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# Low Temperature Formation of Titanium Aluminide Films Using Physical Vapor Deposition

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<p>The crystallization of the two intermetallic phases, <math>\alpha_2</math> and <math>\beta</math>, which form in <math>Ti_3Al</math> alloyed with Nb was investigated in films deposited using direct current magnetron sputtering. Phase formation was studied in post-deposition annealed films as well as in films deposited on heated substrates. Analysis was carried out using X-ray diffraction, scanning electron microscopy, and scanning Auger microprobe analyses. The oxygen content of films formed on heated substrates was 6 at.%, which is considerably lower than the 26 at.% oxygen content of post-deposition annealed films. This difference in the oxygen content is postulated to be a result of the microstructural differences in the films. Formation of the intermetallic phases in the films begins at approximately 100°C.</p>						
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# LOW TEMPERATURE FORMATION OF TITANIUM ALUMINIDE FILMS USING PHYSICAL VAPOR DEPOSITION

## Introduction

Titanium-aluminum intermetallics such as TiAl and Ti<sub>3</sub>Al exhibit high specific strength and stiffness at elevated temperatures as well as increased oxidation resistance when compared with many commercial titanium alloys. This combination of properties has generated a growing interest in titanium aluminides in recent years [1-4]. However, a critical drawback of aluminides is their low room temperature ductility. A few methods for improving their ductility have been successful. For example, the addition of approximately 10 weight percent Nb to Ti<sub>3</sub>Al increases the room temperature ductility to a tensile strain to failure of approximately five percent [4].

Even higher specific strength and stiffness at elevated temperatures maybe obtained by reinforcing titanium aluminides with ceramic fibers if a low temperature technique is used for their synthesis [5]. The usual temperatures employed in consolidating composites with titanium aluminide powders are in the range of 900 to 1200°C. These high temperatures often cause interfacial reactions which result in the formation of a brittle matrix/fiber interphase region and a significant reduction of the fiber strength. Introducing buffer layers between fiber and matrix prevents interfacial reactions during consolidation and in-service. These buffer layers as well as the matrix aluminide elements may be deposited onto the fibers by a physical vapor deposition (PVD) technique to form precursors that may then be consolidated to full density by uniaxial or hydrostatic pressing at temperature [6]. The implications of using this synthesis technique are two-fold: 1) Because the typical fibers (of interest) are of small diameter and since it is desirable for the composite to have high fiber volume fraction, both the buffer and matrix coatings must be of film thicknesses; 2) Consolidation of precursors maybe accomplished at relatively low temperatures (below 900°C) because the diffusion distances involved in forming the desired matrix compounds are much smaller and the contamination is lower than those encountered in powder metallurgy. However, though a desired ratio of the matrix compound elements, in this case Ti, Al, and Nb, may be deposited, the formation of the compound is not assured since it is a function of temperature and time. This maybe approached in two ways: a) by controlling the substrate (fiber) temperature during deposition; or b) by post-deposition annealing such that it parallels the consolidation temperature history.

The present investigation aims at studying the temperatures required to form  $\alpha_2$  and  $\beta$  phases of Ti<sub>3</sub>Al alloyed with Nb in films deposited on heated substrates (denoted as HS films) and in films, deposited without using the substrate heater and subsequently annealed (denoted as post-deposition

annealed, PDA, films). Films of  $Ti_3Al$  with 10 weight percent Nb were exposed to these temperature histories to promote the nucleation and growth of the hexagonal  $\alpha_2$  and bcc  $\beta$  phases of  $Ti_3Al$ .

