

The Effect of Annealing under Non-vacuum on the Optical Properties of TiAlN Non-vacuum Solar Selective Absorbing Coating Prepared by Cathodic Arc Evaporation

GONG Dianqing¹, CHENG Xudong^{1*}, YE Weiping², ZHANG Pu¹, LUO Gan²

(1. State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, Wuhan University of Technology, Wuhan 430070, China; 2. School of Materials Science and Engineering, Wuhan University of Technology, Wuhan 430070, China)

Abstract: TiAlN solar selective absorbing coatings which were deposited on 304L stainless steel using cathodic arc evaporation method were annealed under non-vacuum at different temperatures with different times. The optical properties (absorptance and emittance) of the coatings were measured by a spectrophotometer. It was found that, after being annealed for 2 hours at different temperatures, the absorptance of the coatings reached the highest value of 0.92 at 700 °C while the emittance got the lowest value of 0.38 at 800 °C. When the coatings were annealed at 600 °C for 24 hours, the optical properties changed to 0.92/0.44 (absorptance/emittance). By measuring the structure, morphology, elements and surface roughness of the coatings, it was found that both the elemental composition and the surface roughness of the coatings changed as a result of annealing, and these changes caused the change of the optical properties of the coatings.

Key words: annealing; optical properties; cathodic arc evaporation; solar selective absorbing coating

1 Introduction

Solar selective absorbing coating has attracted attention for more than 50 years because it is able to improve the efficiency of solar energy plant. Many materials have been fabricated as candidates, like black chromium^[1,2], ZnO, NiO^[3,4], TiN^[5], AlN^[6-8], Mo-Al₂O₃^[9]. Black chromium, ZnO and NiO put on good performance at low temperature, but they are out of action when operating temperature is above 400 °C. In 1984, TiN was introduced into solar energy field, and first prepared as high temperature solar selective absorbing coating. Since 1990 s, AlN, Mo-Al₂O₃ coatings have been developed for using in high temperature, and the absorptance of both these coatings can reach 0.96 while the emittance of them was as low as 0.10. Comparing to AlN, Mo-Al₂O₃, the optical performance of TiN was not so well. As a replacement of TiN, TiAlN has been applied as solar selective absorbing coating^[10].

In recent years, TiAlN/AlON tandem coating, TiAlN/TiAlON/Si₃N₄ tandem coating and SS/ TiAl/ TiAlN/ TiAlON/ TiAlO coating have been studied as advance of TiAlN coating^[11-13]. These tandem coatings achieved high absorptance as 0.93 and low emittance as 0.06. As a sound candidate of solar selective absorbing coating, TiAlN was used as main absorbing layer because it displays a low reflectance below 0.30 and a high absorptance above 0.80 in the visible-near ultra-spectral range.

However, all selective absorbing coatings reported have released few details of the effect of annealing under non-vacuum. These details are demanded when the coatings are applied in solar plant. According to this demand, we studied the effect of annealing under non-vacuum on the optical properties (absorptance and emittance) of the TiAlN coatings, and the results are presented in this paper. The coatings were prepared by cathodic arc evaporation and annealed under non-vacuum at different temperatures with different times. The optical properties of these coatings were measured by a spectrophotometer. Scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), atomic force microscopy (AFM) and X-ray diffraction (XRD) were used to characterize the coatings. The mechanism of the effect was studied.

©Wuhan University of Technology and SpringerVerlag Berlin Heidelberg 2013

(Received: July 19, 2012; Accepted: Oct. 8, 2012)

GONG Dianqing (宫殿清): Ph D Candidate; E-mail: gdq12052@163.com

*Corresponding author: CHENG Xudong (程旭东): Ph D, Prof.; E-mail:

xdcheng54@163.com

Funded by the "863" Hi-Tech Project of China (No.2009AA05Z440)

2 Experimental

TiAlN solar selective absorbing coatings were deposited in vacuum on 307L stainless steel substrates (dimensions: 20 mm×30 mm) using cathodic arc evaporation. High-purity Al-Ti (Al 67%, Ti33%) target was used for plating. To strengthen the combination of the coating and the substrate, CrN layer as transition layer was plated at bias of 200 V with the pressure of 0.3 Pa for 5 min. Then, TiAlN coating was plated at bias of 150 V with a pressure of 0.3 Pa, and the arc current was 70 A for 60 min. All the samples divided into 7 groups. Group 1 was the control group without being annealed. From group 2 to group 6, they were annealed under non-vacuum for 2 hours with different temperatures (shown in Table 1). Group 7 was annealed at 600 °C which is higher than the service temperature of the coatings for 24 hours to test the effect of long-time annealing on the coatings, because in one cycle, the time of the coating staying at high temperature is shorter than 24 hours.

