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Surface segregation and oxidation of Ti in a V–Ti alloy

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Abstract

The oxidation and reduction of surface oxides of the V–4%Ti alloy were examined by X-ray photoelectron spectroscopy. A specimen sheet of the alloy covered by oxide films was heated between 513 and 1223 K for 10 min in vacuum. Vanadium oxides started to be reduced to the metallic state at 673 K owing to oxygen dissolution in the bulk, while titanium remained in oxidized states up to 983 K. Titanium segregated to the surface above this temperature, and the surface concentration reached up to 40% at 1223 K. The specimen surface enriched in Ti was thus prepared and oxidized at 573 and 773 K under oxygen pressures between 10^{-5} and 10^{-3} Pa. At 573 K, titanium was selectively oxidized at 10^{-5} Pa, while vanadium remained in a metallic state. Such selective oxidation of Ti took place also at 775 K under the pressure of 10^{-4} Pa. Titanium segregating to the surface appeared to provide the barrier effect against tritium inventory and permeation under high temperature, low oxygen partial pressure conditions through selective oxidation.

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1. Introduction

Vanadium alloys are recognized as candidates of the structural materials for fusion reactor blankets because of their low induced radioactivity by neutron irradiation and favorable mechanical properties [1,2]. Oxidation is, however, one of the critical issues for the application of these alloys because mechanical properties are significantly degraded by oxygen uptake [2]. Tritium permeation and inventory are also important problems since the solubility and diffusivity of hydrogen isotopes are large in vanadium alloys in comparison with other metals [3].

Surface oxides on metals generally act as effective barriers against dissociative chemisorption of hydrogen isotope molecules, while clean surfaces are active for ingress of hydrogen isotopes [4]. Therefore, tritium permeation and inventory should be high provided that vanadium alloys are used under low oxygen pressures where the oxide film is scarcely retained. On the other hand, a low oxygen pressure atmosphere is favorable to prevent the oxygen uptake. Hence, it is necessary to examine the surface chemistry of vanadium alloys under low oxygen pressures to evaluate the applicability of these alloys. A surface modification to reduce tritium permeation/inventory improves the compatibility of these alloys with various coolant materials.

In the present study, changes in surface chemistry of the V–4%Ti alloy were investigated at elevated temperatures in an ultra-high vacuum system. A specimen covered by an oxide film was heated up to 1223 K and the oxide reduction was examined by X-ray photoelectron spectroscopy (XPS). The specimen surface was modified by Ti segregation, and the oxidation was examined under oxygen pressures from 10^{-5} to 10^{-3} Pa. The influence of Ti on the tritium permeation/inventory was discussed.

2. Experimental

A sheet of the V–4%Ti alloy measuring 15 × 15 × 1 mm^3 was cut from an ingot prepared by arc melting. The

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Table 1
Chemical composition of V–4%Ti alloy specimen (in mass ppm)

Element	Ti	N	O	C	Fe	Si	Al	W	Mo	Cu	V
Concentration	42 500	629	565	219	235	190	175	115	30	20	Balance

chemical composition of the specimen is summarized in Table 1. The surface of the specimen was polished with SiC abrasive papers and finished with 0.06 μm Al_2O_3 powder.

The specimen thus prepared was set on a Ta heater installed in an ultra-high vacuum chamber. The pressure of residual gas was lower than 1×10^{-7} Pa. The reduction of surface oxides was examined by heating the specimen at given temperatures between 513 and 1223 K for 10 min. The change in surface chemical state was analyzed by means of XPS at room temperature. Non-monochromatized Mg Kα radiation (1253.6 eV) was used for photoelectron excitation. The energy spectrum of photoelectrons was measured with a double pass cylindrical mirror analyzer. The concentrations of each element were estimated from the peak areas of the photoelectron spectra and the sensitivity factors reported by Wagner et al. [5]. The influence of escape depths of the photoelectrons was taken into consideration.

The surface enriched in Ti was prepared through surface segregation by heating the specimen in vacuum at 1273 K for 1 h. After cooling-down to room temperature, the specimen was oxidized at 573 and 773 K in O_2 atmosphere of 10^{-3}, 10^{-4} and 10^{-5} Pa. Then the chemical state of the surface was analyzed by XPS.

3. Results and discussion

The change in XPS spectra by vacuum heating is shown in Fig. 1. At room temperature, the peaks of V, O and C were observed, while no Ti peak was detected. Below 593 K, no significant change was observed except the decrease in C peak intensity. At 673 K, however, the intensity of the O peak started to decrease, while that of the V peak increased. The Ti peak clearly appeared at 823 K, and its intensity increased with temperature.

