Uppsala University

This is an accepted version of a paper published in *Solar Energy Materials and Solar Cells*. This paper has been peer-reviewed but does not include the final publisher proof-corrections or journal pagination.

Citation for the published paper:

Zhu, D., Mao, F., Zhao, S. (2012)

"The influence of oxygen in TiAlO_xN_y on the optical properties of colored solar-absorbing coatings"

Solar Energy Materials and Solar Cells, 98: 179-184

URL: <http://dx.doi.org/10.1016/j.solmat.2011.11.001>

Access to the published version may require subscription.

Permanent link to this version:

<http://urn.kb.se/resolve?urn=urn:nbn:se:uu:diva-164134>

<http://uu.diva-portal.org>

The Influence of oxygen in TiAlO_xN_y on the optical properties of colored solar-absorbing coatings

Dechun Zhu

Department of Chemical and Materials Engineering, Hefei University, 230022, Hefei, P.R. China

Fang Mao, Shuxi Zhao¹

Department of Engineering Sciences, Uppsala University, Box 534, SE-751 21, Uppsala, Sweden

Abstract:

Low cost and ease of fabrication are important factors for solar-thermal applications in energy-efficient buildings. This contribution reports the influence of oxygen on structure, optical properties and chromaticity of TiAlO_xN_y thin films prepared by DC magnetron sputtering. It is an extension of a previous study on colored solar-thermal absorbers based on titanium-aluminum nitride. The purpose is to investigate the possibility of using TiAlO_xN_y as middle layer to achieve a gradient effect. The results reveal that the structure and optical properties of the TiAlO_xN_y coatings are sensitive to the oxygen content under certain sputtering conditions. The ratio of oxygen/nitrogen of 0.7:10 is the most appropriate to form the crystalline structure of TiAlON . The optical constants of TiAlN and TiAlON were deduced by fitting the experimental data. It shows that both the refractive index (n) and the extinction coefficient (κ) are decreased when oxygen is introduced to form titanium-aluminium nitro-oxide. The gradient effect can be achieved and controlled by adjusting the ratio of oxygen/nitrogen flow during the process to enhance solar absorptance while keeping the desired color appearance.

Key words: Titanium-aluminum nitride/nitro-oxide; colored solar-thermal absorber; optical properties; chromaticity.

1. Introduction

Materials of solar-thermal energy conversion have been studied for several decades [1, 2]. A variety of selective surfaces have been proposed and fabricated for solar thermal applications. Among them, most of the commercially selective surfaces are constructed as absorber-reflector tandems [3-5]. A tandem absorber consists of at least two layers with different optical properties: a coating having high absorptance in the solar wavelength range is

¹ Corresponding author. Tel: +46 18 471 1085, Fax: +46 18 471 3270
E-mail: shuxi.zhao@angstrom.uu.se

deposited onto a highly IR-reflecting metal substrate. These layers together show spectrally selective properties. Widely used absorbing materials for solar-thermal coatings are composites which consist of very fine metal particles embedded in a dielectric matrix, also known as cermet materials [6]. Such composites are strongly absorbing in the solar spectral range due to the nano-size of the metallic particles. In the infrared spectral range, they rapidly become highly transparent with increasing wavelength. However, there is always a risk of aggregation and oxidation of the metallic particles in the cermet layer, so growing attention is paid to chemical compounds which are thermally stable and have intrinsic absorption in the solar range. Transition metal (or alloys) nitrides/nitro-oxides, such as TiN, TiN_xO_y and TiAlN , TiAlO_xN_y , have become popular as solar energy materials due to their good optical properties in combination with their thermal and chemical stability [7].