Table 1 The annealing temperatures of all the samples

Sample	1	2	3	4	5	6	7
Annealing temperature /°C	-	400	500	600	700	800	600

After being annealed, the optical properties of all the samples were measured at room temperature. The near-normal spectral reflectance of the samples $R(\lambda)$ was measured in the wavelength of 0.3-2.5 μm by a Shimadzu UV3600 UV/VIS spectrophotometer. Solar absorptance (α) was calculated by the Eq.(1) which is of both the incident spectrum $I_{\text{sol}}(\lambda)$ and the reflectance of the samples $R(\lambda)$:

$$\alpha = \frac{\int_{0.3\mu\text{m}}^{2.5\mu\text{m}} I_{\text{sol}}(\lambda)(1-R(\lambda))d\lambda}{\int_{0.3\mu\text{m}}^{2.5\mu\text{m}} I_{\text{sol}}(\lambda)d\lambda} \quad (1)$$

And the thermal emittance of the samples was measured at 2.5-25 μm by a Bruker Tensor 27 Fourier Transform spectrometer. The surface morphology of samples was studied with JSM-5610LV SEM, and the ingredients of the coatings were detected by EDS. The surface imaging of the samples was carried out by AFM. The maximum scan ranges for AFM in the X-, Y- and Z- axis were 30 μm ×30 μm ×3 μm . The phase structures of the samples were studied by XRD using Rigaku D/MAX-RB.

3 Results and discussion

3.1 The effect of annealing temperature

The elements of the coatings which were measured by EDS are presented in Table 2. The change of oxygen content could be divided into two phases as annealing temperature rose. When annealing temperature was below 500 °C, the oxygen content changed little. But when annealing temperature was above 600 °C, nitrogen was replaced with oxygen and the coating changed into TiAlNO coating.

Table 2 The elements of the coatings /at%

No.	1	2	3	4	5	6
N	45.4	50.5	47.2	41.5	21.5	11.1
O	4.6	5.7	10.0	14.3	31.7	48.6
Al	27.2	29.9	29.1	30.5	28.9	27.4
Ti	12.9	13.9	13.8	13.7	17.4	12.9

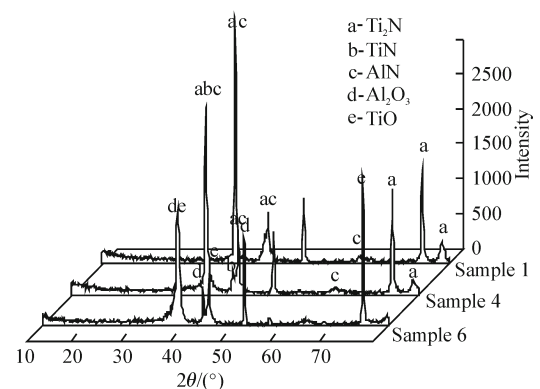


Fig.1 The XRD patterns of the samples

As shown in Fig.1, the X-ray diffraction of the coatings (samples 1, 4, 6) was performed to analyze the phase structures of the coatings. Both sample 1 and sample 4 are composed of Ti_2N and AlN. But the main diffraction peak of TiN at 42.6° is only displayed in sample 4, while in sample 1, at 42.6° , the peak is blurred. The change of the diffraction peak of TiN expresses that the process of annealing under 600 °C is the process of the phase formation of TiN. However, after annealed at 800 °C, because of oxidation at high temperature, sample 6 is composed of Al_2O_3 and TiO.