## Experimental Procedure

A DC magnetron sputtering system was used to deposit films ranging from two to five micrometers in thickness. A  $Ti_3Al$  base alloy with  $10.0 \pm 0.5$  weight percent Nb sputtering target was used to take advantage of the findings of Mendiratta and Choudhury [7] who have shown that when  $Ti_3Al$  is alloyed with Nb, the alloy has improved oxidation resistance in addition to improved room temperature ductility. The composition of the target material was determined with energy dispersive X-ray emission analysis in a scanning electron microscope (SEM) using a standardless semiquantitative analysis routine. The substrate temperature was either the ambient temperature, which was monitored during a calibration run and found to increase to  $85^\circ C$  after two hours of sputtering (Fig. 1), or a temperature in the range of 100 to  $600^\circ C$  that was obtained using a substrate heater. Although mica, sapphire, glass, and quartz (fused silica) were considered as possible substrate materials, polished quartz was chosen because it permitted the largest temperature range for the annealing experiments, and, because of its amorphous structure, it simplified the X-ray diffraction analysis. The vacuum prior to sputtering was below  $6.7 \times 10^{-5}$  Pascals ( $5.0 \times 10^{-7}$  Torr), while the sputtering was performed in a partial argon atmosphere of 2.6 Pascals (20 mTorr). Although this argon pressure would be considered high for most magnetron sputtering applications, it was employed here to minimize the kinetic energy of the sputtered particles. Thus, the energy available for compound formation was primarily the thermal energy supplied by either the substrate heater during deposition or the vacuum furnace during post-deposition annealing.

A resistance furnace, shown in Fig. 2, was used to maintain the substrates at the desired temperatures. It consisted of a stainless steel tube 75 mm long and 35 mm in diameter, with two stainless steel end caps. A tungsten filament was centered inside the tube with one end of the filament insulated from one end-cap by an alumina sleeve. The other end of the filament was connected directly to the opposite end-cap using a set screw. This cap and the oven body were held at ground potential. An opening, 50 mm by 25 mm, in the stainless steel tube was used to place the substrates. A chromel-alumel thermocouple was used to monitor the temperature of the substrate during deposition. The thermocouple was mounted inside the oven body to prevent plating of the lead wires and a pressure contact was used to attach the thermocouple bead on the center of the back of the substrate. During calibration runs, either in vacuum or in air, the temperature of the substrate was monitored at various places and found to vary no more than  $\pm 5^\circ C$ . A three-layer cylindrical tantalum shield was used to protect the rest of the chamber and O-rings from radiant heat. To reduce the oxygen content in the films, a titanium hood was used to enclose the volume between the magnetron and the substrate. The sputtered titanium deposited on the hood acted as an oxygen getter.

