Journal of Alloys and Compounds 671 (2016) 254–266

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

Effects of annealing temperatures on the morphological, mechanical, surface chemical bonding, and solar selectivity properties of sputtered TiAlSiN thin films

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ARTICLE INFO

Article history:
Received 21 December 2015
Received in revised form
5 February 2016
Accepted 8 February 2016
Available online 11 February 2016

Keywords:
Magnetron sputtering
Thin film coatings
Optical properties
Solar absorptance
Solar emittance
Selective solar surface

ABSTRACT

Quaternary sputtered TiAlSiN coatings were investigated for their high temperature structural stability, surface morphology, mechanical behaviors, surface chemical bonding states, solar absorptance and thermal emittance for possible solar selective surface applications. The TiAlSiN films were synthesized, via unbalanced magnetron sputtered technology, on AISI M2 steel substrate and annealed at 500 °C - 800 °C temperature range. SEM micrographs show nanocomposite-like structure with amorphous grain boundaries. Nanoindentation analyses indicate a decrease of hardness, plastic deformation and constant yield strength for the coatings. XPS analysis show mixed Ti, Al and Si nitride and oxide as main coating components but at 800 °C the top layer of the coatings is clearly composed of only Ti and Al oxides. Synchrotron radiation XRD (SR-XRD) results indicate various Ti, Al and Si nitride and oxide phases, for the above annealing temperature range with a phase change occurring with the Fe component of the substrate. UV–Vis spectroscopy, FTIR spectroscopy studies determined a high solar selectivity, *s* of 24.6 for the sample annealed at 600 °C. Overall results show good structural and morphological stability of these coatings at temperatures up to 800 °C with a very good solar selectivity for real world applications.

1. Introduction

Transition metal nitride based quaternary TiAlSiN coatings are attractive candidates as cutting tools, protective and decorative coatings due to their many outstanding properties [1]. In recent years they have seen significant interest as solar selective absorbers for harvesting solar energy in various applications such as thermal solar collectors, solar steam generators and steam turbines for producing the electricity at mid and mid-to high temperatures [2–13]. A good selective surface must have high absorptance (α) in the visible spectrum up to 2.5 μm and low emittance (ε) in the infra-red (IR) region ≥ 2.5 μm at the operating temperatures. In recent years, transition metal nitride based tandem coatings (e.g., TiAlN/AlON, and TiAl/TiAlN/TiAlON/TiAlO) have been suggested for use in solar selective surfaces to be used in photothermal applications [4,14]. Barshilia et al. [15] developed a high thermal stable TiAlN/TiAlON/Si_3N_4 tandem absorber on a copper substrate for high temperature solar selective applications that exhibited an absorptance of 0.958 and an emittance of 0.07. Until now these materials have not been commercially produced [4,11,16]. Transition metal oxides based thin film coatings with good optical properties have

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http://dx.doi.org/10.1016/j.jallcom.2016.02.077
0925-8388/

been also developed for solar selective surface applications [17–22].

Most of the solar selective coatings exhibit good stability in a vacuum but in air they have very limited thermal stability. However, in a high temperature or for long period application purposes, these solar selective absorbers should have stable structural configuration minimal degradations. The oxidation resistance behavior of these coatings is also very important as they are frequently exposed at high temperature atmospheres in air. The addition of Al and Si to the TiN coatings increases their oxidation resistance by forming oxide layers around the surface which eventually work as a barrier for further oxygen penetrations at high temperatures. The formation of amorphous phases also provides better stability against degradation, corrosion and oxidation than that of crystalline metallic nitride phases. TiAlSiN coatings provide good thermal stability at temperatures above 800 °C [26,27]. These coatings have been explored mostly for their extraordinary mechanical properties, but as applications in solar selective surfaces in thermal collector devices are relatively unexplored [28–31].

The synchrotron radiation X-ray diffraction SR-XRD technique is successfully used to probe the crystalline and electronic structure of various systems in a wide range of fields such as physics, chemistry, environmental sciences, materials sciences, biology, medicine, and geophysics. The SR-XRD offers many advantages over the conventional laboratory based XRD techniques such as: highly collimated and intense photon beams, photon-energy tune ability, exceptional photon wavelength resolution ($\Delta\lambda/\lambda \approx 2 \times 10^{-4}$), polarization control, coherence, very high signal-to-noise and signal-to-background ratio. The synchrotron techniques are extensively used in the identification of phases in compounds and unknown structural forms developed during the synthesis processes of the films. In recent years these techniques successfully investigated the local electronic structure of metal nitride thin films in pure and doped states [23–25].

To the best of our knowledge, investigations on structural thermal stability and oxidation resistance behaviors of these coatings via SR-XRD technique are yet to be established. This study addresses the temperature dependent surface morphology, mechanical properties, surface chemical bonding states, high temperature solar selective behaviors, and high temperature structural stability of magnetron sputtered TiAlSiN coatings via mechanical, SEM, XPS, UV–Vis and FTIR, and SR-XRD techniques.

