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Surface oxide dissolution in titanium subhydrides studied by Auger electron spectroscopy and X-ray photoelectron spectroscopy

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The surface sensitive spectroscopic techniques of Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS) have been applied to the study of oxide dissolution of titanium subhydrides. In an earlier study using AES, it was shown that the rate of oxygen dissolution into titanium increased sharply at ~ 350° C. These data correlated well with physical property measurements that indicated an exothermic reaction was occurring at these temperatures which corresponded to the reaction of free titanium with atmospheric oxygen. In the present study the work has been expanded to include studies of TiH_x ($x = 1.15, 1.62$). It has been found that dissolution of the native oxide on titanium subhydrides occurs at a temperature substantially higher (~ 500° C) than that required for titanium. It appears that the outward diffusion of hydrogen is inhibiting the inward diffusion of oxygen on the subhydride samples at temperatures below 500° C.

1. Introduction

Earlier work has shown that, in the ignition of the pyrotechnic mixture $Ti/KClO_4$, the surface oxide on the titanium fuel plays an important role [1–3]. Studies with Auger electron spectroscopy (AES) have shown that the dissolution of the native oxide on titanium increases sharply at 350° C [2]. The reaction between titanium and $KClO_4$ in air will become self-sustaining, however, only at temperatures above 500° C. At lower temperatures, the dissolution reaction is too slow to produce a sufficient amount of the powder particles for sustained oxidation to occur. Oxygen diffusivities in titanium in the temperature range of 450 to 550° C have been calculated from AES depth profiles to be 10^{-15} to $10^{-16}\,cm^2\,sec^{-1}$ by Fick's second diffusion law [4, 5]; the activation energy was calculated to be $30 \pm 3\,kcal\,mol^{-1}$ ($1\,cal = 4.18\,J$).

Titanium subhydride (TiH_x, $x < 2.0$) has been found to be a more electrostatically insensitive material than titanium. In fact, in the $TiH_x/KClO_4$ mixtures, sensitivity has been found to be inversely proportional to x [1]. It has been established that titanium subhydride particles are coated with thin layers of titanium oxide, suboxide, and/or hydroxide [6]. In the present work, hydrided foils were analysed with AES and XPS in order to determine the dissolution characteristics of the surface oxide. Foils with stoichiometries of $TiH_{1.15}$ and $TiH_{1.62}$ were used.

2. Experimental methods

2.1. Spectrometers

AES spectra were obtained with a Varian Auger spectrometer, Model 981-2707, using a beam energy of 5 keV and a beam current density of $20\,mA\,cm^{-2}$ ($2\,\mu A$ beam rastered over $10^4\,\mu m^2$).

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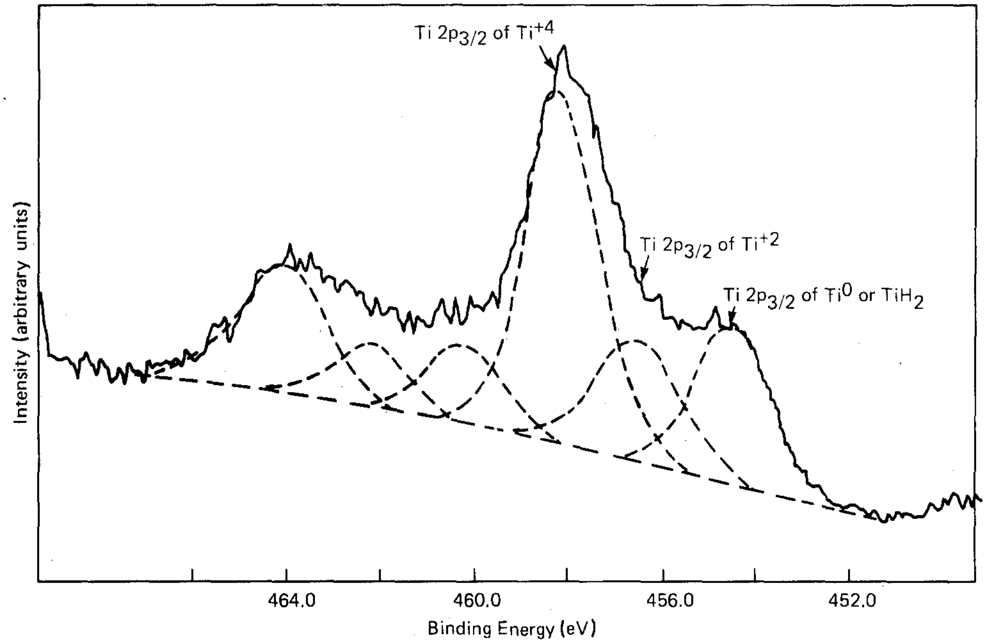

Figure 1 Titanium 2p XPS spectrum of $TiH_{1.62}$ surface.

