Increased thermal stability of Ti$_{1-x}$Al$_x$N/TiN multilayer coatings through high temperature sputter deposition on powder-metallurgical high-speed steels

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ABSTRACT

Although spinodal decomposition of metastable cubic Ti$_{1-x}$Al$_x$N-based coatings and the underlying mechanisms are widely understood, investigations on the influence of high deposition temperatures are lacking. It is thus the aim of this work to elucidate structure, properties, thermal stability and wear performance of Ti$_{1-x}$Al$_x$N/TiN multilayer coatings sputter deposited on powder-metallurgical high-speed steels at substrate temperatures between 375 and 575 °C. At higher substrate temperatures, sharper column boundaries and sharper transition zones in the multilayer arrangement yield increased hardness in the as-deposited state, while the detrimental formation of wurtzite AlN during vacuum annealing is retarded by 50 °C according to Rietveld refinement of X-ray diffractograms. Tribological tests at room temperature and up to 650 °C corroborate the high potential of increased coating temperatures, while demonstrating the crucial importance of using a substrate material with adequate hot hardness. Cutting tests with coated high-speed steel end mills verify the high temperature deposition approach showing a tool life increase of ~40%.

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1. Introduction

Both scientific and industrial significances have yielded extensive research on the thermal stability along with spinodal decomposition of metastable cubic Ti$_{1-x}$Al$_x$N (c-Ti$_{1-x}$Al$_x$N) over the last decade [1–5]. The steadily growing knowledge on the underlying mechanisms [6–12] enables the optimization of the coating's response to distinct thermal and mechanical loads during application e.g. as wear-protective coating on cutting tools [2,8,13]. The objective is to promote the isostructural spinodal decomposition toward cubic TiN (c-TiN) and AlN (c-AlN) due to the resulting age-hardening effect, while the detrimental transformation of metastable c-AlN to its stable wurtzite

structure (w-AlN) needs to be suppressed as it deteriorates both mechanical and tribological coating properties [2,6].

A well accepted approach to enhance the thermal stability of Ti$_{1-x}$Al$_x$N is alloying, e.g. with Si, Cr, Zr, Hf or Ta [14–19]. Furthermore, multilayered coating structures of Ti$_{1-x}$Al$_x$N and TiN have proven to yield enhanced mechanical properties and thermal stability [13, 20–23]. However, investigations on the influence of the coating deposition temperature, which plays a crucial role on the evolving Ti$_{1-x}$Al$_x$N microstructure according to structure zone models [24,25], are lacking. Commonly, chamber temperatures in the 300–500 °C range, in particular for industrial deposition processes, are reported [2,5,10,11,13,20,21, 23,26]. Therefore, the aim of this work is to investigate structure and properties as well as thermal stability and tribological performance arising from sputter deposition of multilayered Ti$_{1-x}$Al$_x$N/TiN coatings at temperatures of up to 575 °C. Consequently, the use of powder-metallurgical high-speed steel (PM-HSS) substrates with substantial hot hardness was crucial, as will be demonstrated. Transmission electron microscopy (TEM) and X-ray diffraction (XRD) in the as-deposited state and after vacuum annealing combined with Rietveld refinement, nanoindentation, tribological tests at room temperature (RT), 560 and 650 °C as well as cutting tests were performed to elucidate the benefits of high substrate temperatures during industrial-scale sputter deposition of Ti$_{1-x}$Al$_x$N/TiN multilayer coatings on PM-HSS substrates.

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2. Experimental details

2.1. Coating deposition

The investigated coatings were deposited by reactive direct current (DC) magnetron sputtering using an industrial-scale CemeCon CC 800/9® ML facility. Three of its four unbalanced magnetrons (500×88 mm^2) were equipped with Ti–Al mosaic targets of type TiAl48 GM (described in more detail in Refs. [27 and 28]), while a pure Ti target was mounted on the fourth one. The substrates were ground and polished disks of the size $\varnothing$ 30 $\times$ 10 mm made of PM-HSS grades Böhler S390PM (HS10-2-5-8 type) and S290PM (HS14-2.5-5-11 type), quenched and tempered to a hardness value of 67 $\pm$ 1 HRC, and rectangular Si (100) samples of 0.4 mm thickness. Furthermore, S290PM end mills were coated for cutting tests. Two-fold rotation at a speed of 1 rpm was applied for the PM-HSS disks and Si, while the end mills were coated under three-fold rotation. As a consequence of both substrate rotation and target configuration [29,30], which implies differing sputter emission distributions from the Ti–Al targets and the Ti target [31,32], the formation of a compositionally modulated structure as obtained by Chen et al. [22] can be anticipated. The substrate temperatures during coating deposition were varied from 375 to 575 °C in five deposition runs and measured by positive temperature coefficient resistors at lower temperatures and by a pyrometer at higher temperatures. In order to achieve the desired temperature variation during deposition, the heating power of the plant's inbuilt heaters was varied, while the settings for the heating and the plasma etching steps prior to the coating step remained unchanged. The magnetrons were operated in a constant power mode with 9500 W for the Ti–Al targets and 4000 W for the Ti target. The DC bias voltage during deposition was set to −90 V. The noble gas flows (Ar and Kr) were kept constant, while the N$_2$ flow was regulated to achieve a predetermined total pressure of 0.57 Pa corresponding to a pressure ratio of N$_2$/(Ar + Kr) of 0.24. The base pressure in the deposition chamber was $\leq 4 \cdot 10^{-3}$ Pa.