The titanium/titanium-aluminum nitride films were initially applied to hard coatings on cutting and drilling tools due to their excellent mechanical properties and good oxidation resistance at high temperatures [8, 9]. TiAlO_xN_y films have also been applied as a diffusion barrier and electrically insulating layers in semiconductor memory devices [10, 11]. Furthermore, $\text{TiN}_x\text{O}_y/\text{TiAlO}_x\text{N}_y$ attracts much attention as a solar absorbing layer after M. Lazarov *et al.* reported that TiO_xN_y thin films deposited on copper exhibited excellent solar selective properties [12, 13] and R. Luthier *et al.* reported that TiAlON as a black decorative coating had good optical properties: low reflectance in the visible-near-UV spectral range (below 0.16) and high absorption coefficient ($1\sim 4\times 10^5\text{ cm}^{-1}$) [14]. Maria Brogren *et al.* reported that $\text{Ti}_x\text{Al}_y\text{N}_z$ coatings offered good possibilities when used for their optical selectivity in satellite temperature control [15]. H.C. Barshilia *et al.* reported the highest absorptance (0.958) and low emittance (0.07 at 82°C) achieved by $\text{TiAlN}/\text{TiAlON}/\text{Si}_3\text{N}_4$ tandem absorbers [16]. We have reported the solar-absorbing coating based on $\text{TiAlON}/\text{TiAlN}$ with regard to its colored appearance as energy-saving materials used in buildings [17]. Energy consumption of houses and buildings contributes a large part of the total energy consumption in developed countries as well as in China. Solar-thermal applications in buildings can play more important roles if the integration of solar collector installations into buildings and the color appearance of the absorbers can be improved. An attractive appearance of the solar collectors in the construction of buildings is very important for architects and inhabitants. The integration of colored, decorative absorbers will lead to a wider acceptance among building architects and users. Furthermore, low cost and ease of production is also important for large scale applications. Using the same target to get a

gradient effect is an easy way to reduce cost. For a cermet material, which is produced by reactive dc sputtering, gradually increasing oxygen (during processing) is an effective way to produce gradient coatings. When producing nitro-oxide, different amounts of oxygen in the compound change the optical properties of the films. In this study, the optical properties of titanium-aluminium nitride/nitro-oxide prepared by DC magnetron sputtering are presented and the influence of oxygen in TiAlO_xN_y on the optical properties is discussed. The purpose is to show that it is possible to use TiAlO_xN_y as middle layer material (in triple constructions [18]) to achieve a desired gradient effect.

2. Sample preparation

The samples were prepared in a reactive dc magnetron sputtering unit Balzer UTT400 which is described in detail elsewhere [17]. Alloy titanium-aluminium at 50% of atomic ratio (99.99% pure) was used as target to produce TiAlN and TiAlO_xN_y thin film. The substrates were Corning glass (7059) and aluminum sheets of size 50mm by 50mm. The substrates were cleaned in an ultrasonic bath, followed by de-ionized water rinsing and nitrogen gas drying.

Argon flow (99.999% pure) and nitrogen flow (99.999% pure) were fixed at 60 and 10 ml/min respectively for nitride film deposition. Oxygen (99.99% pure) flow was varied in a range from 0.14 to 1.5 ml/min under the fixed argon and nitrogen flows for nitro-oxide film deposition. The base pressure was 10^{-5} Pa. The operation pressure was around 1 Pa. Deposition was carried out under a sputtering power density of 35 W/cm^2 . In order to get a crystalline structure, the substrate was heated up to 350°C . Detailed information of the samples used in this study is listed in table 1.

Table 1

3. Optical and structure characterization

The optical performance of the TiAlN and TiAlO_xN_y thin films deposited on Corning glass was characterized by a Perkin-Elmer Lamda 900 UV/VIS/NIR double beam spectrophotometer. It is a dispersive type which uses a white light source and a grating monochromator to create light with a specified wavelength. The instrument is equipped with an integrating sphere to allow for measurements on a rough substrate such as rolled aluminium sheets [19]. A Spectralon sample was used for reference. The measured wavelength range is between 300 and 2500 nm with an interval of 5 nm.

To study the solar-thermal conversion of TiAlO_xN_y thin films, aluminum substrates were used to get tandem samples. The thermal emittance was characterized by the optical reflectance in the infrared range. The instrument used for such measurements was a TENSOR 27 from Bruker Optics. It is a type of Fourier Transform Infrared Reflectance (FTIR) spectrometer. In FTIR, the data are collected as an interference pattern by the connected computer and are processed with a Fast Fourier Transform technique to reform the spectrum. The Bruker Tensor 27 is equipped with an integrating sphere coated with gold. The measuring wave number range is from 4000 to 450 cm^{-1} with a resolution of 4 cm^{-1} .

