On the Structure of (Ti, Al)N-PVD Coatings*

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Introduction

The development of new materials, particularly in the field of refractory hard compounds, is limited by various metallurgical interrelationships. In consequence new materials can only be produced by means of sophisticated and therefore less economical production methods. The deposition of solids from the vapor phase enables the production of a wide range of new materials without having the problems of liquid phases.

These PVD (Physical Vapor Deposition) processes are gaining more and more prominence in semiconductor and coating technology. Materials with high melting points and high reactivity can be deposited easily. Homogeneous multicomponent phases as well as multilayer coatings can be produced with completely new material properties. In reactive mode the stoichiometry of hard phases can be varied easily. By controlling the substrate temperature, materials can be deposited in different structures as there is the amorphous microcrystalline and the crystalline structures. The following investigation deals with the constitution of (Ti, Al)N-PVD coatings, which cannot be achieved by any other production method.

Most of the recent publications concerning wear-resistant hard compound films deal with TiC or Ti(C, N), and in particular TiN. Deposited by CVD or various PVD-techniques these titanium-based hard coatings achieved a high standard of performance. Due to major improvements of the processes such as magnetron sputtering, sputter ion plating, and various other evaporation techniques, a wide range of substrate materials have been coated with excellent adhesion and good reproducibility. A lot of activities in the past have been concerned with process development and with application of TiN on various substrate materials as well as on parts of complicated geometry. Little work however has been done on the improvement of the coating material itself. Although TiN shows good wear and oxidation resistance, new materials with significantly improved properties concerning wear and corrosion resistance will be able to replace TiN at numerous applications.

In order to deposit multicomponent films as the ternary (Ti, Al)N, sputtering seems to be the most appropriate technique. In contrast to other PVD processes the trans-

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formation of the original material into the gaseous state does not involve an intermediate liquid phase, but instead occurs directly as a result of impulse ablation.

New Multicomponent Hard Materials

One promising idea concerning the further development of current wear-resistant coatings deals with the production of compositions of a more complicated structure as there are ternary and quaternary phases. This could be stated by the cutting performance of Ti(C, N) coated carbide inserts (*1*). Instead of adding further metalloids to the titanium nitrogen composition, aluminium as a substitute of titanium has been embedded with good results concerning wear and oxidation resistance (*2, 3*). Aluminium was chosen, as the formation of stable aluminium oxide layers on top of the (Ti, Al)N coating could be expected when exposed at elevated temperatures. This thin oxide film could be able to diminish diffusion out or into the coating. Accordingly the diffusion wear, one of the major wear mechanisms on cutting tools, would be reduced.

The Ternary System Ti–Al–N

Information about the system Ti–Al–N (*12*) describes the formation of two additional compounds besides the well-known ternary phase Ti_2AlN (*4, 5*). The ductility and hardness of this phase is the reason for the growing interest in this composition.

Ti_2AlN belongs to the group of H-phases (*6*). H-phases are hexagonal carbides and nitrides of the general formula T_2MX (T = transition metal, M = metametal, X = metalloid). The crystal structure of H-phases has been studied on Cr_2AlC and is generally called Cr_2AlC type. H is built of an octaedric group T_6X and of a trigonalprismatic group T_6M (Fig. 1).

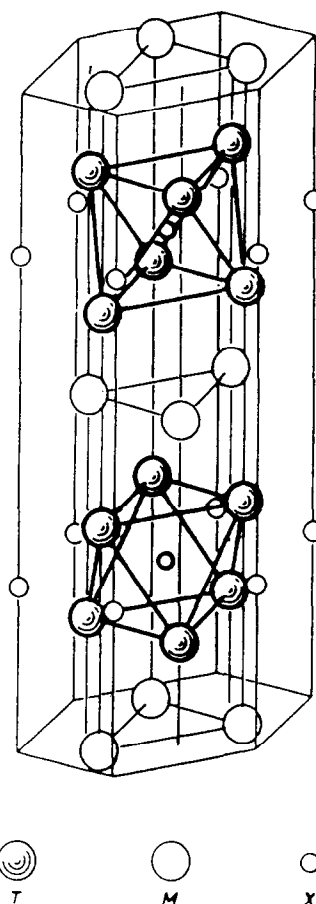There is rather weak bonding between aluminium and carbon (nitrogen). The met-

FIG. 1. Octaedric T_6X group in the structure of T_2MX phases (*6*).

alloids (C, N) obviously prefer the octaedric interstices of the transition metal atoms and by this stabilize the lattice.

