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**SURFACE CHARACTERIZATION OF HYDROGEN CHARGED AND UNCHARGED
ALPHA-2 AND GAMMA TITANIUM ALUMINIDE ALLOYS USING AES AND REELS**

by

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ABSTRACT

The surfaces of selected uncharged and hydrogen charged alpha-2 and gamma titanium aluminide alloys with Nb additions have been characterized by Auger electron (AES) and reflected electron energy loss (REELS) spectroscopy. The alloy surfaces were cleaned before analysis at room temperature by ion sputtering. The low energy (500 eV) ion sputtering process preferentially sputtered the surface of all the alloys, significantly enhancing the Nb surface concentration. The surface concentrations were determined by comparing AES data from the alloys with corresponding data from elemental references.

No differences were observed in the Ti or Nb Auger spectra for the uncharged and hydrogen charged alloys, even though the alpha-2 alloy had 33.4 atomic % dissolved hydrogen. Also, no differences were observed in the AES spectra when hydrogen was adsorbed from the gas phase. Bulk plasmon energy shifts were observed in all alloys. The energy shifts were induced either by dissolved hydrogen (alpha-2 alloy) or hydrogen adsorbed from the gas phase (alpha-2 and gamma alloys). The adsorption induced plasmon energy shifts were greatest for the gamma alloy and cp-Ti metal.

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INTRODUCTION

This report contains results from two on-going studies of the surfaces of titanium aluminide alloys. The first study is to assess the effect of ion sputtering on the surface composition of selected titanium aluminide alloys with niobium (Nb) additions. The second study is to investigate the interaction of hydrogen with selected titanium aluminide alloys and, in particular, to evaluate potential techniques for detecting hydrogen on the surface or in the near surface region.

The preparation of "clean" surfaces is a prerequisite to conducting detailed investigations of surface phenomena and conditions, and for certain manufacturing processes. Energetic ion sputtering is the standard technique used to produce "clean" surfaces under high vacuum conditions. Ion sputtering is known, however, to differentially sputter components of multi-component material systems. This can lead to the surface composition differing significantly compared with the bulk composition. The ion sputtering, for the work reported herein, was done with the sample at room temperature. The sputtered surfaces were not given a high temperature anneal after the sputtering process was completed. For these conditions, it will be shown that the surface concentration of Nb in titanium aluminide alloys is significantly enhanced over the bulk concentration.

The surface compositions were determined using Auger electron spectroscopy (AES) and two analysis methods. In the first method, an element's Auger "signal" amplitude was compared directly to the corresponding amplitude of a pure elemental reference sample. In the second method, published AES relative elemental sensitivity factors were used to estimate the surface composition from the relative Auger derived "signal" amplitudes [1]. The two methods produced reasonable agreement and has allowed a calibration of the AES relative elemental sensitivity factors for this alloy system and the particular instrument used in this work. This will facilitate the AES composition determination of titanium aluminide alloy surfaces when elemental reference standards are not present or cannot be utilized in the experimental arrangement [2].

The second study, that of hydrogen surface interactions, employs Auger electron spectroscopy and reflected electron energy loss spectroscopy (REELS) to detect surface hydrogen. The direct detection of hydrogen with Auger electron spectroscopy is not possible, but the Auger spectrum of a metal, especially a hydride forming metal, is often modified by dissolved hydrogen. In addition, the presence of dissolved hydrogen often modifies the reflected electron energy loss spectra (REELS) in the same metals. In this work, no effect of either dissolved or absorbed hydrogen was observed in Auger spectra taken at room temperature. Significant shifts were observed in the surface plasmon loss peak observed with REELS, both for dissolved hydrogen and absorbed hydrogen.

EXPERIMENTAL CONSIDERATIONS

Alloy Composition

Five titanium aluminide alloys were investigated in this study. Three have primarily the alpha-2 chemistry (Ti_3Al) and two, the gamma chemistry ($TiAl$). The measured bulk compositions for each of the alloys is shown in Table I. One of each alloy chemistry was charged with hydrogen. They were charged at 600 C for four (4) hours in about 760 torr. (1×10^5 N/m²) of gaseous hydrogen and slow cooled in hydrogen to room temperature. The hydrogen content for these alloys is shown in Table I.

To remove any significant pre-existing surface layer from prior processing or machining, the surface of each alloy sample to be analyzed and each reference material was given a metallurgical polish to at least a 3 micron finish. This surface was then given a light acid etch to remove any evidence of the polishing material. After being thoroughly rinsed in de-ionized water and dried, the sample was ready for analysis.