The total solar absorptance α calculated at normal angle of incidence is a weighted average, weighted by the solar spectral radiation. AM 1.5 solar spectrum was used, which is defined by the ISO standard 9845-1 (1992) [3]. The near normal thermal emittance ε is calculated as a weighted average, weighted by the blackbody radiation, $I_b(\lambda, T)$, for a given temperature.

X-ray diffraction measurements for TiAlN and TiAlO_xN_y thin films were performed by a Siemens D5000 diffractometer operating with a grazing incidence angle of one degree in parallel beam geometry using CuK_α radiation (this wavelength is $1.540598\text{ \AA}$) and the diffraction pattern was analyzed between 24° to 58°

Film resistance R_f was measured by a square-probe which directly touches on the sample surface with a certain pressure. The probe consists of two parallel rows of four pin type contacts. The four contacts in a row are electrically connected and work as one pole, so the measured distance is kept the same. The reciprocal of film resistance is defined as film conductance.

4. Optical constant deduction

The optical constants of sputtered materials are usually different from the optical constants of the corresponding bulk materials. The calculation of reflectance spectra consisting of sputtered thin film requires experimentally determined optical constants. Many methods for the determination of optical constants have been reported [20-22]. Combined reflectance and transmittance measurement for the determination of optical constants is one among them. The method involves two measurements: reflectance and transmittance at a near normal angle of

incidence on a semi-transmitting sample. Traditionally, the optical constants are then deduced by the cross point between iso-reflectance and iso-transmittance curves in the $n-k$ plane for each wavelength, i.e. calculated point by point. Major problems can occur when the R- and T- contours are almost parallel at their intersection, which causes uncertainties.

Instead of calculating point by point at each wavelength, the determination of the optical constants for the entire measured wavelength range was developed in our study for sputtered composite materials based on models of dielectric functions. Reflectance and transmittance spectra of modeled thin films on glass substrates can then be calculated and compared to the experimental reflectance and transmittance spectra. The dielectric function of each component usually contains more than one variable. These variables, as well as the film thickness, are then used as fitting parameters. Thus, the optical constants were deduced by fitting the theoretical reflectance and transmittance spectra to the experimental ones in the whole experimental wavelength range.

Modern computer technique provides a way to make the fitting procedure easy. The software we used is ‘CODE’ (Coating Designer) [23] where simulated spectra can be fitted to experimental data. Fitting results depend on models. Previous work shows that it is a good way to help design experiments.

5. Chromaticity

The color of the samples was numerically represented in CIE chromaticity diagram described in the Handbook of Optics [24]. A set of three color-matching functions, $x(\lambda)$, $y(\lambda)$ and $z(\lambda)$ provide the numerical description of the chromatic response of the observer. Tristimulus values X , Y and Z are calculated from three similar integrations of the measured or simulated spectral power distribution data $P(\lambda)$:

$$\begin{aligned} X &= \int P(\lambda)x(\lambda)d\lambda \\ Y &= \int P(\lambda)y(\lambda)d\lambda \\ Z &= \int P(\lambda)z(\lambda)d\lambda \end{aligned} \tag{1}$$

The spectral power distribution $P(\lambda)$ can be the product of a source spectrum and a measured or simulated reflectance spectrum of a sample. In the case of a neutral light source,

$$P(\lambda) = R(\lambda) \tag{2}$$

where $R(\lambda)$ is the measured reflectance spectrum.

From the tristimulus values, the color coordinates x , y , z are defined as

$$\begin{aligned} x &= X/(X + Y + Z), \\ y &= Y/(X + Y + Z), \\ z &= 1 - (x + y) \end{aligned} \quad (3)$$

In this paper, only the case of a neutral light source is discussed for simplicity. Data of three color-matching functions can be found in the Handbook of Optics [24].

6. Results and discussion

6.1. XRD Structure of TiAlN coating

Figure 1 shows the XRD pattern of a single layer pure nitride thin film, which shows the TiAlN structure characterized by the peak at $2\theta=37.5^\circ$ with preferred orientation (111) [25]. The sample was sputtered at a nitrogen flow of 10 ml/min with a substrate temperature of 350°C . The small peak centered at $2\theta=43.5^\circ$ indicates that there is a trace of TiAlON (200) [26], showing the effect of remaining oxygen in the sputtering chamber.