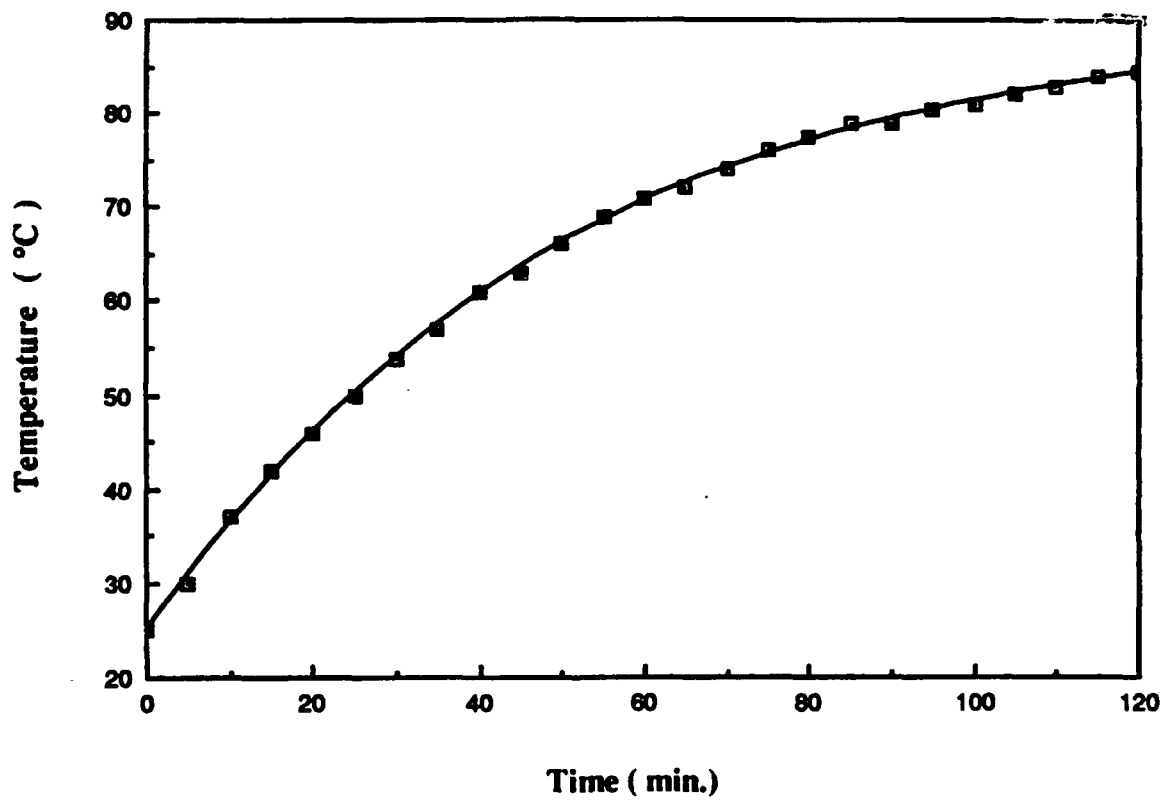
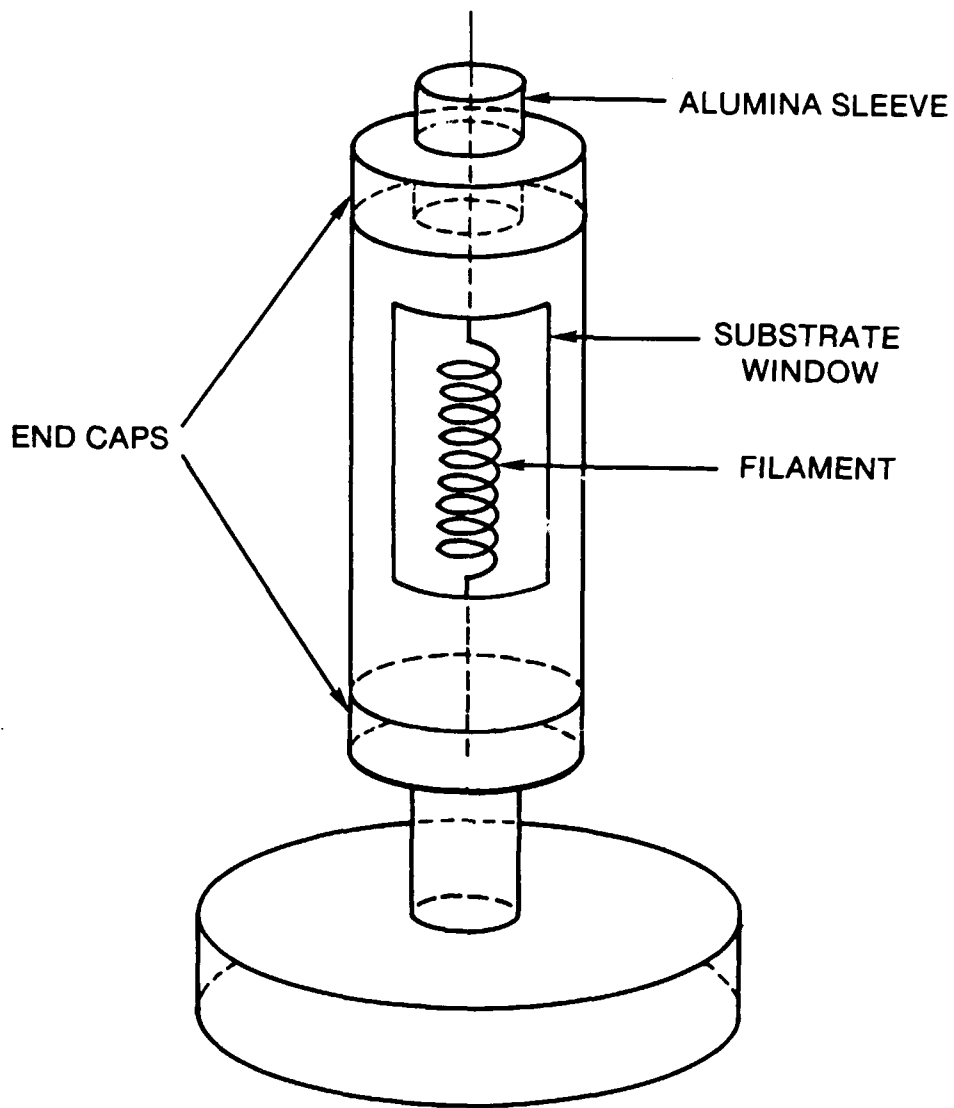


Fig. 1 - Increase in the temperature of the unheated substrate monitored during a two-hour deposition run.



