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Thermal conductivity of titanium aluminum silicon nitride coatings deposited by lateral rotating cathode arc

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ABSTRACT

A series of physical vapour deposition titanium aluminum silicon nitride nanocomposite coating with a different (Al + Si)/Ti atomic ratio, with a thickness of around 2.5 μm were deposited on stainless steel substrate by a lateral rotating cathode arc process in a flowing nitrogen atmosphere. The composition and microstructure of the as-deposited coatings were analyzed by energy dispersive X-ray spectroscopy, and X-ray diffraction, and cross-sectional scanning electron microscopy observation. The titanium nitride (TiN) coating shows a clear columnar structure with a predominant (111) preferential orientation. With the incorporation of Al and Si, the crystallite size in the coatings decreased gradually, and the columnar structure and (111) preferred orientation disappeared. Thermal conductivity of the as-deposited coating samples at room temperature was measured by using pulsed photothermal reflectance technique. Thermal conductivity of the pure TiN coating is about 11.9 W/mK. With increasing the (Al + Si)/Ti atomic ratio, the coatings' thermal conductivity decreased monotonously. This reduction of thermal conductivity could be ascribed to the variation of coatings' microstructure, including the decrease of grain size and the resultant increase of grain boundaries, the disruption of columnar structure, and the reduced preferential orientation.

1. Introduction

Nowadays, thin wear-resistant hard coatings are extensively applied on cutting and forming tools to improve their lifetime and performance. Hard coating deposition has now become a routing processing step in tools industry. Currently, a wide range of physical vapour deposition (PVD) hard coatings are available for a variety of applications. Ti-based coatings (e.g. titanium nitride (TiN) and titanium aluminium nitride (TiAlN)) represent state-of-the-art of commercial PVD tools coatings. In the past few years [1–6], nanocomposite coatings, which are composed of a nanocrystalline hard material (e.g. TiN, TiAlN, or CrAlN) embedded in an amorphous matrix (e.g. Si_3N_4) with strong interfaces between the two phases, have attracted great attention all over the world due to their excellent properties, including super hardness (≥40 GPa), enhanced toughness, high temperature thermal stability and oxidation resistance, outstanding abrasive and erosive wear resistance, etc., over the commercial TiN and TiAlN coatings [7–9]. These nanocomposite coatings have been shown to be thermodynamically stable and resistant to oxidation in air at temperatures over 800 °C, and they have exhibited very promising applicability in high temperature wear components and various forming tools. Tanaka et al. [3] reported a greatly improved oxidation resistance of titanium aluminum silicon nitride (TiAlSiN) coatings, with a few atomic percentages of Si, up to 1100 °C in air. And a better cutting performance, particularly under high speed machining conditions, of TiAlSiN-coated cermet cutting tools has been demonstrated over both the TiAlN and commercial chemical vapour deposition multilayer TiCN/Al_2O_3/TiN-coated tools.

In addition to the protection requirements against oxidation and wear, thermal properties, particularly thermal conductivity, are also important for hard coatings. In physics, thermal conductivity, K, is the property of a material's ability to conduct heat. Materials of high thermal conductivity are widely used in heat sink applications and materials of low thermal conductivity are used as thermal insulation. In some specific tool applications, e.g. high speed machining, hot forging/casting, a lower thermal conductivity of the hard coatings is favourably desired, which serves as a thermal barrier layer and can effectively delay the temperature rise on the tool substrate materials. Recently, Fox-Rabinovich, et al. [10] have demonstrated that a nano-multilayered AlTiN/Cu PVD coating performed evidently better than an AlTiN coating in turning the hard-to-machine aerospace Ni-based Inconel 718 superalloy. They partially attributed the better cutting performance to the lower thermal

