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SYNTHESIS AND CHARACTERIZATION OF HARD LAYERS OBTAINED BY VACUUM ARC TECHNOLOGY

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Abstract: TiN/(Ti,Al)N layers were deposited by reactive cathodic arc method on turbine blade materials. Microchemical, microstructural and mechanical characteristics of the layers were analyzed, resulting stoichiometric films with high microhardness and adhesion, with high oxidation resistance determined by the formation of a thin alumina film on the surface.

Key words: TiN//TiAlN layers, hard coating, oxidation resistance, cathodic arc deposition.

INTRODUCTION

Over the past years, TiN and (Ti,Al)N hard coatings have gained increasing importance in the cutting tool and different mechanical parts coating to increase their life time and performance, due to their attractive properties such as high hardness, chemical stability, good wear and oxidation resistance[1-2]. In gas turbine engines, higher life time of the rotor blades can be achieved using coatings which provide a better oxidation resistance. [3-4].

Hot section components of the rotors such as combustors, blades and vanes are generally made from nickel-based super alloys such as Inconel 718 and nickel based alloy such as NCK 18 TDA. The operating temperature is limited to 650^0 C for Inconel 718 and at approx. 850^0 C for NCK 18 TDA. Above 650^0 C the Inconel 718 alloy primary strengthening precipitate particles coarsen rapidly and induce loss in strength [5]. NCK 18 TDA alloy presents a higher oxidation resistance in comparison with Inconel 718 due to Al migration from the bulk material to its surface and the formation of alumina in oxygen atmosphere. However, it presents a decrease of its strength at both increase or decrease in the aluminum bulk content [6]. The idea of this study was to prevent the depletion or the enrichment with Al of the bulk NCK 18 TDA alloy, by depositing a TiN layer as a diffusion barrier for Al. In order to have a thin protective layer of alumina on the surface of the rotor blade, a layer of (Ti,Al)N was deposited on top of TiN layer. (Ti,Al)N is a protective layer with high oxidation resistance [7-8] and presents the advantage of naturally forming on its surface, in open atmosphere, of a dense, highly adhesive, protective Al_2O_3 film, which prevents further diffusion of environmental oxygen to the coated material. (Ti,Al)N also is also intended to work as an aluminum reservoir for the continuous formation of the alumina top layer in oxygen atmosphere. TiAl layers were also deposited in order to study the condition for Al migration towards the surface and the change in surface composition at the temperature increase.

The aim of the present paper is to investigate the properties of TiN/(Ti,Al)N double stack layered coating, in order to extend the life time of the rotor blades of the gas turbines under conditions of high temperature oxidation.

EXPERIMENTAL DETAILS

The experimental set-up has been described in details elsewhere [9]. Coatings of TiN, (Ti,Al)N and TiAl were deposited on a variety of substrates (Si, high speed steel and Ni base alloy NCK 18 TDA) using arc cathodic method and Ti and Al cathodes in different atmospheres (N_2 and Ar for the titanium aluminide).

Prior to the deposition, the samples were ultrasonically cleaned with organic solvents, mounted on a rotating holder inside the deposition chamber, and then sputtered by Ti ion bombardment (1000 V; 5 min.). Before TiN deposition a Ti interlayer (about 100 nm thick) was deposited on the samples, which has no side effect on the properties of the coatings, but to increase the adhesion on the substrate of the first deposited layer.

The deposition parameters (arc current- $I_{Ti,\ Al}$, nitrogen pressure-p_{N2}, bias voltage-V_s) for TiN and (Ti,Al)N coatings are the following: TiN - $p_{N2} = 5.10^{-3} \div 1$Pa, $V_s = 150 \div 230$V, $I_{Ti} = 90 \div 120$A; (Ti,Al)N - $p_{N2} = 10^{-2} \div 10^{-1}$ Pa, $I_{Al} = 50$ A, $I_{Ti} = 90$ A, $V_s = 150 \div 230$ V. TiAl coating was deposited in argon atmosphere in the following deposition conditions: $p_{Ar} = 2 \div 4.\ 10^{-3}$ Pa; $I_{Ti} = 80 \div 120$ A; $I_{Al} = 50 \div 70$ A $V_s = 220$. For all the depositions the substrate temperature was in the range $150 \div 200\ {}^0$C. The deposition time was in the range $45 \div 60$ min, to obtain about 2 μm layer thickness.

The microchemical and microstructural characterization was made for TiN and (Ti,Al)N layers, separately deposited. "The deposition recipe" resulted from the best obtained properties of the individual deposited layers (in terms of stoichiomety, texture, adhesion and microhardness), was used to obtain the double stack layered coating of TiN/(Ti,Al)N.

Chemical composition was determined (on Si substrates) by X-ray Photoelectron Spectroscopy (XPS) and energy dispersive X-ray analysis (EDX) methods. XPS analysis was done with Al K_α radiation, using a SSX-100 spectrometer. The elemental composition of the films was obtained by EDX analysis using a scanning electron microscope type XL-30-ESEM TMP. The crystallographic structure was determined by XRD measurements using Cu K_α radiation. Oxidation behavior was studied by mass spectrometry of the recoiled ions (MRSI) and XPS methods.

