Engineering studies of Thin Films for Biomedical Applications: Structural and Compositional Analysis of NiAl and Ni-Al-N films

R. Said[1], W. Ahmed[2], J. O. Uhomoibhi[3], M.J. Jackson[4]

[1,2]School of Computing, Engineering & Physical Sciences,
University of Central Lancashire, Preston, PR1 2HE. UK
[3]Faculty of Computing and Engineering, University of Ulster,
Newtownabbey, Northern Ireland, BT37 0QB, UK
[4]Department of Mechanical Engineering and Centre for Manufacturing Research,
Tennessee Technological University, Cookeville, TN 38505, USA

wahmed4@uclan.ac.uk[2], j.uhomoibhi@ulster.ac.uk[3], jacksomj@purdue.edu[4]

Abstract

Thin films have been used widely for a range of biomedical applications. These include human implants and surgical tools. Examples of these include diamond like carbon (DLC) films and others deposited by closed unbalanced magnetron sputter ion plating. The addition of dopant gas to the carbon source results in doped DLC. Considerable modification of the surface and structural properties of films are caused by a lot of factors. In this study NiAl and Ni-Al-N thin films were deposited from elemental Ni (99.5 % pure) and Al (99.5 % pure) targets onto glass and stainless steel 316 substrates using closed field unbalanced magnetron sputter ion platting (CFUBMSIP) process. These films have important uses in tribological and thermal barrier system applications. The thickness of the films deposited was approximately 1μm. A range of techniques including energy dispersive spectroscopy (EDAX), X-ray diffraction (XRD), stylus profilometry, and atomic force microscopy (AFM), nanoindentation were used to characterise the as – grown films. A CSM scratch tester was used to determine the critical load, the coefficient of friction and wear rate of the films on stainless steel substrates. X-ray diffraction spectra for both types of thin films confirmed the presence of _-NiAl phase. EDAX results revealed that the NiAl thin films contained the nearly equal atomic composition of Ni and Al at 300 Watts DC power for Ni and 400 Watts DC power for Al targets, respectively. However, the Ni-Al-N thin films showed a Nickel rich NiAl phase. AFM results of both types of films on glass samples showed that the coatings displayed a smooth surface finish with surface roughness in the nanometre range less than 100nm. The nanoindentation results for coatings on glass substrates displayed hardness and elastic modulus of 7.7 GPa and 100 GPa respectively. The hardest coating obtained were produced at 10% of N content. Scratch test on the stainless steel coated samples showed the critical load, friction of coefficient and wear rate of 24N, 0.24 and 1x10 -6 mm3 /m respectively. The film properties were related to the film adhesion and wear behaviour.

Introduction

Thin film materials based on _-NiAl have been used for a wide variety of engineering applications including under layers in magnetic recording media, thin film thermistors in microelectronic devices, high temperature environmental coatings, and high current vacuum circuit breakers [1-6]. These coatings are also extensively used as bond coats in hot section components such as turbine blades and vanes of aerospace gas turbine engines [7-10]. Some NiAl based composite coatings such as NiAl-AlN are believed to possess improved mechanical and oxidation resistance [11]. Several route have been applied for the deposition of NiAl coatings including pack cementation, chemical vapor deposition (CVD), RF magnetron sputtering, ion- assisted sputter deposition and electron beam evaporation [9].

The B2 intermetallic compound _-NiAl is an attractive material for many engineering applications. This component has excellent properties such as high melting point (1638 oC), low density (5.90 g/cm3) high Young's Modulus (240

GPa), high thermal conductivity (76 W/m K) which is four to eight times higher than Ni-based super alloys, and excellent oxidation resistance at elevated temperatures [11-14]. NiAl is formed at a composition range of about 45-58 atomic% Ni with a high melting point peaking at 638 0C. The melting point of the alloy is considerably lower at lower values of atomic weight%. At elevated temperatures NiAl exhibits poor ductility, low strength and low creep resistance which limits the range of practical applications [1, 2, 15-17].

