Int. Journal of Refractory Metals and Hard Materials xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Int. Journal of Refractory Metals and Hard Materials

journal homepage: www.elsevier.com/locate/IJRMHM

Nanostructured coatings for tooling applications

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A R T I C L E   I N F O

Article history:
Received 16 March 2016
Received in revised form 9 June 2016
Accepted 24 June 2016
Available online xxxx

Keywords:
HR-CVD
Nanostructured coatings
AlTiN

A B S T R A C T

Since the technical means for the preparation and examination of nanostructured materials have been provided, a new generation of wear resistant coatings with grain sizes and structural effects in the nano-scale has emerged. In this contribution the authors will present a short summit of the state of the art in the field of nanostructured coatings and will then emphasise on the most recent developments in preparing CVD AlTiN.

1. Introduction

Modern cutting tools for the machining of metals and non-metallic compounds are expected to withstand a broad range of thermal, mechanical and chemical loads in order to enable short processing cycles and high productivity. In many cases the base tool materials (e.g. ingot metallurgy high speed steels, powder metallurgic HSS or cemented carbides) are no longer sufficient to meet the challenges and have to be supported by protective coatings. Consequently, a tremendous amount of research activities around the world dealt with either the optimization of already existing wear resistant coatings, or the development of new types of coatings which showed excellent hardness, oxidation resistance, thermal stability, fracture toughness and a good adhesion to the substrate also at high temperatures. Both of these tendencies have gained massive support by novel analytical methods (e.g. HR-SEM, FIB, TOF-SIMS etc.), which enabled to study the micro- and nanostructure of the coating materials.

The first so called nano-structured coatings have been derived from multilayer PVD coatings in which the almost planar single layers are only a few nanometers thick and form a so called superlattice [1]. Later the studies of S. Veprek [2] revealed that the production of three-dimensional nanocomposite materials was possible by combining the classical PVD AlTiN and AlCrN layers with a small amount of Si_3N_4, in which they are insoluble. All these developments primarily aimed at the increase of the thermal stability and the high temperature hardness of the coating materials enabling the use of higher cutting speeds during machining and consequently a reduction of process cycle times. The preliminary endpoint in this research was reached with the production of nanostructured coatings via CVD methods.

The beginning of this development was set ten years ago, when Boehlerit GmbH & Co.KG announced products containing a nanostructured TiCN coating made by high temperature CVD. Further research in the CVD process established the new HR-CVD (highly reactive chemical vapor deposition) process and the deposition of CVD-AlTiN-coatings, which was thought impossible at the time [3]. Since two or more chemical reactions are usually influencing and hindering each other, according to the laws of kinetics, it was not to be expected that the simultaneous growth of different kinds of materials with different crystal structures could be achieved within one coating. But recently a novel $Ti_{0.05}Al_{0.95}N$ coating consisting of self-organized nanolamellae based on alternating cubic Ti(Al)N and hexagonal (wurtzite type) AlN lamellae was developed by Boehlerit GmbH & Co.KG and examined by the Department of Materials Physics at Montanuniversität Leoben [4]. The following contribution will emphasise on the historical but also on the most recent developments concerning the possible changes in the coating architectures of nanostructured coatings, which can be achieved by changing some of the process parameters.

2. Experimental data

All coatings were prepared in an industrial hot wall CVD reactor at temperatures between 900 and 1050 °C (TiCN) respectively 800 and 900 °C (AlTiN) and pressures between 70 and 150 mbar (TiCN) respectively 15 and 25 mbar (AlTiN). The reaction gas mixture consisted of $AlCl_3$, $TiCl_4$, N_2 and NH_3 for AlTiN and $TiCl_4$, N_2, CH_4 for TiCN. H_2 was used as carrier gas.

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http://dx.doi.org/10.1016/j.ijrmhm.2016.06.017
0263-4368/

The following examination techniques available at Montanuniversity Leoben were used for coating characterization: The morphology and chemistry of the samples were analysed using a scanning electron microscope (SEM, LEO 1525 from Zeiss) and a dual beam focused ion beam (FIB) workstation (AURIGACrossBeam from Zeiss with FIB column from Orsay-Physics) equipped with an energy dispersive X ray spectroscopy (EDX) detector.

X ray diffraction (XRD) phase analysis of the samples was performed using a 5-circle X ray diffractometer (SmartLab from Rigaku Co.) equipped with Cu Kα radiation, a parabolic multilayer mirror in the primary beam and a secondary graphite monochromator. The XRD characterization was carried out in grazing incidence geometry with 1° incidence angle.

The microstructure of the coatings was further investigated using a high resolution transmission electron microscope (HR TEM, Jeol 2100F) equipped with an imaging spherical aberration (Cs) corrector and a Tridiem imaging filter from Gatan that delivered an atomic resolution of better than 1.4 Å.

Depth-resolved hardness measurements were carried out by nanoindentation with a Hysitron Triboscope transducer mounted on an atomic force microscope (Veeco Dimension 3100) using a Berkovich diamond indenter tip.

Depth gradients of phase composition and residual stresses were determined through cross-sectional X ray nanodiffraction by analysing 100 μm thick sample slices at the nanofocus extension of the ID13 beamline at the European Synchrotron Radiation Facility (ESRF) in Grenoble, France [5,6]. The beam size was 50 nm by 2 μm, with the larger dimension oriented perpendicular to the scanning direction and parallel to the coating surface.

Annealing experiments have been conducted for one hour in ambient air and at temperatures in the range of 700–1200 °C. After oxidation, the samples stayed in the furnace for cooling down to room temperature, which took approximately four hours.

