The thermal cycling stability
of V-Ti based alloy

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Abstract

The intrinsic degradation behavior of $(V_{0.53}Ti_{0.47})_{0.925}Fe_{0.075}$ alloy with BCC structure and the two plateau regions (the low and high plateau region) has been investigate during the temperature-induced hydrogen absorption-desorption cycling (thermal cycling). After 400 thermal cycles between room temperature and $600°C$ under 10atm H_2, the total reversible hydrogen absorption capacity decreased by about 40%. From thermal desorption analysis it was found that the degradation behavior at each plateau region was different. In addition, XRD analysis showed that the crystal structure of the sample in de-hydrided state was changed from BCC to BCT after degradation, and that of the sample in hydrided state it was maintained as FCC although peaks were broadened after degradation. From the result of static isothermal hydrogenation treatment it were found that crystal structure change from BCC to BCT was caused by the thermal energy. TEM analysis showed that the peak broadening was due to the formation of an amorphous phase in FCC matrix.

1. Introduction

In recent years, much attention has been paid to metal hydrides for application in thermal energy conversion systems such as heat pump and steam regeneration plants[1)-5)]. In such applications, one of the most important factors to be considered is the intrinsic degradation behavior of the alloys with hydrogen absorption - desorption cycling. Many of the studies have been carried out to elucidate the intrinsic degradation behavior and its corresponding mechanisms in several metal hydride systems[6)-12)].

It was reported that BCC solid solution alloys were promising candidate materials because of their high hydrogen storage capacity of about 3~4 wt% and large hydride formation enthalpy[13)]. In particular, $(V_{0.53}Ti_{0.47})_{0.925}Fe_{0.075}$ alloy has many advantages like easy activation and fast hydrogen desorption reaction[13)]. However, this alloy has two plateau pressure regions at high and low pressure. The plateau pressure of the low plateau region is too low at room temperature to be used in usual conditions. In addition, it is well known that the plateau region rises up as the temperature of alloy increases. The low plateau region can rise up to the ambient pressure at high temperature and the total stored hydrogen in this alloy can be used. Therefore, this alloy is very promising in application for thermal energy conversion systems operated at high temperature. But, there has been no experimental reports on intrinsic degradation behavior of this alloys used in such energy conversion system. In this study, the degradation behaviour of $(V_{0.53}Ti_{0.47})_{0.925}Fe_{0.075}$ BCC solid solution alloy was investigated before and after thermal cycling at high temperature.

2. Experimental details

The $(V_{0.53}Ti_{0.47})_{0.925}Fe_{0.075}$ BCC solid solution alloy sample was prepared by arc melting under argon atmosphere. To ensure homogeneity, it was remelted four times. XRD measurement made for the determination of its crystal structure using Cu Ka. From the XRD measurement it is confirmed to be a homogeneous single BCC solid solution phase. The alloy was mechanically crushed into powder with a size of 100~200 mesh in air. Powder samples of about 1g were loaded into the reactor of P-C isotherm measurement apparatus. P-C isotherm measurements, static isothermal hydrogenation treatment, and thermal desorption analysis were carried out in an automatic Sievert-type apparatus described elsewhere[14)]. The samples were activated by heat treatment at 600℃ for 30 min under a hydrogen pressure of 40atm. Thermal cycling from room temperature to 600℃ was performed on the activated samples with a 20min cycle time under a charging pressure of 40atm H_2. In order to observe the degradation behavior in the aspect of hydrogen storage capacity, the P-C isotherm measurements were carried out at several temperatures before and after thermal cycling. The thermal desorption analysis was performed on samples in both activated and degraded states. For the thermal desorption analysis, each sample was first hydrided under a hydrogen pressure of 40atm at room