In this paper we report on the deposition and characterization of NiAl and Ni-Al-N thin films using closed field unbalanced magnetron sputter ion platting (CFUBMSIP) process. In particular the wear and adhesion behavior has been investigated. Coatings of this type are useful as bond coats for thermal barrier coatings requiring improved oxidation resistance and mechanical properties.

Methodology

In this study, unbalanced magnetron sputtering was used to deposit NiAl coatings from pure Ni and Al targets. Unbalanced magnetron sputtering is an extension of the basic planar sputtering process that relies on a momentum-exchange mechanism in which positive ions are generated in glow discharge plasma and are then bombarded to a target material to remove target atoms. These removed target atoms are then deposited as thin films on a substrate material. The whole process takes place in a vacuum chamber in the presence of an inert gas such as Argon, in which plasma can be initiated and maintained by applying a negative DC or RF voltage to the target plate. Conventional planar sputtering process is associated with low deposition rates, low ionisation efficiency and high substrate heating effects. To overcome these problems unbalanced magnetron sputtering has been developed and employed in this study [18].

Both conventional and unbalanced magnetron essentially consists of a water cooled target with magnets arranged behind it in such a way that a magnetic trap is created for charged particles, such as Ar ions, in front of the target. This arrangement also produces a magnetic field perpendicular to the electric field at the target which confines the electrons in the plasma to a region near the target resulting in an increased ionisation and much denser plasma in this region [18]. The main difference between conventional and unbalanced magnetron sputtering is the degree of confinement of the plasma. In conventional magnetrons, the plasma is strongly confined to the target region and the substrates placed beyond this region lie in very low- density plasma resulting in a little ion bombardment of the growing film necessary to produce good quality and fully dense coatings of certain materials. However, by using unbalancing the magnetrons the plasma can be made able to follow the magnetic-field lines and thus can be flowed out towards the substrate. In this way, the dense plasma can be confined between the target and the substrate resulting in increased ion bombardment at the substrate thus producing high quality and fully dense coatings [18].

A variation of the unbalanced magnetron sputtering is the closed field unbalanced magnetron sputter ion plating process (CFUBMSIP) which is now widely recognized as a state of the art technique capable of depositing high quality coatings. The CFUBMSIP configuration, acts to increase the ion current density in magnetron sputter ion platting. Unbalanced magnetrons are used in a configuration where at least one pair is of the opposite polarity [18]. This traps the plasma, preventing the loss of ionising electrons thus providing significant plasma enhancement. The ion current is maximised at a relatively low substrate bias voltage (-50 V), so that deposition occurs under high-density bombardment of low energy ions, the ideal conditions for growing high quality dense films.

Measurements and Analysis

NiAl and Ni-Al-N thin films were deposited onto glass and stainless steel 316 substrates in a Teer coatings Ltd system UDP 450/4 by co-sputtering elemental targets of Ni and Al (99.5 % pure). Due to its magnetic nature, Ni target was placed at a strong magnetron (Mag-3, Strong North) whereas Al target was placed at weak magnetrons (Mag-2, Weak South). A vacuum was achieved by using a combination of turbo molecular and rotary pumps. The base pressure of the
deposition chamber was below 5 x 10-6 Torr. Ar was used as a sputter gas and N2 was added with Ar for Ni-Al-N

coatings in 5, 10 and 20 % ratios. For Ni-Al-N coatings fixed sputter powers of 300 Watts for Ni and 400 Watts for Al targets were used respectively. Coatings were deposited without additional heating of the substrates at an overall gas pressure of 10 mTorr. The sputter time was fixed at 50 minutes in order to get a 1 mm coating. The substrates were rotated at a speed of 60 rpm in order to obtain a homogeneous film thickness. The deposition conditions for both types of coatings are summarized in Table 1. The composition, films structure and surface morphology of the films were characterized using stylus profilometry, energy dispersive spectroscopy (EDS), X-ray difrectometry (XRD), X-ray photoelectron spectroscopy (XPS), and atomic force microscopy (AFM).