### SUBSTRATE HEATER

Fig. 2 - Schematic of the substrate heater.

The films deposited on unheated substrates were annealed in a vacuum furnace for two hours at various temperatures in the range of 100 to 600°C. The films to be annealed were placed in a tantalum boat and covered with a titanium foil to getter oxygen. The pressure in the vacuum furnace during the heat treatment did not exceed  $4.0 \times 10^{-4}$  Pascals ( $3.0 \times 10^{-6}$  Torr). All films were stored in vacuum until they were analyzed. The films were characterized using X-ray diffraction, scanning Auger microprobe (SAM) analysis, and scanning electron microscopy (SEM).

## Results and Discussion

Niobium in  $Ti_3Al$  can be either in an  $\alpha_2$  hexagonal  $DO_{19}$  crystal structure or in a  $\beta$  bcc crystal structure [8]. Niobium expands the  $\alpha_2$  lattice and hence shifts the position of the diffraction peaks from those of unalloyed  $Ti_3Al$ . The  $\alpha_2$  lattice parameters found in the present work are in good agreement with those reported by Nartova and Sopochnik [8] for  $Ti_3Al$  with 10 weight percent (wt. %) Nb. Note that the  $\alpha_2$  lattice parameters of  $Ti_3Al$  with Nb remain constant for more than 5 wt. % Nb because, with increasing Nb content, a two-phase field of  $\alpha_2$  and  $\beta$  develops [8]. The X-ray diffraction patterns from the films deposited on heated substrates, presented in Fig. 3, show that the formation of the  $\alpha_2$  and  $\beta$  phases begins at 100°C. Figure 3 also shows the diffraction peaks for titanium oxide. The reduction in the number of peaks with increasing substrate temperature may indicate a tendency for preferred orientation of both  $\alpha_2$  and  $\beta$  phases in the films. This preferred orientation phenomenon was investigated further by depositing a film on an unpolished quartz substrate which was heated to 600°C during deposition. The fact that the diffraction pattern for this film (Fig. 3d) exhibited a majority of the peaks not found in Figs. 3b and 3c supports the hypothesis that using a polished quartz substrate in conjunction with the substrate heater increases texturing in the film.

The diffraction patterns for a film deposited on an unheated substrate and for the PDA films are shown in Fig. 4. The pattern for the film deposited on the unheated substrate is the same as it is expected for an amorphous material. This is somewhat surprising because the temperature of the unheated substrate was found to increase to 85°C monotonically after two hours of sputtering (Fig. 1) and this temperature is only 15 degrees less than the temperature required to form the phases when the substrate heater is used (Fig. 3). The series of X-ray diffraction patterns for the PDA films again show that formation of the  $\alpha_2$  and  $\beta$  phases begins at 100°C. The minor fluctuations in the peak heights in the patterns for higher post-deposition annealing temperatures (Fig. 4) may be due to texturing of the grains, more complete crystallization, or oxide formation. It should be noted that the quality of the diffraction patterns from HS films (Fig. 3) was inferior to that obtained from PDA films (Fig. 4). This difference in the quality of the patterns is partly explained by the different thicknesses of the respective films. Although the films in this study were produced under identical sputtering conditions except for the substrate temperature, the HS films turned out thinner than the PDA films, as verified by SEM micrographs and depth-profiling using SAM.