The XPS data were obtained with an extensively modified AEI ES-100 photoelectron spectrometer. Modifications to this instrument included the addition of a 200 l sec^{-1} turbomolecular pump and a 110 l sec^{-1} ion pump for evacuation of the sample chamber. The heater assembly in the AES and XPS systems has been used in cathode studies and is described elsewhere [7].

2.2. Sample preparation

The titanium subhydride foils used in this work were prepared from Materials Research Corporation electron beam melted, cold fabricated titanium in the form of 0.020 inch x 1.000 inch strips. A strip was cut, cleaned in acetone followed by ethanol, dried with argon, then weighed to ± 0.1 mg. The sample was placed in a reactor vessel in a furnace and heated under vacuum at 400° C for 1 h. Hydrogen gas from a calibrated reservoir held at room temperature was then admitted, and the furnace temperature was raised to 700° C. Absorption occurred rapidly and the furnace was allowed to cool. When the pressure in the reservoir dropped to a predetermined level, the inlet valve was closed. When the furnace returned to room temperature, the sample was removed and again weighed to ± 0.1 mg, and the weight difference was used to calculate stoichiometry.

3. Results and discussion

XPS has been shown to be useful in distinguishing the different oxidation states of titanium present in passive titanium oxide films [2, 3, 8, 9]. In Fig. 1, the titanium 2p spectrum of $TiH_{1.62}$ surface is shown. The signal can be deconvoluted into three titanium $2p_{3/2}$ peaks with binding energies of 458.3, 456.3, and 454.5 eV due to TiO_2, TiO_x, Ti (or TiH_2) respectively. The most prominent peak in this spectrum at 458.3 eV is the titanium $2p_{3/2}$ peak from Ti^{+4}. Parte *et al.* [9] have shown that TiO_x can have the form of TiO, Ti_2O_3 or Ti_3O_5 with titanium $2p_{3/2}$ binding energies ranging over only 2.3 eV. We do not have evidence to identify the form of this suboxide; however, it is assigned to be Ti^{+2} for simplicity. The peak at 454.5 eV is either from Ti^0 or from titanium in TiH_2. The detection of this peak indicates that the oxide layer is rather thin. Lamartine *et al.* [10] have shown that there is only a 0.6 eV separation between the titanium $2p_{3/2}$ peaks of titanium and TiH_2. Thus, in the situation where both titanium and TiH_2 are present, it is not possible to resolve their respective contributions to the XPS peak at $\sim$454 eV.

Other evidence that the surface oxide is thin for both the $Ti_{1.15}$ and $TiH_{1.62}$ samples is found in the AES data. Fig. 2 shows an AES depth profile

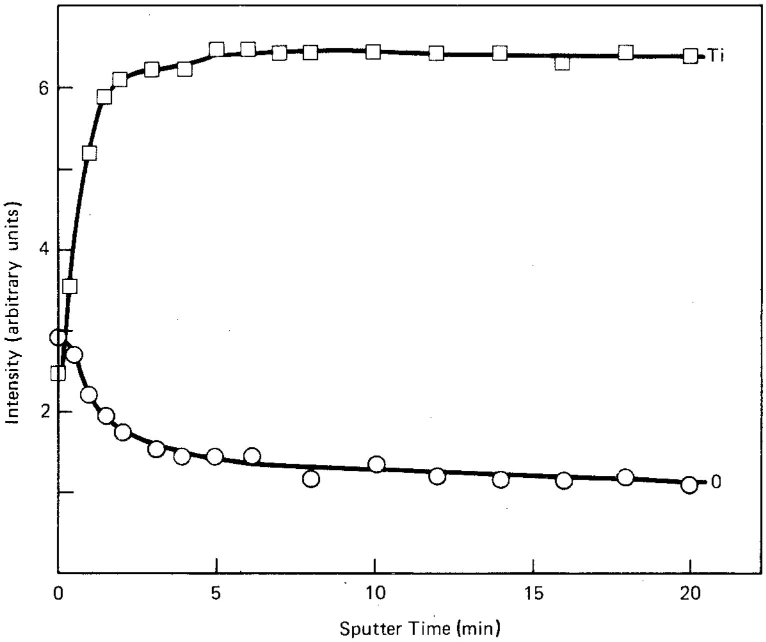

Figure 2 AES depth profile of $TiH_{1.15}$ sample.

