesellschaft Oberursel. 1993.) p. 73, D. Schulz and R. Wilberg describe a CrAlN layer that, during a filling test, doubled the service life of a drill that was coated with TiAlN. The layer was precipitated by a hollow cathode process that, however, caused a pronounced variation

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of the chromium/aluminum distribution in the (CrAl)N layer because of an intermittent vapourization process..

In their paper titled "Oxidation Resistance of $\text{Cr}_{1-x}\text{Al}_x\text{N}$ and $\text{Ti}_{1-x}\text{Al}_x\text{N}$ Films," Surf. & Coat Tech., Vol. 165, 2, (2003), pp. 163-167, M. Kuwate et al. describe a $\text{Cr}_{1-x}\text{Al}_2\text{N}$ layer that, with a high aluminum content and wurzite structure, displayed improved resistance to oxidation as compared to conventional TiAlN layers.

In their paper titled "Investigations of Mechanical and Tribol Properties of CrAlN + C Thin Coatings Deposited on Cutting Tools," E. Lugschneider, K. Bobzin, and K. Lackner compare arced CrAlN layers and CrAlN layers that additionally have an even harder covering layer that contains carbon. All the layers display a coefficient of friction that rise rapidly to higher values.

It is the objective of the present invention to describe work pieces coated with $(\text{Al}_y\text{Cr}_{1-y})\text{X}$, for example, machining tools, cutting and forming tools, or components for machine building and die making, as well as a method for depositing such layers on a work piece, and at the same time avoid the disadvantages found in the prior art.

This includes work pieces, for example, that are of an adjustable, even or variable layer composition, at least with reference to the Al/Cr ratio, and which display greater wear resistance, at least in specific applications, than work pieces that have previously known layers.

In order to investigate the wear resistance of $(\text{Al}_y\text{Cr}_{1-y})\text{N}$ or -CN layers on different tools, Cr layers with various aluminum contents were deposited on different work pieces in Type RCS industrial machinery (Balzer company), as described in EP 1186681 in Figure 3-6, Description page 12, lines 26 to page 14, line 9.

To this end, the cleaned work pieces were secured, depending on their diameters, on two- or, in the case of diameters smaller than 50 mm, on threefold rotating substratum carriers, and two titanium targets and four

targets produced by powdered metallurgy which were of different AlCr alloys were built into six cathodic arc sources attached to the walls of the coating machinery. Next, the work pieces were initially brought to a temperature of approximately 500°C by irradiation heaters similarly installed in the machinery, and the surface was subjected to etching cleaning by applying a bias voltage of -100 to -200 V in an Ar atmosphere at a pressure of 0.2 Pa.

Subsequently, by operating the two Ti sources with a power of 3.5 kW (140 A) in a pure nitrogen atmosphere at a pressure of 3 Pa and a substrate voltage of -50 V for a period of five minutes, a TiN adhesive layer, approximately 0.2 µm thick, and an AlCrN layer was next deposited by operating the four AlCr sources with a power of 3 kW for a period of 120 minutes. In order to achieve an optimum layer transition, the sources were operated jointly for a period of two minutes. Then a nitride layer on an AlCr base was deposited in a pure nitrogen atmosphere, also at a pressure of 3 Pa and a substrate voltage of -50 V. In principle, the process pressure in each of these steps can be set in a range of 0.5 to approximately 8 Pa, preferably between 2.5 and 5 Pa, and either a pure nitrogen atmosphere or a mixture of nitrogen and a noble gas such as argon can be used for a nitride layers, or a mixture of nitrogen and a gas that contains carbon which can, if necessary, have a noble gas added to it, can be used for carbon nitride layers. Accordingly, in order to deposit layers that contain oxygen or boron, oxygen or a gas that contains boron can be added, as known.

Layer properties such as the crystal structure of the layer, and layer thickness, layer hardness, wear resistance, and the adhesion of AlCrN layers as a function of the chemical composition and crystal structure, as well as the composition of the targets that were used, are set out in Table 1. Process parameters such as target power, substrate bias voltage, and process pressure and temperature, are set out in Table 2.

Table 3 shows a measurement series in which the AlCr layers were deposited using targets with an Al/Cr ratio of 3, during the application of various substrate voltages. When this is done, the wear resistance as determined with a precision wear tester

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manufactured by Fraunhoferinstituts-IST Brunswick, when a calotte-grinding method that had been modified from DIN EN 1071-2 was used in order to determine the rate of wear. The details of this method can be found in Michler, Surf. & Coat. Tech., Vol. 163-164 (2003), p. 547, Col. 1, and Figure 1.

The present invention will be described in greater detail below on the basis of the drawings appended hereto. These drawings show the following:

Figure 1: XRD spectrum of an AlCrN with B1 and B4 structure;

Figure 2: XRD spectrum of an AlCrN as a function of the chemical composition Al/Cr:
A = 75/25, C = 50/50, D = 25/75.

As can be seen from Table 1 and Figure 1, and as is known from Kawate, "Micro-hardness and lattice parameter of $\text{Cr}_{1-x}\text{Al}_x\text{N}$," J. Vac. Sci. Technol. A 20 (2), Mar/Apr 2002, pp. 569-571, an hexagonal (B1) layer structure could be established for Al proportions of > 70 AT% of metal content in the layer, and a cubic (B1) lattice structure could be established for smaller Al proportions. For hexagonal layers, HV values of approximately 2100 $\text{HV}_{0.05}$ could be measured, although for cubic layer structures higher HV values of approximately 2800-3100 $\text{HV}_{0.05}$ could be measured (see Table 1). At higher Cr contents (Sample D), a hardness of approximately 2300 $\text{HV}_{0.03}$ was established. At this composition, as distinct from the AlN lattice with a high aluminum content, as is shown in Figure 2A, there is a CrN lattice as in Figure 2D.

Next, the service life of 6 mm HSS drills coated with AlCrN was determined on DIN 1.2080 steel material with a hardness of 230 HS at a feed of 0.12 mm and a cutting speed of 35 m/min as in Example 1 below. When this was done, it was revealed that, in contrast to the range of $(\text{Al}_y\text{Cr}_{1-y})\text{N}$ $0 < y \leq 0.7$ that was described as being particularly favorable in JP 09-041127, a chromium content of greater than 0.3 was advantageous. At chromium contents of greater than or equal to 0.8, the productivity fell once again for

this range of application because of the existing CrN lattice. In this case, the increase in service life of cubic as compared to hexagonal AlCrN layers amounted to 235%.