The chemical composition of the films was determined using SAM analysis using a standardless routine for quantitative analysis that results in

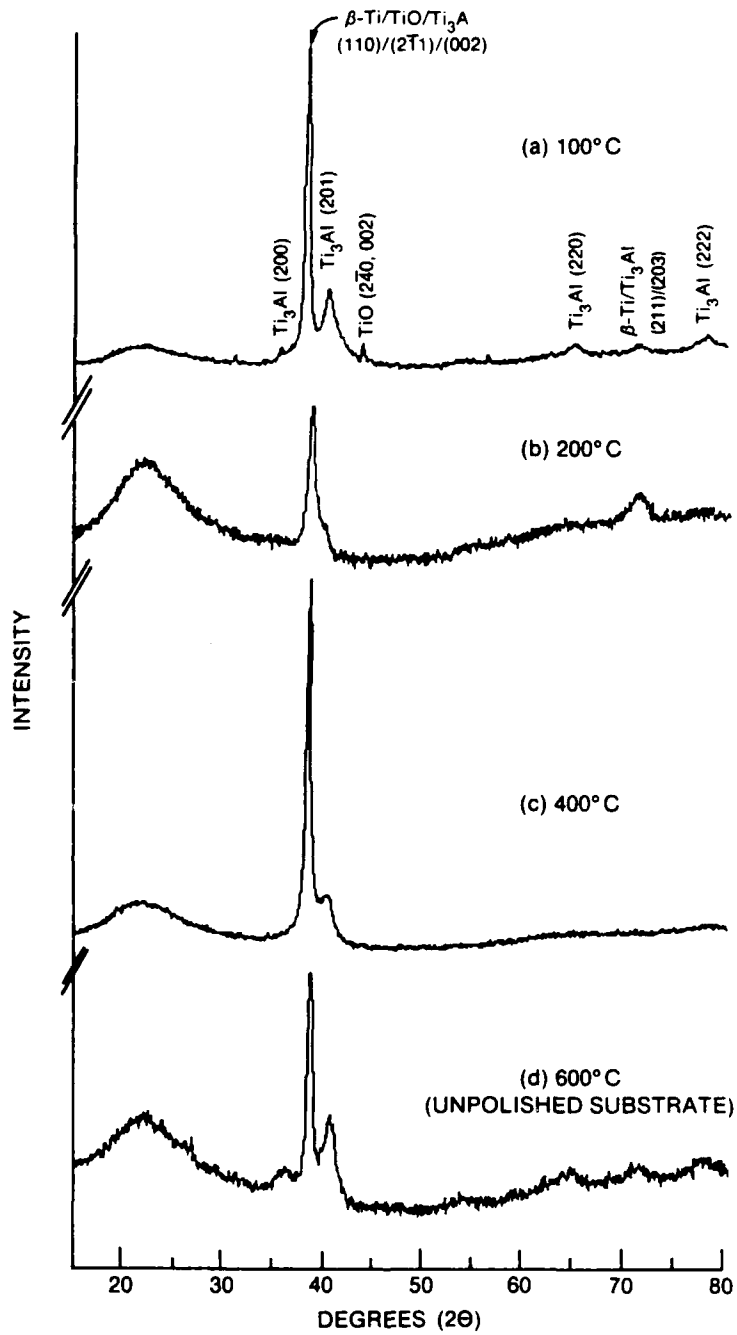


Fig. 3 - X-ray diffraction patterns from HS films. Substrate Temperature: (a) 100°C, (b) 200°C, (c) 400°C, and (d) 600°C.

an accuracy of  $\pm 20\%$ . Results of the SAM analysis are presented in Table I and show a major reduction in oxygen content in the films when the substrate heater was used. The reduced oxygen content may be attributed to the increased density of the HS films. The films deposited on heated substrates (Fig. 5a) appear denser and more uniform than the films deposited on unheated substrates. The latter films exhibit fine columnar grains (Fig. 5b). A dense film may prevent oxygen from penetrating beyond the surface oxide layer by eliminating fast diffusion paths such as columnar boundaries. The

Table I - Chemical Composition of Titanium Aluminide Films.

Film	Composition in atomic concentration (at. %)			
	Ti	Al	Nb	O
Unheated Substrate	46	19	17	18
HS Films (600°C)	54	18	22	6
PDA Films (600°C)	41	18	15	26

microporosity associated with columnar growth allows oxygen to diffuse into the film during deposition. This diffusion process could account for the increased oxygen content in the PDA films (Table I). Depth-profiling using the SAM was also performed on the films. Figure 6 is a plot of film composition versus sputtering time, the sputtering rate being approximately 10 nm per min. The compositions remain constant after three minutes (30 nm) of sputtering.