The stability of the composition is related to strong connections between transition metal and metalloid atoms. The T–X distances are shorter than in binary compositions. The T–M and the T–T connections are additionally stabilizing factors beside the strong T–X connection within the octaedric group T_6X.

Experimental

Using magnetron sputtering in a DC reactive mode, thin coatings were deposited on

cemented carbide type M15 (82 at.% WC, 11 at.% (Ti, Ta, Nb)C, 7 at.% Co) on high-speed steel (S 6–5–2) and on stellite (Co–Cr–W–C) alloys). The coatings have been prepared in a sputtering plant of Leybold-Heraeus Z 400. Dominant parameters and experimental procedures have been described previously (*1, 2*). Different target materials have been used:

–"Mechanical" targets: aluminium stoppers have been fitted into a titanium and into a sintered titanium–zirconium target.

The velocity of particles in the plasma–gas caused a complete mixing of the metallic component.

–Sintered targets: Ti–Al targets with different aluminium contents; one Ti–Zr target with about 30 at.% zirconium.

–Metallurgical target: Ti Al 6 V 4.

With all targets dense and homogeneous coatings were deposited. By means of X-ray diffraction and microprobe analysis no inhomogeneities or differences in concentration have been stated. Metallographic examinations as microhardness and scratch-tests give a first characterization of the films.

High deposition rates are one advantage of Ti–Al–N compounds. At mean powers of 6 W/cm^2 the deposition rates of sintered targets amounted to 7 μm/hr compared to TiN deposition rates of 4 μm/hr.

At different nitrogen partial pressures depending on the aluminium content, the microhardness achieved values between 2200 and 2400 HV 0.05. The adhesion of the Ti–Al–N coatings was proved by a scratch-test apparatus. Critical loads of 60 N were determined on coatings, which also show maximum microhardness.

Constitutional Investigations

X-ray analysis has been carried out with monochromatic Co–K radiation (λ =

0.17902 nm). The X-ray examination proved that no H-phases of the form Ti$_2$AlN as originally planed have been deposited. Instead interference bonds of a cubic face centered structure appeared. Figure 2 shows the well-known TiN X-ray pattern and the shifted peaks of the Ti–Al–N material.

Clearly one can see that the (Ti, Al)N material has a smaller lattice parameter. As there are no other peaks besides those of the substrate material, this pattern only means a (Ti, Al)N solid solution.

Titanium atoms of the TiN lattice are replaced by aluminium atoms and compositions of the form (Ti, Al)N come into existence.

The X-ray patterns also showed that the lattice parameter obviously decreases when a target with higher aluminium content was used.

Electron probe microanalysis was used for quantitative determination of the film composition. In comparison to other methods of surface analysis the EPMA is the only reliable technique that quantitatively determines microscopical areas.

In order to analyze thin films it was necessary to choose the right preparation method. The deep action of the previously mentioned technique requires films of a minimum thickness of 5 μm. The microprobe analysis of nitrogen in TiN or (Ti, Al)N is generally difficult because of relatively small yields of the NK$_\alpha$ radiation. Additionally the NK$_\alpha$ line is overlapped by the TiL$_1$ line.
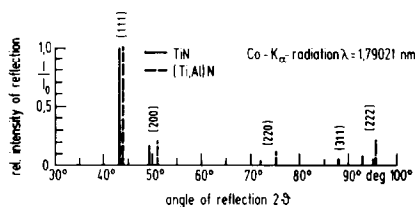

FIG. 2. X-ray pattern of (Ti, Al)N in comparison to TiN coatings.