Ion Sputtering Parameters

A Physical Electronics (Perkin-Elmer) model C02-300 differentially pumped ion gun was used as the sputtering source. The ion gun was run with a gas pressure of 1.5×10^{-4} torr. (2×10^{-2} N/m²) in the ionizer region and a pressure of about 1×10^{-7} torr. (1.3×10^{-5} N/m²) in the analyzer chamber. Beam current to the sample was about 1 microamp. Gross surface cleaning (the clean surface is very reactive and quickly forms an air-oxide coating when cleaned outside the ultra-high-vacuum environment) was done at an ion beam energy of 4 keV. Long term (at least one hour) sputtering of the clean surface was done with a beam energy of 500 eV to produce a stable "steady-state" low energy sputtered surface.

Over the course of this work, different sputtering angles (the angle between the sample surface normal and the incident ion beam direction) and different sputtering gases were used to clean the surface of the materials. The majority of the sputter cleaning was done at a grazing incidence angle of about 75° from the sample normal. Some work was done at a nearly normal incidence angle of 15° from the sample normal. Two different sputtering gases were used, initially Argon (Ar) and eventually Xenon (Xe). It was discovered that a significant amount of the sputtering gas becomes embedded in the titanium aluminide samples during sputtering. The Auger electron spectrum for Ar overlaps portions of the Nb spectrum, complicating the interpretation of the Nb spectrum. To remove this uncertainty, the Ar was replaced with Xe. These variations in the sputtering parameters did not appear to influence the results to be described below.

TABLE I

The bulk metallic concentrations and AES surface concentrations for the titanium aluminide alloys studied in this work.

Sample		Concentration, Atomic %			
		Ti	Al	Nb	H
alpha-2-1	bulk	66.2	20.7	12.7	0.92
	surface	55.0	20.6	18.0	
	surface/bulk	0.83	0.99	1.42	
alpha-2-2	bulk, nominal [1]	65.0	24.0	11.0	
	surface	58.9	25.1	21.3	
	surface/bulk	0.91	1.05	1.94	
alpha-2-3	bulk	67.9	21.7	10.2	33.43[4]
	surface	64.6	20.4	15.0	
	surface/bulk	0.95	0.94	1.47	
gamma-1	bulk	50.5	47.0	2.2	0.001
	surface [2]	46.4	49.1	4.6	
	surface/bulk	0.92	1.04	2.1	
gamma-2	bulk	52.4	47.3	0.1	1.68
	surface [2]	52.3	47.7	[3]	
	surface/bulk	0.99	1.01		

Notes:

1. The bulk concentration for this alloy was not measured. The values shown are the nominal design values.
2. These surface concentration were estimated using the revised AES Relative Elemental Sensitivity Factors shown in Table II.
3. AES signal not observed, below the sensitivity limit.
4. X-ray analysis of this sample shows a significant change in the dominant crystal structure and suggests that the sample is predominantly hydrided. Identification of the hydride phase is, however, not complete and this is only a tentative identification.

Electron Spectroscopy

The Auger electron spectrum (AES) and the reflected electron energy loss spectrum (REELS) were measured with a Physical Electronics model 10-155 cylindrical mirror analyzer (CMA) with an integral-axis electron gun. The integral-axis electron gun provided normal (to the sample surface) or near normal (about 15° from the normal) excitation of the electron processes. An

off-axis electron gun was used for grazing incidence excitation (about 75° from the sample normal). Although grazing incidence excitation tends to enhance the surface sensitivity of the Auger measurements, no significant differences between the two excitation modes were observed in this work. The AES and REELS data presented, herein, are for near-normal excitation.

The analyzer was mounted in a bakable ultra-high-vacuum system. After bakeout at 250 C, the base pressure of the vacuum system was about 5×10^{-5} torr. (6.6×10^{-8} N/m²) with all the electronics operating. The specimens and reference materials were mounted on a rotating carousel supported from a precision UHV manipulator. This allowed measurements to be made repeatedly on the same area of each specimen or on different areas, if desired.

When used to measure the Auger spectrum, the CMA was operated in the "derivative detection mode", where the derivative of the electron energy distribution with regard to electron energy is detected. The modulation on the CMA in the "derivative detection mode" was set at 4 eV peak-to-peak. The excitation electron beam energy was fixed at 3 keV with the beam current to the sample adjusted to 5.00 ± 0.05 microamps.