For layers in a transition range with an aluminum content between 60% and 75 at%, it is possible to adjust not only the preferred orientation, but also the underlying structure of the crystal lattice, by way of the process parameters. Thus, for example, in Test B (Table 2) at a low pressure of 1 Pa and a substrate voltage of -50 V, an hexagonal structure is generated, whereas in a pressure range from 3 Pa and the substrate voltage of -50 V, a cubic structure is generated. The hexagonal structure is thus deposited at a relatively lower bias voltage and low pressure, whereas the preferred cubic structure is deposited at higher pressure or at the amount according to a higher bias voltage. It is no longer possible to generate a cubic layer structure at higher aluminum contents.

Work pieces according to the present invention are thus distinguished by a cubic $(\text{Al}_y\text{Cr}_{1-y})\text{X}$ coating of the following composition: $\text{X} = \text{N}$ or CN , but preferably N , and $0.2 \leq y < 0.7$, preferably $0.40 \leq y \leq 0.68$. The layer structure is microcrystalline with a median grain size of approximately 20-120 nm.

The methods according to the present invention are distinguished by a sequence of operations in which a cubic $(\text{Al}_y\text{Cr}_{1-y})\text{X}$ layer of a composition as defined above is deposited. Target compositions of 75 to 15% aluminum content can be used advantageously for the cathodic arc method described above. At high aluminum contents, process parameters are to be set as described above in order to generate a cubic crystal structure.

When this is done, it is advantageous to use targets produced by powder metallurgy, in particular by cold pressing; these targets display greater strength than Al/Cr targets produced by fusion or sintering, which mostly contain brittle phases, particularly at high aluminum contents.

Such targets are cold pressed by mixing the powdered starting materials and then compacted by repeated forming, for example in a forging press, at temperatures below 660 °C during flow and low-temperature welding, and brought to an end state with a theoretical density of approximately 96-100%.

In addition, it could also be established that with an AlCrN coating that was deposited, for example, using targets of a composition $\text{Al/Cr} = 3$, wear resistance could be influenced by the substrate bias voltage. As the substrate bias voltage rises, resistance to abrasive wear declines (see Table 3). Even at a very small-substrate voltage, which is not shown explicitly in the table, of only a few volts (3-10 V and any intervening values), it is possible to achieve a clear improvement as compared to floating substrates (no external voltage supply). At approximately -20 V, wear resistance for $\text{AlCr} = 3$ reaches a maximum and falls once again at higher voltages. An optimal range of substrate voltage between 3 to 150 V, in particular between 5 and 40 V, can be derived from the test to determine wear behavior; a very low rate of wear between 0.4 and 1.0, in particular between 0.4 and $0.8 \text{ m}^3 \text{m}^{-1} \text{N}^{-1} 10^{-15}$ can be derived, was measured in these. The same applies for layers according to the present invention, which is to say, cubic layers with different Al/Cr composition at which no wear rates above $1.5 \text{ m}^3 \text{m}^{-2} \text{N}^{-1} 10^{-15}$ were measured. It should be noted however, that the wear resistance of floating layers deposited at a higher substrate voltage is significantly greater than the wear resistance of known TiAlN layers, the wear coefficient of which is significantly greater. For example, a wear rate of $3.47 \text{ m}^3 \text{m}^{-1} \text{N}^{-1} 10^{-15}$ was measured for a TiAlN layer deposited analogously to the AlCrN layers (Experiment 2, Al 47 at%, Ti 53 at%).

Using TiAl targets produced by the method described above, in particular by powder metallurgy, it is possible to deposit layers having a low level of roughness. The measured Ra values lie in the range between 0.1 and 0.2 μm and are thus in the same range as comparably produced CrN layers. Further smoothing of the layers will result from the use of a magnetic field generator that includes two magnetic systems of opposing polarity and which is so configured that the B_1 component of the resulting magnetic field that is perpendicular to the surface displays essentially constantly small

values across the major part of the service, or is zero. At the same time, the value of the perpendicular B_1 component is less than 30 and preferably less than 20, and in particular is less than 10 Gauss. The Ra value of the (Al_yCr_{1-y}) X layers that are deposited thereby lie in the range from 0.05 to 0.15 μm . The magnetic field was generated by two coils of opposing polarity arranged coaxially behind the target.

In addition, during the precipitation of (Al_yCr_{1-y}) X layers, other preferably highly conductive nitride or metallic adhesive layers can be used, or the use of such an adhesive layer can be dispensed with for certain applications. For example, in order to achieve particularly high productivity, an AlCr-/AlCrN- adhesive layer can be applied in place of a TiN adhesive layer, which makes it possible to provide all the arc sources of a coating machinery with AlCr targets and increase the coating rates.

In the same way, it is also possible to deposit gradient layers with, for example, aluminum contents that increase towards the surface, if two target types with a different Al/Cr ratio are used or if, proceeding from a Cr and/or CrN adhesive layer, a change in the layer composition is achieved by, for example, continuous or incremental regulation of the corresponding target powers of a coating chamber that is equipped with Cr as well as AlCr targets. What is important for an industrial application of such a coating system is the possibility of setting up the process parameters so that they can be replicated essentially across the whole coating sequence, and thus across the whole thickness of the layer. Minimal variations in the composition, like those brought about by substrate movement, for example, on a single or multiple rotating substrate carrier, can be used additionally for nanostructuring that is formed partially or across the whole thickness of the layer, i.e., lamination in the nanometer or micrometer range. If unalloyed chromium and aluminum targets are used, a more coarsely structured hard layer will be precipitated than is the case when alloyed AlCr targets are used.

Less suitable for this purpose, however, are processes known from the prior art in which, for example, the vaporization process of a least one component is difficult to manage or is intermittent, since no reproducible layer quality can be achieved thereby.

It is, of course, possible to produce layers of this kind using other vacuum coating machinery or, for example, by sputtering processes, although ionization of the process gases, which is in principle lower, must under certain circumstances be balanced out by known measures such as special adhesive layers, additional ionization, etc., in order to achieve comparable layer adhesion.

In principle, using the $\text{Cr}_{1-x}\text{Al}_x\text{N}$ layers with a cubic structure it is possible to coat very different work pieces. Examples of these are cutting tools such as milling tools, hob cutters, round-head, flat, and profile milling tools, as well as drills, threading taps, reamers, and turnover cutting plates for turning and milling work, or forming tools such as, for example, stamps, matrices, drawing rings, ejector cores or thread formers. Injection molding tools, for example, for metal injection molding alloys, plastics, or thermoplastic, in particular injection molding tools such as those used for producing molded plastic parts or data carriers such as CDs, DVDs etc., can also be used and can to advantage be protected by layers of this kind. A further range of applications includes components that demand wear resistance which under certain circumstances is coupled with great resistance to oxidation. For example, sealing rings, pistons, stamps, gear wheels, and valve gear such as barrel tappets and rocker arms, or needles for injectors, compressor shafts, pump spindles, or many components to which one or plurality of meshing elements are attached.