Table-1: Process parameters for sputter deposition of NiAl and Ni-Al-N coatings

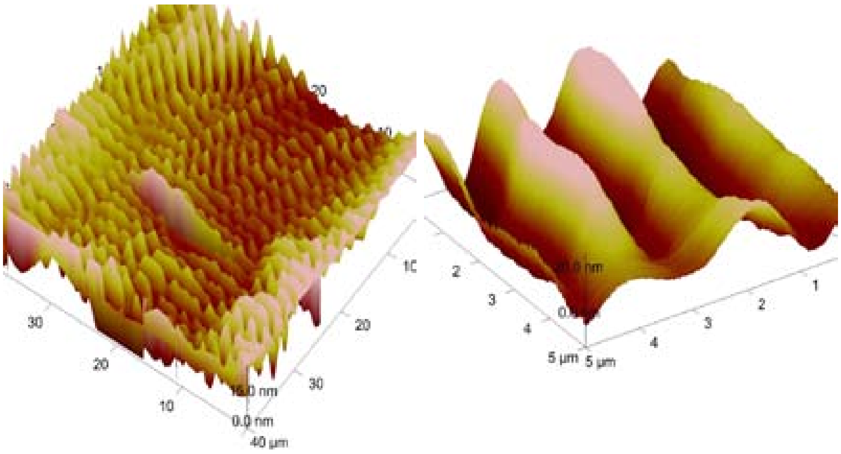
Parameter	**Range of Values**
Chamber pressure during deposition mTorr	10
Substrate to target distance	150
Magnetron power for Ni & Al targets for Ni-Al-N coatings Watt	Ni-300 Al-400
Substrate rotation speed rpm	60
Amount of N2 in Ar-N2 atmosphere for Ni-Al-N films %	5, 10, & 20

The nanoindentation technique was used to measure the hardness and elastic modules. A CSM (scratch tester) was used to determine the critical load, coefficient of friction and wear rate.

Results and Discussions

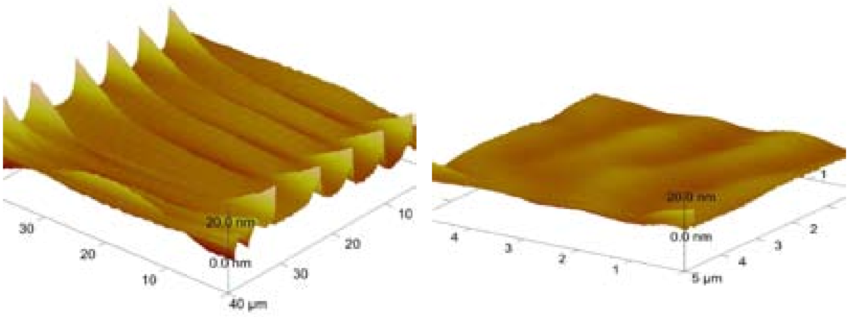
Atomic Force Microscope (AFM) was used to characterize the roughness of the surface of NiAl and Ni-Al-N thin films deposited by CFUMBS onto substrates. Two scales were used for measurements: the first a 40x40 μm square and the second a 5x5 μm square. Two scales were used to effectively capture the roughness generally found on the coated surfaces. AFM results are shown in figures 1a and 1b that both types of films on glass substrates exhibited surface roughness values in the nanometre range (4-10nm). The Ni-Al-N films exhibited a finer surface roughness than NiAl films with values of 1.2nm and 4.7nm respectively at a scan size 40x40μ m. This is common in many types of coatings where the addition of an impurity or dopant result in a decrease in the crystallinity yielding much smoother films.

