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Microstructural size effects on the hardness of nanocrystalline TiN/amorphous-SiN_x coatings prepared by magnetron sputtering

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Abstract

It has been postulated that equiaxed nanocrystalline (<10 nm) TiN grains embedded in a thin amorphous silicon nitride (a-SiN_x) phase are a prerequisite to obtain ultrahard TiN/a-SiN_x coatings. The present study correlates hardness and microstructure of TiN/a-SiN_x coatings with Si contents between 0 and 17 at.%. The coatings have been deposited by magnetron sputtering in industrial-scale physical vapour deposition systems. Transmission electron microscopy studies revealed that increasing the silicon content causes the TiN grain size to decrease. This is accompanied by a change in grain morphology: At Si contents lower than 1 at.% TiN grains become columnar, while at Si contents higher than 6 at.% equiaxed grains with diameters of 6 nm form. For silicon contents between 1 and 6 at.%, a transition region with nanocrystalline columnar grains exists. This nanocrystalline columnar microstructure causes maximum hardness values of more than 45 GPa for TiN/a-SiN_x coatings as determined by nanoindentation. The elongated and equiaxed nanocrystalline TiN grains exhibit almost theoretical strength as dislocation-based deformation mechanisms are constrained.

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1. Introduction

The reduction of wear is a major goal in today's machining industry which could profit from longer lifetimes of tools and therefore from lower production costs. One strategy to prevent tool degradation is to apply wear-resistant coatings. Single-layer coatings consisting of nanocrystalline phases are expected to exhibit outstanding properties, combining, e.g. ultrahigh hardness, high toughness, high-temperature stability and low friction. A possible material system is the TiN/a-SiN_x system, which allows formation of hard and immiscible nitrides [1]. TiN/a-SiN_x-based coatings with hardness values exceeding 50 GPa were first described by Shizhi et al. [2] and further developed by Vepřek et al. [3,4] using chemical vapor deposition (CVD). The high hardness of these coatings is supposed to originate from a microstructure consisting of nanocrystalline TiN embedded in an amorphous silicon nitride (a-SiN_x) matrix phase [5]. A nanocrystalline TiN phase with average particle diameters of 3 to 4 nm was identified by Vepřek et al. using X-ray diffraction (XRD) [4] and transmission electron microscopy (TEM) [6] techniques.

The major drawback of CVD-grown TiN/a-SiN_x coatings is their limited temperature stability, caused by chloride-induced corrosion as a consequence of $TiCl_4$ and $SiCl_4$ precursor gases. This problem can be overcome by using unbalanced magnetron sputtering as a deposition method [7,8]. By this method, Diserens et al. [8] were able to prepare TiN/a-SiN_x-based coatings with a hardness of 38 GPa

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and an oxidation rate at 800 °C in air that was one order of magnitude lower than that of standard TiN coatings. The correlation between hardness and microstructure of the TiN/a-SiN_x coatings has been discussed in the literature, based on different experimental results [9–11]. For example, Meng et al. [9,12] found a nanocrystalline TiN/a-SiN_x composite microstructure, but a decrease in hardness with increasing silicon content. Diserens et al. [8] observed a hardness maximum at 4 at.% silicon, while Vepřek et al. [5] and Rebouta et al. [13] observed maximum hardness values at about 9 at.% silicon.

In the present study, TiN/a-SiN_x coatings with a silicon content ranging from 0 to 17 at.% were deposited by magnetron sputtering in industrial-scale physical vapour deposition equipment to systematically study the relationship between coating composition, microstructure and mechanical properties. The optimum microstructure was found to be connected to an optimum Si content, giving rise to hardness values in excess of 45 GPa.