### Summary

In summary, it has been found that the  $\alpha_2$  and  $\beta$  phases of  $Ti_3Al$  with Nb begin to form at temperatures as low as 100°C in films deposited on heated substrates or in films deposited on unheated substrates and post-deposition annealed. Films deposited on unheated substrates were amorphous. The HS films were found to be very uniform and dense while the PDA films showed a columnar growth pattern. PDA films contained 26 at. % oxygen while HS films contained only 6 at. % oxygen. The difference in oxygen content is believed to be due to the higher density of the films formed on heated substrates; these dense films have no fast diffusion paths for the oxygen.

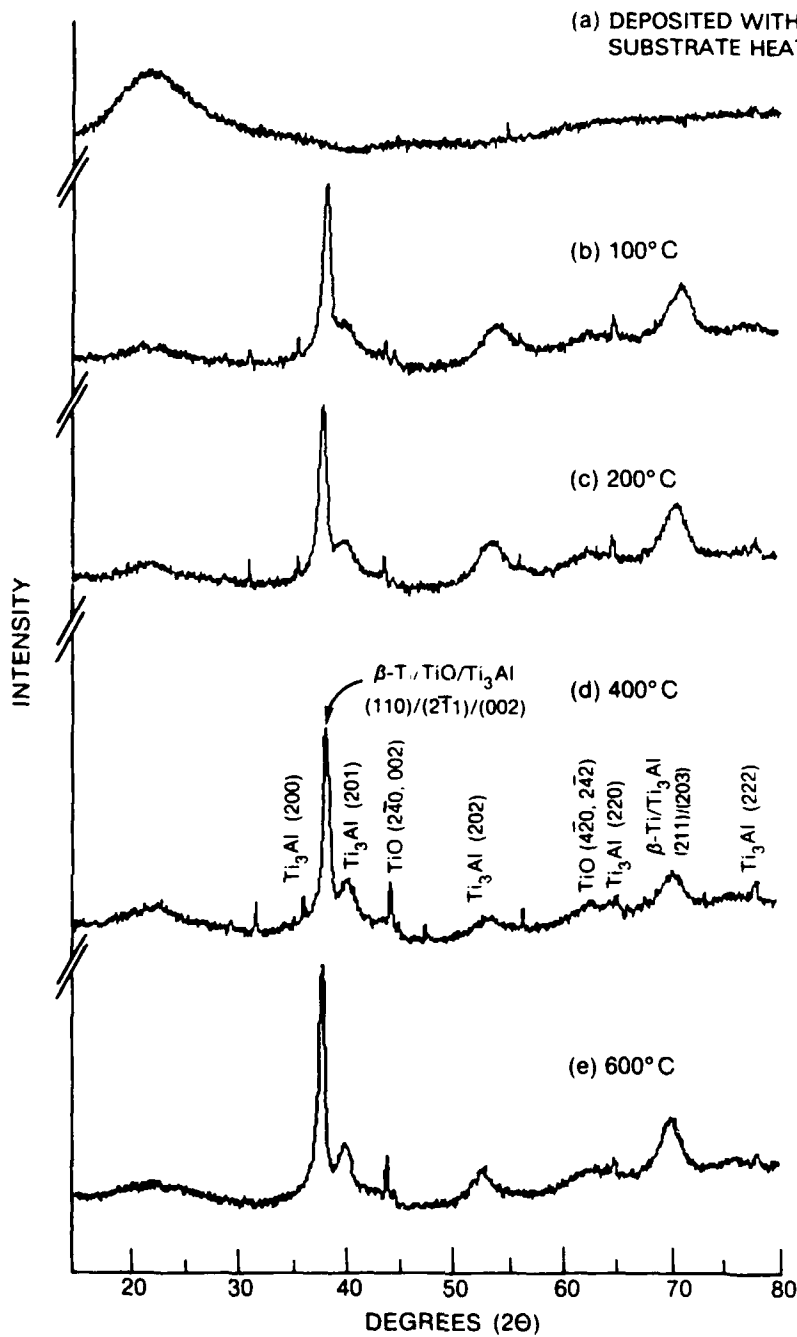
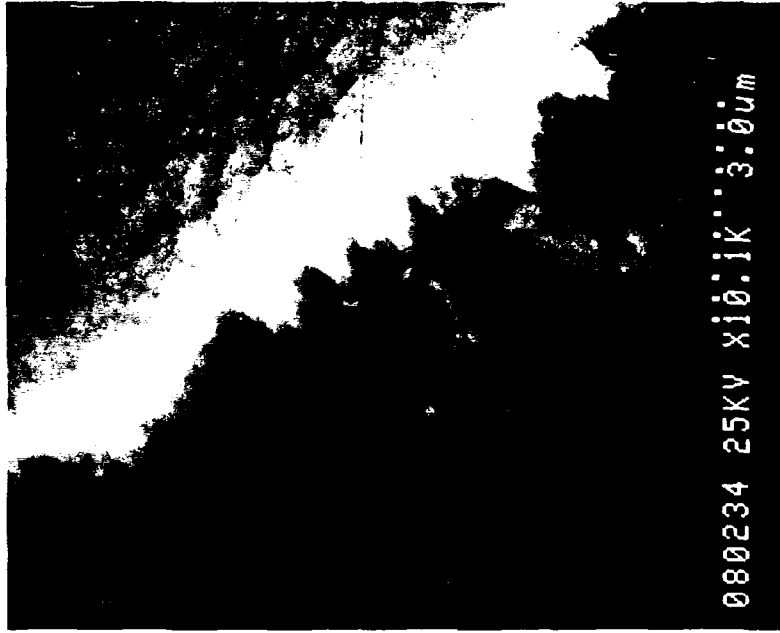