2. Experimental techniques

2.1. Film deposition process

TiAlSiN films were deposited onto AISI M2 tool steel substrates via a closed field unbalanced magnetron sputtering system (UDP650, Teer Coating Limited, Droitwich, Worcestershire, UK). The magnetron sputtered system is equipped with a four-target configuration. Before coating, the substrates were ultrasonically cleaned in an acetone and methanol solution and then dried using high purity nitrogen gas. A pressure of 0.24 Pa was maintained in the chamber throughout the deposition process. Prior to synthesizing the samples, all of the targets were cleaned properly and the steel substrates were safeguarded by shutters through the magnetrons. In order to achieve a homogeneous film thickness, the substrate was rotated at a speed of 10 rpm throughout the synthesis process. The substrates were sputter cleaned with Ar plasma at a bias of −450 V for 30 min. The coatings were deposited in an $Ar + N_2$ mixed gas atmosphere. The partial pressure of Ar and N_2 were 0.133 Pa and 0.106 Pa throughout the deposition processes. The bias currents for Ti, Al and Si target were 5 A, 7 A, and 5 A, respectively. The final products were then annealed at 500, 600, 700 and 800 °C. Details of the deposition conditions of TiAlSiN coatings are displayed in Table 1.

2.2. Characterisations

Scanning electron microscopy (SEM) was conducted to determine the surface morphology of the thin film coatings with a high resolution microscope (SEM, PHILIPS XL 20, Eindhoven, The Netherlands). A secondary electron (SEI) detector was used to characterize the overall surface morphology of thin film structures. The SEM machine was operated at 25 kV. The samples were glued with double sided carbon tape affixed to the sample holders.

A depth-sensing indentation system (Ultra-Micro Indentation System, UMIS-2000, CSIRO, Australia) equipped with a Berkovich indenter was used to measure the Young's modulus and hardness of the coatings. The indenter tip was calibrated by conducting single-cycling indentation tests on fused silica (a standard material having a known modulus of 72 GPa) at different loads. Load–unload tests were run in a closed-loop under load control to determine the mechanical properties of the samples. A maximum load of 20 mN was applied in 10 increments. The loading rate set to 2.5 mN/s represents the static response of the materials. Following each increment there were 10 decrements, from which the Young's modulus and hardness were calculated. Five indentation tests were performed on each specimen. The load vs displacement response obtained by nanoindentation is a very powerful technique for analyzing mechanical properties. The elastic behavior of, and deformation mechanisms within, the coating systems can be realized by analyzing the nanoindentation data. In order to investigate the thermal stability of the sputtered films, mechanical hardness of the coatings was tested with the samples before annealing and after being annealed between 500 °C and 800 °C in steps of 100 °C in air atmosphere.

The XPS data will reveal information on chemical structure, elemental compositions and bonding states in the outermost 5 nm surface of the films. The XPS measurements of the TiAlSiN coatings were taken using an XPS (Kratos Axis Ultra XPS spectrometer, Manchester, UK) machine operating with an Al-K_α monochromatic radiation ($h\nu = 1486.6$ eV) source with a power of ~10 mA and ~15 kV. The XPS machine was also equipped with a cold stage, and an Ar ion gun for etching the coatings. The samples were mounted on a steel sample holder and put in the analysis chamber where the pressure was reduced to 2.9×10^{-9} Torr. The XPS survey spectra were collected before etching, and after 6 min etching. Ar ion sputtering was used for etching the films. Etching was done to remove any surface oxide layers and to reduce the Ti^{4+} ions in order to lower oxidation states. The high resolution XPS data was recorded after a 6 min Ar^+ sputtering. The typical high resolution XPS core level spectra of TiAlSiN samples before and after being annealed show Ti2*p*, Al2*p*, Si2*p*, N1*s* and O1*s* energy regions. Information on the existence of various chemical bonding states was acquired by subtracting the background with the Shirley's method and deconvoluting the spectra with curve-fitting methods using CASA XPS software (version 2.3.1.5) [32].

The optical properties of the thin film coatings were analyzed by measuring the optical reflectance as a function of wavelength from ultraviolet through the visible to infrared range of the solar spectrum via UV–Vis and FTIR spectrometers. A double-beam UV–Vis spectrophotometer (Model: UV-670 UV–Vis spectrophotometer, JASCO, USA) equipped with a unique, single monochromator design covering a wavelength range from 250 to 2500 nm was used to measure the solar absorptance of the coatings. The monochromator itself was designed with 1200 grooves/mm grating and a photo multiplier tube (PMT) detector. A PERKIN Elmer Spectrum 100 FTIR Spectrometer (USA) was used for measuring the reflectance, $R(\lambda)$, of