Additionally, because of the behavior of $(\text{Al}_y\text{Cr}_{1-y})\text{X}$ layers, which is, in principle, similar, an improvement in wear behavior can also be anticipated if in the following layer systems target composition and coating parameters are so selected that a cubic layer structure is achieved.

$(\text{Al}_y\text{Cr}_{1-y})\text{X}$ wherein $\text{X} = \text{N}, \text{C}, \text{B}, \text{CN}, \text{BN}, \text{CBN}, \text{NO}, \text{CO}, \text{BO}, \text{CNO}, \text{BNO}, \text{CBNO}$, preferably, however, N or CN , and $0.2 \leq Y < 0.7$, preferably $0.40 \leq Y \leq 0.68$

(Al₆₆Cr₃₄) NO layers with different N/O ratios were deposited thus and then their layer properties were tested. The coating parameters were selected so as to be similar to those selected above. The total pressure was between 1 and 5 Pa at an oxygen flow between 20 and 60 sccm (remainder nitrogen), the substrate voltage was between -40 to -150 V, the temperature was 450°C, and the source power at a current of 140 A was set at 3.5 kW. This produced layers with O/N ratios of approximately 0.2, 0.6, and 2.2. The layers with the low oxygen content proved to be superior in different milling tests. The results were clearly better than the service lives achieved with conventional TiN or TiCN.

Because of the improved slip properties of the (Al_yCr_{1-y}) X layers discussed above, there is the possibility -- which is interesting from both economic and ecological standpoints -- of dispensing with lubricants when operating tools, in particular cutting tools and forming tools, or else use only minimal quantities of such lubricants. From the economic standpoint, one must take into account the fact that the costs for cooling lubricant, in particular in the case of cutting tools, can be greater than the cost of the tool itself.

An even more far-reaching possibility for improving the slip properties of a layer system according to the present invention, which contains an (Al_yCr_{1-y}) X layer, will result if a slip layer is applied as the outermost layer. It is advantageous if the slip layer is of a lower hardness than the (Al_yCr_{1-y}) X layer and possesses break-in characteristics.

The slip-layer system can be built up from at least one metal or from a carbide of a least one metal and dispersed carbon, MeC/C, the metal being a metal from the group IVb, Vb and/or VIb and/or silicon. For example, a WC/C cover layer of a hardness that can be adjusted between 1000 and 1500 HV, and which possesses excellent break-in characteristics, is well-suited for this. Cr/C layers display a similar behavior, although at a somewhat higher coefficient of friction.

In the case of deep-hole drill bits coated in this way, after the production of one to three bore holes, it was possible to see excellent break-in smoothing which, up to now, could only be achieved by means of costly mechanical machining. Such properties are

interesting, in particular, for component applications that are subjected to slip, friction, or rolling stresses, with little lubrication or when running dry, or if an uncoated opposing body is to be protected at the same time.

Additional possibilities for forming a finishing slip layer are metal-free, diamond-like, carbon layers, or layers containing MoS_x , WS_x , or MoS_x or MoW_x layers that contain titanium.

As discussed, the slip layer can be applied directly on the $(\text{Al}_y\text{Cr}_{1-y})\text{X}$ layer or after application of an additional adhesive layer, which can be formed as metal, nitride, carbide, or carbon nitride, or as a gradient layer with, for example, a continuous transition between $(\text{Al}_y\text{Cr}_{1-y})\text{X}$ and slip layer, in order to bring about the best possible adhesion of the layer bond.

For example, after the application of a sputtered or arced Cr or Ti adhesive layer, WC/C or CrC/C layers can be produced, advantageously by sputtering of WC targets during the addition of a gas that contains carbon, when the proportion of gas that contains carbon is increased over time in order to arrive at a greater proportion of free carbon in the layer.

Further advantageous applications for different $(\text{Al}_y\text{Cr}_{1-y})\text{X}$ hard coated tools are described below, their use for different cutting operations serving as examples.

Example 1: Milling structural steel

Tool: Shank-type cutter

Diameter $D = 8$ mm, tooth count 3

Material: Ck 45 structural steel, DIN 1.1191

Milling parameters:

Cutting speed: $v_c = 200/400$ m/min

Feed speed v_t : 2388/4776 mm/min

Width of radial contact a_r : 0.5 mm

Width of axial contact: a_p : 10 mm

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Cooling: Emulsion 5%

Process: Constant speed milling

Wear criterion: Free-surface wear $VB = 0.12$ mm

Experiment Nr. ①	Metallanteil [At%] ② Schicht			Standzeit t bei $VB = 0.12$ mm in Minuten ③	
	Ti	Al	Cr	$v_c = 200$ m/min	$v_c = 400$ m/min
1 (TiCN)	100	-	-	71	9
2 (TiAlN)	53	47	-	42	15
3 (AlCrN) B1	-	69.5	30.5	167	40
4 (AlCrN) B4	-	72	28	41	7
5 (AlCrN) B1	-	41.5	58.5	150	12
6 (AlCrN) B1	-	19	81	17	4

Key: 1 – Experiment Number; 2 – Proportion of metal (At%) Layer; 3 - Standard times t at $VB = 0.12$ mm in minutes

Example 1 shows a comparison of the standard times of coated HM milling tools that were tested using different cut parameters.

It is clear that the AlCrN layers referred to have longer service lives as compared to the layer systems used in industry up to the present time, such as TiCN and TiAlN. In addition, the results show that, as in Example 1, the service life behavior improves as the aluminum content increases, to the extent that the cubic B1 structure is maintained, as is the case in Example 1 (compare Experiments No. 3, 5, 6). This can be attributed above all to the improved resistance to oxidation and hardness that can be seen with the increasing aluminum content (see Table 1). The very good resistance to oxidation of the AlCrN coating becomes particularly noticeable in the range of dry and high-speed machining (e.g., $v_c = 400$ rpm). Furthermore, this test, too, shows that when the crystal lattice is collapsed from B1 to B4, the structure of the wear behavior is degraded (compare Experiments 3 and 4).