Fig. 4 - X-ray diffraction patterns from a film deposited on an unheated substrate and PDA films: (a) Deposited without substrate heating; annealed for two-hours at (b) 100°C, (c) 200°C, (d) 400°C, and (e) 600°C.



(a)



(b)

Fig. 5 - Microstructure of films revealed by through-thickness SEM fractographs: (a) film deposited on heated substrate and (b) film deposited on unheated substrate.

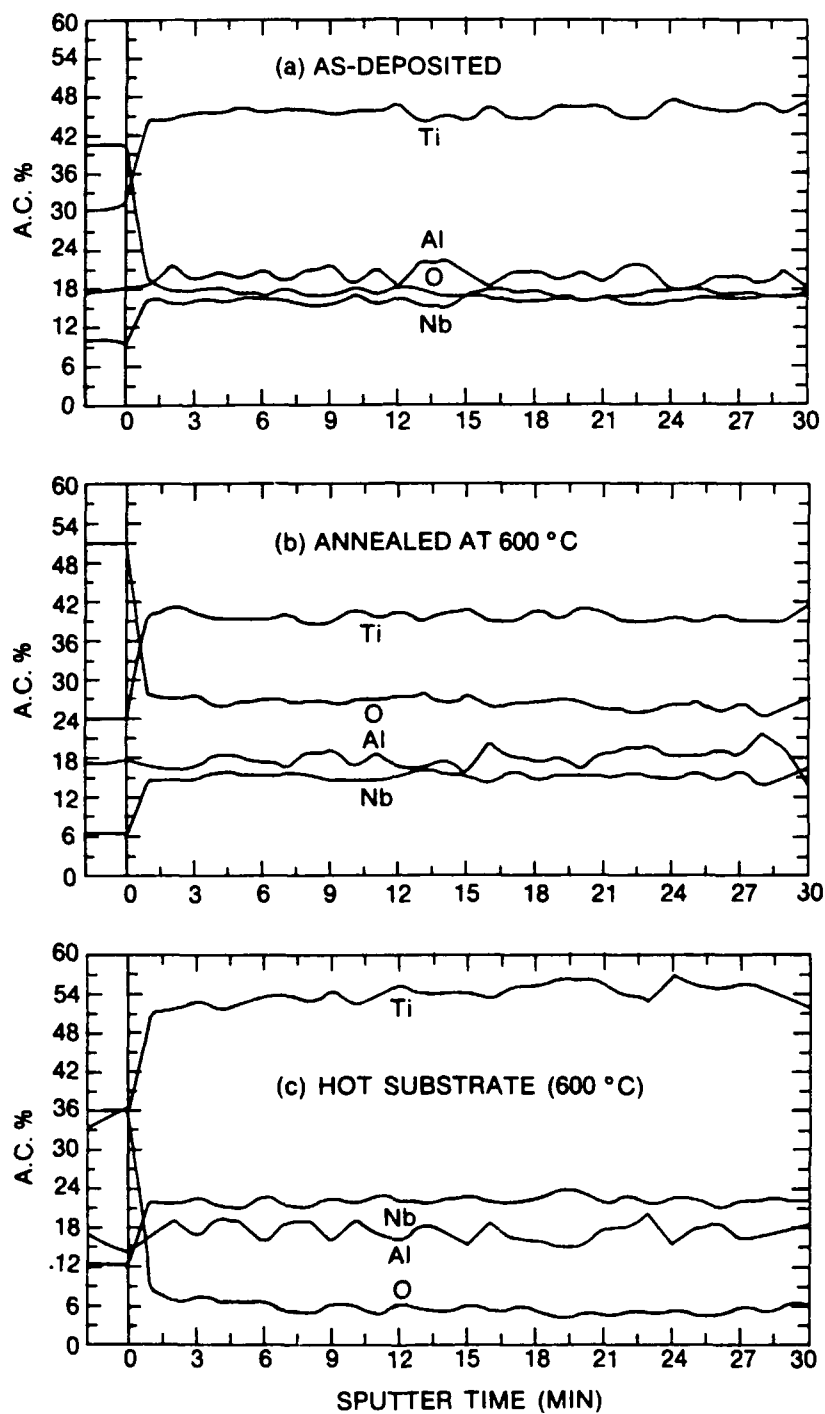


Fig. 6 - Atomic concentration (at. %) depth-profile of films obtained from a scanning Auger microscope: (a) film deposited on unheated substrates, (b) PDA film (600°C), and (c) HS film (600°C).

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## References

1. R.K. Ball and A.G. Todd, "The Formation of Titanium, Chromium, Niobium and Zirconium Aluminides for Interconnections," *Thin Solid Films*, **149**, 1987, pp. 269-282.
2. S.M.L. Sastry and H.A. Lipsitt, "Ordering Transformations and Mechanical Properties of  $Ti_3Al$  and  $Ti_3Al-Nb$  Alloys," *Metallurgical Transactions*, **8A**, 1977, pp. 1543-1552.
3. R. Strychor, J.C. Williams and W.A. Soffa, "Phase Transformations And Modulated Microstructures in Ti-Al-Nb Alloys," *Metallurgical Transactions*, **19A**, 1988, pp. 225-235.
4. P.L. Martin, H.A. Lipsitt, N.T. Nuhfer, and J.C. Williams, "The Effects of Alloying on the Microstructure and Properties of  $Ti_3Al$  and  $TiAl$ ," in *Titanium '80 : Science & Technology*, Vol. 2, Proceedings of the Fourth International Conference on Titanium, H. Kimura and O. Izumi, eds, AIME, Warrendale, Pa, 1980, pp. 1245-1253.
5. R.K. Everett *et al*, "Thin Sheet Titanium Aluminide Metal Matrix Composites," *NASP Technical Memorandum Report No. 1010*, January 1988.
6. S.C. Sanday *et al*, "Fiber Reinforced Metals by Ion-Plating," *NRL Memorandum Report No. 5686*, April 1986.
7. M.G. Mendiratta and N.S. Choudhury, "Properties and Microstructure of High Temperature Materials," *Technical Report, AFML-TR-78-112*, Systems Research Laboratories Inc., Dayton, Ohio, 1978, pp. 47-59.
8. T.T. Nartova and G.G. Sopochnik, "Investigation of the Phase Structure of  $Ti_3Al-Nb$  Alloys," *Russian Metallurgy*, No. 2, 1970, pp. 138-141.