The reflected electron loss spectrum could be observed in either the "derivative mode" or by measuring the electron energy distribution directly (integral detection mode). All of the REELS results quoted herein were obtained from data obtained in the integral detection mode. As a matter of operating procedure, the apparatus was adjusted and calibrated first in the REELS "derivative mode" before acquiring either Auger spectrum data or integral REELS data. The excitation electron beam energy for the REELS measurements was 1000 eV. In the "derivative mode," the beam current to the sample was set at 5.00 ± 0.05 microamps and the CMA modulation set at 1 eV peak-to-peak. In the "direct" mode, the CMA is not modulated, but the electron beam current is modulated. The average beam current to the sample was about 40% of the constant value.

RESULTS and DISCUSSIONS

AES: Surface Concentrations

Presented in Fig. 1 are examples of the Auger electron spectrum for sputter cleaned surfaces of a representative alpha-2 and gamma alloy which have not been hydrogen charged. The initial, unsputtered surface Auger spectrum is dominated by oxygen and carbon surface species. After the initial oxide surface is removed, the specimens were ion sputtered for about one hour with an ion beam energy of 500 eV to produce a steady-state low-energy sputtered surface. The principal elemental Auger transitions, Ti(LMV)-418 eV, Nb(MNV)-167 eV, and Al(LVV)-68 eV are indicated in the Fig. 1.

The surface concentrations for the metallic components in the alpha-2 alloys obtained after prolonged sputtering are shown in Table II. These surface concentrations were obtained by two methods. In the first method, the amplitude of a particular element was compared directly to the corresponding Auger amplitude from a pure elemental reference sample. The ratio of the two amplitudes gives a direct measure of the surface concentration of that particular element. These are the surface concentrations shown in Table II as being obtained with the "direct" analysis method. In the second method, published relative elemental sensitivity factors [1] were used to convert the peak-to-peak derivative Auger amplitudes into "normalized" Auger amplitudes for each element. The concentration of a particular element is then given by the ratio of that element's normalized Auger amplitude to the sum of all the normalized Auger amplitudes. The surface concentrations obtained by this "indirect" method are shown in Table II along with the published values of the relative elemental sensitivity factors used in the analysis. The error bars shown in Table II represent the statistical deviations for at least four separate random measurements.

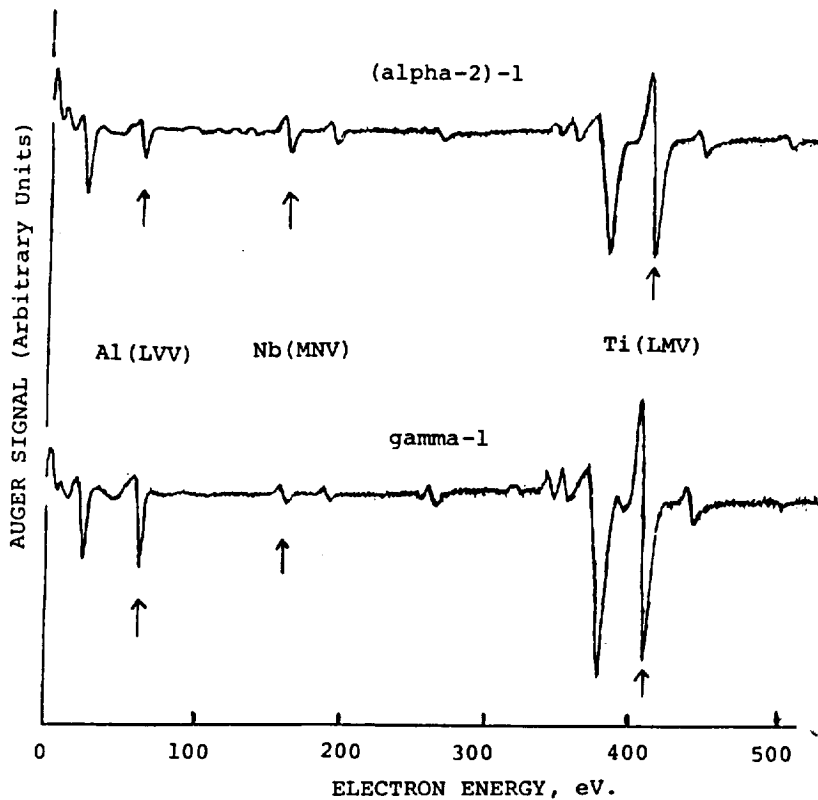


Fig. 1 AES spectra of the sputter cleaned surfaces of an uncharged representative alpha-2 and gamma titanium aluminide alloy.