Example 2: Milling austenitic steel

Tool: Shank-type cutter, hard steel

Diameter $D = 8$ mm, tooth count 3

Material: X 6 CrNiMoTi 17 12 2 austenitic steel, DIN 1.4571

Milling parameters:

Cutting speed $v_c = 240$ m/min

Tooth feed speed $f_z = 0.08$ mm

Width of radial contact $a_p = 0.5$ mm

Width of axial contact: 10 mm

Cooling: Emulsion 5%

Process: unidirectional milling

Wear criterion: free-surface wear $VB = 0.1$ mm

Experiment Nr. ①	Metallanteil (At%) ② Schicht			Standweg l_r bei $VB = 0.1$ mm in Meter ③
	Ti	Al	Cr	
7 (TiCN)	100	-	-	33
8 (AlTiN)	35	65	-	45
9 (AlCrN) B1	-	69,5	30,5	54

Key: 1 – Experiment Number; 2 – Proportion of metal (At%) Layer; 3 – Standard path l_r at $VB = 0.1$ mm in meters

Example 2 shows a comparison of the service lives of coated HM milling tools. Here, in the same way as with the AlCrN layer, it is possible to achieve an improvement of wear as compared to the layers of hard material used in industry. In the case of AlCrN, the improvement in service life could be achieved, on the one hand, by a lesser inclination -- as compared to the Ti in TiAlN layers -- of the second alloying element Cr to spread, which up to now remains unproved and, on the other hand, by the clearly good resistance to wear displayed by AlCrN layers (A, B, D) according to the present invention, as set out in Table 1, at a simultaneously high degree of hardness.

Example 3: Milling hardened steel

Tool: Ball-head cutter

Diameter $D = 10$ mm, tooth count $z = 2$

Material: K 340 (62 HRC), corresponding to C 1.1%, Si 0.9%, Mn 0.4%, Cr 8.3%, Mo 2.1%, Mo2.1%, V 0.5%

Milling parameters:

Cutting speed $v_c = 0 - 120$ m/min

Tooth feed speed $f_x = 0.1$ mm

Width of radial contact $a_s = 0.2$ mm

Width of axial contact a_p : 0.2 mm

Cooling: Dry

Process: Unidirectional and bidirectional milling, planishing

Wear criterion: Free-surface wear $VB = 0.3$ mm

Experiment Nr. ①	Metallanteil [At%] ② Schicht			Standweg l_s bei $VB = 0.3$ mm in Meter ③
	Ti	Al	Cr	
10 (TiAlN)	53	47	-	70
11 (AlCrN) B1	-	69.5	30.5	90

Key: 1 – Experiment Number; 2 – Proportion of metal (At%) Layer; 3 - Standard path at $VB = 0.3$ mm in meters

Example 4: Rough milling tool steel

Tool: Shank-type cutter, hard steel

Diameter $D = 10$ mm, tooth count $z = 4$

Material: X 38 tool steel X 38 CrMoV 5 1, DIN 1.2343 (50 HRC)

Milling parameters:

Cutting speed $v_c = 60$ m/min

Tooth feed speed $f_x = 0.02$ mm

Width of radial contact $a_{??} = 2$ mm

Width of axial contact a_p : 10 mm

Cooling: Dry

Process: Unidirectional milling, roughing

Wear criterion: Free-surface wear $VB = 0.1$ mm

Experiment Nr.	Metallanteil [At%] Schicht			Standweg l_s bei $VB = 0.1$ mm in Meter
	Ti	Al	Cr	
12 (AlTiN)	35	65	-	90
13 (AlCrN) B1	-	69.5	30.5	130

Key: 1 – Experiment Number; 2 – Proportion of metal (At%) Layer; 3 - Standard path at $VB = 0.1$ mm in meters

Example 3 and Example 4 display an improved standard path of the AlCrN layer as opposed to the TiAlN layers used in industry. AlCrN is particularly well-suited for dry machining that imposes great demands with respect to resistance to oxidation and resistance to wear.

Example 5: Drilling in tool steel

Tool: HSS drill bit (S 6-5-2) Diameter D = 6 mm,

Material: X 210 tool steel, Cr 12 DIN 1.2080 (230 HB)

Cutting speed $V_c = 35$ m/min

Drilling parameters:

Feed $f = 0.12$ mm

Bore hole depth $z = 15$ mm, blind hole

Cooling: Emulsion 5%

Wear criterion: torque shutoff (corresponding to erosion wear of ≥ 0.3 mm)

Experiment Nr. ①	Metallanteil [At%] Schicht ②		Standweg ③ [Lochzahl / μ m Schichtdicke]
	Al	Cr	
14 (AlCrN) B1	19	81	21
15 (AlCrN) B1	41,5	58,5	52
16 (AlCrCN) B1	41,5	58,5	65
17 (AlCrN) B1	69,5	30,5	108
18 (AlCrN) B4	72	28	46

Key: 1 – Experiment Number; 2 – Proportion of metal (At%) Layer; 3 - Standard path (hole count/ μ m layer thickness)

Example 6 shows a comparison of the hole count, standardized on the basis of layer thickness and achieved with HSS drill bits with $Al_yCr_{1-y}N$ / $Al_yCr_{1-y}CN$ layers with different Al contents.

The layers were produced with the parameters set out in Table 2. As the aluminum content increase, there was an increase in the service life up to not quite 70% aluminum in the metal content. In the case of a further increase, and thus the precipitation of a layer with an hexagonal crystal structure, performance falls off. In the range between 41.5 and

69.5% aluminum (Experiment 15, 17) it is possible to establish a clear increase in performance in this application as compared to the prior art (Experiment 18).

Example 6: Deep hole drilling 5 x D in Ck 45

Tool: Drill bit hard metal, Diameter D = 6.8 mm,

Material: Structural steel, 1.1191 (Ck 45)

Drilling parameters:

Cutting speed $v_s = 120$ m/min

Feed $f = 0.2$ mm

Bore hole depth $z = 34$ mm, blind hole

Cooling: Emulsion 5%

Wear criterion: Erosion wear $VB = 0.3$ mm

Experiment Nr. ①	Metallanteil [At%] ② Schicht			Standzeit t bei $VB = 0.3$ mm in ③
	Ti	Al	Cr	Anzahl Bohrlöcher
18 (TiAlN)	70	30	-	890
19 (TiAlN)	53	47		1135
20 (AlCrN) B1	-	69,5	30,5	2128

Key: 1 – Experiment Number; 2 – Proportion of metal (At%) Layer; 3 - Standard time t at $VB = 0.3$ mm in number of bore holes

Example 6 shows an improved service life of the AlCrN layer as compared to the TiAlN layers, as used industrially, in a drilling application. Here, the improved resistance to abrasive wear of the AlCrN coating according to the present invention becomes obvious. In addition, drill bits coated as in Experiment No. 20 were provided with a WC/carbon slip layer after application of a Cr adhesive layer, whereupon a clearly improved service life could be achieved under otherwise identical test conditions. Torque measurements conducted at the same time revealed a clearly smaller torque moment than is observed without a slip layer. In addition, it is possible to see a better surface quality and, until shortly before the end of the service life, no coloration brought about by excessive temperature stress.

Example 7: Tapping 2xD in austenitic steel

Tool: HSS screw tap , thread dimension M8

Material: Austenitic steel, 1.4571 (X6CrNiMoTi 17/12/2)

Drilling parameters:

Cutting speed $v_c = 3$ m/min

Thread depth: 2XD

Thread type: blind hole

Number of threads: 64

Cooling: Emulsion 5%

Wear criterion: Torque progression over thread count, visual assessment of wear after 64 threads.