of the $TiH_{1.15}$ sample. The profile of the $TiH_{1.62}$ sample was similar. In both cases, the oxygen intensity decreases to 10% of its surface intensity after only ~4 min of sputtering with 1 keV Ar^+. This indicates that the oxide thickness is < 3.0 nm. Samples of the $TiH_{1.15}$ and $TiH_{1.62}$ foils have been heated in the AES system. The peak-to-peak heights of the Ti $L_3M_{2,3}M_{2,3}$ transition and the oxygen KLL transition are ratioed and plotted as a function of temperature for $TiH_{1.15}$ and $TiH_{1.62}$ in Figs. 3 and 4, respectively. In each case, the titanium oxygen ratio begins to increase at temperatures above 450° C. In the previous study on titanium foil, it was found that the onset of oxide dissolution occurred at a lower temperature, in the range 300 to 350° C [2].

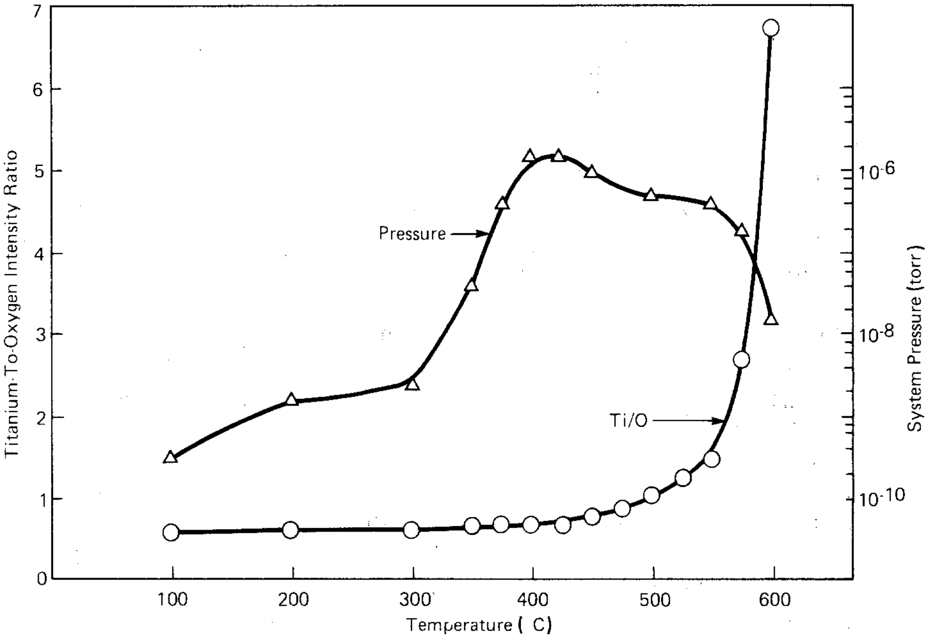

Figure 3 Pressure due to hydrogen evolution and AES intensity ratio of titanium $L_3M_{2,3}M_{2,3}$ to oxygen KLL in $TiH_{1.15}$ sample as a function of temperature.