2. Experimental details

The TiN/a-SiN_x-based coatings were prepared by reactive magnetron sputtering. All coatings were deposited with industrial-scale production equipment. Magnetron sputtering was carried out with a mixed titanium/silicon target containing 10 at.% silicon or with two separate elemental targets (co-sputtering). All mechanical properties presented in this paper stem from magnetron sputtered TiN/a-SiN_x films made with two separate targets, since only in this case the silicon content could be varied substantially without changing other deposition parameters. The target to substrate distance was 28 cm. The chamber pressure during the deposition of the coatings ranged between 2.0×10^{-1} and 2.5×10^{-1} Pa depending on the nitrogen flux. The deposition parameters bias voltage (0 to −400 V), nitrogen flux (50% to 150% of the argon flux) and sputter power ratio between the two elemental targets (Ti-Target: 3 to 6 kW; Si-Target 1 to 3 kW) were varied to optimize the hardness and to achieve different microstructures. The Si-content was mainly controlled via the power ratio of the two targets, but the Si-content also decreases with increasing bias voltage due to a preferred resputtering of the Si atoms. The thickness of the deposited coatings was approximately 2 μm. Silicon single crystal wafers and high-speed steel plates were used as substrate materials.

The silicon content of the TiN/a-SiN_x coatings was analyzed with a microprobe (CAMECA SX 100). The atomic composition was determined from the measured intensities at the silicon and the titanium K_α-edges in comparison to elemental silicon and titanium standards. Because the nitrogen K-edge and the titanium L-edge overlap significantly, the nitrogen content was calculated from the difference of the combined titanium and silicon contents to 100%. This slightly overestimated the nitrogen content due to the presence of impurities such as oxygen. Values quoted are mean values of 10 measurements per specimen.

Crystalline phases and textures of the coatings were identified by XRD θ–2θ measurements, with diffraction angles scanned between 2θ=35° and 90°. The diffractometer (Siemens M18XHF-V at 40 kV and 300 mA) was operated in steps of 0.05° and with acquisition times of 5 s per data point.

The microstructure of the coatings was studied by focused ion beam microscopy (FIB) using an FEI 200, as well as TEM (JEOL 2000 FX) and high resolution TEM utilizing a JEOL ARM1250 with a point resolution of 0.12 nm [14].

Cross-sectional TEM samples were prepared with the FIB [15]. Specimens with a length of 3 mm and a thickness of 2 mm were cut from the coated substrate with a diamond wire saw and mechanically thinned to a thickness of about 70 μm. Subsequently, these specimens were glued onto a copper half-ring with a diameter of 3 mm. Electron transparent regions of 30 μm in width and 4 μm in height were milled in the FIB using Ga^+-ions as described in Ref. [15].

Additionally, cross-sectional TEM samples were prepared using a conventional technique developed by Strecker et al. [16]. The conventionally prepared TEM specimens were Ar^+-ion thinned using a precision ion polishing system (GATAN 691). However, high internal stresses in the films often caused cracking of the conventionally prepared TEM samples, while FIB made specimens were less prone to cracking, since only a small region is thinned to electron transparency. Both types of TEM specimen preparation routes gave identical microstructural results, indicating that noticeable preparation artifacts caused by incorporation of Ga ions did not occur.

X-ray photoelectron spectroscopy (XPS) studies were performed to obtain further information on the chemical oxidation states of Ti, Si and N by analyzing their binding energies. The XPS spectra were recorded with a VG ThetaProbe instrument equipped with a spherical sector analyzer. Monochromatic Al-K_α radiation was used to generate photoelectrons. The X-ray beam with a diameter of 400 μm was focused on the sample. In order to obtain XPS depth profiles, material was removed by sputtering with a 3.0 keV Ar^+-ion beam scanned over an area of about 1×1 mm^2. Spectra with a step size of 0.1 eV and a pass energy of 100 eV from the interior of the coating were recorded after the oxygen content in the samples remained constant. The results of the XPS measurements were only used to determine the binding energies, the composition of the coatings was measured with a microprobe to avoid errors caused by preferential sputtering.

The hardness of the coatings was analyzed with a nanoindenter (NanoXP) using the continuous stiffness method proposed by Oliver and Pharr [17], in which an oscillation of the indenter tip is superimposed on the normal