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AN INVESTIGATION OF THE EFFECT OF SURFACE IMPURITIES ON THE ADSORPTION KINETICS OF HYDROGEN CHEMISORBED ONTO IRON

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1.0 INTRODUCTION

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The goal of this program ~~has been~~ to develop an understanding of heterogeneous kinetic processes for those molecular species which produce gaseous hydrogen degradation of the mechanical properties of metallic structural materials. Although hydrogen degradation of metallic materials is believed to result from dissolved protonic hydrogen ~~[1]~~, the heterogeneous hydrogen interface transport processes often dominate the kinetics of the degradation process. ~~[2]~~ The initial step in the interface transport process is the dissociative chemisorption of the molecular species at the metal surface followed by hydrogen absorption into and transport through the bulk. ~~[3]~~.

Modern advanced aerospace applications often require the use of structural materials in high pressure hydrogen environments at temperatures which range from low cryogenic temperatures to very high temperatures (1300 K and greater). ~~[4]~~. Materials proposed for these applications, such as the titanium aluminides, beta-titanium alloys, nickel- and cobalt-based superalloys, molybdenum-rhenium alloys, beryllium, and various beryllides, need to possess a high degree of immunity from hydrogen induced degradation of mechanical properties. ~~In addition, most of these materials require the use of ceramic protective coatings to inhibit high temperature oxidation. [5,6]. Little is known about the interaction of hydrogen with many of these materials and the possible influence of hydrogen on the material's mechanical properties or the coatings protective performance. [7]. It can be expected that the interaction of gaseous environmental hydrogen with these materials will be influenced by the gas phase-surface reaction process.~~

~~To develop a understanding of the interaction of gaseous hydrogen with these materials and to evaluate hydrogen transport through them, the present study was initiated in 1988. This present study supersedes, for the present, the work begun earlier under this agreement, which was to study the influence that surface impurities have in modifying the kinetics for hydrogen chemisorption on pure iron.~~

In the present program, the interaction of hydrogen with the surfaces of alpha-2 (Ti_3Al) titanium aluminide ~~[8]~~, gamma (TiAl) titanium aluminide ~~[9]~~, and beryllium [~~10~~] ~~have been~~ were studied. The interaction of low pressure hydrogen with gamma titanium aluminide and beryllium was found to be relatively weak, ~~Weak~~ in the sense that adsorption leads to a low surface concentration of dissociated hydrogen, ie., the chemisorption process is reversible at room temperature (300 K) for gamma titanium aluminide and the sticking coefficient for chemisorption is extremely small for beryllium. Hydrogen was found to interact readily with alpha-2 titanium aluminide to form a stable surface hydride at 300 K. These results correlate well with other recent studies which show that the mechanical properties for alpha-2 titanium aluminide are readily degraded in hydrogen while gamma titanium aluminide exhibits less

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degradation and beryllium essentially no degradation, [~~11~~]. The interaction of oxygen with the surface of these materials has been studied, also, in the present program .[~~12~~].

— end

The remainder of this document presents a narrative summary of the research activities completed during the award period, January 1, 1991 to December 31, 1991.

2.0 SUMMARY OF RESEARCH ACTIVITIES

As in the past, work supported by this agreement has covered a spectrum of activities during the present award period. The focus of the technical activities has been to complete the characterization of the interaction of oxygen with clean titanium aluminide and other titanium alloy surfaces; complete development of the hydrogen permeation facility; and initiate computer modeling studies of hydrogen permeation in metals. A portion of this time was spent on non-research activities, providing technical-management support to the National Aero-Space Plane (NASP) Hydrogen-Materials Compatibility Task and NASP Government Work Package #92. Progress in completing the technical areas are summarized below.

There were several areas in which planned activities did not occur or where the level of activity was too small to be reported. These areas are: (1) characterization of the thermal stability of thin oxides on titanium aluminide alloys, (2) development of REELS (Reflected Electron Energy Loss Spectroscopy) as a tool to study hydrogen chemisorption kinetics, and (3) development of an environmental-mechanical test facility for high temperature, low hydrogen pressure mechanical studies of titanium aluminide alloys. There was not enough time available during the award period to significantly develop these areas. They will not be discussed further.

2.1 Chemisorption Kinetics

An extensive analysis of data from measurements of CO adsorption onto Fe films was completed. These measurements were made earlier in this program, but the data analysis had not been completed. The adsorption of CO onto the Fe films was determined using the chemisorption-induced resistance change technique [13]. Carbon monoxide was adsorbed at constant pressure (6.6×10^{-5} N/m^2) onto clean Fe films with temperatures of 230 K or 305 K. The CO gas was at ambient room temperature.