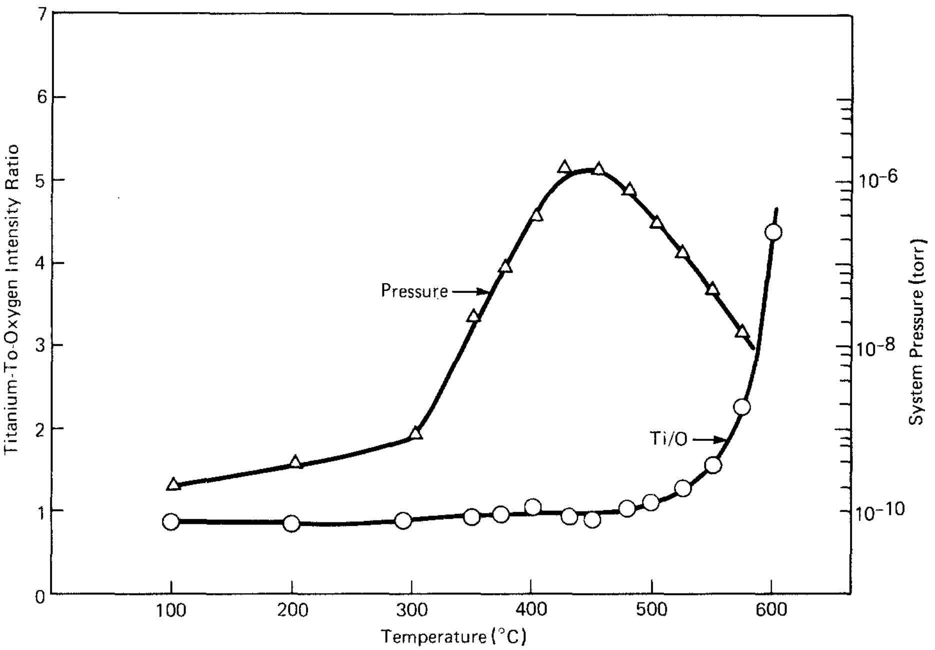

Figure 4 Pressure due to hydrogen evolution and AES intensity ratio of titanium $L_3M_{2,3}M_{2,3}$ to oxygen KLL in $TiH_{1.62}$ sample as a function of temperature.

While the titanium hydride samples were heated in the AES sample chamber, a pressure rise due to a dehydriding of the samples was noted. The system pressure was also plotted as a function of the temperature of the titanium subhydride samples in Figs. 3 and 4. For both the $TiH_{1.15}$ and $TiH_{1.62}$ samples, the rates of hydrogen evolution peaked at about 400 to 450° C. The AES data would then seem to indicate that the outward diffusion of hydrogen is inhibiting the dissolution of oxide. There is a slight difference in the dissolution rate for the two samples. If Figs. 3 and 4 are compared, it can been seen that the titanium oxygen ratio increases more rapidly at temperatures above 500° C for the $TiH_{1.15}$ sample.

XPS spectra are shown in Fig. 5 for the $TiH_{1.62}$ sample at several representative temperatures. The scans of the titanium 2p peaks show an increase in the amount of Ti, TiH_2 and/or TiO on the sample surface as the sample is heated. At temperatures above 500° C the sample surface is composed chiefly of Ti^0. The area under each of the titanium $2p_{3/2}$ peaks for TiO_2, TiO and Ti^0 (or TiH_2) was ratioed to the total titanium $2p_{3/2}$ area and plotted as a function of temperature in Fig. 6. When this figure is compared with earlier data for titanium metal [2], it can be seen that the Ti^{+4} level begins to decrease at a higher temperature for the $TiH_{1.62}$ than for titanium metal. This is consistent with the AES data discussed previously.

In Fig. 7 it can be seen that as the temperature of the $TiH_{1.62}$ sample is increased, there are changes in the oxygen 1s spectra. The peak at ~530 eV has been attributed to TiO_2 [2, 8] while the peak at ~532 eV is thought to be due to either OH^- [2] or absorbed oxygen on the surface [8]. At temperatures above 650° C, oxygen is no longer detectable.

The carbon 1s spectra show that there is a transformation in the carbon chemistry that occurs during heating as shown in Fig. 8. The peak at 281.5 eV, which increases as the sample is heated, has been assigned to either a carbide or dissolved carbon [8].

The $TiH_{1.15}$ sample has also been analysed using XPS. There were some differences between the dissolution characteristics of this sample and those of the $TiH_{1.62}$ sample discussed previously. The initial Ti^{+2} level on the surface of the $TiH_{1.62}$ sample was higher than for the $TiH_{1.15}$ sample. The titanium $2p_{3/2}$ spectrum was again deconvoluted into peaks due to TiO_2, TiO, and Ti^0 (or TiH_2). The area under each of these titanium $2p_{3/2}$ peaks was ratioed to the total titanium $2p_{3/2}$ area and plotted as a function of temperature in Fig. 9. When this figure is compared with Fig. 6, it