TABLE II

The AES surface concentrations and AES relative elemental sensitivity factors for the metallic components in the alpha-2 alloys studied.

Sample	Analysis Method	Surface Concentration, Atomic %		
		Ti LMM(418 eV)	Al LVV(68 eV)	Nb MNN(167 eV)
alpha-2-1	Direct [1]	55.0±7.7	20.6±2.7	18.0±3.2
	Indirect [2]	62.1±5.0	21.0±3.6	16.9±2.2
alpha-2-2	Direct [1]	58.9±8.8	25.1±3.7	21.3±3.8
	Indirect [2]	59.8±4.8	20.9±3.6	19.2±2.5
alpha-2-3	Direct [1]	64.6±5.2	20.4±2.6	15.0±2.6
	Indirect [2]	55.9±7.9	24.2±3.2	13.9±2.4

AES Relative Elemental Sensitivity Factors

Literature Value [ref. 1]	0.44	0.235	0.26
Revised, This Work	0.51±0.06	0.20±0.04	0.29±0.04

The "indirect" analysis procedure, using relative elemental sensitivity factors, is often utilized where it would be difficult during the measurements to compare with elemental reference samples [2]. The small differences obtained for the surface concentrations using these two methods result from the specific instrument characteristics used to measure the Auger spectrum and matrix effects in the particular alloys. The published sensitivity factors were corrected to agree with the concentrations obtained with the reference samples. The corrected sensitivity factors are shown in Table II. These sensitivity factors were used to obtain the surface concentrations for the metallic components in the gamma alloys. The final corrected surface metallic elemental concentrations for both the alpha-2 and gamma alloys are presented in Table I.

It can be anticipated that sputtering the surface of these multi-component alloys will produce differences between the surface concentrations and the bulk concentrations. Shown in Table I is the ratio of the surface concentration to the bulk concentration for the sputtered alloy surfaces. Least affected by the sputtering process is the aluminum composition, which has a surface-to-bulk concentration ratio of about one for all the alloys. The titanium composition is reduced slightly in the surface region. The reduction in the Ti surface concentration may be correlated with the presence of Nb in the composition, since the niobium concentration is significantly enhanced in the

surface region by the sputtering process. The minimum niobium surface enhancement is about 40%, while the maximum enhancement is about 100% over the bulk concentration. Enrichment of the surface niobium may increase the surface reactivity, especially of the alpha-2 alloys, since niobium is very reactive with most gases, especially hydrogen. It remains to be determined if the niobium surface enrichment is thermally stable. High temperature vacuum annealing may dissolve the niobium and produce a surface matching the bulk composition.

AES: Hydrogen Interactions

Shown in more detail in Fig. 2 is the Ti(MVV) Auger spectrum at about 27 eV for an uncharged and the hydrogen charged alpha-2 alloy. The point to be noted here is that there is no apparent effect of the absorbed hydrogen on the Ti(MVV) Auger transition, even though the hydrogen charged specimen contains 33.4 at.% hydrogen. Similarly, no differences are observed in the Ti(LMM) and Ti(LVV) Auger spectra for these two alpha-2 alloys. These comments can be extended, also, to the gamma alloys where no differences in the Auger spectra were observed between the charged and uncharged alloy.

The absence of an effect of absorbed hydrogen on the Ti Auger spectra is surprising, since there are several reports in the literature of absorbed hydrogen affecting the Auger spectra of pure (alpha) Ti. In particular, it is reported that the Ti(MVV) spectrum is reduced in amplitude and distinctly split into two spectra with a splitting of about 5 eV for hydrogen charged Ti [3, 4]. The Ti(LMM) and the Ti(LVV) spectra are affected by hydrogen with the splitting of some spectra and energy shifts