The relative sticking coefficient during adsorption was obtained from the time derivative of the CO uptake curve, the variation of the resistance change with time during adsorption at constant pressure. The behavior of the sticking coefficient is qualitatively different at the two different substrate temperatures. At the lower temperature, 230 K, the sticking coefficient demonstrates an anomalous behavior, going through a maximum with increasing adsorption time, whereas at the higher temperature, 305 K, the sticking coefficient monotonically decreases with increasing adsorption time.

These results can be modeled by a simple chemical reaction model which assumes that the molecular CO chemisorption occurs via an adsorbed molecular, or precursor, state. The Ahrenius temperature dependence of the rate constants produces the dramatic difference in the behavior of the sticking coefficient. This work demonstrates that the anomalous sticking coefficient behavior observed in other studies is primarily a manifestation of the dynamics of the precursor adsorption process, and not the result of adsorbate-adsorbate interactions [14]. A manuscript describing these results is in preparation for submission for publication in early 1992.

2.2 Surface Characterization - Initial Oxidation Kinetics

Measurements of the adsorption at room temperature of oxygen onto the surface of a variety of titanium alloys containing aluminum, including alpha-2 (Ti_3Al) and gamma (TiAl) titanium aluminide were completed using Auger Electron Spectroscopy. The initial analysis of the Auger data has been completed, a detailed analysis of the Auger data, including lineshape analysis in in progress. The data demonstrate that the initial rate for oxygen chemisorption and the rate for the formation of the initial oxide state are essentially independent of the alloy surface composition, which varies from 0 to about 50% aluminum. This result is surprising because there is a very big difference between similar kinetics obtained with pure titanium and with pure aluminum; the aluminum kinetics are very slow compared with the titanium kinetics [12].

The data suggest that oxygen chemisorption occurs via a mobile molecular precursor with dissociative chemisorption occurring near the surface titanium atoms. The dissociated oxygen atoms diffuse into the near surface region where they bond with equal probability to titanium or to aluminum. The initial oxide state formed at room temperature has a thickness of about 0.5 nm. This initial oxide state does not appear to be thermodynamically complete, ie, an intermediate oxide state, not Al_2O_3, is formed.

These results imply, also, that the kinetics for low temperature (less than 900 K) oxidation of alpha-2 and gamma titanium aluminide are not controlled by surface processes. Since the observed low temperature oxidation kinetics for the titanium aluminides are very similar to the oxidation kinetics for pure aluminum (not titanium), it can be concluded that even at low temperatures, the oxidation process is controlled by bulk diffusion and not a surface adsorption process. Further details of this work can be found in the publication manuscript included as Appendix A in this report.

2.3 Hydrogen Permeation - Experimental

Progress in establishing the experimental hydrogen permeation facility has been disappointingly slow. The experimental apparatus has under gone several modifications to eliminate problems encountered in the original design. Several pieces of equipment failed and were replaced or repaired. The apparatus is near operational status at this time.

Significant delays have been encountered, also, in fabricating the permeation specimens. Although the specimen design is not complicated, the present Fabrication Shop procedures at NASA-Ames Research Center have produced lengthy delays to correct poor machining practices and procedures.

2.4 Hydrogen Permeation - Modeling

There was a significant activity in modeling hydrogen transport for engineering situations of interest to the National Aero-Space Plane. Numerical procedures were developed to calculate hydrogen permeation through composite structures consisting of multiple metallic layers or metal-insulator layers. In addition to calculating the steady-state hydrogen flux for given conditions of inlet pressure and temperature, the equivalent hydrogen interface pressures were estimated. Holidays in the interface region can act as voids which fill with diffusing hydrogen. High pressure gaseous hydrogen in the interface voids could potentially act to degrade the interface region, leading to failure of the interface bond.

Numerical techniques were used, also, to estimate the effect of oxidized surfaces on the permeation of hydrogen through thick ferrous materials (one inch thickness and greater) at relatively low temperatures. Inlet and exit heterogeneous kinetic processes were modeling and evaluated to estimate the degree of surface reaction poisoning necessary for the surfaces to become rate controlling. The effectiveness of poisoning on the inlet surface is a function of the inlet hydrogen pressure. At high pressures (greater then about 1 atm.), dissociation poisoning at the inlet surface becomes less effective at low permeation fluxes. For example, even if the probability of dissociating the gaseous hydrogen in reduced by a factor of 10^{-6}, sufficient dissociation can occur to provide the necessary flux of hydrogen atoms. Recombination poisoning at the exit surface is effective only for high permeation fluxes. Otherwise, a significant amount of poisoning (a reduction in the recombination probability by 10^{-4}) can be accommodated for low permeation fluxes without affecting the steady-state distribution. There was not sufficient data available to be able to relate the model calculations directly to actual field situations.