Oxidation is not the only consequence of annealing at high temperature such as 800 °C, so is the change of surface morphology of the coatings. According to the SEM image of the coatings in Fig.2(b), after being annealed at 800 °C, the coating cracked because the thermal strains of the coating and the substrate were with different thermal expansion coefficients.

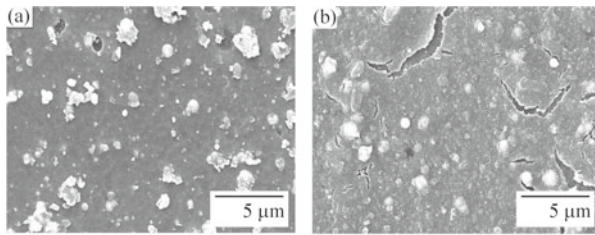


Fig. 2 SEM images of the samples. (a) annealed at 600 °C; (b) annealed at 800 °C

The surface roughness of the coatings was measured by the three-dimensional AFM images which are shown in Fig.3. It was 63.4 nm originally, and then turned to 96.0 nm after being annealed at 600 °C, and turned to 86.0 nm after being annealed at 800 °C.

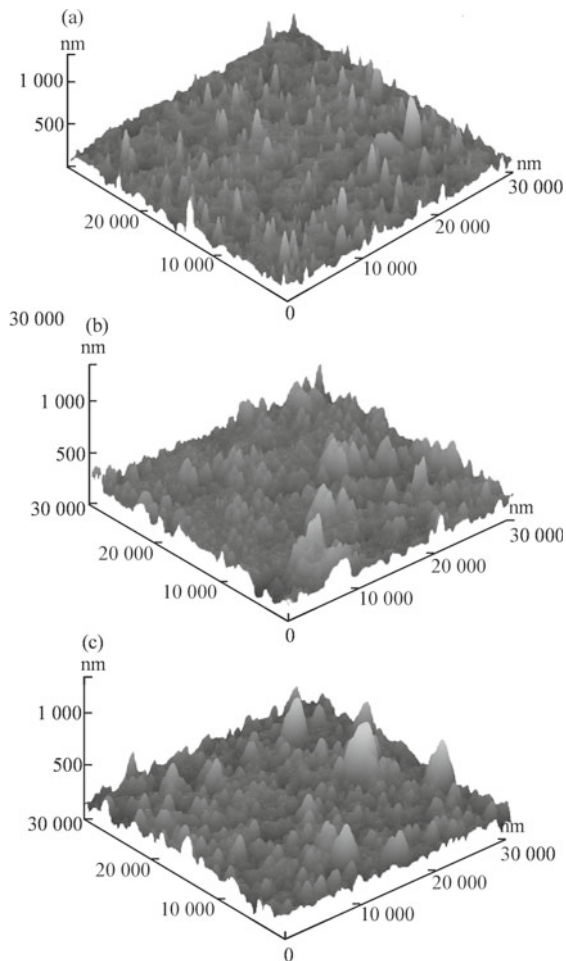


Fig.3 Three-dimensional AFM images of coatings:(a) sample 1; (b) sample 4; (c) sample 6

The optical properties of the samples which were annealed at different temperatures are shown in Fig.4. The absorptance (α) of the samples fluctuates in the range between 0.77 and 0.92, and emittance (ϵ) of them fluctuates in the range from 0.36 to 0.54. At first, both the absorptance and the emittance increased as annealing temperature rose, but then, the optical properties decreased when the annealing

temperature rose above a singularity. For absorptance, the singularity of annealing temperature is 700 °C, but for emittance, it is 500 °C. The ratio of the absorptance to the emittance (α/ϵ) reflects the efficiency of the optical selective absorption of the samples. The curve of the ratio in Fig.4(b) shows a 'V' as the annealing temperature rises, which means as annealing temperature rose, the efficiency reduced first, and then increased when annealing temperature was above the singularity about 500 °C. The singularity of annealing temperature expresses there is an optimum annealing temperature.