Fig. 1a: Surface morphology and roughness parameters for NiAl coatings



Parameter	Scan Size 40 x 40 μm	Scan Size 5 x 5μm
RMS	6.28 nm	12.0 nm
Ra	4.70 nm	9.77 nm

Figure-1 (b): Surface morphology and roughness parameters for Ni-Al-N coatings.



Parameter	Scan Size 40 x 40 μm	Scan Size 5 x 5μm
RMS	1.94 nm	1.05 nm
Ra	1.20 nm	0.861 nm

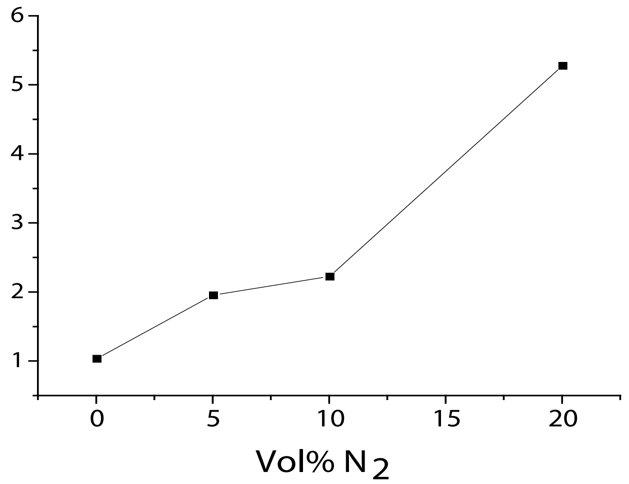
The EDAX results revealed that all of the NiAl thin films produced exhibited the near equiatomic NiAl phase with the best results being given by the one deposited using 300 Watts DC power for Ni and 400 Watts DC power for Al targets respectively. However, the Ni-Al-N thin films showed a Ni-rich NiAl phase. The quantitative results of EDAX for both types of coatings are tabulated and are shown in Table 2. The results revealed that Ni/Al ratio for NiAl coatings to 1.042 thus indicating the formation of nearly equiatomic NiAl phase. However for NiAl-N coatings, the Ni/Al ratio varies from 1.9626 to 2.2321 for 10 % N2 whereas for 20 % N2 this ratio is 5.2839.

Table 2: Composition of Ni-Al-N thin films deposited by CFUBMSIP using elemental Ni and Al targets

Deposition Power (W)		Volume % N_2	Substrate Material	Characterization Method	Atomic Concentration (%)				Ni/Al Ratio
Ni	Al				Ni	Al	N	O	
300	400	0	Glass	EDAX	51.03	48	-	24	1.042
300	400	5	Glass	EDAX	40.88	20.83	15.04	23.25	1.9626
300	400	15	Glass	EDAX	36.83	16.50	18.01	28.66	2.2321
300	400	20	Glass	EDAX	42.80	8.10	23.74	25.36	5.2839

When the N2 was added to the UBMS system there was a significant increase in the NiAl ratio. Table 2 this increase may be due to the premature reaction between Al and atomic nitrogen being introduced into the system as shown in figure 2.

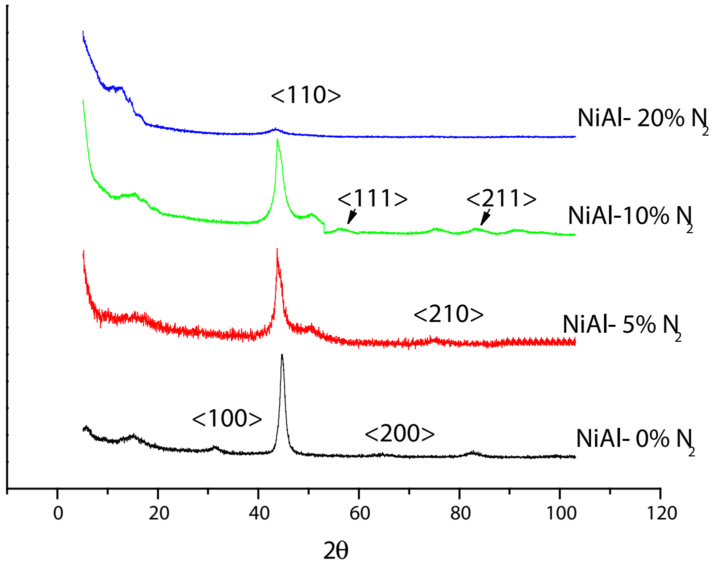
Figure 2: EDAX analysis of NiAl,NiAl-N films for various N2 Concentration.