2.5 Other Activities

A. Meetings Attended

The following meetings were attended during the present award period:

1. The 10th National Aero-Space Plane Symposium, April 23-26, 1991, Monterey, California; participant.

2. Fourteenth Surface/Interface Research Meeting of the Northern California Chapter of the American Vacuum Society, June 27, 1991, Stanford, California; participant.

3. The Gordon Research Conference on Metal-Hydrogen Systems, July 15-19, 1991, Tilton, New Hampshire; participant.

4. NASP Workshop for Government Work Package #92 (Hydrogen-Materials Compatibility), August 13-14, 1991, Moffett Field, California; invited participant.

5. International Conference on High Temperature Aluminides and Intermetallics, September 16-19, 1991, San Diego, California; presenter and participant.

6. The 1991 TMS Fall Meeting, October 20-24, 1991, Cincinnati, Ohio, participant.

7. The 38th Annual Symposium of the American Vacuum Society, November 11-15, 1991, Seattle, Washington; presenter and participant.

B. Presentations Made

1. "The Initial Oxidation of Alpha-2 (Ti_3Al) and gamma (TiAl) Titanium Aluminide Alloys," contributed presentation, International Conference on High Temperature Aluminides and Intermetallics, San Diego, California (1991).

2. "The Coverage Dependence of the Sticking Coefficient for CO Adsorption onto Evaporated Fe Films and the Effect of Adsorbate Temperature," contributed presentation, 38th Annual Symposium of the American Vacuum Society, Seattle, Washington (1991).

C. Publications

The following have been published, submitted for publication, or were in preparation for publication during the present award period:

1. "The Initial Oxidation of Alpha-2 (Ti_3Al) and Gamma (TiAl) Titanium Aluminide Alloys," to be published in The Journal of Materials Science and Engineering.

2. "Coverage Dependence of the Sticking Coefficient for CO Adsorption onto Evaporated Fe Films and the Effect of Substrate Temperature," in preparation for submission to The Journal of Vacuum Science and Technology.

3. "Observation of a Maximum in the Coverage Dependence of the Sticking Coefficient for O_2 Chemisorption onto Fe Films," in preparation for submission to Surface Science.

D. Technical Reports

1. Quarterly Technical Progress Report (for October through December, 1990) for Hydrogen-Materials Compatibility TMP Task 4.2.06.1, submitted to Howard Nelson of NASA-Ames Research Center.

2. Quarterly Activity Report (for January through March, 1991) for NASA Cooperative Agreement NCC-2-63, submitted to Howard Nelson of NASA-Ames Research Center.

3. Quarterly Technical Progress Report (for January through March, 1991) for Hydrogen-Materials Compatibility TMP Task 4.2.06.1, submitted to Howard Nelson of NASA-Ames Research Center.

4. "Estimate of Hydrogen Permeation through a High Pressure, High Temperature Composite Pipe," technical memo submitted to Howard Nelson of NASA-Ames Research Center.

5. "Estimate of the Through-Thickness Hydrogen Concentration in KSC High Pressure Hydrogen Storage Vessels," technical memo submitted to Howard Nelson of NASA-Ames Research Center.

6. Quarterly Activity Report (for April through June, 1991) for NASA Cooperative Agreement NCC-2-63, submitted to Howard Nelson of NASA-Ames Research Center.

7. Quarterly Activity Report (for July through September, 1991) for NASA Cooperative Agreement NCC-2-63, submitted to Howard Nelson of NASA-Ames Research Center.

8. "An Investigation of the Effect of Surface Impurities on the Adsorption Kinetics of Hydrogen Chemisorbed onto Iron," M.R. Shanabarger, Annual Status Report, NASA-Ames Cooperative Agreement No. NCC-2-63, January 1 to December 31, 1990, submitted to Howard G. Nelson, NASA-Ames Research Center, December 17, 1991.

9. Quarterly Activity Report (for October through December, 1991) for NASA Cooperative Agreement NCC-2-63, submitted to Howard Nelson of NASA-Ames Research Center.

E. Student Participation

The following students participated in various stages of this program during the present award period:

Mr. Kevin Harlson (Foothill-DeAnza Community College),
Mr. James Park (Foothill-DeAnza Community College), and
Mr. Bryant Rayngay (Bennington College).

3.0 REFERENCES

1. H. G. Nelson, in **Treatise on Materials Science and Technology, Embrittlement of Engineering Alloys**, C. L. Briant and S. K. Banerji, eds. (Academic Press, New York, 1983), vol. 25, p. 344.

2. H. G. Nelson, D. P. Williams, and A. S. Tetelman, Metall. Trans. 2(1971)953.

3. **Chemisorption of Gases on Metals**, F.C. Tompkins (Academic Press, New York, 1978).