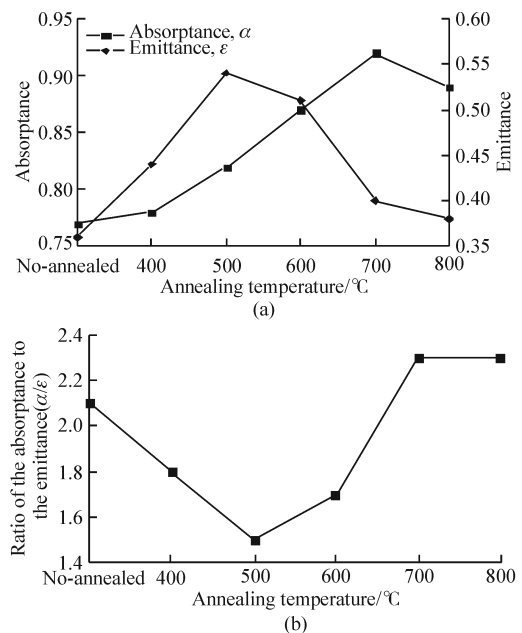


Fig 4 The curves of the optical properties of the samples annealed at different temperatures: (a) the curves of absorptance and emittance; (b) the curve of ratio of absorptance to emittance

Absorptance of the coatings, which is related to the reflectance of the coatings, depends on the elemental composition which determines the cut-off wavelength and the refractive index of the coatings. According to Eq.(2), the cut-off wavelength (λ_c) is related to the forbidden gap and wide forbidden gap related to short cut-off wavelength. For TiAlN coatings, titanium nitrides (Ti_2N and TiN) are of metallic character and with narrow forbidden gap (1.64 eV for TiN), while aluminum nitride (AlN) is a dielectric with wide forbidden gap (6.2 eV). When the coatings are annealed at high temperature, the products of oxidation have wider forbidden gaps. So, the cut-off wavelength got longer when the TiN content increased. And the change of the cut-off wavelength of the coatings caused the redshift of onset of the reflection shown in Fig.5, in which the letters a, b, c, d are the symbols for the onsets of the reflection of

samples 1, 4, 5, 6, respectively. But for the abnormal change of the onset of the reflection of sample 6, it is because of the cracks on the surface of the coatings and the light was reflected by the transition layer of CrN of which the forbidden gap is only about 0.09 eV. The refractive index (n) determines the reflectance (R) and the relation between them is shown in Eq.(3). By annealing, the oxide content of the coatings increased, and the titanium oxide possesses higher refractive index than the titanium nitride does. According to Eq.(3), as a result of the increase of titanium oxide, the reflectance of the coatings decreased, which resulted in an increase of the absorptance of the coatings. In short, the absorptance of the coatings changed because the reflectance of the coatings changed by annealing.

$$\lambda_c = \frac{h_c}{E_g} \quad (2)$$

$$R = \frac{1-n}{1+n} \quad (3)$$

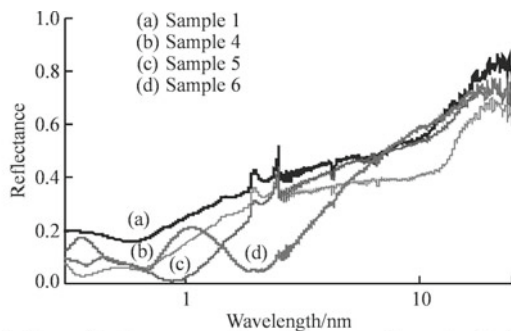


Fig.5 The reflectance-wavelength curves of samples 1, 4, 5, 6

Emittance of the coatings is a surface property and depends on the surface condition of the coatings such as the surface roughness and the oxides of the coatings^[14]. When annealing temperature rose, the emittance of the coatings increased because the surface of the coating got rough. But the emittance decreased when annealing temperature was above 500 °C because the content of oxides which possess high infrared reflectance increased as a result of oxidation at high temperature.

3.2 The effect of annealing time

The optical properties of samples 1, 4, 7 are listed in Table 3, and samples 4 and 7 were annealed at the same temperature of 600 °C but with different times. Comparing with sample 4 which was annealed for 2 hours, the optical properties of sample 7 which was annealed for 24 hours got better from 0.87/0.51 (absorptance/emittance) to 0.92/0.44 (absorptance/emittance).