Microhardness (Vickers) measurements were performed with a microhardness tester (30 g load), using high-speed steel substrates. Film thicknesses were measured by optical microscope examination of the cross section through the coatings. The scratch test, under standard conditions, was used to measure the films adhesion.

RESULTS AND DISCUSSION

XPS and EDX measurements revealed the dependence of the chemical composition of TiN and (Ti,Al)N layers on the nitrogen pressure, cathodic arc currents and substrate bias. Examples of EDX spectra for TiN and (Ti,Al)N films are given in figures 1 and 2, respectively. The chemical composition of the films, as obtained by XPS, are given in table 1, showing that the obtained coatings were almost stoichiometric (the ratio N/ (Ti + Al) is about 0.95).

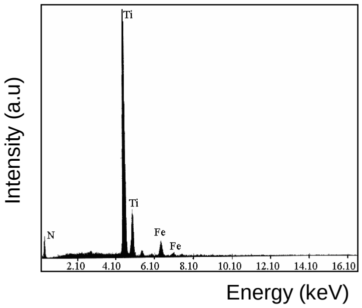


Fig.1 – EDX spectrum for a TiN coating
$p_{N2} = 10^{-1}$Pa, I_{Ti} = 90A, V_s=220 V

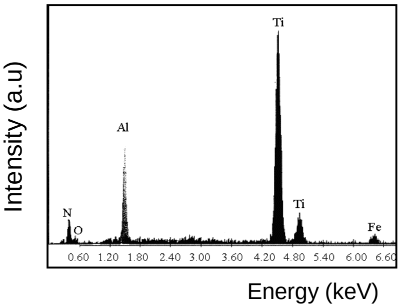


Fig.2 – EDX spectrum for a (Ti,Al)N coating
$p_{N2} = 10^{-1}$ Pa, I_{Al} =50 A, I_{Ti} =90 A, V_s=220 V

Table 1

Chemical composition of TiN and (TiAl)N coatings

Film	Elemental concentration (at. %)				
	Ti	Al	Fe	N	O
TiN	41.2	-	2.9	53.2	2.7
(TiAl)N	30.9	14.8	2.0	43.6	8.7

For TiN films, the study of the influence of the N_2 pressure on the N/Ti ratio, showed that, for a constant arc current, a pressure variation in the range $10^{-2} \div 1$ Pa slightly influences the film stoichiometry, while in the range $10^{-2} \div 5 \times 10^{-3}$ Pa it results in a sharp drop of N/Ti coefficient value from 1.2 to 0.7.

Typical diffraction pattern for stoichiometric TiN is illustrated in Fig. 4. A strong (111) preferred orientation is observed, as it was also reported for the films deposited by this method [10].

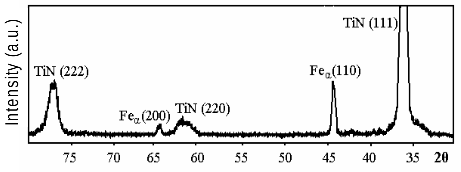


Fig. 4 – XRD spectra of stoichiometric TiN layer

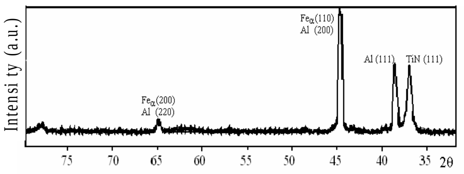


Fig. 5 – XRD spectra of a (TiAl)N layer

The Ti/Al ratio in (Ti,Al)N layers can be controlled mainly by the arc current intensities at the corresponding cathodes. For example, an increase of the I_{Ti} from 50 to 90 A resulted in a variation of the Ti/Al ratio from 0.74 to 2.09, while I_{Al} was kept constant at 50 A. (Ti,Al)N coatings generally exhibit a texture with a strong (111) orientation. An X-ray diffraction pattern for a (Ti,Al)N coating with Ti/Al ratio >1 is shown in Fig.5. The diffraction peaks belonging to Al indicates that some of the aluminum atoms did not react with nitrogen. This enables the (Ti,Al)N layer, with Al in excess, to act as an aluminum reservoir for Al_2O_3 formation onto its surface in oxygen atmosphere.

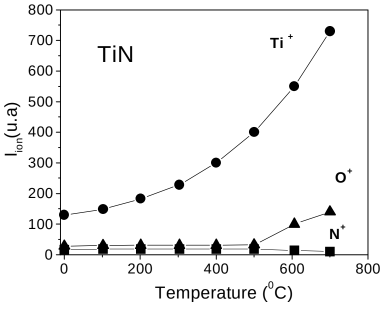


Fig. 6 – Temperature dependence of the ionic currents intensities at TiN film oxidation