4. "Advanced Materials to Fly High in NASP," T. M. F. Ronald, Advanced Materials and Processes 135(May, 1989)29.

5. **Oxidation of High-Temperature Intermetallics**, T. Grobstein and J. Doychak, eds. (The Minerals, Metals & Materials Society, Warrendale, 1988).

6. M.R. Shanabarger and A. Khan, in **Proceedings of the Eighth National Aero-Space Plane Technology Symposium** (NASA Langley Research Center, Langley, Virginia, 1990), Volume IV-Materials, p.107.

7. **Summary Proceedings of the Workshop on Hydrogen-Materials Interactions**, NASP Workshop Publication 1001, H.G. Nelson and M.R. Shanabarger, eds., (NASP Joint Program Office, Wright-Patterson AFB, Ohio, 1987).

8. M.R. Shanabarger, in **Hydrogen Effects on Material Behavior**, N.R. Moody and A.W. Thompson, eds. (The Minerals, Metals & Materials Society, Warrendale, 1990), p.507.

9. M.R. Shanabarger, in **Summary Proceedings of the Third Workshop on Hydrogen-Material Interactions**, NASP Workshop Publication 1007, H.G. Nelson, ed. (NASP Joint Program Office, Wright-Patterson AFB, Ohio, 1990) p.205.

10. M.R. Shanabarger, "An Investigation of Hydrogen Adsorption on Beryllium," to be published in the **Proceedings of the Fourth NASP Workshop: Hydrogen-Material Interactions**, Scottsdale, Arizona, 1990.

11. See articles in **Proceedings of the Fourth NASP Workshop: Hydrogen-Material Interactions**, Scottsdale, Arizona, 1990, to be published.

12. M.R. Shanabarger, "The Initial Oxidation of Alpha-2 (Ti_3Al) and Gamma (TiAl) Titanium Aluminide Alloys," to be published in the Journal of Materials Science and Engineering.

13. M.R. Shanabarger, Surface Science 150(1985)451.

14. E.S. Hood, B.H. Toby, and W.H. Weinberg, Phys. Rev. Lett. 55(1985)2437.

<u>APPENDIX A</u>

THE INITIAL OXIDATION OF ALPHA-2 (Ti_3Al) AND GAMMA (TiAl) TITANIUM ALUMINIDE ALLOYS

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ABSTRACT

Auger Electron Spectroscopy has been used to measure the room temperature interaction of low pressure, gaseous oxygen with alpha-2 (Ti_3Al) and gamma (TiAl) titanium aluminide alloy surfaces. The kinetics of the initial oxidation process were determined and the initial oxide overlayer was characterized. The data indicate that oxygen adsorbs with high probability into a precursor molecular state on the surface. Dissociation from the precursor molecular state occurs primarily on the titanium surface atoms after which the oxygen atoms diffuse throughout the surface region. The presence of less reactive aluminum on the surface has no obvious influence on the adsorption kinetics. The initial oxide overlayer has an estimated thickness of 0.45-0.55 nm. No metallic species were detected in the overlayer nor were any complete oxides.

to be published in
The Journal of Materials Science and Engineering.

1. INTRODUCTION

It has been known for some time that the oxidation kinetics at temperatures below 700 C for alpha-2 (Ti_3Al) and gamma (TiAl) titanium aluminide alloys in air or oxygen environments approximate the growth kinetics of alumina (Al_2O_3) on aluminum [1,2]. The initial step in the oxidation process is the dissociative chemisorption of molecular oxygen at the gas-solid interface to produce adsorbed atomic oxygen. Data in the literature show that the kinetics for dissociative chemisorption of oxygen on clean aluminum at 300 K [3] is extremely slow compared with the corresponding kinetics for a titanium surface [4,5]. The question arises as to whether adsorption kinetics have a role in determining the low temperature oxidation kinetics on the titanium aluminides and, if so, does the presence of aluminum atoms on the alloy surface impede (or modify) the adsorption process by making the adsorption kinetics more "aluminum" like?

The present study is an attempt to answer these questions and develop an understanding of the role the oxygen chemisorption reaction may have in influencing the initial oxidation of several alpha-2 and gamma titanium aluminide alloys. Measurements were made using Auger Electron Spectroscopy (AES) to monitor oxygen adsorption on clean specimen surfaces and to monitor changes in the valence state of the metallic surface species. Clean surfaces were produced with ion sputtering techniques. Differential sputtering of different molecular weight surface atoms produced changes in the surface composition of the alloys compared with the bulk composition. These changes were quantified as part of this work.