It is shown that long annealing time promotes the selective absorbing ability of the coating.

Table 3 The optical properties of samples 1, 4, 7

Sample	1	4	7
α	0.77	0.87	0.92
ε	0.36	0.51	0.44
α/ε	2.1	1.7	2.1

Table 4 The elements of the coatings /at%

Sample	1	4	7
N	45.44	41.45	31.67
O	4.61	14.30	27.04
Al	27.22	30.51	28.01
Ti	12.89	13.74	13.26

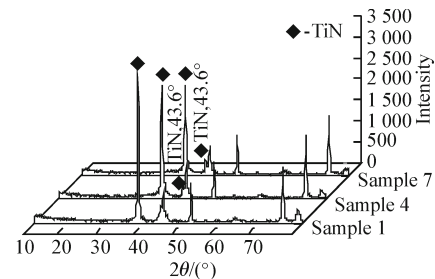


Fig.6 The XRD patterns of samples 1, 4, and 7

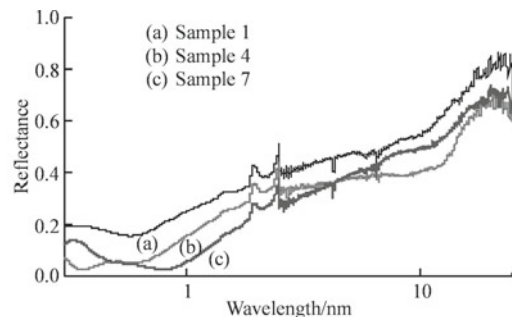


Fig.7 The reflectance-wavelength curves of samples 1, 4, 7

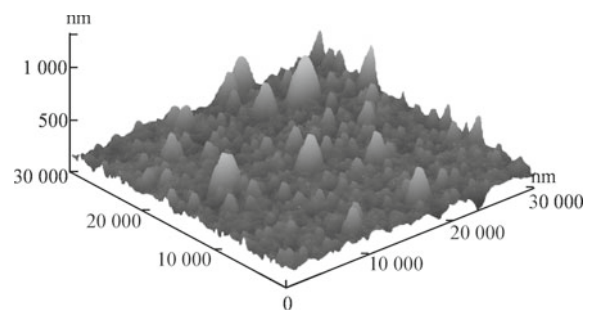


Fig. 8 Three-dimensional AFM image of sample 7

The increase of absorptance is caused by the change of elemental composition. According to Table 4, the coating was oxidized slowly when it was annealed at 600 °C. According to the XRD patterns of samples 1, 4, and 7 shown in Fig.6, as annealing time became long, the main diffraction peak of TiN at 42.6° became

clear, which means the process of annealing at 600 °C was also a process of formation and stabilizing of TiN. In Fig.7, which shows the reflectance-wavelength curves of samples 1, 4, 7, the letters a, b, c show the onsets of the reflection of samples 1, 4, 7 respectively. Comparing with the wavelength of b, the wavelength of c became longer because the content of TiN with narrow forbidden gap increased, which means the change of reflectance of the coatings was mainly caused by the redshift of onset of the reflection. In other words, the absorptance of the coatings which was annealed at 600 °C for long time of 24 hours was optimized by the increase of the TiN content.

The alteration of emittance of the coatings was caused by the change of surface condition of the coatings. By AFM imaging of sample 7 in Fig.8, the surface roughness of sample 7 is 76.9 nm. It is lower than of sample 4, but slightly higher than of sample 1. As annealing was going on, the surface of coating became flat, and the emittance of the sample was lowered.

4 Conclusions

In this paper, we researched the effect of annealing under non-vacuum on the TiAlN coatings and found the optical properties of the coatings changed when annealing parameters changed. After being annealed below 500 °C, the coatings oxidized little, and the absorptance of them increased from 0.77 to 0.82 because of redshift of the cut-off wavelength, and the emittance of them increased from 0.36 to 0.54 because of the increase of the surface roughness. However, after being annealed above 600 °C, the coatings oxidized greatly that they changed into TiAlNO coatings, and the absorptance of the coatings increased to 0.92 at 700 °C, then decreased to 0.89 at 800 °C because the cut-off wavelength and the oxides contents changed, but the emittance of the coatings decreased to 0.38 because of the changed of both the oxides and the surface roughness. The optical properties of the coatings attained the best value of 0.92/0.40 (absorptance/emittance) when the coatings were annealed at 700 °C.