Figure 1

6.2. XRD structure of TiAlO_xN_y – Oxygen effect on structure

Under certain sputtering conditions, the effect of oxygen on TiAlO_xN_y is clear. Figure 2 shows the influence of the oxygen flow on the XRD pattern of TiAlO_xN_y , where the nitrogen flow was fixed at 10 ml/min and the oxygen flow was increased from 0.14 to 1.5 ml/min. Generally, introducing oxygen during sputtering will produce TiAlON. Even a small ratio of oxygen to nitrogen flow, such as 0.14:10, reduced the peak intensity of TiAlN dramatically, and at the same time the peak of TiAlON appeared, indicating that oxidization of titanium-aluminum alloy is more active than nitrogenization.

Increasing the oxygen flow from 0.2 to 0.7 l/min, the peak intensity of TiAlN gradually decreased to zero (merged in background). Meanwhile, the peak intensity of TiAlON gradually increased to its maximum and both peaks of TiAlN and TiAlON shifted slightly to a higher angle position as the oxygen flow increased, which indicates that the lattice parameter decreased with the increase of O_2 flow. This is because both TiAlN and TiAlON are B1 cubic structures and the lattice constant of TiAlON (4.13 Å) is slightly smaller than TiAlN (4.17 Å)

[27, 28]. Increasing the oxygen flow further from 0.7 to 1.5 l/min caused the peak intensity of TiAlON to drop again and the peaks became broad, which indicates that the amount of crystalline TiAlON decreased and the cell size became smaller. This is possibly due to the formation of amorphous (TiAl)O₂ with increasing oxygen flow [26].

Figure 2

From the results of figure 1 and 2, we can see that oxygen in a wide flow range together with nitrogen reacts with titanium-aluminum alloy forming TiAlO_xN_y. When the ratio of oxygen/nitrogen is less than 0.7:10, the result is a mixture of TiAlN and TiAlON. When the ratio of oxygen/nitrogen is larger than 0.7:10, TiAlN disappears and only TiAlON is found (perhaps with amorphous (TiAl)O₂). The influence of oxygen flow on the structure can also be illustrated in figure 3 which shows how the peak intensity of TiAlN and TiAlON changes with oxygen flow under fixed nitrogen flow of 10 ml/min during sputtering. These results indicate that the ratio of oxygen/nitrogen of 0.7:10 is the most appropriate for the formation of crystalline TiAlON.

Figure 3

The film thickness of the above samples was controlled by the sputtered time and checked by an instrument, a Tencor Alpha-step 200, which uses a mechanical stylus to measure the thickness of the film around a film edge. The samples in figures 1 to 5 have the same thickness within 10 percent deviation.

6.3. Optical properties

The optical properties were also strongly influenced by the oxygen/nitrogen flow ratio. Figure 4 shows that the transmittance of the thin films gradually increases with the increasing oxygen flow in the whole oxygen flow range. Figure 5 shows that the absorptance of the thin film decreases with increasing oxygen flow. The absorptance A was deduced according to

$$A = 1 - R - T \quad (4)$$

where, R and T are the measured reflectance and transmittance values.

As well known, the gradient index coatings are important for solar absorbers because they are an efficient way to reduce the front surface reflectance loss, hence enhanced solar absorptance

[29]. A three-layer absorbing coating is widely used as a simple structure for gradient coatings [18]. For a three-layer solar absorber, the base-layer is the main absorbing layer, so higher transmittance of the middle-layer will create a gradient effect when it is deposited on top of the base layer. From this point of view, TiAlON will be a good choice to be used as the middle-layer in the solar thermal absorbing coatings.

Figure 4

Figure 5

6.4. Optical constants

Two samples of thin films coated on glass were used to deduce the optical constants of TiAlN and TiAlON (prepared at the oxygen/nitrogen ratio of 0.7:10). The principle of deduction was described in section 4. From measured reflectance and transmittance data, a model based on the Bruggeman theory was built to fit the experimental data. The dielectric function of the transition metal was also based on a model where the free charge carrier was described by the Drude model, and the Lorentz model was used to describe the transition of d-electrons. The fitting results from the sample of TiAlON thin film are shown in figure 6, where circles and squares represent the experimental R and T, respectively. The blue and red lines are the fitting results.