2. EXPERIMENTAL PROCEDURES

2.1 Specimen Preparation and Characterization

Data were obtained for four titanium aluminide alloys, two alpha-2 (Ti_3Al) and two gamma (TiAl) alloys. Since there were no significant differences in the data within each alloy class, the presentation of the results will be simplified by presenting data from only one alloy of each class. The bulk composition of the two alloys is shown in Table 1. Data were obtained, also, with pure aluminum, titanium, and niobium metals, which were used to generate reference Auger spectra.

The alpha-2 alloy has an atomic composition of Ti-20.7Al-12.7Nb. This is an ingot cast and rolled, two phase alloy consisting of about 80 vol% alpha-2 phase and 20 vol% beta phase. The beta phase occurs along the boundaries of the alpha-2 platelets, which have characteristic dimensions of 10 microns. The gamma alloy, which was HIP consolidated from Rapid Solidification Rate (RSR) powder, has an atomic composition of Ti-53.1Al-3.5Nb. This material is essentially 100 vol% gamma phase with a mean grain diameter of 34 microns. The phase distribution and characterization was done using established X-ray and optical metallography techniques.

To remove any significant pre-existing surface contamination, specimen surfaces were polished using standard metallographic techniques followed by a light acid etch. Under vacuum conditions, the specimens were cleaned further using grazing incidence ion sputtering with xenon (Xe) ions. An ion current of 1 microamp was used in all the sputtering procedures. Initial sputter cleaning was done with an ion energy of 4 keV. A final, long time (about one hour) sputter etch was done at an ion energy of 1 keV to stabilize the surface composition. Sputtering with ion energies of 1 keV was done, also, to clean the specimen surface after exposure to oxygen.

To determine the composition of the sputter-cleaned specimen surface, the Auger electron spectrum from the alloy was compared under identical analysis conditions with the spectra from the identically prepared reference metals. The surface compositions obtained with this procedure are presented in Table 1. The major effect of the ion sputtering procedure on all the alloys was to significantly enhance the Nb surface concentration compared with the bulk value. Smaller changes occur in the titanium and aluminum concentrations.

2.2 Auger Electron Spectroscopy

The electron energy distribution, n(E), of electrons emitted from the specimen surface was measured using a cylindrical mirror analyzer (CMA) containing an integral-axis electron gun (Physical Electronics Model 10-155) [6]. The specimen surface normal was about 15^{o} from the axis of the electron gun, which provided excitation of the Auger and other electron processes.

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 6.6×10^{-8} N/m^2 (5×10^{-10} torr) with all the electronics operating. The alloy specimens and reference specimens were mounted on a carrousel supported from a precision UHV manipulator. This allowed measurements to be made routinely under identical analysis conditions on the same area of each specimen or on different areas as required.

The CMA was operated in the "derivative" detection mode, where the derivative, d(E n(E))/dE, of the electron energy distribution with respect to the electron energy, E, is detected as a function of electron energy [6]. The modulation on the CMA was maintained at 4 eV peak-to-peak. The electron beam energy was 3 keV with a beam current to the sample of 10 microamps. The beam diameter is about 30 microns at focus. The amplitudes of specified Auger spectral lines presented in this work refer to the peak-to-peak amplitude, and following convention, the energy of the Auger spectra were measured at the position of the negative peaks [7].

2.3 Oxygen Adsorption Procedure

A standardized procedure was used in exposing the specimen surfaces to high purity oxygen. For oxygen exposures of 10 Langmuirs* or less, the clean specimen surface was exposed to oxygen at a constant pressure of 2.7×10^{-6} N/m^2 (2×10^{-8} torr) for varying lengths of time. After completing the Auger measurements, the specimen surface was sputter cleaned to remove the previously adsorbed oxygen before proceeding with the next oxygen exposure. For exposures greater than 10 Langmuirs, the exposures were additive; the specimen surface was not cleaned between successive exposures. For total exposures above 30 Langmuirs the oxygen pressure was increased to 1.3×10^{-5} N/m^2 (1×10^{-7} torr) to keep the exposure time reasonable.

During the oxygen exposures, the specimen surface was turned away from all hot filaments. The electron gun was also put into a standby mode. It was found from extensive testing that a significant oxygen Auger signal would rapidly develop under high vacuum conditions if the specimen surface faced the electron gun filament, even with the beam biased off. Under these same conditions, enhancement of the oxygen adsorption kinetics would occur when oxygen was introduced.

3.0 RESULTS and DISCUSSION

3.1 Auger Spectra - the Clean Surface

Characteristic electron energy spectra for the alpha-2 alloy are shown for the clean surface in Fig. 1a and in Fig. 1b after exposure to 20 Langmuirs of oxygen. Corresponding spectra for the gamma alloy are shown in Figure 2. Auger spectra from the clean alloy surfaces are identified as follows: 27 eV, Ti(MVV); 387 eV, 418 eV, and 450 eV, Ti(LMV); 66 eV, Al(LVV); 167 eV and 198 eV, Nb(MNV); and 510 eV, O(KLL) [5,6]. A complete listing of all the major Auger spectral energies for the clean and oxygen exposed alloy surfaces is presented in Table 2. Included in this listing is an unidentified spectral line at about 15 eV on the clean surface and 7.6 eV on the oxygen covered surface.