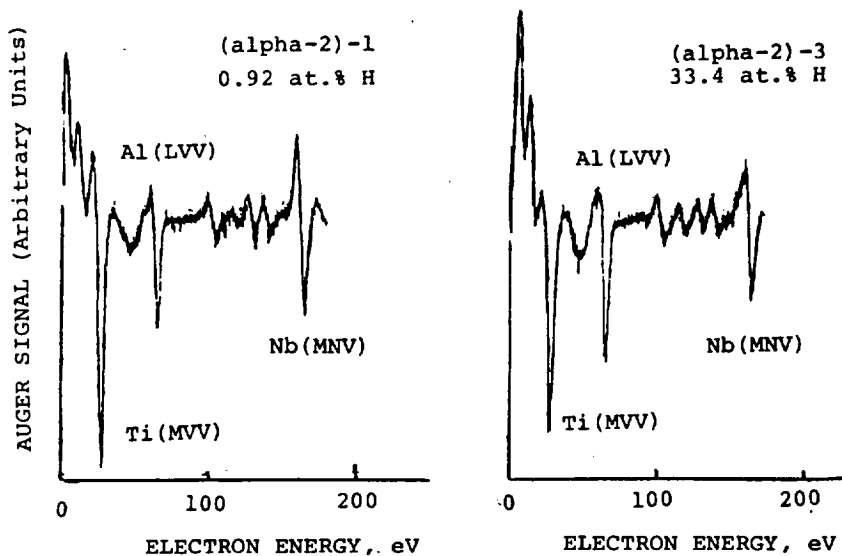


Fig. 2 Detail of the Ti(MVV) Auger spectrum for an uncharged and a hydrogen charged alpha-2 titanium aluminide alloy. The hydrogen charged alloy has a hydrogen concentration of 33.4 at.% H.

in others [4]. Hydrogen interaction with pure niobium produces, also, measurable energy shifts in the Nb(MNV) spectrum [5]. No comparable-magnitude Auger spectra energy shifts or splittings were observed with the titanium aluminide alloys studied in this work.

To evaluate whether the absence of a hydrogen effect on the Auger spectra is an intrinsic effect or the result of hydrogen loss in the surface region due to the sputtering process, gaseous hydrogen was adsorbed onto the surface while observing the Auger spectra. The hydrogen gas pressure was 5×10^{-5} torr. (6.6×10^{-3} N/m²) [6]. The Auger signal amplitudes were slightly reduced, but no significant changes in the Auger spectra of either the alpha-2 or gamma alloys were observed. This does not, however, conclusively establish that surface hydrogen does not have an effect on the Auger spectra of the titanium aluminides, since the hydrogen surface coverage is unknown. As will be presented in the next section, however, adsorbed and desorbed hydrogen does affect the REELS. This suggests that the hydrogen surface concentration is not insignificant at the absorption pressure used. It suggests, also, that the surface hydrogen concentration was not significantly reduced by the Auger (or REELS) electron excitation beam.

REELS: Hydrogen Interactions

Presented in Fig. 3 are representative examples of the REELS spectra obtained from uncharged alpha-2, uncharged gamma, and a chemically pure (cp) Ti reference sample. The dominant peak is the elastically scattered exciting electron beam. The first major loss peak in the inelastically scattered electrons has been identified as the bulk plasmon peak [4]. Measurements of the energy of the bulk plasmon energy with respect to the elastic peak (at 1000 eV) are shown in Table III. These measurements were made on uncharged and hydrogen charged alloys as well as after having hydrogen adsorbed onto their surfaces.

For the alpha-2 alloy charged with hydrogen (alpha-2-3), the bulk plasmon occurs at about 1 eV higher energy than for the uncharged alloy (alpha-2-2). The fact that the large amount of adsorbed hydrogen in the alpha-2-3 alloy (33.4 at.% H) is affecting the bulk plasmon energy is consistent with published studies on other hydrogen charged hydride forming metals. It was shown, for example, that the bulk plasmon energy can be correlated with the degree of hydriding of titanium [7]. The maximum shift for TiH₂ is about 3 eV [4]. The lack of a shift in the gamma alloy may be related to the relatively small amount of hydrogen adsorbed by this alloy (1.7 at.% H).

To determine the effect of adsorbed hydrogen on the bulk plasmon energy, gaseous hydrogen was adsorbed onto the sputter cleaned surface and maintained on the surface by a constant background hydrogen pressure of 5×10^{-5} torr. (6.6×10^{-3} N/m²) [6] while acquiring REELS data. Shifts were observed in the bulk

TABLE III

Bulk plasmon energies for hydrogen absorbed in the bulk and adsorbed on the surface of selected titanium aluminide alloys.

