

Positron Lifetime Study on Degradation of TiCrV Hydrogen Storage Alloy

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Abstract. Using positron lifetime spectroscopy, we examined the evolution of defects in the $\text{Ti}_{24}\text{Cr}_{36}\text{V}_{40}$ alloy prepared by arc-melting method during hydriding cycles. We found that the positron lifetime increases with increasing the pressure swing cycles. This behavior is well correlated with the degradation of hydrogen transfer change with the pressure swing cycles. The prolonged positron lifetime is attributed to dislocation-related defects. Both dislocations and vacancies bound at dislocations may act as positron trapping centers. After the heat treatment at 400°C, a partial recovery of positron lifetime was observed.

Introduction

To realize the hydrogen fuel cell vehicles in future, the rechargeable hydrogen capacity of storage material should be improved to more than 4 mass% [1]. The Ti-Cr-V solid solution alloy is a promising hydrogen storage material for fuel cells since this alloy exhibits a relatively higher initial storage capacity (3.9 mass%) as compared to the other alloys [2]. After one hydriding cycle, the effective hydrogen capacity is approximately 2.6 mass%. Subsequently, this is gradually reduced with the further hydriding cycles. The strain accumulation and pulverization during hydriding cycles are thought to be the reasons in addition to the surface contamination and the formation of stable hydrides. Microscopically, excess vacancy defects and dislocations may be generated during hydriding cycles [3]. These internal defects trap hydrogen to reduce the rechargeable hydrogen capacity. It is needed to reveal the physical origins of harmful defects acting as hydrogen trapping centers during hydriding cycles. In this paper, using positron lifetime spectroscopy, we investigated the evolution of defects in the $\text{Ti}_{24}\text{Cr}_{36}\text{V}_{40}$ alloy prepared by the arc-melting method during hydriding cycles [4].

Experiment

Ti-Cr-V alloys were prepared by arc melting under an argon atmosphere in a water-cooled Cu crucible. The target composition was $\text{Ti}_{24}\text{Cr}_{36}\text{V}_{40}$. Ingots were subjected to annealing at 1400°C in order to homogenization. Pressure composition isotherms (P-C-T) were measured in a conventional Sieverts-type apparatus. From the P-C-T curves, the hydrogen transfer change was determined at 20°C. X-ray powder diffraction (XRD) analysis using Cu-K α radiation was carried out to determine phases and lattice constants after degassing at 100°C for 1 hour. Dislocation density was determined from transmission electron microscopy (TEM) observation. After the one hydriding, samples are pulverized. The pulverized samples were put into small cases with titanium windows (2 μm thick). Positron lifetime measurements were performed using a conventional fast-fast spectrometer with a time resolution of 200 ps and using a sodium-22 source of 370 kBq after degassing at 100°C and 400°C for 1 hour. Lifetime spectra were analyzed using the PATFIT-88 program [5].

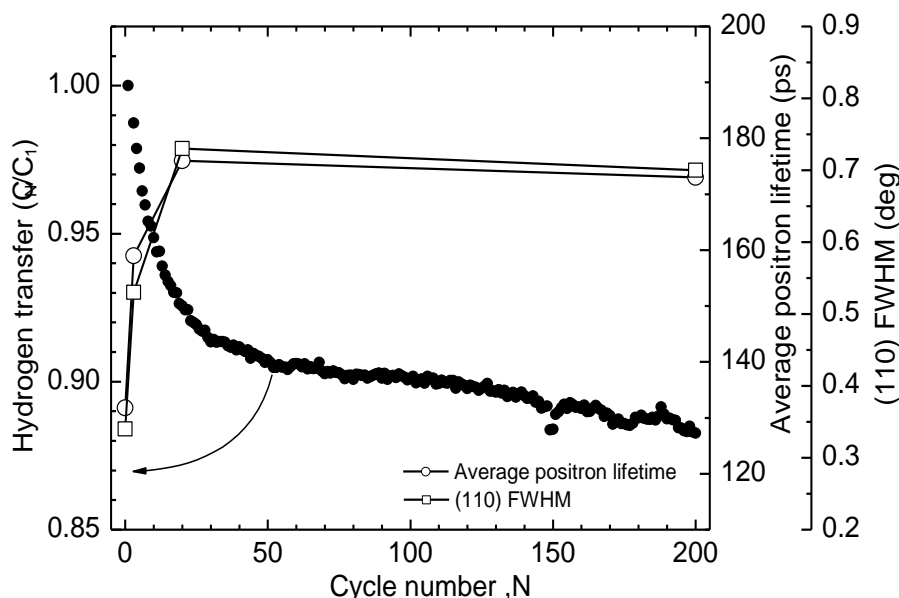


Fig. 1 Hydrogen transfer change, average positron lifetime and full width at half maximum of XRD (110) peak as a function of pressure swing cycles.