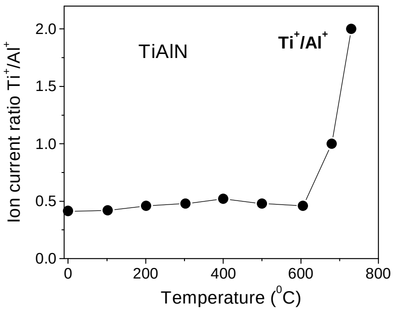
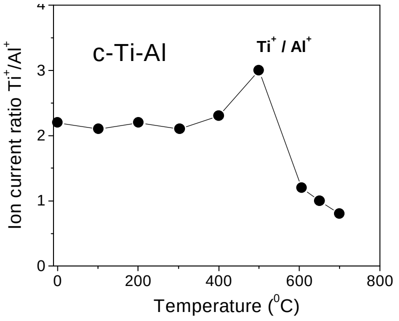


Fig. 7 – Temperature dependence of the ionic ratio at (Ti,Al)N film oxidation

(Ti,Al)N has higher oxidation resistance as compared with TiN. TiN oxidized at temperatures higher than 200^0C (Fig. 6), whereas (Ti,Al)N shows resistance to oxidation up to a temperature of 600^0C (Fig. 7).

The diffusion of Al to the surface of TiAl films, resulting in the formation of Al_2O_3 layers onto the surface (Fig. 8) was observed in the case of polycrystalline c-TiAl coatings. In the case of amorphous a-TiAl films, obtained at higher argon pressures and lower arc current on Al cathode than c-TiAl, a negligible diffusion of Al towards the surface took place; this could be deduced from higher values of Ti^+ MSRI signal in Fig. 9. In addition, XRD (Fig.5) and XPS measurements revealed that Al in c-TiAl is not oxidized remaining in metallic form. The results obtained for TiAl alloy coatings indicate that the presence of the grain boundaries, may play a critical role in the oxidation processes, due to grain boundary-enhanced diffusion of Al to the surface and subsequent its oxidation at the surface. On the contrary, the amorphous a-TiAl appeared to inhibit the diffusion of Al to the surface, resulting only a partial oxidation of Ti.



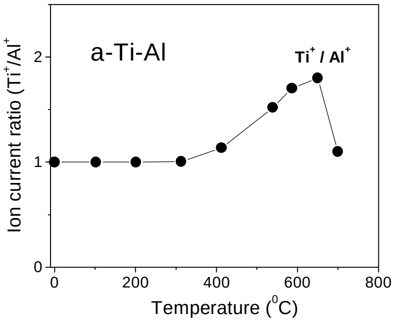
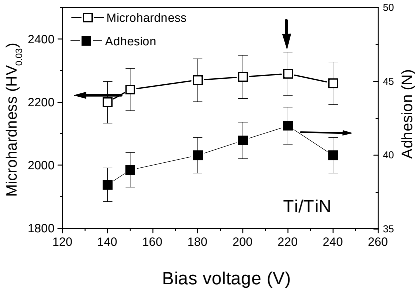


Fig. 8 – MSRI spectra for crystalline TiAl alloy   Fig. 9 – MSRI spectra for amorphous TiAl alloy

For TiN films it was observed that over a large range of the deposition parameters (p_{N2} = 2. 10^{-2} ÷ 5. 10^{-1} Pa, I_{Ti} = 60 ÷ 130 A and V_s = 50 ÷ 225 V), the microhardness variation is not important (values ranging from 2200 to 2300 $HV_{0.03}$ were measured). On the other hand, the microhardness of (Ti,Al)N films is greatly influenced by the relative amount of Ti and Al, present in the coating. As it was also reported [11-12], Ti/Al ratio has a marked influence on the film properties.



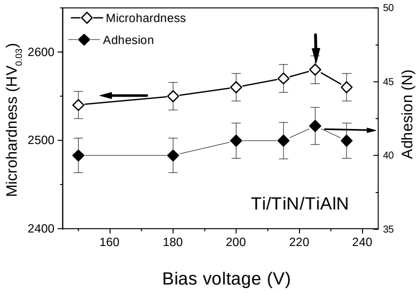


Fig.10 – Microhardness and adherence (L_c)   Fig. 11 – Microhardness and adherence (L_c)
of TiN films on NCK 18TDA   of TiN/(Ti,Al)N films on NCK 18TDA

The influence of the substrate bias on microhardness and adherence is presented for TiN films and for the double stack TiN/(Ti,Al)N films in Fig. 10 and Fig.11, respectively. In the case of TiN coatings with thickness of about 2 µm, critical loads in the range 36÷42 N were measured. (Ti,Al)N/TiN coatings, with individual layer thicknesses of about 2 µm each, and microhardness of about 2540 $HV_{0.02}$ and 2580 $HV_{0.02}$ exhibit a good adhesion on NCK 18 TDA substrate. The critical loads measured before exfoliation took place was in the range 38÷46 N.

CONCLUSIONS

Double stack layers of TiN/(Ti,Al)N were obtained as protective layers for high temperature oxidation for turbine rotors blades. Stoichiometric TiN layer acts as a diffusion barrier for Al migration in or out the Ni base alloy. Crystalline (Ti,Al)N layers, with higher content of metallic Al, has been shown to improve the oxidation resistance, acting in the same time as a reservoir for alumina thin films formation on the surface, to protect the rotor blades from further oxidation.

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