temperature and then heated at a uniform heating rate of 5 K/min. The amount of evolved hydrogen was measured. The evolution rate was defined as the amount of desorbed hydrogen during the pressure change from 0.05 to 0.5atm in a unit time and then plotted against temperature. This alloy has three phases, α solid solution phase, β, and γ hydride phase. To observe the structural change after degradation, it was necessary to obtain XRD data for both samples in de-hydrided and hydrided state before and after cycling, respectively. To maintain the sample in de-hydrided state, sample was heated at 600°C in vacuum state. The α phase remained unchanged with this treatment. since α phase is very stable form. To maintain the sample in hydrided state, the sample was fully hydrogenated under a hydrogen charging pressure of 40atm. The sample was quenched in cold water and then exposed in dry air. A static isothermal hydrogenation treatment at high temperature was performed to verify the effect of thermal energy during thermal cycling. In this experiment, the activated sample in the reactor was heat treated at 600°C for 48h under charging pressure of 40atm H_2. Its microstructure was investigated using TEM. The TEM specimen was prepared by crushing the degraded sample in acetone.

3. Results and discussion

Fig. 1 shows the P-C isotherms obtained before cycling at several temperatures. To observe the degradation behaviour of $(V_{0.53}Ti_{0.47})_{0.925}Fe_{0.075}$ having two plateau regions (high and low plateau region) it is

necessary to investigate the P-C isotherms at several temperatures. The high and low plateau regions are clearly observed at 150°C and 600°C, respectively. After P-C isotherm measurements at several temperatures to establish the hydrogen storage capacity and pressure of plateau region from as-received sample, thermal cycling was initiated on this sample to identify a degradation extent. Fig. 2(a) shows the P-C isotherms only including the low plateau region after several cycles. The hydrogen storage capacity decreases by about 24% after 400 cycles, but the major capacity loss takes place during the initial 243 cycles. Fig. 2(b) shows the P-C isotherms only including the high plateau region after several cycles. The total hydrogen storage capacity obtain from Fig. 2(b) decreases by about 40% after 400cycles. It decreases gradually with increasing cycle. Therefore the hydrogen storage capacity of the high plateau region, regard as that of the low plateau region, decreases by about 16% after 400cycles. To investigate the degradation behavior in detail thermal desorption analysis was performed on samples before and after thermal cycles (243 and 400cycle). Fig. 3 shows the results of the thermal desorption of hydrogen from hydrided samples before and after cycling. Two peaks in the thermal desorption spectra are seen in each sample. Since the position of peaks is closely related to the interaction energy between hydrogen atoms and occupied sites[15], two peaks at the low and high temperature correspond to the low and high interaction energy, respectively. Therefore the peaks at the low and high temperature can be related to the desorption of hydrogen evolved in high and low plateau
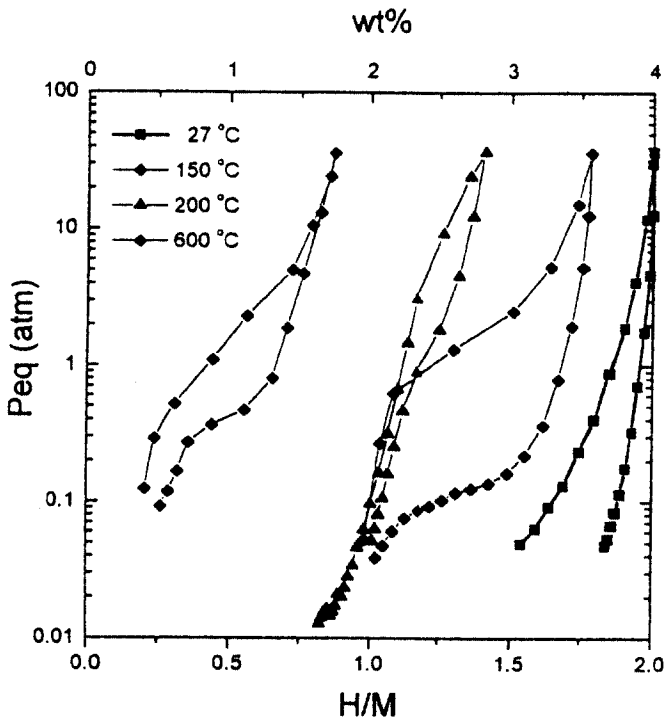
박정건, 김동명, 장국진, 한재성, 이재영