Experiment Nr. ①	Metallanteil (At%) Schicht ②			Ø max. ③ Schnittmoment [Nm]	Optischer Verschleiß (1) ④
	Ti	Al	Cr		
21 (TiCN)	100	-	-	4,72	+
22 (AlCrN)B1	-	69,5	30,5	4,05	++
23 (AlCrN)B1	-	41,5	58,5	4,23	+++
24 (AlCrN)B1	-	19	81	4,27	+

Key: 1 – Experiment Number; 2 – Proportion of metal (At%) Layer; 3 – Ø maximum cut moment (Nm); 4 – Visual wear (1)

Explanation of (1)

+ Wear behaviour satisfactory during tapping

++ Wear behaviour good during tapping

+++ Wear behaviour very good during tapping

A reduction of the average maximal cutting moment is achieved with all the layers compared to the prior art. In addition, because of the very good wear resistance of the layers with the higher aluminum content, there is improved wear behavior compared to TiCN. Certainly, in this example, presumably because of the adhesive tendency of the aluminum, which leads to material spreading and subsequently to layer breakdown, the

layer in Experiment 23 displayed a better wear image than Experiment 22. Additionally, screw taps coated as in Experiment Nos. 22 and 23, were provided with a WC/carbon slip layer or, after application of a Ti adhesive layer, were provided with a MoS₂ layer containing Ti, whereby an improvement in service life and better surface quality of the machined material could be achieved under otherwise equal test conditions.

Example 8: Hobbing in CrMo steel

Tool: Hob milling machine

Material: DIN 86-7-7-10 (ASP60)

Diameter: D = 80 mm, length L = 240 mm, Modulus m = 1.5

25 chip grooves

Angle of engagement $\alpha = 20^\circ$

Reference profile 2, tooth count 50, thread width 25 mm

Material: Cr-Mo steel DIN 34CrMo4

Cutting parameters:

Cutting speed $V_c = 260$ m/min

Feed: 2 mm/U

Piece count: 300

Cooling: dry cut, compressed air to remove chips.

Experiment Nr. ①	Metallanteil [At%] Schicht ②			Verschleissmarkenbreite in [mm] ③	
	Ti	Al	Cr	Freiflächenv. ④	Kolkverschleiss ⑤
25 (TiCN)	100	-	-	0,32	0,062
26 (TiAlN)	53	47	-	0,25	0,042
27 (AlCrN)B4	-	72	28	0,29	0,053
28 (AlCrN)B1	-	19	81	0,26	0,051
29 (AlCrN)B1	-	41,5	58,5	0,13	0,022
30 (AlCrN)B1	-	69,5	30,5	0,14	0,018

Key: 1 – Experiment Number; 2 – Proportion of metal (At%) Layer; 3 – Width of wear marks in (mm); 4 – Free surface wear; 5 – Erosion wear

In Tests 25 to 30, different hobbing cutters made from high-speed steel (HSS) produced by powder metallurgy and with different layer systems were tested during dry cutting. A significant improvement as compared to known TiCN or TiAlN coated cutters could be

achieved with tools coated as in the present invention (Experiment 29 and Experiment 30). In the same way, it must be acknowledged that AlCrN layers with a low (No. 28) to high aluminum content offer a lesser degree of protection against wear if an hexagonal crystal structure is present (No. 27).

The following examples, Nos. 31 to 33, also shows the clear superiority of an AlCrN layer according to the present invention, with a cubic crystal lattice in the essentially stoichiometric nitrogen proportion and an aluminum content of 66%. Milling cutters made from PM HSS or hard metal were tested both for dry and for emulsion-lubricated cutting.

Experiment No. 31: Hobbing

Tool: PM HSS

Diameter: $D = 80$ mm, length $L = 240$ mm

Cutting speed: 180 m/min

$(Al_{0.42}Ti_{0.56})N$, balinite NANO:	1809 pieces
$(Al_{0.63}Ti_{0.39})N$, balinite X.CEED	2985 pieces
$(Al_{0.65}Cr_{0.36})N$	5370 pieces

Experiment No. 32 Hobbing

Tool: Hard metal (HM)

Diameter: $D = 60$ mm, length $L = 245$ mm

Modulus: 1.5

Angle of engagement $??? = 20^\circ$

Material: 42 CrMo4

Cutting speed: 350 m/min, dry

$(Al_{0.41}Ti_{0.39})N$, balinite X.TREME	1722 pieces
$(Al_{0.53}Ti_{0.37})N$, balinite X.CEED	2791 pieces
$(Al_{0.65}Cr_{0.34})N$	> 3400 pieces

Experiment No. 33: Hobbing

Tool: PM HSS

Diameter: $D = 80$ mm, length $L = 240$ mm

Modulus: 2.5

Material: 16MnCr5

Cutting speed: 140 m/min, emulsion

TiCN, BALINITE B: 1406 pieces

(Al_{0.42}Ti_{0.56})N, balinite NANO: 1331 pieces

(Al_{0.66}Cr_{0.34})N 1969 pieces

Additional tests, not described herein, showed that even at still higher speeds, up to $v_s = 450$ m/min, durability remained good. Standard times of hard-metal hob cutters could also be improved noticeably during wet and, in particular dry, machining.

Example 9: Rough milling tool steel

Tool: Shank-type cutter

Diameter $D = 10$ mm, tooth count $z = 4$

Material: X 40 tool steel CrMoV 5 1, DIN 1.2344 (36 HRC)

Milling parameters:

Cutting speed $v_c = 60$ m/min

Tooth feed speed $f_a = 0.05$ mm

Width of radial contact $a_x = 3$ mm

Width of axial contact a_p : 5 mm

Cooling: Emulsion 5%

Process: Unidirectional milling, roughing

Wear criterion: Free-surface wear $VB = 0.1$ mm

Experiment Nr. ①	Metallanteil (At%) ② Schicht			Standweg l, bei VB = 0,1 mm in Meter ③
	Ti	Al	Cr	
34 (AlTi)N	35	65	-	6 - 8
35 (AlTi)N	58	42	-	3 - 4
36 (AlTi)CN	50	50	-	3 - 4
37 TiCN	100	-	-	8 - 11
38 (AlCr)N	HS	64	36	12 - 21
39 (AlCr)N	puls	66	34	21 - 28
40 (AlCr)N	-	66	34	12 - 18

HS = Adhesive layer of TiN

puls = pulsed

Key: 1 – Experiment Number; 2 – Proportion of metal (At%) Layer; 3 - Standard path
l ??? at VB = 0.1 mm in meters

Example 10: External machining of hardened carburizing steel

Tool: Turning tool with soldered-in CBN insert

Material: Carburizing steel 16 MnCr 5, DIN 1.7131 (49 – 62 HRC)

Turning parameters: hard-soft machining with interrupted cut and partially thinner wall
thickness

Cooling: dry

Wear criterion: piece count up to achievement of free-surface wear of VB = 0.1 mm

Experiment Nr. ①	Metallanteil (At%) ② Schicht			Standmenge bei VB = 0,1 mm ③
	Ti	Al	Cr	
41 (AlTi)N	35	65	-	90
42 (AlCr)N		66	34	144

Key: 1 – Experiment Number; 2 – Proportion of metal (At%) Layer; 3 - Standard
quantity at VB = 0.1 mm in meters

Similar results were also obtained with cermets produced by powder metallurgy
consisting of a TiN, TiC, or a Ti(CN) hard phase, to which molybdenum and or tantulum
was added. Ni or Ni/Co was used as a binding phase.