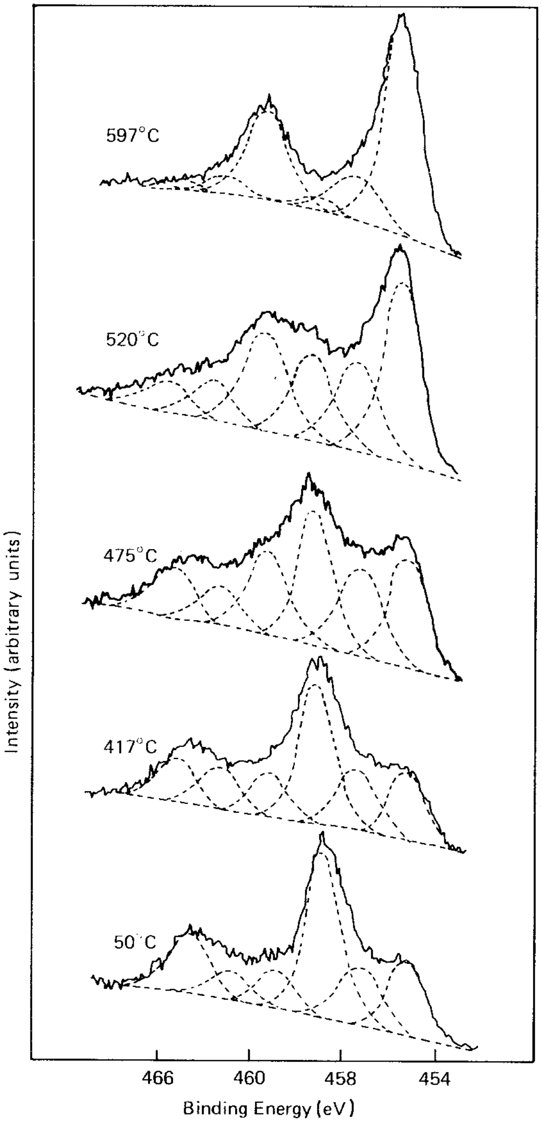

Figure 5 Titanium 2p XPS recorded to $TiH_{1.62}$ sample during dissolution of native oxide.

can be seen that the Ti^{+4} level begins to decrease at a somewhat lower temperature on the $TiH_{1.15}$. The oxygen and carbon spectra for the $TiH_{1.15}$ sample showed changes with temperature which were very similar to those observed for $TiH_{1.62}$ as plotted in Figs. 7 and 8.

4. Conclusion

In the present study, the AES and XPS techniques have shown that the solubility of oxygen in titanium subhydride (TiH_x where $x = 1.15$ or 1.62) increases sharply at temperatures above 500° C. There was a difference between the two samples in that the dissolution proceeded

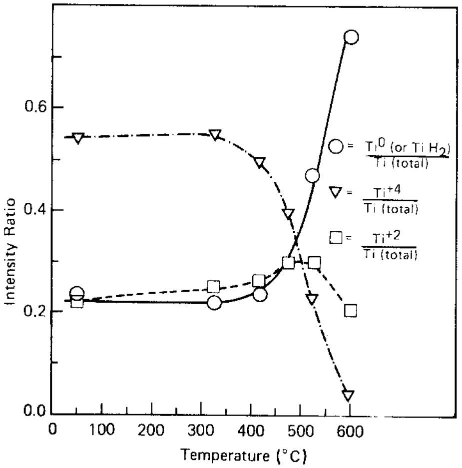

Figure 6 Ratio of titanium $2p_{3/2}$ intensity from Ti^{+4}, Ti^{+2} and Ti^0 (or TiH_2) to total titanium $2p_{3/2}$ intensity as a function of temperature for a $TiH_{1.62}$ sample.