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conductivity of the nano-layered AlTiN/Cu coating [4]. Up to now, experimental investigation on thermal conductivity of hard coatings is still quite limited. Taylor et al. [11] measured thermal conductivity of bulk TiN to be around 27 W/mK in the temperature range of 200–2000 °C by using flash diffusivity and radial heat flow diffusivity. Similarly, Aivazov et al. [12] also demonstrated that the thermal conductivity of TiN over a wide temperature range from 77 to 1100 °K is almost independent on temperature. Using the picosecond time domain thermoreflectance, Fox-Rabinovich et al. [10] measured the temperature dependence of thermal conductivity of AlTiN and AlTiN/Cu multi-layered coatings and the reported thermal conductivity from room temperature to 450 °C for AlTiN and AlTiN/Cu are around 3.5–4.5 W/mK and 2.5–3.5 W/mK, respectively. In our previous work [13], the thermal conductivity of a series of TiAlN coatings with a different Al/Ti atomic ratio was investigated using pulsed photothermal reflectance (PPR) technique at room temperature. A significant decrease in thermal conductivity was found with increasing Al/Ti atomic ratio. A minimum thermal conductivity of about 4.63 W/mK was obtained at the Al/Ti atomic ratio of around 0.72. In the present work, a series of TiAlSiN nanocomposite coatings were prepared by a cathode arc technique with a different (Al + Si)/Ti atomic ratio on American iron and steel institute 304 (AISI 304) stainless steel substrates. The thermal conductivity of these coatings was investigated by using the PPR technique.

2. Experiment

TiAlSiN nanocomposite coatings with a thickness of 2.2–2.6 μm were deposited by a lateral rotating cathode arc technique, which has been described in detail elsewhere [14]. For deposition of the TiAlSiN nanocomposite coatings, one elemental Ti cathode and one Al + Si alloy cathode (with ~ 11 at.%Si) were used. These two cathodes were laterally rotating during the coating deposition. Mirror-finished AISI 304 stainless steel coupons with a dimension of $25 \times 25 \times 1$ mm^3 were used as substrates for coating deposition. At first, the substrates were ultrasonically cleaned in a series of alkaline solutions, washed in deionized water, and dried by nitrogen gas blowing and further dried in an oven at 100 °C. Then the pre-cleaned substrates were mounted on a carrousel substrate holder which rotated continuously around the vertical central axis at a speed of 12 rpm. The coating deposition was conducted in a flowing pure nitrogen atmosphere with a working pressure controlled at 1.5 Pa. In order to control composition of the as-deposited coatings, the direct current applied on the two cathodes, $I_{(Al + Si)}$ and I_{Ti} was separately changed between 0 and 125A with different current ratio, $I_{(Al + Si)}/I_{Ti}$. During the deposition, a negative bias of −70 V was applied to the substrate, and substrate temperature was controlled at 480 °C. Composition of the as-deposited coatings was measured by energy dispersive X-ray spectroscopy (EDX) analysis, which is attached to a scanning electron microscope, at 8 keV and the INCA quantitative analysis software. The coating crystalline structure is analysed by X-ray diffraction (XRD) which was performed on a Philips X-ray diffractometer in a θ–2θ scan mode using CuK$_\alpha$ radiation (40 kV, 30 mA). The scanning step size and the counting time at each step were set as 0.05° and 10 s, respectively. Nanotest 550 nanoindenter equipped with a Berkovich diamond indenter (a three-sided pyramid) was used to measure microhardness of the coatings. The cross-sectional microstructure of the coating samples was observed by a field emission scanning electron microscope (FESEM) (JEOL, 7600F) at a low 1 kV accelerating voltage.