Fig. 1 P-C isotherms of $(V_{0.53}Ti_{0.47})_{0.925}Fe_{0.075}$ at several temperatures 30, 150, 200, and 600℃
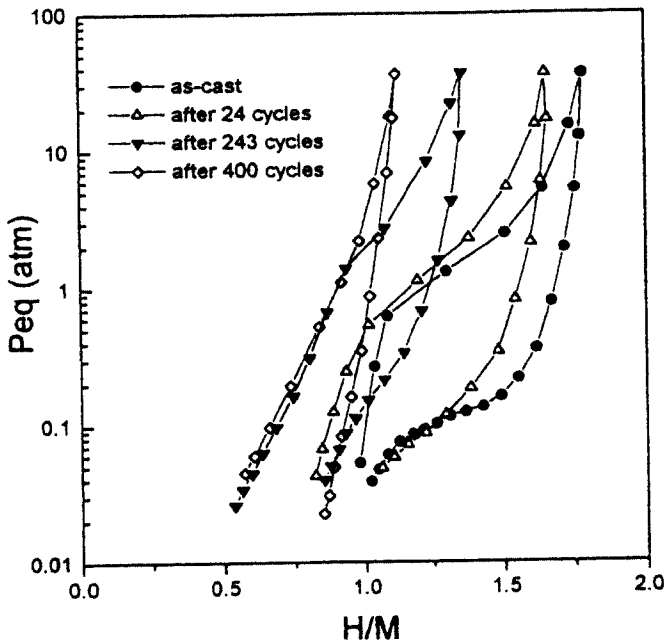

Fig. 2(a) P-C isotherms of sample at 150 ℃ before and after thermal cycling(24, 243, and 400 cycles, Temperature = RT~600℃, P=10atm H_2, cycle time = 20min)