The optical properties of the coatings got better when the annealing time extended at 600 °C. They changed from 0.87/0.51 (absorptance/emittance) for 2 hours to 0.92/0.44 (absorptance/emittance) for 24 hours. The increase of the absorptance was mainly caused by redshift of the cut-off wavelength, while the decrease of the emittance was caused by the change of surface roughness.

References

- [1] McDonald GE. Spectral Reflectance Properties of Black Chrome for Use as a Solar Selective Coating[J]. *Solar Energy*, 1975, 17(2): 119-122
- [2] Andersson A, Hunderi O, Granqvist CG. Nickel Pigmented Anodic Aluminum Oxide for Selective Absorption of Solar Energy [J]. *Journal of Applied Physics*, 1980, 51(1): 754-764
- [3] Zhao S, Ribbing CG, Wackelgard E. Optical Constants of Sputtered Ni/NiO Solar Absorber Film-depth-profiled Characterization [J]. *Solar Energy Materials and Solar Cells*, 2004, 84(1-4): 193-203
- [4] Katumba G, Olumekor L, Forbes A, et al. Optical, Thermal and Structural Characteristics of Carbon Nanoparticles Embedded in ZnO and NiO as Selective Solar Absorbers [J]. *Solar Energy Materials and Solar Cells*, 2008, 92(10): 1 285-1 292
- [5] Martin PJ, Netterfield RP, Sainty WG, et al. The Preparation and Characterization of Optical Thin Films Produced by Ion-assisted Deposition[J]. *Journal of Vacuum Science and Technology*, 1984, A 2(2): 341-345
- [6] Zhang QC. Stainless-steel-AlN Cermet Selective Surfaces Deposited by Direct Current Magnetron Sputtering Technology[J]. *Solar Energy Materials and Solar Cells*, 1998, 52(1-2): 95-106
- [7] Zhang QC, Shen YG. High Performance W-AlN Cermet Solar Coatings Designed by Modelling Calculations and Deposited by DC Magnetron Sputtering[J]. *Solar Energy Materials and Solar Cells*, 2004, 81(1): 25-37
- [8] Zhao S, Wackelgard E. The Optical Properties of Sputtered Composite of Al-AlN [J]. *Solar Energy Materials and Solar Cells*, 2006, 90(13): 1 861-1 874
- [9] Teixeira V, Sousa E, Costa MF, et al. Spectrally Selective Composite Coatings of Cr-Cr₂O₃ and Mo-Al₂O₃ for Solar Energy Applications [J]. *Thin Solid Films*, 2001, 392(2): 320-326
- [10] Schüler A, Tommen V, Reimann P, et al. Structure and Optical Properties of Titanium Aluminum Nitride Films (Ti_{1-x}Al_xN) [J]. *Journal of Vacuum Science and Technology*, 2001, A19(3): 922-929
- [11] Barshilia HC, Selvakumar N, Rajam KS, et al. Deposition and Characterization of TiAlN/TiAlNO/Si₃N₄ Tandem Absorbers Prepared Using Reactive Direct Current Magnetron Sputtering [J]. *Thin Solid Films*, 2008, 516(18): 6 071 - 6 078
- [12] Barshilia HC, Selvakumar N, Rajam KS, et al. Optical Properties and Thermal Stability of TiAlN/AlON Tandem Absorber Prepared by Reactive DC/RF Magnetron Sputtering [J]. *Solar Energy Materials and Solar Cells*, 2008, 92(11): 1 425- 1 433
- [13] Hao L, Wang SM, Jiang LJ, et al. Preparation and Thermal Stability on Non-vacuum High Temperature Solar Selective Absorbing Coatings [J]. *Chinese Science Bulletin*, 2009, 54(8): 1 451-1 454
- [14] Seraphin BO. Solar Energy Conversion: Solid State Physics Aspects[C]. In: *Topics in Applied Physics*, Berlin, Springer, 1979:24