Fig. 2(a) shows the V 2p spectrum for the as-prepared specimen. This spectrum was deconvoluted into the component by taking account of the binding energies in V, VO, V_2O_3/VO_2 and V_2O_5 reported in the literature [5–10]; V_2O_3 and VO_2 could not be separated from each other because their binding energies are too similar. The spectra of each component thus obtained are also shown in this figure. The major oxides were VO and V_2O_3/VO_2. The change in the fraction of the chemical states by heating is shown in Fig. 2(b). It is obvious that the reduction of V oxides started at around 673 K. Fig. 3(a) shows the Ti 2p spectrum at 823 K where the Ti peak appeared. The spectra of each component shown in this figure were obtained by taking account of binding energies in Ti, TiO and TiO_2 reported in the literature [5]. The major phase was TiO at this temperature. The fraction of the chemical states is plotted against temperature in Fig. 3(b). The reduction of Ti oxides started at 1063 K. The temperature where the reduction of Ti oxides started was higher than that of V oxides by 390 K. The atomic ratio of Ti to V is also shown in this figure. It is apparent that the Ti concentration increased with temperature. Such surface segregation of Ti took place after the reduction of Ti oxides. Namely, Ti segregated to the surface in the metallic state.

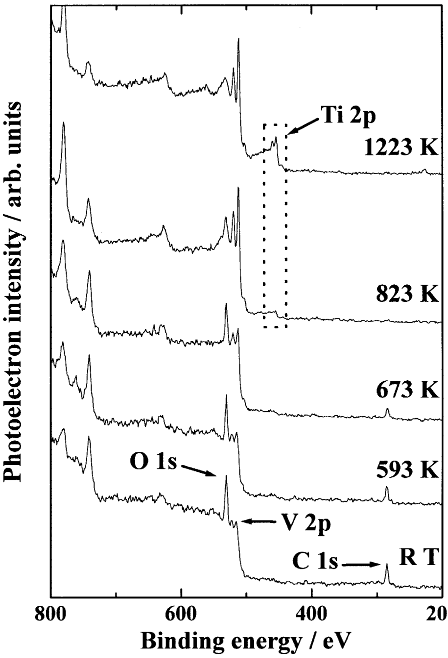

Fig. 1. Change in photoelectron spectrum from V–4%Ti alloy by heating in vacuum.

The surface enriched in Ti was prepared by heating the specimen at 1273 K for 1 h. The concentration of Ti at the surface became ≈50 at.% by this heat treatment. Both the Ti and V were metallic after heating. This specimen was oxidized at 573 and 773 K under oxygen pressures of 10^{-3}, 10^{-4} and 10^{-5} Pa for a period of time from 10 to 45 min. Before oxidation at each temperature and pressure, the specimen was heated at 1273 K in

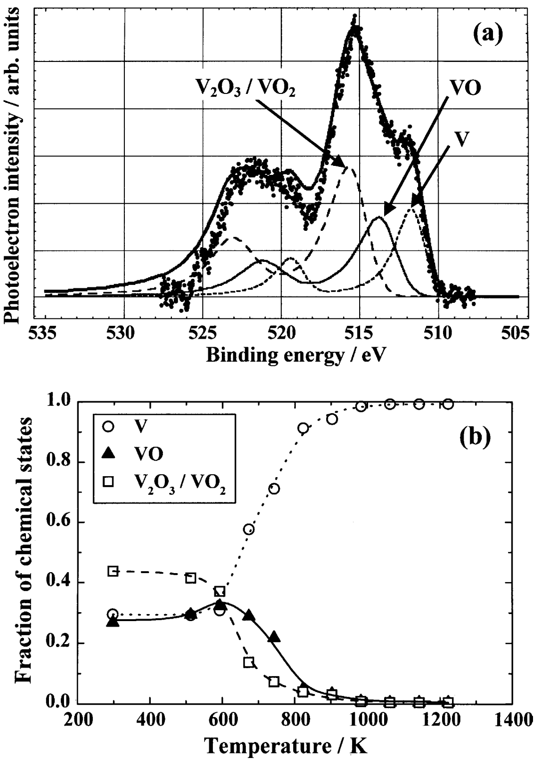

Fig. 2. (a) V 2p photoelectron spectrum before heat treatment. (b) Change in fraction of chemical state of V with temperature.

vacuum (10^{-6} Pa) to start the oxidation with clean surface.