region, respectively. Also the peak area represents an amount of hydrogen evolved from the cite[15], therefore the degradation state can be confirmed qualitatively by measuring the change of the integrated peak area. As shown in Fig. 3, two peaks at around 180℃ and 470℃ for the activated sample, two peaks at around 180℃ and 370℃ for the degraded samples after 243 and 400 cycles, respectively. And the position of the low temperature peak is not changed but the peak area gradually decreases with increasing the number of cycle. However the position of the high temperature peak is shifted to a low temperature region and the peak area is decreased largely during the initial 243 cycles. And then, the peak position and area are nearly not changed up to the 400th cycle. Fig. 4 shows the result of XRD analysis before and after thermal cycling for the samples in de-hydrided state. This sample (α phase) before cycling exhibits a homogeneous single phase having BCC structure. However the degraded sample after 243 cycles exhibits BCT structure. Fig. 5 shows the result of XRD analysis before and after cycling for the samples in hydrided state. The sample (γ phase) before cycling exhibits a homogeneous single phase with FCC structure. The degraded sample after 400cycles also exhibits FCC structure, but its XRD peaks are broadened. On the basis of these facts, the results of thermal desorption analysis shown in Fig. 3 can be interpreted as follows; The high temperature peak represents hydrogen atoms that occupy the cites related to the α phase. Because the structure is changed from BCC to BCT after 243 cycles, which means less stable phase with lower capacity, the
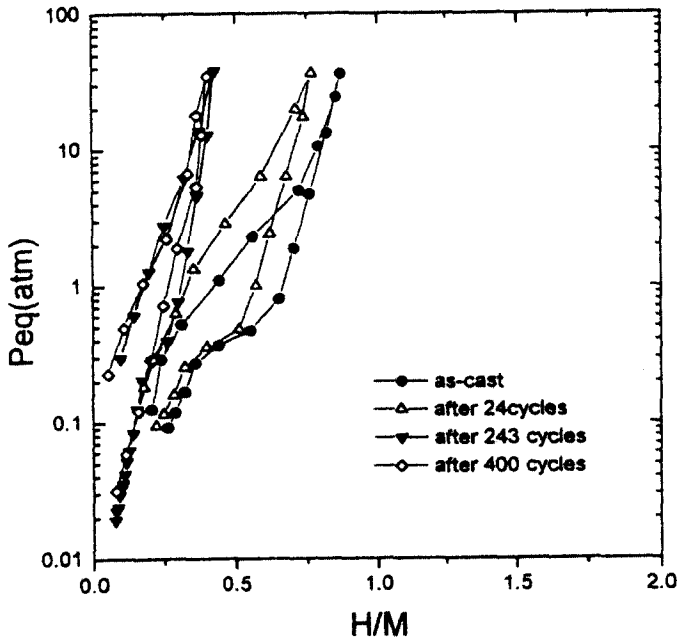
Fig. 2(b) P-C isotherms of sample at 600℃
before and after thermal cycling(24, 243, and
400 cycles, Temperature = RT~600℃,
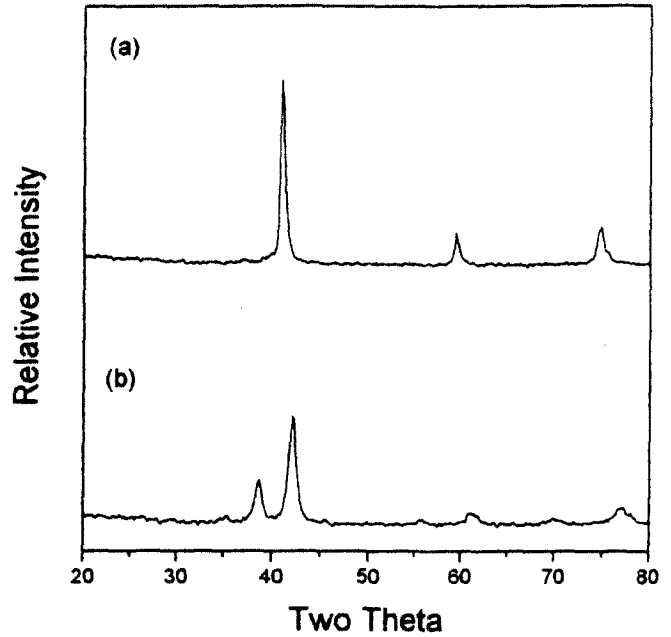P=10atm H_2, cycle time = 20min)

Fig. 4 XRD patterns of samples (a) activated
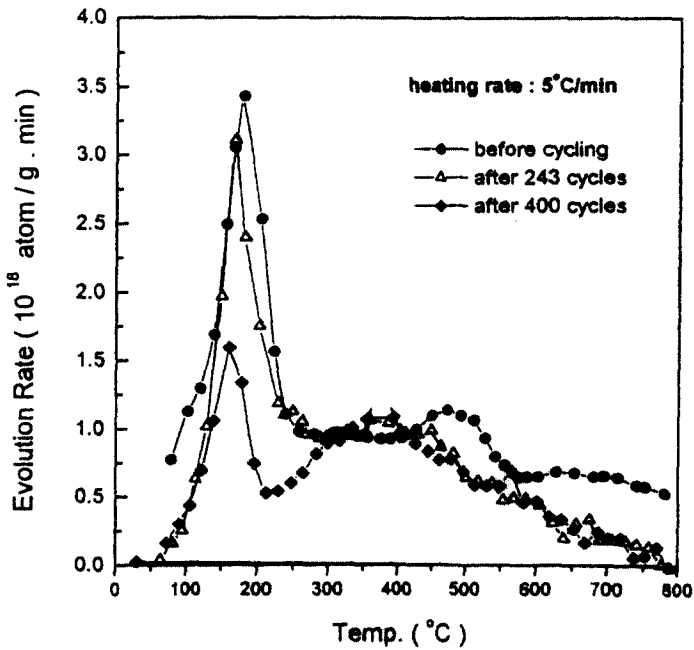and (b) degraded in de-hydrided state