Figure 6

The deduced optical constants of TiAlN and TiAlON are shown in figure 7. It is clear that both the refractive index and the extinction coefficient are decreased as titanium-aluminium nitro-oxide is formed. The dispersion behaviour is similar to the nickel-nickel oxide cermet when metallic volume fraction was varied [30]. This behaviour gives the possibility of forming a desired gradient effect in solar absorbing coatings.

Figure 7

6.5. Conductance

The reciprocal of the measured film resistance is defined as the film conductance. TiAlN shows the behavior as a good semiconductor (film resistance was about 30 k Ω with film

thickness about 320 nm). However, the conductance decreases as oxygen flow is increased during preparation. When the oxygen flow reaches the value of 0.7 ml/min, the resulting TiAlON is almost an insulator (film resistance is about 4M Ω). Figure 8 shows how the conductance changes with differing oxygen flow and fixed nitrogen flow.

Solar radiation is very high frequency electro-magnetic wave radiation. For solar absorbing coatings, absorption is mainly due to the displacement of “free” or weakly bonded electrons with respect to molecular charges and interband absorption. This explains why the semiconductor behavior of TiAlN gives strong absorption in the solar wavelength range. The absorption effect decreases with increasing oxygen flow as indicated by the reduced conductance (forming more TiAlON). Thus, the gradient requirement for solar absorbing coatings can be carried out by gradually increasing the oxygen flow in this way: from zero for base layer to some value for middle layer. Such properties simplify the procedure for large scale production and conductance measurement provides a simple and quick way to control the process.

Figure 8

6.6. Color vision

Colored solar absorbing coatings are becoming more popular for integrated energy-efficient buildings [15]. Therefore, the color appearance influenced by oxygen is also of interest in this study. Generally, single layers of TiAlON coatings show color, but the solar absorptance is not very high. If it is used as middle layer deposited on top of a colored TiAlN layer, it not only modifies the color, but also enhances the solar absorptance. Figure 9 shows an example: a single layer of TiAlN coated on aluminum substrate shows red color with solar absorptance of 0.86 (sample *C-ILR*); the color appearance becomes green with an enhanced solar absorptance of 0.92 when TiAlON layer was deposited on top of the TiAlN layer (sample *C-2LG*).

Figure 9

7. Conclusions

The titanium-aluminium nitro-oxide TiAlON is a promising coating material to be the middle-layer on top of colored titanium-aluminum nitride TiAlN to enhance the solar absorptance while keeping a desired color appearance. The results reveal that the structure and optical properties of the TiAlO_xN_y layer are sensitive to the oxygen content under certain sputtering conditions. The XRD results show that, together with nitrogen, oxygen within a wide flow range reacts with titanium-aluminum alloy to form TiAlO_xN_y . The ratio of oxygen/nitrogen of 0.7:10 is the most appropriate to form a crystalline structure of TiAlON. The TiAlN shows the behavior of a good semiconductor, while TiAlON is almost an insulator. The transmittance of TiAlO_xN_y increases with increasing oxygen content in TiAlO_xN_y , while the absorptance of TiAlO_xN_y decreases as the oxygen content increases. The deduced optical constants of TiAlON and TiAlN reveal a difference in both values and dispersion. TiAlON thin film as middle layer deposited on top of a colored TiAlN layer on an Al substrate not only modifies the color of the absorber tandem but also enhances its solar absorptance.

Acknowledgement

The authors would like to thank the Faculty of Science and Technology, Uppsala University for financial support for the international cooperation between Hefei and Uppsala University, and the Natural Science Foundation of Anhui Educational Commission (KJ2009B036) for the work.

The authors would also like to thank Professor Arne Roos for his assistance in the optical characterization and for kindly helping to correct the English.