It was not possible to produce a surface completely free of oxygen as demonstrated by the spectra in Figs. 1a and 2a. This initial oxygen Auger signal amounts to 4-6% of the maximum signal which occurs for exposures greater than about 25 Langmuirs. It is believed that this oxygen signal originates from bulk oxygen in the alloy which has diffused into the surface region. The oxygen signal was not present during sputtering, but appeared shortly after termination of the sputtering process. This oxygen signal was, also, not present during the characterization of the reference metals.

3.2 Auger Spectra - the Initial Oxide Surface

At an exposure of 20 Langmuirs, the initial oxidation process is essentially complete as will be demonstrated later. The low electron energy, valence band Auger spectra for the alpha-2 and gamma alloys presented in Figs 1b and 2b, respectively, show

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* One Langmuir is defined as an exposure to gas at a pressure of 1×10^{-6} torr for 1 sec; 1 Langmuir = 1×10^{-6} torr-sec. For oxygen, 1 Langmuir is equivalent to 3.54×10^{14} molecules/cm^2 impacting the surface in one second.

primarily spectra associated with titanium oxide, 24 eV and 40 eV [4], and aluminum oxide, 38 eV and 55 eV [3]. The splitting of the Ti(418eV) Auger signal is characteristic of the formation of titanium oxide in the overlayer where there is overlap between the oxide spectrum and the attenuated Ti(LMM) spectrum from the substrate [8]. Changes in the niobium Auger spectra resulting from oxygen adsorption were not studied in detail, because, other than attenuation, the changes in spectral lineshape and position were small.

Analysis of the attenuation of the Ti(450eV), Nb(167eV), and Nb(198eV) Auger signals due to inelastic electron scattering by the oxygen-oxide overlayer at 20 Langmuirs gives an overlayer thickness of 0.45-0.55 nm [6]. An overlayer of this thickness would significantly attenuate the low energy Ti(27eV) and Al(66eV) Auger signals originating from the substrate. For the higher aluminum concentration gamma alloy, there is a very small Al(66eV) signal at 20L whose amplitude is consistent with a 0.5 nm thick overlayer. A similar comparison of the attenuation of the Ti(27eV) Auger signal was not successful, since it could not be separated from a larger and overlapping oxide signal at 24 eV. These observations imply there are no titanium or aluminum metal species in the initial oxide overlayer, otherwise larger and more easily detected Auger signals would have been observed.

Auger electron spectroscopy is generally not sensitive enough to quantify multiple oxidation states, such as titanium, which has oxidation states of Ti^{+2}, Ti^{+3}, and Ti^{+4}. Aluminum, however, has only one oxidation state, Al^{+3}. Differences in the valence band spectral energy can give information on bond strength or the degree of bond formation [6]. Using data from Table 2, the difference between the energy of the metallic Al(LVV) spectrum (66.2eV) and the corresponding oxide spectrum (56.4eV) is estimated to be 9.8 eV for alpha-2 and 10.4 eV for gamma. These values can be compared with 17 eV for bulk Al_2O_3 [7]. The measured differences imply that the binding of oxygen to aluminum in the initial oxide is slightly greater on the gamma alloy compared with the alpha-2 alloy, but for neither alloy is it as great as Al_2O_3.

3.3 Oxygen Adsorption Kinetics

The kinetics for oxygen adsorption onto alpha-2, gamma, titanium, and aluminum are shown in Figure 3. Here, the oxygen Auger signal is plotted as a function of the oxygen exposure. The data for titanium and aluminum were obtained using the same experimental procedures as for the alloys. The difference between the slow oxygen adsorption kinetics on aluminum and the rapid adsorption kinetics on titanium and the titanium aluminides is clear from the data in the Figure 3. The oxygen amplitude reaches an apparent "constant" value on the titanium aluminides after an exposure of about 20 Langmuirs, whereas on aluminum, the corresponding situation is not achieved until an exposure of about 250 Langmuirs.

The oxygen Auger signals for exposures greater than 20 Langmuirs are actually not constant, but very slowly increasing. The initial rapid increase in the oxygen Auger signal occurs during chemisorption on the clean surface and growth of the initial oxide layer. The very slow growth region marks the transition to "logarithmic" oxide growth kinetics, the study of which is beyond the scope of this work [9].