2.2. Substrate and coating characterization

A Rockwell HRC hardness tester type EMCO-test M4R-075 was used to measure the PM-HSS substrate hardness in the quenched and tempered state and after being coated at the five different deposition temperatures as well as the coating adhesion. For the latter, the VDI Rockwell indentation test was used, whereupon damage to the coatings in the vicinity of a Rockwell C indent is assigned to adhesion classes between HF 1 and HF 6 according to DIN report 39 [33]. The overall chemical composition of the coatings was determined by energy-dispersive X-ray spectroscopy (EDX) using an Oxford Instruments INCA extension in a Zeiss EVO 50 scanning electron microscope (SEM). The thickness of the coatings was measured via ball cratering with a CSM Instruments Calotest unit.

Crystallographic investigations on as-deposited coatings were performed by X-ray diffraction (XRD) in Bragg–Brentano as well as grazing incidence (GIXRD) geometry in a Siemens D500 diffractometer with Cu K$_\alpha$ radiation. For GIXRD measurements, a beam incidence angle of 4° was chosen. Furthermore, investigations on uncoated PM-HSS disks were performed in Bragg–Brentano configuration using the same device. Transmission electron microscopy (TEM) was conducted on coatings deposited onto Si substrates at 375 and 575 °C using a Philips CM20 microscope operating at 200 kV. Energy-filtered TEM (EFTEM) in an imaging mode was performed for Ti mapping using a Gatan Imaging Filter. A focused ion beam (FIB) lift-out technique was chosen for the TEM sample preparation, using a FEI Nova 200 NanoLab Dual Beam SEM/FIB microscope.

Coating hardness and Young's modulus were determined after slight diamond-polishing of the coating surface with a UMIS (Ultra Micro Indentation System, Fischer-Cripps Laboratories) nanoindenter equipped with a Berkovich tip from at least 10 measurements. The load–displacement data of the conducted plateau tests was analyzed according to the Oliver and Pharr method [34], including area functions determined experimentally using a silica standard of known elastic modulus to account for unavoidable microscopic indenter shape imperfections. Residual stress measurements using the substrate curvature method [35,36] were performed on coated Si platelets, measuring the sample curvature with two parallel laser beams.

2.3. Annealing experiments

An HTM Reetz furnace was used for isothermal vacuum annealing of coated Si samples in the range of 800–950 °C in 50 °C steps for 10 min. All annealing treatments were performed with a base pressure of $<5 \cdot 10^{-4}$ Pa and virgin specimen. The heating rate was 20 K·min^{-1}, and an isothermal step of 30 min at 250 °C was implemented to remove volatile contaminants. After annealing, the samples were furnace cooled. The thermally induced microstructural changes were investigated via GIXRD at a beam incidence angle of 2° using Cu K$_\alpha$ radiation in a Bruker-AXS D8 Advance diffractometer equipped with parallel beam optics and an energy-dispersive detector (Sol-X from Bruker-AXS). Rietveld refinement of the diffractograms recorded in the angular range of $32° \leq 2\theta \leq 46°$ was subsequently applied using the TOPAS software package (version 4.2; Bruker-AXS) to gain quantitative information on the evolution of the constituent phase fractions, the respective mean crystallite sizes (the mean sizes of the diffracting domains, to be more precise) and the corresponding average lattice constants.

2.4. Tribological investigations

Tribological tests were performed using a CSM Instruments high temperature ball-on-disk tribometer with corundum balls of $\varnothing$ 6 mm, 5 N normal load, a sliding speed of 0.1 m·s^{-1}, a sliding distance of 500 m, a wear track radius of 5 mm and testing temperatures of 25, 560 and 650 °C. All tests were performed in ambient atmosphere at relative humidities of 25 $\pm$ 5%. The wear tracks were investigated by white light optical profilometry, using a Veeco Wyko NT1000 device in a vertical scanning interferometry mode, to derive the volume of the worn area determined by three-dimensional cross-sections at four different positions along the wear track. The wear rates (K) were calculated from the measured wear volumes, the wear track circumference, the normal load and the number of laps. Cutting tests were conducted on cold work steel 40CrMnMoS8-6 (DIN 1.2312, tensile strength: 1000 MPa) with a Deckel Maho milling facility. End mills with $\varnothing$ 16 mm made of S290PM with four flutes, a cutting speed of 100 m·min^{-1}, a rotation speed of 1990 min^{-1}, a feed per tooth of 0.08 mm, a feed rate of 636 mm·min^{-1}, a width of cut of 1 mm, a depth of cut of 16 mm and a cutting distance of 70 m were used under dry conditions.

Unless otherwise noted, all investigations were done on both coated S390PM and S290PM samples. Measurement of coating hardness and Young's modulus was done on coated S290PM samples because of their higher hot hardness and thermal stability (cf. Section 3.1), to avoid possible influences due to softening of the PM-HSS substrates especially after coating deposition at 575 °C.

3. Results and discussion

3.1. Thermal stability of the PM-HSS substrates

The substrate temperatures T$_S$ determined during the five deposition runs were 375, 420, 470, 530 and 575 °C, where the latter two were measured by means of a pyrometer. The Böhler PM-HSS grades S390PM and S290PM exhibit remarkably high softening temperatures of ~530 and ~560 °C, respectively [37,38]. The difference in thermal stability can be attributed to their different alloy compositions, as summarized in Table 1. On the one hand, the S290PM exhibits a higher