References

1. G.A. Niklasson, C.G. Granqvist, Surfaces for Selective Absorption of Solar Energy: An Annotated Bibliography 1955-81, *J. Mater. Sci.* 18 (1983) 3475-3534.
2. C.G. Granqvist, Solar Energy Materials-Overview and some Examples, *Applied Physics A*, 52 (1991) 83-93.
3. E. Wäckelgård, G. Hultmark, Industrially sputtered solar absorber surface, *Solar Energy Materials and Solar Cells*, 54 (1998) 165-170.
4. B.O. Seraphin, Chemical vapor deposition of thin semiconductor films for solar energy conversion, *Thin Solid Films*, 39 (1976) 87-94.
5. M. Janai, D.D. Allred, D.C. Booth and B.O. Seraphin, Optical properties and structure of amorphous silicon films prepared by CVD, *Solar Energy Materials*, 1 (1979) 11-27.
6. R.A. Buhrman, H.G. Craighead, Composite Film Selective-Absorbers, in *Solar Materials Science*, edited by Lawrence E. Murr, 1980, Academic Press, New York, 277-292.
7. E. Wäckelgård, G.A. Niklasson and C.G. Granqvist, Selectively Solar-Absorbing Coatings, in *Solar Energy-the State of the Art*, edited by Jeffrey Gordon, 2001, James & James Ltd, London, 123-127.
8. Y. H. Yoo, D. P. Le, J. G. Kim, S. K. Kim, P. V. Vinh, Corrosion behavior of TiN, TiAlN, TiAlSiN thin films deposited on tool steel in the 3.5 wt.% NaCl Solution, *Thin Solid Films* 516 (2008) 3544-3548.
9. B.Y. Man, L. Guzman, A. Miotello, M. Adami, Microstructure, oxidation and H₂-permeation resistance of TiAlN films deposited by DC magnetron sputtering technique, *Surface and Coatings Technology* 180-181 (2004) 9-14.
10. H.C. Kim, T.L. Alford, Investigation on diffusion barrier properties of reactive sputter deposited TiAl_xNyOz thin films for Cu metallization, *Thin Solid Films* 449 (2004) 6-11.
11. A. Schöler, V. Thommen, P. Reimann, P. Oelhafen, Structure and optical properties of titanium aluminum nitride films (Ti_{1-x}Al_xN), *J. Vac. Sci. Technol. A*, 19 (3) (2001) 922-929.
12. M. Lazarov, P. Rath, H. Metzger, and W. Spirk, Optical constants and film density of TiN_xO_y solar selective absorbers, *J. Appl. Phys.* 77 (1995) 2133-2137.
13. M. Lazarov, A. Brunotte, T. Eisenhammer, R. Sizmann and W. Graf, V. Wittwer, Effects of roughness on TiN_xO_y-Cu selective absorbers, *SPIE*, 1727 (1992) 34-45.
14. R. Luthier, F. Lévy, Magnetron sputtered TiAlON composite thin films. II. Optical and electrical properties, *J. Vac. Sci. Technol. A*, 9 (1) (1991) 110-115.
15. M. Brogren, G.L. Harding, R. Karmhag, C.G. Ribbing, G.A. Niklasson, L. Stenmark, Titanium-aluminum-nitride coatings for satellite temperature control, *Thin Solid Films*, 370 (2000) 268-277.
16. H.C. Barshilia, N. Selvakumar, K.S. Rajam, Thermal stability of TiAlN/TiAlON/Si₃N₄ tandem absorbers prepared by reactive direct current magnetron sputtering, *J. Vac. Sci. Technol. A*, 25 (2) (2007) 383-390.
17. D. Zhu, S. Zhao, Chromaticity and optical properties of colored and black solar-thermal absorbing coatings, *Solar Energy Materials & Solar Cells*, 94 (2010) 1630-1635.
18. Q.C. Zhang, D. R. Mills, New cermet film structures with much improved selectivity for solar thermal applications, *Applied Phys. Lett.*, 60 (5) (1992) 545-547.
19. A. Roos, Use of an integrating sphere in solar energy research, *Solar Energy Materials and Solar Cells*, 30 (1993) 77-94.