The results after oxidation for 10 min are summarized in Fig. 4. After oxidation at 573 K and 10^{-4} Pa, the peak of the V $2p_{2/3}$ photoelectron spectrum appeared at 515.3 eV corresponding to the binding energy in V_2O_3/VO_2, while the peak of the Ti spectrum was observed at 458.0 eV being assigned to TiO_2. At 10^{-5} Pa, however, the V $2p_{2/3}$ peak was observed at 512.0 eV corresponding to the binding energy of metallic V. On the other hand, the spectrum of Ti indicated that titanium was oxidized as observed at 10^{-4} Pa. Namely, the selective oxidation of Ti took place at 10^{-5} Pa. At 773 K, both vanadium and titanium were oxidized at 10^{-3} Pa, while vanadium remained in the metallic state at 10^{-4} Pa. At this oxygen pressure of 10^{-4} Pa, the Ti $2p_{2/3}$ peak was observed at 454.4 eV corresponding to the binding energy of metallic Ti, while the intensity in the higher energy region was slightly higher than that in the spectrum of metallic Ti. This observation indicates that a small portion of Ti was oxidized. At 10^{-5} Pa, both the V and Ti remained in the metallic states. Fig. 5 shows the time course of oxidation at 773 K and 10^{-4} Pa where a slight oxidation of Ti was observed in Fig. 4. No significant change was observed in the V 2p spectra. The peaks in the Ti 2p spectra, on the other hand, obviously shifted to the higher energy side. Therefore, it was concluded that the selective oxidation of Ti took place at 10^{-4} Pa and 773 K.

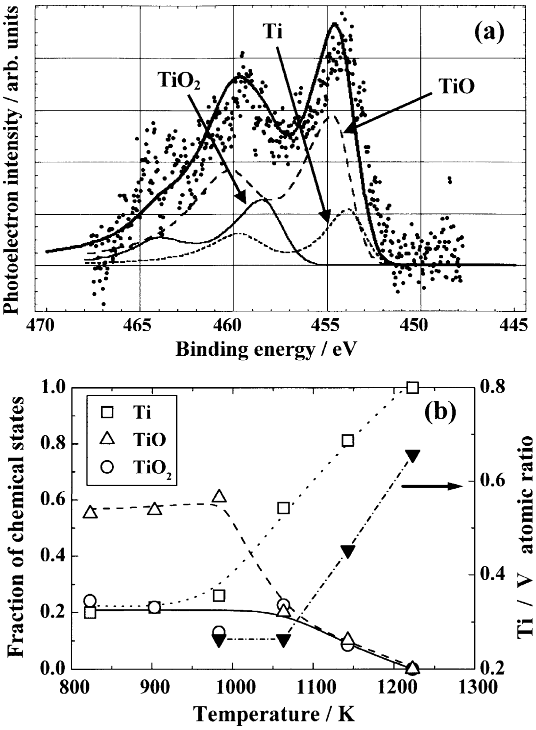

Fig. 3. (a) Ti 2p photoelectron spectrum after heating at 823 K. (b) Change in fraction of chemical state of Ti with temperature.

The reduction of surface oxides by vacuum heating was ascribed to the dissolution of oxygen into the bulk because the solubility and diffusivity of O in V are large. For example, the solubility and diffusivity can be estimated from the literature [11,12] to be ≈4 at.% O and 4×10^{-16} $m^2 s^{-1}$, respectively, at 673 K where the significant reduction of V started, see Fig. 2(b). These values appear to be high enough to accommodate the oxygen present as a thin surface oxide film in the bulk. The difference of the reduction temperatures between Ti and V was attributed to the difference in the chemical affinity to oxygen. The Gibbs energies of formation of bulk Ti oxides are more negative than those of V oxides. For example, the Gibbs energies of formation of TiO and VO at 773 K are −467 and −363 kJ mol^{-1}, respectively [13]. Hence, it is plausible that the surface oxide of Ti is more stable than that of V.

During oxidation, the oxygen potential at the surface is determined by the balance between the incident flux of oxygen from the gas phase and the diffusion flux of oxygen into the bulk. The higher incident flux of oxygen is required for the oxide formation at higher temperature because of increased diffusivity. This is a reason that V was oxidized under the oxygen pressure of 10^{-4} Pa at