Results and Discussion

Figure 1 shows the hydrogen transfer change, the average positron lifetime and the full width at half maximum (FWHM) of XRD (110) peak as a function of pressure swing cycles (N). It is seen that the hydrogen transfer change decreases rapidly at the initial stage of pressure swing cycles and gradually decreases up to $N=200$. The FWHM of XRD (110) peak increases up to $N=20$ and keeps nearly constant value up to $N=200$. In the XRD rocking curve new peaks indicating the change of crystal structure from BCC to BCT appeared at $N \geq 200$ cycles. These results suggest that some strain is accumulated due to hydriding up to $N=20$ and the vanadium hydride formation starts at $N \geq 200$. From the TEM observation, the dislocation density was found to increase from $5 \times 10^8 \text{ cm}^{-2}$ to $1 \times 10^{10} \text{ cm}^{-2}$ with N .

As shown in Fig. 1, the average positron lifetime also rapidly increases up to $N=20$ and keeps a constant up to $N=200$. The results of positron lifetime measurements are summarized in table 1. Before hydriding ($N=0$), only one short-lived component ($\tau=132 \text{ ps}$) was obtained. The bulk lifetime of $\text{Ti}_{24}\text{Cr}_{36}\text{V}_{40}$ was calculated to be 123 ps using the atomic superposition method [6]. This means that positrons mostly annihilate in the perfect lattice region before hydriding. After the partial hydriding (1.3 mass%), the lifetime increases to 142 ps . Up to $N=3$, the lifetime increases to $\sim 160 \text{ ps}$. At $N \geq 20$, the positron lifetime increases to 173 ps and keeps a constant value up to $N=1000$.

The increase of positron lifetime with the pressure swing cycles indicates that some open volume type defects such as vacancies and dislocations are generated due to hydriding. Although we attempted to decompose the lifetime spectra, no further lifetime components were obtained. Therefore, the lifetime component ($\tau=173 \text{ ps}$) is hardly attributed to large vacancy clusters. The FWHM of XRD (110) peak similarly increases with the pressure swing cycles. This implies that the increase of positron lifetime may be caused by the dislocation generation and degradation of crystallinity. Since the dislocation density is very high after a few swing cycles, most positrons annihilate at dislocations and hence the positron lifetime keeps a constant value after the further swing cycles.

According to Shirai et al. [7], the positron lifetime at dislocations in fcc and bcc metals depends on the burgers vector of the dislocation. For Cu and Au, the positron lifetime at an edge dislocation is approximately 200 ps , while the bulk lifetime 120 ps . The positron lifetimes for the Frank and Shockley partial dislocations are approximately 180 ps and 160 ps , respectively. Kamimura et al. [8] calculated the positron lifetimes for edge dislocations and vacancies in iron considering a realistic

lattice relaxation. Contrary to the Shirai's report, their calculation shows that an edge dislocation and even a jog on it act as very shallow trapping centers. The positron lifetime increases only 7 ps from the bulk lifetime. Whereas vacancies on edge dislocation give rise to a relatively longer lifetime. The increase of positron lifetime observed at $N \geq 20$ is more than 40 ps. Hence, not only dislocations but also vacancies should be considered. Vacancies are probably bound at dislocations. Fukai et al. [9] reported that the thermal equilibrium vacancy concentration increases extremely due to the hydrogen absorption. Vacancies may also be generated due to the interaction among dislocations. Vacancies generated in such ways may be trapped at dislocations.

As shown in table 1, the positron lifetime decreases to 164-166 ps after heat treatment at 400°C. Since the dislocation density does not decrease by this heat treatment, probably, vacancies bound at dislocations are partially annealed out.

From the above results, it is inferred that the degradation of hydrogen transfer change is related to the formation of defects detected by positron lifetime measurement. In bcc metals, hydrogen atoms occupy the octahedral sites surrounded by six metal atoms. Possibly, the effective hydrogen occupation sites decreases due to the formation of defects. Considering the fact that the hydrogen transfer change is also recovered after the heat treatment at 400°C, the presence of vacancies may result in the decrease in the hydrogen exhaust amount.

Summary

In this paper, we examined the correlation between hydrogen transfer change and generation of defects detected by positron lifetime measurement in $\text{Ti}_{24}\text{Cr}_{36}\text{V}_{40}$ alloy. The degradation of hydrogen transfer change is well correlated with the increase of average positron lifetime. From the detailed analyses of lifetime spectra, it was found that after a few pressure swing cycle, dislocation-related defects are introduced. Both dislocations and vacancies bound at dislocations may act as positron trapping centers although the formation of large amount of vacancies due to the lowering of formation energy was not confirmed.

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Table 1 Positron lifetimes and intensities obtained from the lifetime spectra. In the column of 'Cycle #', 1.3 mass% means that the sample is only partially hydrided with this content.

Cycle #	Degass temp. (°C)	τ (ps)
0		132
1.3 mass%	100	142
3	100	159
20	100	176
200	100	173
1000	100	175
200	400	164
1000	400	166

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