As shown in Fig. 3, the "constant" value of the oxygen Auger signal is alloy dependent, decreasing in value with increasing aluminum alloy concentration. This appears to be the result of a matrix effect in the production of oxygen Auger electrons rather than a variation in the oxygen content in the initial oxide overlayer [6]. The attenuation of specific Auger spectra (see Sec. 3.2) with oxygen exposure is essentially independent of alloy composition for all oxygen exposures, including the logarithmic region. This indicates that during the adsorption of oxygen the thickness of the overlayer is independent of alloy composition and dependent only on oxygen exposure. Since the same exposure is required to reach the logarithmic growth region for each titanium alloy, it is reasonable to assume that the total adsorbed oxygen content in the overlayer is independent of the alloy composition.

Given the above arguments, if the oxygen Auger signals, shown in Figure 3, are normalized by their respective "constant" values, then the kinetics for oxygen adsorption onto alpha-2, gamma titanium aluminide, and titanium are identical, within experimental error. There is no effect of the varying surface aluminum concentration on the adsorption kinetics or adsorption rate. The initial sticking coefficient for oxygen adsorption onto these surfaces is estimated to be unity [5] and, as shown in Fig. 3, it is relatively constant over a large portion of the initial adsorption.

The fact that the initial sticking coefficient is so large, is constant initially, and is independent of surface composition suggests that the gas phase oxygen is initially adsorbed into a precursor molecular state [10]. Dissociative chemisorption occurs from the precursor and not the gas phase. If the adsorption kinetics on metallic titanium and aluminum are indicative of the dissociating capabilities of the respective atoms, then it would follow that the dissociation of oxygen on the titanium aluminides must be occurring on the titanium atoms. Since the Auger data show that all the metallic species in the initial oxide overlayer are reacted with adsorbed oxygen, the oxygen atoms must diffuse freely throughout the surface region from the dissociating titanium atoms and are not preferentially bound to the titanium atoms.

4. SUMMARY

The oxygen adsorption kinetics and adsorption rates at room temperature on alpha-2 and gamma titanium aluminide alloys are independent of the aluminum concentration. In fact, the adsorption kinetics and rates observed for these alloys are identical to the corresponding kinetics for pure metallic titanium. The adsorption rate is consistent with an initial sticking coefficient of unity.

The initial oxide overlayer grows with uniform kinetics to a limiting thickness of 0.45-0.55 nm. Definite oxides, for example Al_2O_3, are not observed in the overlayer. There is, however, no evidence of any metallic species in the initial oxide overlayer.

The fact that the oxygen adsorption kinetics at room temperature are independent of the aluminum surface concentration indicates that the adsorption process, at least during the initial oxide growth phase, plays no role in determining the low temperature oxidation growth kinetics. Adsorption from the gas phase appears to occur through an adsorbed molecular state with dissociation occurring via the titanium surface atoms. The surface of the initial oxide overlayer is possibly still chemically reactive (ie, dissociative hydrogen adsorption), since the oxidation states of the surface species are incomplete. Thermal activation should produce a more complete reaction with the adsorbed oxygen and the formation of more stable surface oxides.

ACKNOWLEDGEMENTS

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REFERENCES

1. N.S. Choudhury, H.C. Graham, and J.W. Hinze, in Z.A. Foroulis and F.S. Pettit (eds.), Proceedings of the Symposium on Properties of High Temperature Alloys with Emphasis on Environmental Effects, The Electrochemical Society, Princeton, 1976, p. 668.

2. G. Welsch and A.I. Kahveci, in T. Grobstein and J. Doychak (eds.), Oxidation of High-Temperature Intermetallics, The Minerals, Metals and Minerals Society, Warrendale, 1988, p. 207.

3. M. Bujor, L.A. Larson, and H. Poppa, J. Vac. Sci. Technol., 20 (1982) 392.

4. M.C. Burrell and N.R. Armstrong, Langmuir, 2 (1986) 30.

5. D.J. Hana, J. Vac. Sci. Technol., 13 (1976) 471.
6. G. Ertl and J. Kuppers, Low Energy Electrons and Surface Chemistry, Verlag Chemie, Weinheim, 1974, Chapter 2.

7. L.E. Davis, N.C. MacDonald, P.W. Palmberg, G.E. Raich, and R.E. Weber, Handbook of Auger Electron Spectroscopy, Perkin-Elmer Corp., Eden Praire, 1978, p. 47.

8. G.B. Hoflund, H.-L. Yin, A.L. Grogan, Jr., D.A. Asbury, H. Yoneyama, O. Ikeda, and H. Tamura, Langmuir, 4 (1988) 346.

9. O. Kubaschewski and B.E. Hopkins, Oxidation of Metals and Alloys, Butterworths, London, 1962, p.36-37.

10. W.H. Weinberg, in M. Grunze and H.J. Kreuzer (eds.), Kinetics of Interface Reactions, Springer-Verlag, Berlin, 1987, p.94ff.