Fig. 3 Thermal desorption spectra of
$(V_{0.53}Ti_{0.47})_{0.925}Fe_{0.075}$ hydrides before and
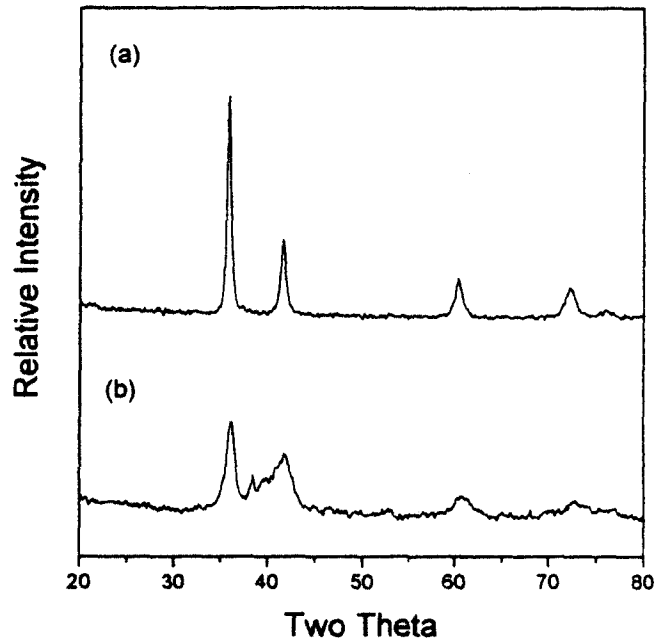after cycling

Fig. 5 XRD patterns of samples (a) activated
and (b) degraded in fully hydrided state

position of peak is shifted to lower temperature region and the peak area decreases largely after 243cycles. And the lower temperature peak represents hydrogen atoms that occupy the cites related to the γ phase. Because the crystal structure is maintained as FCC, which means the existence of the initial hydride at high plateau region, the position of the peak is not shifted. Also the gradual decrease of the peak area which means the decrease of hydrogen storage amount, can be related to the peak broadening in XRD data.

Generally the elastic strain accumulation in the matrix for repetitive cycling and the applied thermal energy derive the sample in a more stable thermodynamic state[16]. Therefore it is suggested that the intrinsic degradation of $(V_{0.53}Ti_{0.47})_{0.925}Fe_{0.075}$ is motivated by the elastic strain and thermal energy. In order to investigate the effect of thermal energy only, a static isothermal hydrogenation treatment at high temperature was performed on the activated sample. With this treatment the effect of elastic strain caused by hydrogen absorption and desorption can be eliminated. Fig. 6 shows the P-C isotherm of a sample hydrogenated at 600℃ under a hydrogen charging pressure of 10atm for 48h. Under these conditions the absorbed hydrogen capacity at low plateau region drastically decreases by about 24%. From Fig. 6, it is proved that the application of thermal energy without elastic strain energy causes a large capacity loss in this alloy. To investigate the change of crystal structure after a static isothermal hydrogenation treatment, a sample in de-hydrided state was prepared and subjected to XRD analysis. Fig. 7 shows that
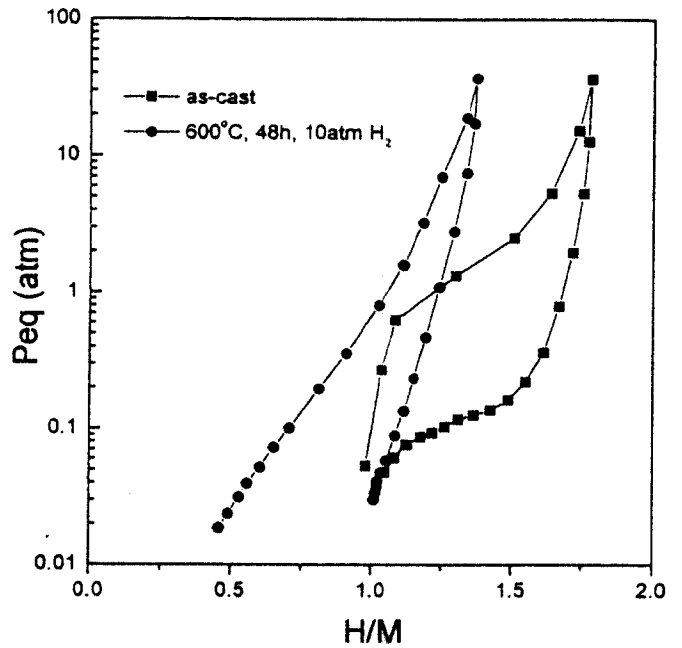