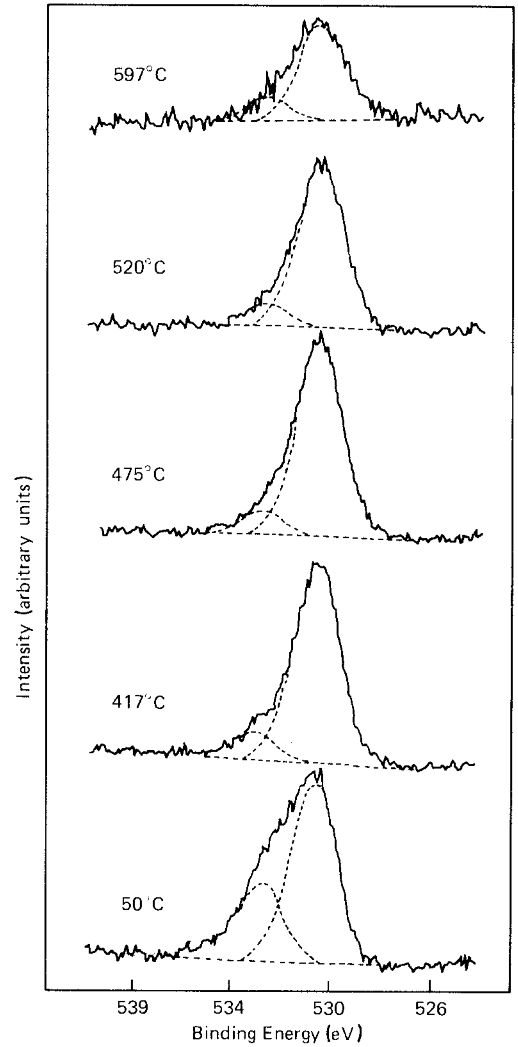

Figure 7 Oxygen 1s XPS spectra recorded for $TiH_{1.62}$ during dissolution of native oxide.

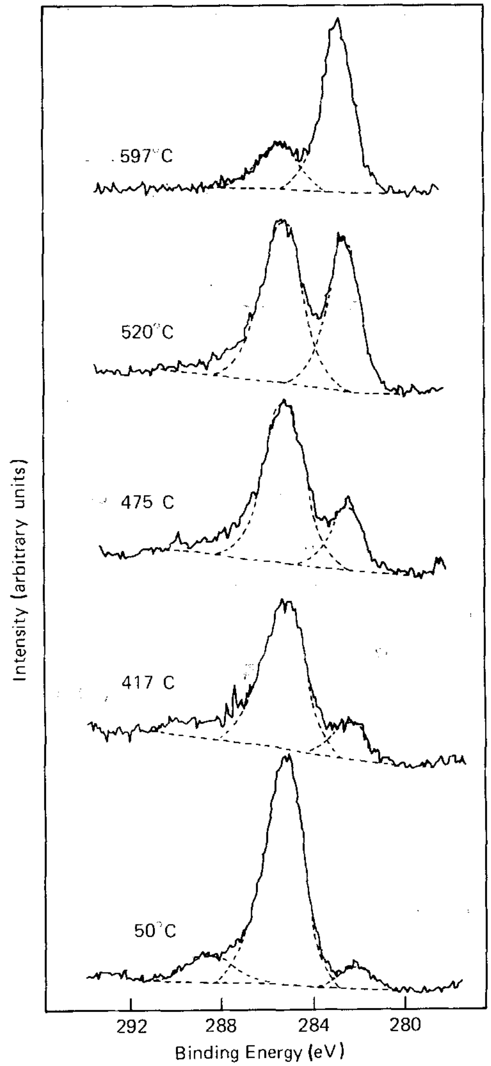

Figure 8 Carbon 1s XPS spectra recorded for $TiH_{1.62}$ during dissolution of native oxide.

somewhat more rapidly on the $TiH_{1.15}$ sample than on the $TiH_{1.62}$. The evolution of hydrogen from these samples peaked at 450° C. It could then be inferred that at temperatues below 500° C the outward diffusion of hydrogen is preventing the inward diffusion of oxygen.

The XPS data on the two subhydride samples showed that the level of TiO increased as the sample was heated reaching a maximum between 400 and 500° C. A similar increase in the TiO level was noted in a previous study on the dissolution of the native oxide on titanium.

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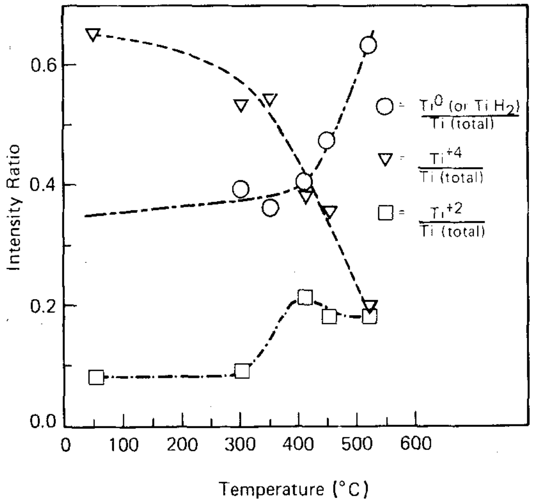

Figure 9 Ratio of titanium $2p_{3/2}$ intensity from Ti^{+4}, Ti^{+2} and Ti^0 (or TiH_2) to total titanium $2p_{3/2}$ intensity as a function of temperature for a $TiH_{1.15}$ sample.

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