2.1. TiCN by high-temperature CVD

The first nanostructured CVD coating reported by Boehlerit GmbH & Co.KG was a Ti(C,N) layer with a graded grain morphology and composition. It was produced by modifying the deposition conditions (namely temperature) during the chemical vapor deposition process itself (CVD) [7]. The basic chemical reaction is described by:

$$\mathrm{TiCl_4(g) + xCH_4(g) + \frac{1}{2}(1-x)N_2(g) + 2(1-x)H_2(g) \leftrightarrow TiC_xN_{1-x}(s) + 4HCl(g)}$$

Out of XRD-measurements it was found that this special Ti(C,N) layer is nitrogen-rich with an overall C/N ratio of 0.16/0.84 although most of the Ti(C,N) grains present a non-uniform distribution of carbon and nitrogen as revealed by TEM investigations. Fig. 1 shows clearly that the size of the crystallites increases from the coating-substrate-interface towards the surface. This corresponds well to the mechanism of selective crystal growth which states that energetically favoured crystal plains grow faster and thus inhibit the growth of other not favoured crystallites. In contrary to the strictly columnar growth, which is generally observed in the medium temperature (MT) TiCN made from CH_3CN, a high amount of secondary nucleation occurred during the initial state of the high temperature process. This resulted in an increased number of small crystallites and kept the overall crystal size rather small (21 nm average). The crystallites themselves showed differences in their composition. While carbon and nitrogen are evenly distributed in the MT-TiCN, the high temperature process resulted in a composition with a "core-rim" type microstructure. Globally the HT-crystallites consist of a TiC/TiN mixture, but instead of a homogeneous distribution presents a nitrogen enriched core and a rim with high carbon content (Fig. 1).

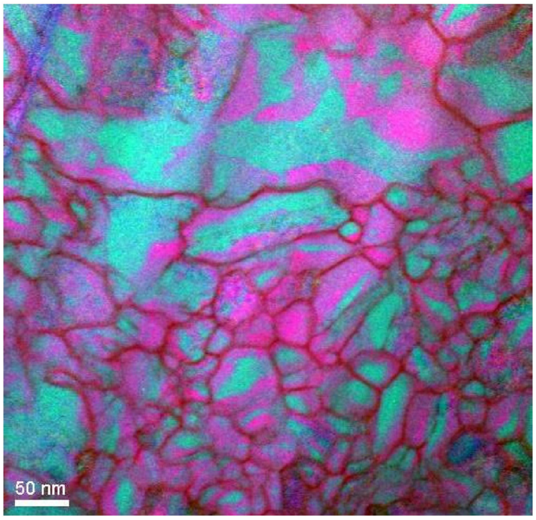

Fig. 1. Microstructure and element distribution of the HT-CVD TiCN as revealed by TEM (red regions are TiC rich; green regions are TiN rich). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

The novel Ti(C,N) phase shows a composite structure, not only in the chemical composition but also regarding the crystal morphology. Two types of Ti(C,N) crystallites simultaneously co-exist within the layer (star-shape and lenticular-like). The basic crystal structure of both types is still cubic but the defect density varies. SEM-Images obtained from samples which have been extracted from the coating process at different times (and temperatures) show clearly that during the initial nucleation phase ball shaped and almost amorphous crystal co-exist with five-star nuclei. These star shaped crystals have a higher growth rate and slowly overgrow the initial spherical particles. At temperatures above 1050 °C the lenticular shaped crystals appear and slowly replace the star shaped ones (Fig. 2).

Within the final coating morphology crystallites protrude from the surface of the Ti(C,N) layer, giving a roughing-effect to the coating layer. This special surface topography significantly improves the adhesion of subsequent coating layers, such as Al_2O_3 layers, due to mechanical anchoring. Within the method described in [7] a graded transition from the Ti(C,N) into the κ-Al_2O_3 without the production of intermediate layers is obtained. The presence of different types of crystals in the HT-Ti(C,N) layer (star-shape and lenticular-like grains) compared with the MT-Ti(C,N) (columnar grains) may act as barriers for dislocations propagation (Fig. 3). On the other hand, the nitrogen-rich Ti $(C_{0.2}N_{0.8})$ layer may improve the crater wear resistance by forming oxide layers on the crystal surface [8], which are not soluble in hot steel chips.

Another positive effect of the graded crystallite morphology of the novel HT-CVD coating is the formation of the needle-like transition (Fig. 4), which results in a better adhesion of the κ-Al_2O_3 toplayer. In Fig. 5 a cross section of the cutting edge of the indexable insert with the novel multilayer at the end tool life is shown. A perfect adherence of κ-Al_2O_3 to the Ti(C,N) in the novel multilayer system is achieved, even though the tip of the insert is completely damaged. It can be then concluded that, both the combination of the graded morphology of the novel HT-Ti(C,N) layer and the improved adhesion of the heat resistant κ-Al_2O_3 layer are then responsible for an enhanced cutting performance of the novel multilayer system which since has been proofed especially in heavy duty machining of steel and cast iron.

2.2. AlTiN by high-reactivity (HR) CVD

Morphology and Composition: Since 2011 the authors have repeatedly presented data [4,9,10] on the first nanostructured HR-CVD AlTiN

Please cite this article as: A. Köpf, et al., Nanostructured coatings for tooling applications, Int J Refract Met Hard Mater (2016), http://dx.doi.org/10.1016/j.ijrmhm.2016.06.017