Example 11: Thread forming in galvanized steel

Experiment No.: 43:

Tool: HSS MS thread former

Material: DC01 corresponding to DIN 1.0330 St 12 ZE

Tapping drill hole diameter: 8.34 mm

Cutting parameter: 55 m/s

Cutting speed: 2000 rpm

Return speed: 3600 rpm

Lubrication: S26 CA

TiN: 3200 threads

TiCN 3200 threads

TiAlN 3500 threads

(Al_{0.66}Cr_{0.34})N 8800 threads

Tests with coated CBN (cubic boron nitride) or cermet tools: turnover cutting plates of different CBN sintered materials with a CBN content between 30-99vol-%, remainder binding agent, were coated, on the one hand, with known TiAlN layers as in Experiment 8, and, on the other hand, with AlCrN layers as in Experiment 3, Experiments 3, and Experiment 6. Because of the non-conductive nature of the CBN sintered material, a pulsed substrate bias in the middle frequency range, preferably in a frequency range from 20 to 250 kHz, was applied for the etching and coating process.

For materials with a CBN content of up to 90%, a bonding agent powder was used that consisted of at least one of the elements from the following group: nitride, carbide, boride, and oxide of the Ti, V, or Cr group, i.e., IVa, Va, and VIa elements, as well as aluminum or aluminum compounds.

For materials with a CBN content of up to 95% a bonding agent powder was used that consisted of titanium nitride and the least one of the elements from the following group: cobalt, nickel, wolfram carbide, aluminum, or an aluminum compound.

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For materials with a CBN content of greater than 90%, a bonding agent powder was also used, consisting of titanium nitride and at least one of the elements from the following group: boride or boron nitride of the alkali or earth-alkali metals.

During turning and milling tests conducted subsequently it was, in most instances, possible to see wear behavior that was greatly improved as compared to TiAlN layers. It was the same in the course of a particularly exhaustive external machining test in which a shaft of complex geometry that was only partially hardened and was machined in part during interrupted cutting.

Example 12: Hot forging

Tool: 4 forging jaws 220x43x30 mm, drill W350, hardness 54 HRC, 4 tools engaged simultaneously

Work piece: round stock, diameter 22 mm, material 42 CrMo4

Method: Temperature of work piece before forming 1050°C Pressing force 57 t per jaw

Cooling: Molicote™ + graphite

Experiment Nr. ①	Metallanteil [At%] ② Schicht				③ Standmenge (Stückzahl)
	Ti	Al	Cr	Nb/Si V/W	
43 unbesch.	-	-	-	-	500
44 TiAlN	58	42	-	-	900
45 AlCrN	-	64	36	-	1900
46 AlCrVN	-	63	31	6	1500
47 AlCrSiN	HS	65	26	9	1800
48 AlCrNbN	-	62	31	7	1550
49 AlCrNN	-	65	26	9	1630
50 AlCrYN	-	62	31	7	1730
51 AlCrMoN	-	62	31	7	1460

HS = Adhesive layer of TiN

Key: 1 – Experiment Number; 2 – Proportion of metal (At%) Layer; 3 - Standard quantity (piece count)

Example 13: Hot bordering

Tool: HM flowdrill, diameter 10 mm

Method: The tool was pressed against the work piece at 2800 rpm, at 3000 N. The work piece was brought to red heat, i.e., approx. 1000°C and formed by kinetic energy.

Experiment Nr. ①	Metallanteil [At%] Schicht ②				③ Standmenge (Stückzahl)
	Ti	Al	Cr	Nb/Si V/W	
52 unbesch.	-	-	-	-	500
53 TiAlN	58	42	-	-	900
54 AlCrN	-	64	36	-	1700
55 AlCrVN	-	63	31	6	1530
56 AlCrSiN	HS	65	26	9	1650
57 AlCrNbN	-	62	31	7	1450
58 AlCrWN	-	65	26	9	1390
59 AlCrYN	-	62	31	7	1660
60 AlCrMoN	-	62	31	7	1340

HS = Adhesive layer of TiN

Key: 1 – Experiment Number; 2 – Proportion of metal (At%) Layer; 3 - Standard quantity (piece count)

Example 14: Stamping

Tool: 1.2379 slot punch 20 x 10 mm

Work piece: TRIP 700, 1.2 mm thick

Method: Shearing, cutting gap 10%, 500 strokes/min

Cutting force: 20 kN

Experiment Nr. ①	Metallanteil [At%] Schicht ②				③ Standmenge (Stückzahl)
	Ti	Al	Cr	Nb/Si V/W	
61 unbesch.	-	-	-	-	100000
62 TiAlN	58	42	-	-	200000
63 AlCrN	-	64	36	-	350000
64 AlCrVN	-	63	31	6	370000
65 AlCrSiN	HS	65	26	9	280000
66 AlCrNbN	-	62	31	7	300000
67 AlCrWN	-	65	26	9	340000
68 AlCrYN	-	62	31	7	320000
69 AlCrMoN	-	62	31	7	290000

HS = Adhesive layer of TiN

Tabelle 1

Versuchs- bez. ①	Al/Cr- verhältnis im Target ②	Kristall- struktur ③	Al At%	Cr At%	Schicht- dicke ④ [µm]	HV 0.03	AV [mN·N ⁻¹ ·10 ⁻¹⁵]	Haftung ⑤
A	3	B1	69.5	30.5	3.2	3200	0.8	HF1
B	3	B4	72	18	4.2	2100	1.0	HF1
C	1	B1	41.5	58.5	3.8	2800	1.5	HF1
D	0.33	B1	19	81	4.2	2300	2.5	HF1

Tabelle 2

Versuchs- bez. ①	Al/Cr- verhältnis im Target ②	P _{Power} [kW]	Unterdruck [N]	P _{Dep} [Pa]	Temp. [°C]
A	3	3	-50	3	450
B	3	3	-50	1	450
C	1	3	-50	3	450
D	0.33	3	-50	3	450