A CVD-TiN coating served as the standard with 75.1% Ti, 21.4% N, and 3.5% O.

The analysis took place on the surface. Trials to measure in a cross section failed. Reproducible results have been achieved only on smooth polished surfaces.

With EPMA it could be proved that a (Ti, Al)N solid solution grows up and the lattice parameter decreases with growing aluminium content. This can be seen in Fig. 3.

According to these results up to 30 at.% aluminium can be embedded into the titanium nitride. It could be proved that there exists a composition of the form (Ti, Al)N which has to be composed slightly understoichiometric with metal contents between 51 and 56 at.%. This range shows the highest stability concerning wear and microhardness.

The range of stability is obviously fixed by the aluminium content; a smaller cubic face centered cell hampers the interstitial metalloids. Subsequently the stability is shifted toward higher metal contents.

Figure 4 shows the TiN monocell with aluminium atoms in solid solution. The aluminium atoms are distributed randomly. There is no superstructure of aluminium atoms and also no preferred orientation has been detected in relation to the aluminium
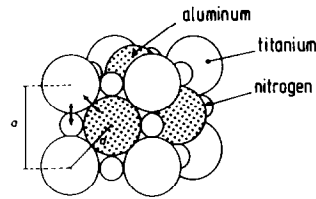

FIG. 4. TiN monocell NaCl type with embedded aluminium atoms.

content. Only by changing the deposition parameters was a preferred orientation possible.

The oxygen content ranges between 4 and 6 at.% depending on the aluminium content. Annealing tests at 1000°C/24 hr in vacuo caused a decomposition of the (Ti, Al)N phase. Aluminium diffuses out and builds Al_2O_3. The lattice parameter goes back to the original TiN values.

The fact that no Ti_2AlN phase has been deposited is due to the deposition temperature of 620°C. Figure 5 shows the ternary Ti–Al–N system with the (Ti, Al)N solid solution.

All compositions near the Ti_2AlN ternary phase showed TiN, Al and Ti_2N peaks but no typical H-phase. Only a higher deposition temperature of about 1000°C might form this ternary compound.
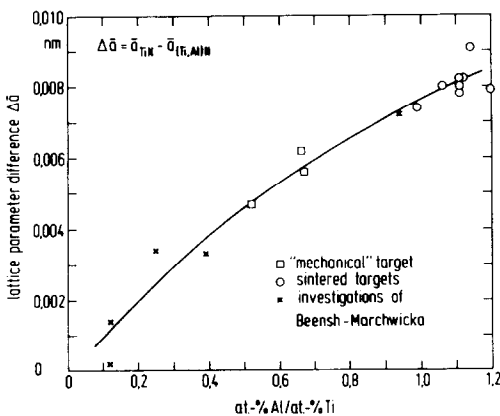

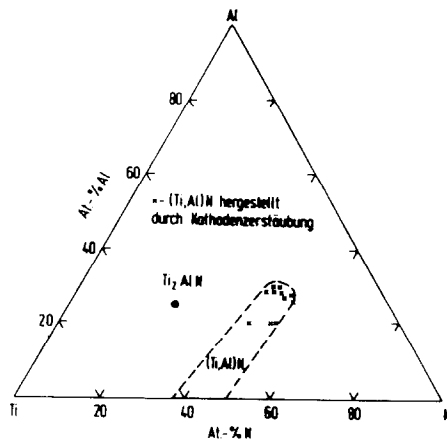FIG. 3. Lattice parameter difference in relation to the Al/Ti ratio.

FIG. 5. (Ti, Al)N solid solution.

Summary

Thin films of the ternary system Ti–Al–N, produced by PVD magnetron sputtering, show excellent wear-resistance and microhardness. It could be proved that a composition of the form (Ti, Al)N grows up a TiN lattice. Up in a 30 at.% aluminium can be solved in this lattice with decreasing lattice parameters. The ternary H-phase Ti_2AlN has not been deposited as the deposition temperatures are too low.

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