Sample	Bulk Plasmon Energy (eV)			
	Clean Surface -No Hydrogen-	Absorbed Hydrogen	Adsorbed Hydrogen	H-Induced Shift[1]
alpha-2-2	16.7		17.7	+1.0
alpha-2-3		17.7	17.7	+1.0
gamma-1	15.6		18.0	+2.4
gamma-2		15.6	17.9	+2.3
cp-Ti	15.7		18.0	+2.3

plasmon energies of the uncharged alloys only. These results are shown in Table III. No shifts were observed for either the hydrogen charged alpha-2 or gamma alloys. The shift (about 1 eV)

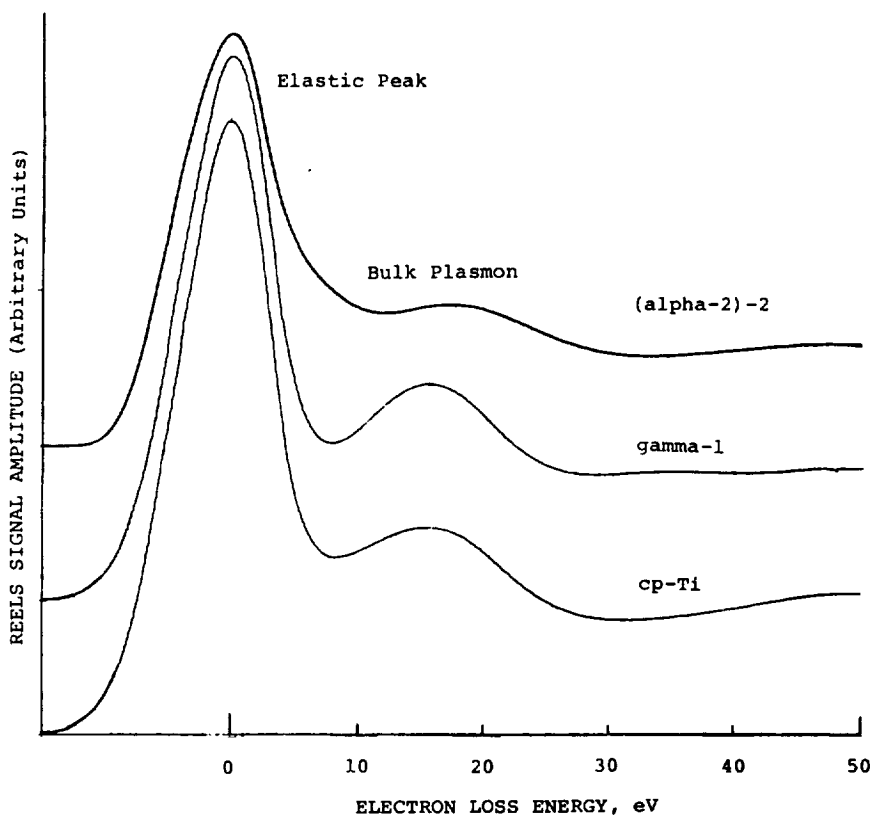


Fig. 3 The reflected electron energy loss spectrum for an uncharged alpha-2 alloy, gamma alloy, and cp-Ti. The first major peak measured from the main elastic peak is the bulk plasmon loss peak.

observed for hydrogen adsorbed on the alpha-2 alloy corresponds to the shift obtained for the hydrogen charged alpha-2 alloy. The largest shifts were observed for hydrogen adsorption onto the uncharged gamma alloy and the cp-Ti reference sample. These shifts are about 2.3 eV.

There is at present no understanding for the magnitude of the bulk plasmon energy shifts. It is interesting to note that the largest adsorption shift occurs with the gamma alloy which has a negligible absorption shift. The gamma alloy has, also, less apparent solubility for hydrogen and less surface Ti (and Nb) to react with, compared with the alpha-2 alloys.

SUMMARY

Measurements have been made of the surface composition of ion sputtered alpha-2 and gamma titanium aluminide alloys containing Nb. For low energy "steady-state" sputtering conditions, the Nb surface concentration is significantly enhanced (40-100%) compared to small changes in the Al and Ti surface concentrations. A calibration of the AES relative elemental sensitivity factors for Ti, Al, and Nb was made for the titanium aluminide alloys.

No hydrogen effects were observed in the Ti or Nb Auger spectra of either alloy. This observation is for absorbed hydrogen (up to 33.4 at.% H in alpha-2) and surface hydrogen adsorbed from the gas phase.

Hydrogen effects were observed in the reflected electron energy loss spectrum. Here hydrogen interactions shifted the bulk plasmon to higher energies; not only for absorbed hydrogen (alpha-2), but, also, for hydrogen adsorbed onto the surface from the gas phase (alpha-2 and gamma). The magnitude of the shifts were distinctly different, +1.0 eV for the alpha-2 alloy and +2.3 eV for the gamma.

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