The XRD results for NiAl and NiAl-N coatings deposited onto glass substrates are shown in Figure 3. The X-ray diffraction patterns of both NiAl and Ni-Al-N type of thin films deposited confirmed the formation of _-NiAl phase. In both types of coatings, the strongest peak observed was with a crystallographic plane of (100) for undoped NiAl films. Some other phases were also present in Ni-Al-N coatings which were left unidentified. However, when N2 is added to the grown mixture <111> and <110> become more pronounced.

The hardness and elastic modulus of the NiAl and NiAl-N coatings onto glass substrates were measured using the nanoindentation technique with Rockwell Diamond Nanoindentor system.The maximum load for nanohardness (H) was determined using the relationship between the plastic depth of penetration and the applied load. The total penetration depth is

Figure3. XRD pattern of NiAl and NiAl-N thin films deposited by CFUBMS onto glass substrates



composed of a plastic component and elastic recovery which occurs during the unloading. The elastic modulus of composites was determined using the unloading curve and the Doerner and Nix equations. Figures 4, 5 show the hardness (H) and elastic modulus (E) of the different films of NiAl and Ni-Al-N with different nitrogen concentrations.

Fig 4:Effect of nitrogen on the hardness of NiAl And NiAl-N films deposited on glass substrates

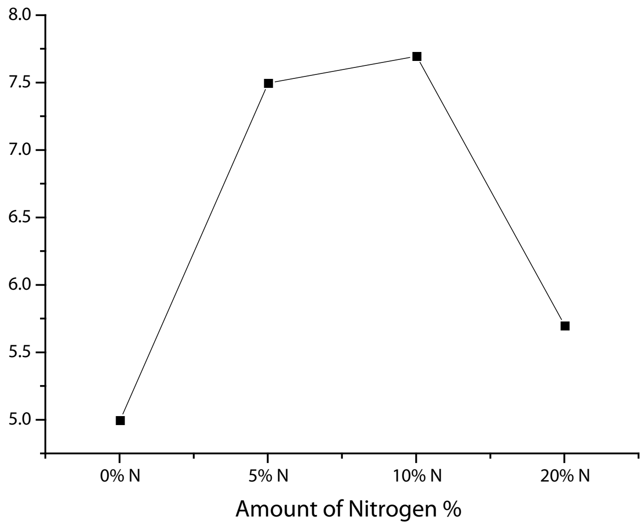
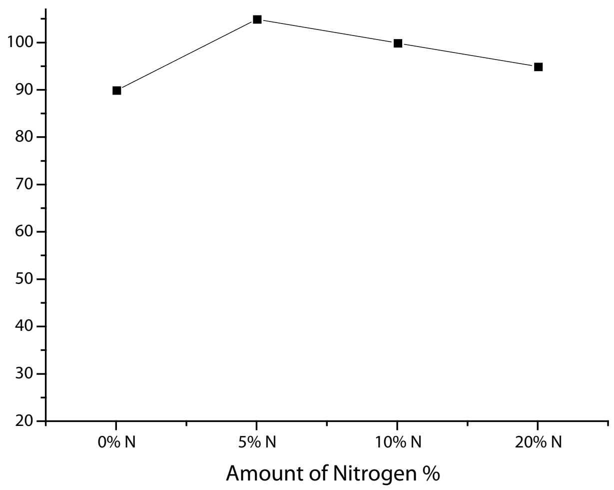


Fig 5: Effect of nitrogen on the Elastic modulus of NiAl and NiAl-N films deposited on glass substrates on glass substrates



These measurements were referenced to silicon dioxide film before and after measurements. Table 3 shows the results of NiAl, Ni-Al-N for hardness and elastic modulus. For coatings of NiAl including 10% N2, hardness and elastic modulus were found to be 7.7GPa and 100 GPa respectively.