20. P.O. Nilsson, Determination of optical constants from intensity measurement at normal incidence, *Applied Optics*, 7 (1968) 435-442.
21. T.C. Pauick, Inversion of normal-incidence (R, T) measurements to obtain $n+ik$ for thin film, *Applied Optics*, 25 (1986) 562-564.
22. D. Pekker, L. Pekker, A method for determining thickness and optical constants of absorbing thin film, *Thin Solid Films*, 425 (2003) 203-209.
23. M. Theiss, Hard and software for optical spectroscopy, 2002, Dr. Bernhard-Klein-Str. 110, D-52078 Aachen, Germany.
24. G. Wyszecki, Colorimetry, Walter G. Driscoll (Ed.), *Handbook of Optics*, Optical Society of American, McGraw-Hill Book Company, New York.
25. R. Luthier, F. Lévy, Magnetron sputtered TiAlON composite thin films. I . Structure and morphology, *J. Vac. Sci. Technol. A* , 9 (1) (1991) 102-109
26. C. Hsu, M. Chen, K. Lai, Corrosion resistance of TiN/TiAlN-coated ADI by cathodic arc deposition, *Materials Science and Engineering A*, 421 (2006) 182-190.
27. S.Y. Lee, S.C. Wang, J.S. Chen, J.L. Huang. Effects of nitrogen partial pressure on electrical properties and thermal stability of TiAlN films by ion beam sputter deposition, *Surface& Coating Technology*, 202 (2007) 977-981.
28. R. Luthier, F. Lévy, TiAlON black decorative coatings deposited by magnetron sputtering, *Vacuum*, 41(7-9) (1990) 2205-2208.
29. I.T. Ritchie, B. Window, Applications of thin graded-index films to solar absorbers, *Applied Optics*, 16 (1977) 1438-1443.
30. S. Zhao, Spectrally selective solar absorbing coatings prepared by dc magnetron sputtering, PhD. Thesis, Uppsala University, Sweden, 2007, ISSN 1651-6214, pp. 36-37.

Table 1

List of samples

Sample label	α	ε	O ₂ /N ₂	Substrate	Coating materials	Color
<i>G-TAN-1</i>			0 : 10	Glass	TiAlN	
<i>G-TAON14</i>			0.14 : 10	Glass	TiAlO _x N _y	
<i>G-TAON20</i>			0.2 : 10	Glass	TiAlO _x N _y	
<i>G-TAON40</i>			0.4 : 10	Glass	TiAlO _x N _y	
<i>G-TAON50</i>			0.5 : 10	Glass	TiAlO _x N _y	
<i>G-TAON60</i>			0.6 : 10	Glass	TiAlO _x N _y	
<i>G-TAON70</i>			0.7 : 10	Glass	TiAlON	
<i>G-TAON100</i>			1.0 : 10	Glass	TiAlON	
<i>G-TAON150</i>			1.5 : 10	Glass	TiAlON	
<i>G-TAN-2</i>			0 : 10	Glass	TiAlN	
<i>G-TAON-2</i>			0.7 : 10	Glass	TiAlON	
<i>C-ILR</i>	0.86	0.04	1 layer	Aluminum	TiAlN	Red
<i>C-2LG</i>	0.92	0.08	2 layers	Aluminum	TiAlN+TiAlON	Green

Figure Captions

Figure 1. The XRD pattern of sample TiAlN (Label *G-TAN-1*) shows the structure of TiAlN at preferred orientation (111).

Figure 2. The XRD pattern of samples labelled *G-TAN-1*, *G-TAON14* to *G-TAON150*, where nitrogen flow was fixed at 10 ml/min, oxygen flow increased from 0.14 to 1.5ml/min.

Figure 3. The XRD peak intensity of TiAlN and TiAlON changes with oxygen flow under fixed nitrogen flow for samples labelled *G-TAN-1*, *G-TAON14* to *G-TAON150*.

Figure 4. The transmittance of thin film changes with increasing oxygen flow for samples labelled *G-TAN-1*, *G-TAON14* to *G-TAON150*.

Figure 5. The absorptance of thin film changes with increasing oxygen flow for samples labelled *G-TAN-1*, *G-TAON14* to *G-TAON150*.

Figure 6. Experimental and fitted reflectance and transmittance spectra of sample labelled *G-TAON-2*: circles, experimental R , blue line—fitting R ; squares – experimental T , red line – fitting T .

Figure 7. Refractive index n and extinction coefficient k of TiAlN and TiAlON deduced from sample *G-TAN-2* and *G-TAON-2* respectively.

Figure 8. The conductance of thin film changes with increasing oxygen flow for samples labelled *G-TAN-1*, *G-TAON14* to *G-TAON150*.

Figure 9. The chromaticity diagram of single layer of TiAlN on aluminium substrate with red colour (*C-1LR*) and two -layer of TiAlON/TiAlN on aluminium substrate with green colour (*C-2LG*).

Figures

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9