Thermal conductivity and diffusivity of the as-deposited TiAlSiN nanocomposite coating samples were measured by the PPR technique, which has been described in detail in our previous works [15,16]. In this approach, thermal properties of thin films are characterized in nanosecond regime by thermoreflectance technique [17]. Before the measurement of thermal conductivity, a gold layer with a thickness of about 0.8 μm is deposited on top of each coating sample surface by thermal evaporation for the purpose of enhancing heat absorption. The sample was struck by a Nd:YAG (532 nm) laser pulse with a full width at half maximum of 7 ns, spot size (diameter of the laser beam) of 3 mm, and pulse energy of 5 mJ. A 1 mW HeNe laser with a 20 μm spot size and 632.8 nm in wavelength was focused at the centre of the excitation spot to monitor the changes in reflected light intensity from the gold surface using a 125 MHz photodiode and pre-amplifier. The temperature excursion of metal surface $\varepsilon(r,z,t)$ (the temperature rise above the ambient temperature T_0, z is vertical direction, r is radial direction, t is time) is measured through the temperature dependence of metal's reflectivity. Since for most metals, the thermoreflectance coefficient ($\Delta R/\Delta T$) is about constant [18], the intensity of reflected probe beam is proportional to the gold surface temperature. Surface temperature excursion profile depends on thermal properties and the thermal resistance of the underlying layers. Because the effective thermal diffusion length $2(\alpha_{Au}\tau_{exp})^{1/2}$ (where τ_{exp} is the measurement duration in the experiment to detect the surface temperature excursion, and α_{Au} is the thermal diffusivity of gold) and the spot size of probe beam are much smaller than the spot size of the excitation beam, the measurement can be completed before any significant lateral heat diffusion occurs. Therefore, the heat conduction problem can be modelled as one dimension vertical heat diffusion in the three-layer (Au/TiAlSiN/AISI 304) structure.

A discontinuity in temperature between the layers is caused by thermal boundary resistance when the adhesion between neighbouring layers is poor. Totally, heat diffusion into underlying layers is slowed down by the thermal boundary resistance. The thermal boundary resistance is small when film adheres well to the neighbouring layers. In a two-layer model [17,19], thin film between the gold film and substrate is modelled as part of thermal resistance, R_{th}. R_{th} is expressed as $R_{th}(d) = d_{film}/K_{in}(d) + R_{12}$, where $d_{film}/K_{in}(d)$ is the internal volume resistance, d is the thickness of the film, K_{in} is the thermal conductivity of the film, and R_{12} is the boundary resistances between the interface layers. Since this thermal resistor is linearly proportional to film thickness, it becomes large for thicker films. Thus for thicker films which are well adhered to the neighbouring layers, the interface thermal resistance is relatively small (as compared to the volume resistance) and can be neglected. Conversely, if the thickness of the film is rather small or the adhesion is poor, we can expect the interface thermal resistance becomes significant and cannot be neglected. In our samples, we can neglect the thermal boundary resistances between the layers. This is because the volume resistance (d/K_{int}) is in the range of 10^{-6} m^{2}K/W whereas the expected thermal boundary resistances (between the Au and the TiAlSiN, and between TiAlSiN and substrate) are more than one order of magnitude lower [20]. Therefore, a three-layer model is used in this work and heat conduction problem is solved for a three-layer structure and thermal boundary resistance between the interfacial layers is neglected [16]. Also, substrate is considered as an infinite medium because the heat diffusivity length in AISI 304 is much less than the thickness of the substrate.

3. Result and analysis

Fig. 1 shows the (Al + Si) to Ti atomic ratio measured by EDX analyses in the as-deposited TiAlSiN coating as a function of the current ratio applied onto the (Al + Si) and Ti cathodes. It is expected that the (Al + Si)/Ti atomic ratio in the coatings increased monotonously with the increase of the current ratio $I_{(Al + Si)}/I_{Ti}$.

Fig. 2 shows the normalized surface temperature profile for Au/TiAlSiN/AISI 304 structure with two different atomic ratios of (Al + Si)/Ti. In order to obtain the thermal conductivity and diffusivity of TiAlSiN, the temperature profile is fitted by using a three-layer heat conduction model to simulate heat transport in the Au/TiAlSiN/AISI 304 structure, the details can be found in our previous work [13]. A least square optimization method is used to fit the experimental data to an analytical solution of heat diffusion for the three-layer model