Table 3: Hardness H and Elastic modules E of NiAl and NiAl-N

Nitrogen content of coating	**Hardness GPa**	**Elastic modules GPa**
0% N	5	90
5% N	7.5	105
10% N	7.7	100
20%N	5.7	95

A Scratch Tester with diamond indenter Rockwell 240 type with radius 200 _m was used to determine the friction and wear under a constant load of 1 N. Progressive linear scratch tests were used with a total linear scratch of 6mm, the speed of the scratch was 2.56 mm/min. The volume loss from the surface of the material was determined by the weight of the substrates before and after scratch testing. From analysis of data it was found that the coefficient of friction decreased with increasing nitrogen content and at 20%N it increased. The critical load was found also to increase with increasing nitrogen content. These studies were carried out by using a CSM scratch tester on stainless steel substrates. They revealed how critically dependent some of these parameters are on conditions of deposition.

Conclusion

We have undertaken detailed studies of the structure and compositional analysis of thin films used for biomedical applications. Of the order of 1 μm thick NiAl and Ni-Al-N thin films were successfully deposited from elemental Ni (99.5 % pure) and Al (99.5 % pure) targets onto glass and stainless steel 316 substrates using the closed field unbalanced magnetron sputter ion platting (CFUBMSIP) technique. Different phases are shown to be present. The XRD patterns of both types of thin films produced confirmed the presence of _-NiAl phase. The EDAX results revealed that all of the NiAl thin films produced exhibited the near equiatomic NiAl phase. The best results were given by the films deposited using 300 Watts DC power for Ni and 400 Watts DC power for Al targets respectively. The Ni-Al-N thin films showed a Ni-rich NiAl phase. AFM results of both types of films produced onto glass substrates exhibited that both type of coatings have surface roughness in the nanometer range with Ni-Al-N films exhibiting finer surface roughness than NiAl films. The hardness and elastic modulus were found to be 7.7 GPa and 100 GPa for a nitrogen content of 10% compared to 5.2 GPa and 85 GPa for films without nitrogen respectively. Further works and anal;ysis are planned to be extended to other thin films deposited using a variety of other techniques and it is hoped to compare and obtain the optimised conditions for best results. Using a scratch tester the critical load, friction coefficient and wear rates were found to be 24N, 0.024 and 1 x 10-6 mm3/m respectively with 10% nitrogen content compared to films without nitrogen of 20N, 0.29 and 5.5 x 10-6 mm3/m respectively. Recent advances in thin films technology with has the potential of improving understanding of film properties need in their manufacture.

Acknowledgements

The authors would like to thank staff at the Nanotechnology and Integrated BioEngineerinring Centre (NIBEC) of the University of Ulster for use of facilities. We also would like to thank the government of Libya for funding and studentship for work carried out as part of this project.