Tabelle 3

Substrat- vorspannung ① [V]	AV [mN·N ⁻¹ ·10 ⁻¹⁵]
0	1,23
-20	0,47
-80	0,76
-100	0,83
-150	2,0
-200	1,36

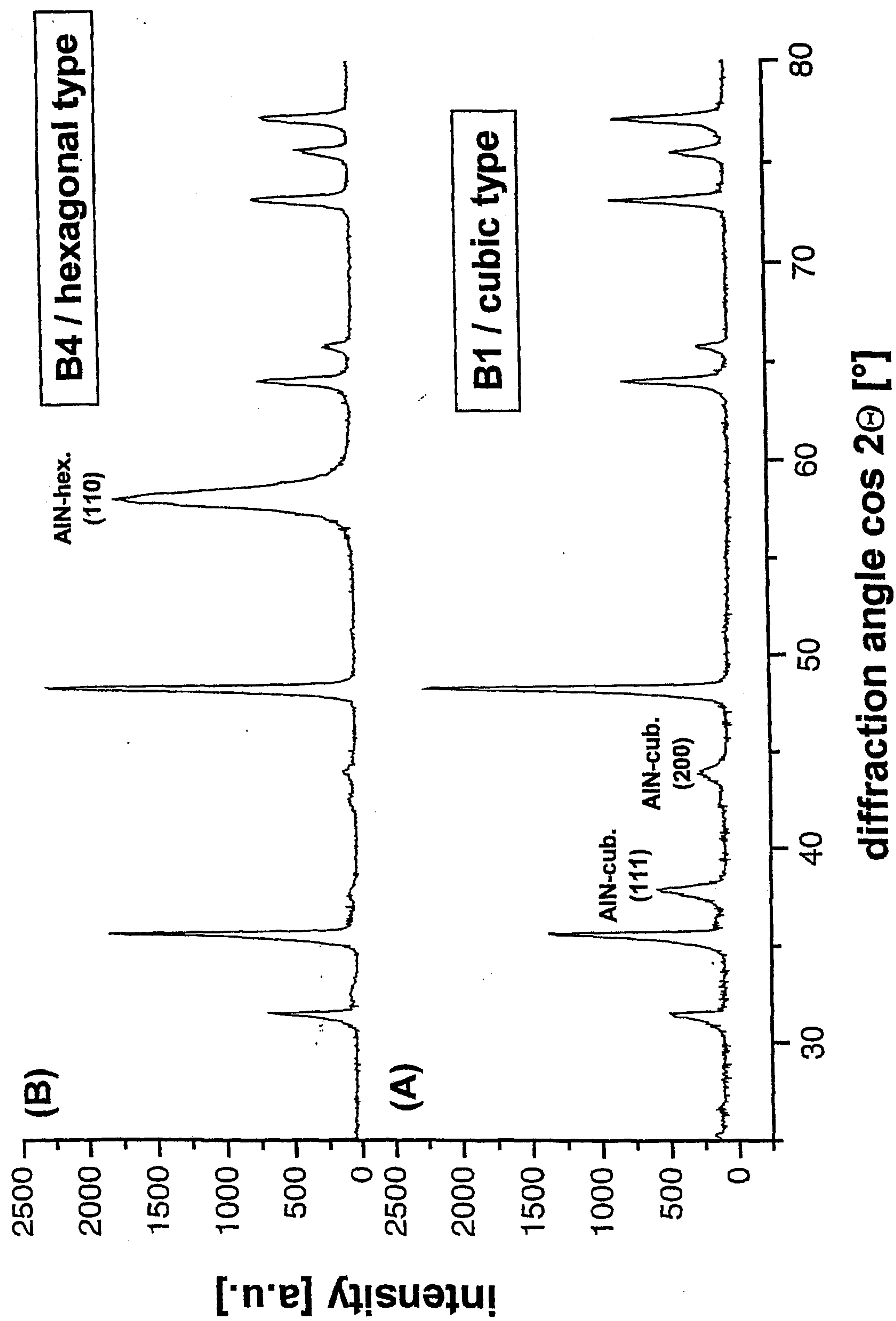
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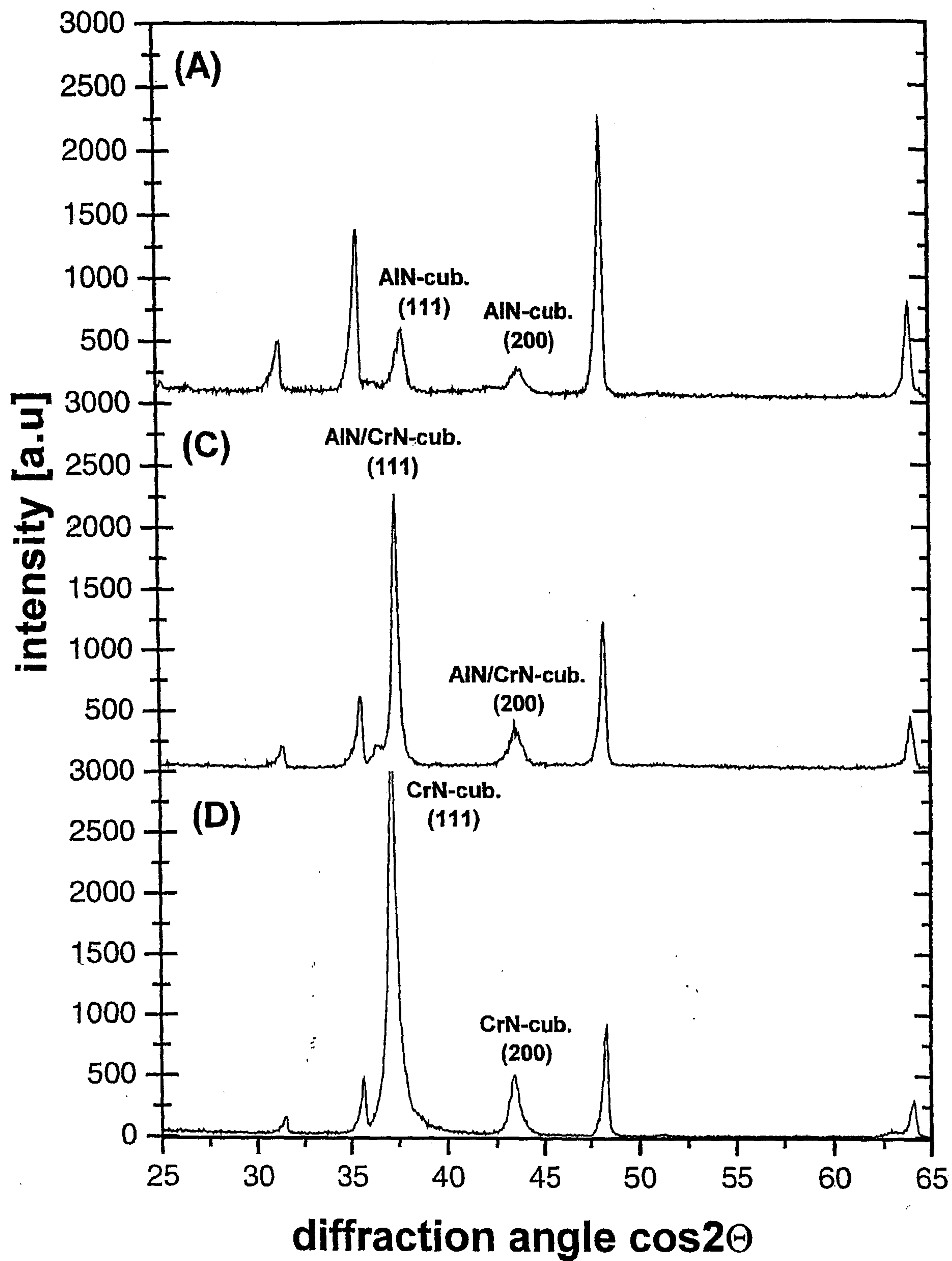
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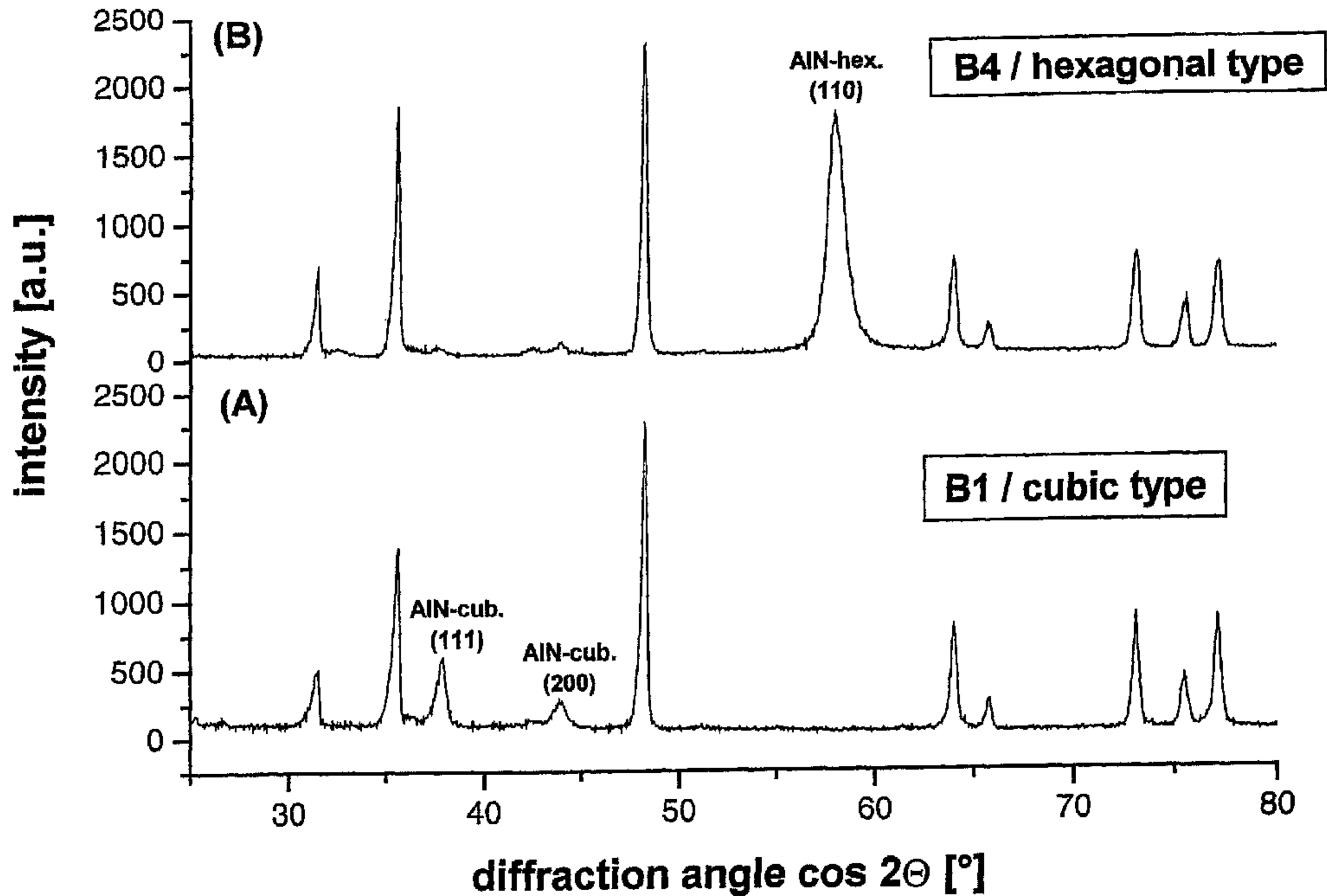
1. A PVD method for depositing at least one (Al_yCr_{1-y}) N layer on a work piece, with $0.415 \leq y \leq 0.695$, wherein the work piece is introduced into a vacuum coating machinery with at least two compositionally different Al_zCr_{1-z} targets with $0.25 \leq z \leq 0.75$
5 and held at a pressure of 0.5 - 8 Pa during the addition of a reactive gas that comprises nitrogen, carbon, boron, or oxygen and the application of a substrate voltage between -3 to -150 V, applied as an arc or sputter source, such that the layer composition within at least one (Al_yCr_{1-y}) N layer changes continuously or incrementally across the thickness of the layer.
2. The PVD method according to claim 1, wherein the reactive gas comprises
10 nitrogen or oxygen.
3. The PVD method according to claim 1 or 2, wherein the substrate voltage is pulsed.
4. The PVD method according to any one of claims 1 to 3, wherein at least one of the Al_zCr_{1-z} targets is a target produced by powder metallurgy.
- 15 5. The PVD method according to claim 4, wherein at least one of the Al_zCr_{1-z} targets is fabricated from mixed powder starting materials which are first cold pressed at temperatures below 660°C and then pressed by multiple reforming to reach an end state with a theoretical density of 96 - 100%.

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Fig. 1 . X-Axis: diffraction angle 2θ (unit: degrees)

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Fig. 2 - X-Axis: diffraction angle $\cos (2 \theta)$, unit: degrees



X-Axis: diffraction angle $\cos (2 \theta)$, unit: degrees