TABLE 1

The metallic bulk and surface concentrations of the titanium aluminide alloys discussed in this report.

Alloy		Concentration, atomic % Ti	Al	Nb	
alpha-2	bulk	66.2	20.7	12.7	
	surface	53.7	23.7	22.6	
		55.0	22.6	22.4	[1]
gamma	bulk	43.5	53.1	3.5	
	surface	42.8	50.3	6.9	

1. Differently prepared specimen of the same alloy.

TABLE 2

Energies of the principal Auger spectra emitted from clean and oxygen exposed (20 Langmuirs) alpha-2 and gamma titanium aluminide.

Surface Condition	Alloy	Spectral Energy (eV) For The Indicated Elements Ti	Al	Nb	O
clean	alpha-2	15.6[1], 27.0 386.7, 418.0, 450.0	66.2	167.1, 198.2	511.3
20 L	alpha-2	7.6[1], 25.3, 40.8 385.0, 417.9, 450.4	40.8 56.4	166.0, 198.2	510.2
clean	gamma	14.5[1], 27.0 386.7, 417.9, 450.7	66.8	167.1, 198.2	512.5
20 L	gamma	7.6[1], 22.5, 40.1 385.0, 417.9, 451.1	40.1 56.4	167.1, 198.9	511.3

1. This spectrum has not been identified as an Auger transition. It occurs, also, in spectra from titanium metal.

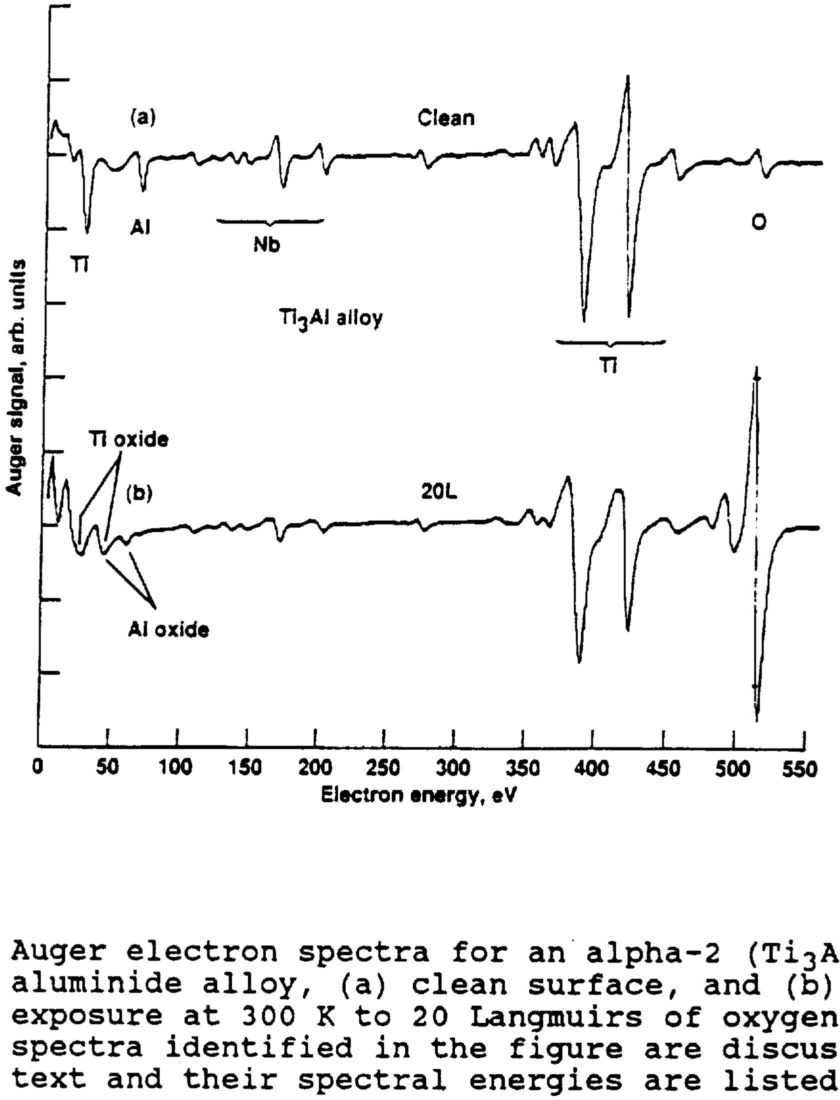

Figure 1 --- Auger electron spectra for an alpha-2 (Ti_3Al) titanium aluminide alloy, (a) clean surface, and (b) after exposure at 300 K to 20 Langmuirs of oxygen. The spectra identified in the figure are discussed in the text and their spectral energies are listed in Table 2.