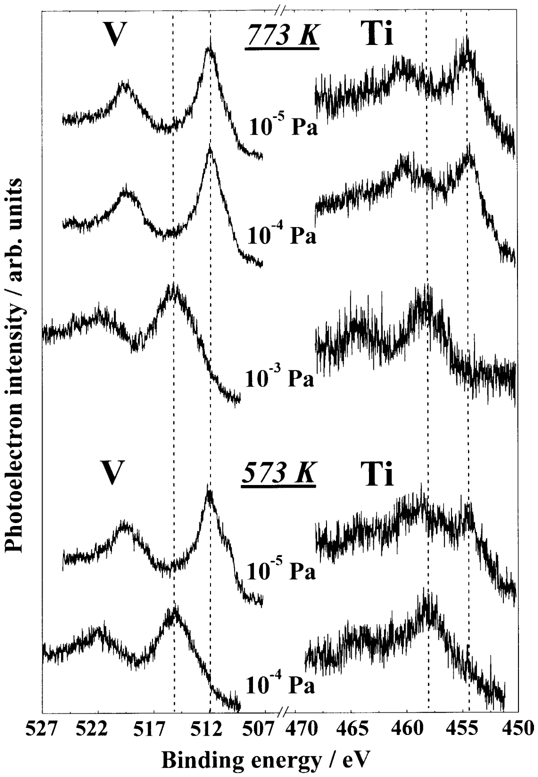

Fig. 4. V and Ti 2p photoelectron spectra after oxidation at 573 or 773 K for 10 min.

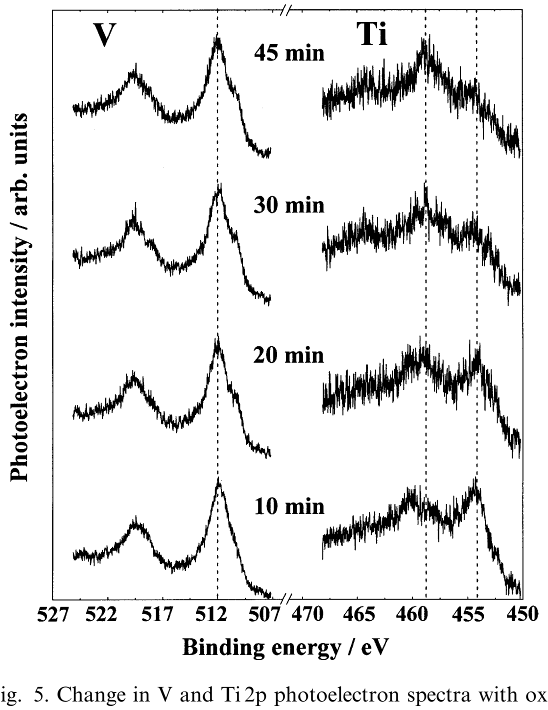

Fig. 5. Change in V and Ti 2p photoelectron spectra with oxidation time at 773 K and 10^{-4} Pa.

573 K and not at 773 K. The selective oxidation of Ti observed in Figs. 4 and 5 was ascribed to the difference in the chemical affinity to oxygen between Ti and V; Ti oxides could be formed at lower oxygen potential than V oxides.

It is known that a monolayer of non-metal impurities significantly reduces the probability of dissociative chemisorption of hydrogen isotope molecules [4]. Therefore, the Ti segregating to the surface appears to provide a barrier against the tritium permeation and inventory under high temperature and low oxygen pressure conditions through the selective oxidation. The favorable barrier effect, however, is obtained in the case where the surface is covered by Ti oxide completely. In order to examine the uniformity of Ti segregation, the specimen heated at 1273 K for 1 h was analyzed by using a scanning Auger microscope. Auger spectra were acquired from randomly selected points with a primary electron beam of ≈10 nm in diameter. The concentration of Ti was not uniform at the surface; it varied from spot to spot in the magnitude of a factor of 2. Nevertheless, Ti was detected from all analyzed points. Therefore, it is plausible that the specimen surface is completely covered by Ti oxides under conditions appropriate for the Ti oxidation. At present, hydrogen permeation experiments through a V–Ti alloy membrane with and without Ti segregation are in preparation in order to examine the barrier effect of Ti oxides against the ingress of hydrogen isotopes.

The mechanism underlying the surface segregation of Ti is not fully understood at present. Measurements of the heat of segregation should provide information on the driving force of segregation. Therefore, it is necessary to examine the temperature dependence of the equilibrium Ti surface concentration in the future.

4. Conclusions

Oxidation and reduction of surface oxides on the V–4%Ti alloy were examined by XPS. Vanadium oxides were reduced to metallic state above 673 K owing to oxygen dissolution into the bulk, while Ti remained in the oxidized states up to 983 K. Titanium segregated to the surface above this temperature, and the surface concentration reached up to 40% at 1223 K. The oxidation of the specimen surface enriched in Ti resulted in the selective oxidation of Ti under an oxygen pressure of 10^{-5} Pa at 573 K and 10^{-4} Pa at 773 K. These observations indicated that titanium segregating to the surface provides a barrier effect against the tritium inventory and permeation under high temperature and low oxygen partial pressure conditions through selective oxidation.

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