References

01. Sierra, C., Vazquez, A.J., (2006) 'NiAl coating on carbon steel with an intermediate Ni gradient layer' Surface and Coatings Technology Vol. 200 pp 4383 – 4388.
02. Tacikowski, M., Sloma, J., Wozniak, M., Wierzchon, T. (2006) 'Structure of the Al–Ni intermetallic layers produced on nickel alloy by duplex treatment' Intermetallics Vol.14, pp. 123–129.
03. Zhong, D., Moore, J.J., Disam, J., Thiel, S., Dahan, I. (1999) 'Deposition of NiAl thin films from NiAl compound target fabricated via combustion synthesis' Surface and Coatings Technology Vols.120–121 pp 22–27.
04. Zhong, D., Moore, J.J., Sutter, E., Mishra, B. (2005) 'Microstructure, composition and oxidation resistance of nanostructured NiAl and Ni-Al-N coatings produced by magnetron sputtering' Surface and Coatings Technology Vol. 200 pp. 1236–1241.
05. Ning, B, Weaver, M.L., (2004) 'A preliminary study of DC magnetron sputtered NiAl-Hf coatings', Surface and Coatings Technology Vols.177-178, pp. 113-120.
06. Ding, Y., Zhang, Y., Derek, O., Northwood, A.T., Alpas, T. (1997) ' PVD NiAl intermetallic coatings: microstructure & mechanical properties, Surface and Coatings Technology Vols. 94-95, pp. 483-489.
07. Ning, B., Shamsuzzoha, M., Weaver, M.L. (2005) 'Microstructure and property analysis of DC magnetron sputtered NiAl–0.6Hf coatings, Surface & Coatings Technology Vol. 200, pp. 1270 – 1275.
08. Voudouris, N., Christoglou, Ch., Angelopoulos,G.N. (2001) 'Formation of aluminide coatings on nickel by a fluidised bed CVD process' Surface and Coatings Technology vol. 141, pp. 275-282.
09. Yu, Z., Hass, D.D., Wadley, H.N.G. (2005) 'NiAl bond coats made by a directed vapor deposition approach', Materials Science and Engineering A Vol. 394, pp. 43-52.
10. Wllner, P., Kraft, O., Dehm, G., Andersons, J., Arzt, E. (2004) 'Channel cracking of thin films on Si substrates' Acta Materialia Vol.52, pp. 2325-2336
11. Zhong, D., Moore, J.J. Ohno, T.R., Disam, J., Thiel, S. Dahan, I. (2000) 'Deposition and characterisation of NiAl and Ni-Al-N thin films from a NiAl compound target', Surface and Coatings Technology Vol.130, pp. 33-38.
12. Peng, L.M., Wang, J. H., Li, H., Gong, M.(2006) 'Microstructure& mechanical behaviour of NixAly-Al2O3 in situ composites by pre-oxidation followed by hot-pressed reactive sintering' Material science and engineering A Vol.425, pp. 339-345.
13. Chang, J.T, Davison, A., He, J.L., Matthews, A. (2006) 'Deposition of Ni-Al-Y alloy films using a hybrid arc ion plating and magnetron sputtering system', surface and Coatings Technology Vol. 200, pp. 5877-5883.
14. Ning, B, Weaver, M.L., (2004) 'A preliminary study of DC magnetron sputtered NiAl-Hf coatings', Surface and Coatings Technology Vols.177-178, pp. 113-120.
15. Lasalmonie, A. (2006) 'Intermetallics: why is it so difficult to introduce them in gas turbine engines?', Intermetallics Vol.14, pp. 1123-1129.
16. Sanchez Bautista, C., Ferrier, A., Rodriguez, G.P., Lopez-Almodovar, M., Barba, A., Sierra, C., Vazquez, A.J. (2006)' NiAl intermetallic coatings elaborated by a solar assisted SHS process' Intermetallics Vol. xx pp.1-6.
17. Reichert, K., Martinez, C., Kyrsta, S., Cremer, R., Neuschutz, D. (2003) 'Sputter deposition and film characterization of NiAl on sapphire fibres' Vacuum Vol. 71 pp. 241-246.

18. Kelly, P.J., Arnell,R.D., Ahmed W., and Afzal, A. (1997) ‘Novel engineering coatings produced by closed-field unbalanced magnetron sputtering’, Materials and Design Vol. 17 pp. 215-219.
19. Kelly, P.J. and Arnell, R.D., (1998) ‘The influence of substrate temperature on the properties of Al, Zr and W coatings deposited by closed-field unbalanced magnetron sputtering’ Vacuum Vol. 49, pp. 43-47.