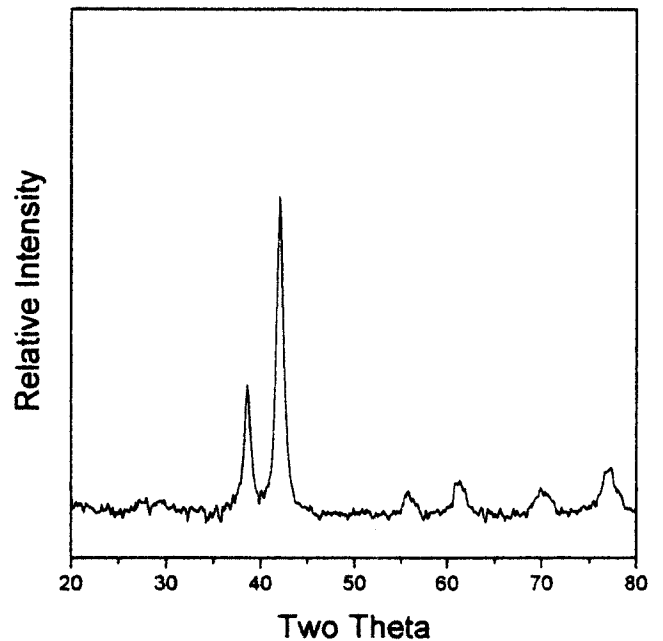Fig. 6 P-C isotherm of sample at 150℃ hydrogenated at 600℃ and 10atm H_2 for 48h

Fig. 7 XRD pattern of sample hydrogenated at 600℃ and 10atm H_2 for 48h in de-hydrided state

initial BCC structure changes to BCT structure only by thermal energy. This phenomenon is the same after thermal cycling. From these facts, it is said that the decrease of hydrogen storage capacity at low plateau region is caused only by thermal energy during thermal cycling. However, the reason of the degradation at high plateau region is still not clear. Since XRD analysis after thermal cycling showed broadened peaks which may be caused from a disordered structure. TEM analysis was carried out to investigate this phenomenon. Fig. 8 shows the bright field image and its corresponding electron diffraction pattern of the degraded sample after 400 thermal cycles. TEM analysis shows a featureless and mottled structure which is typical for amorphous materials and the broad diffuse halo ring pattern corresponding to an amorphous phase are shown. In many rare-earth based intermetallic compounds it is well known that the hydrogen absorption and desorption cycling induces a transformation of crystalline hydride to an amorphous phase[17)-19)]. Especially Chung and Lee[17)] reported that the La_2Ni_7 intermetallic compound could be amorphized by thermal cycling. It was thereby suggested that the amorphization by the thermal cycling was closely related to the lattice distortion caused by repetitive elastic strain accumulation. From these facts it is reasonable to say that the hydrogen storage capacity at high plateau region decreases with the formation of the amorphous phase in FCC matrix phase.
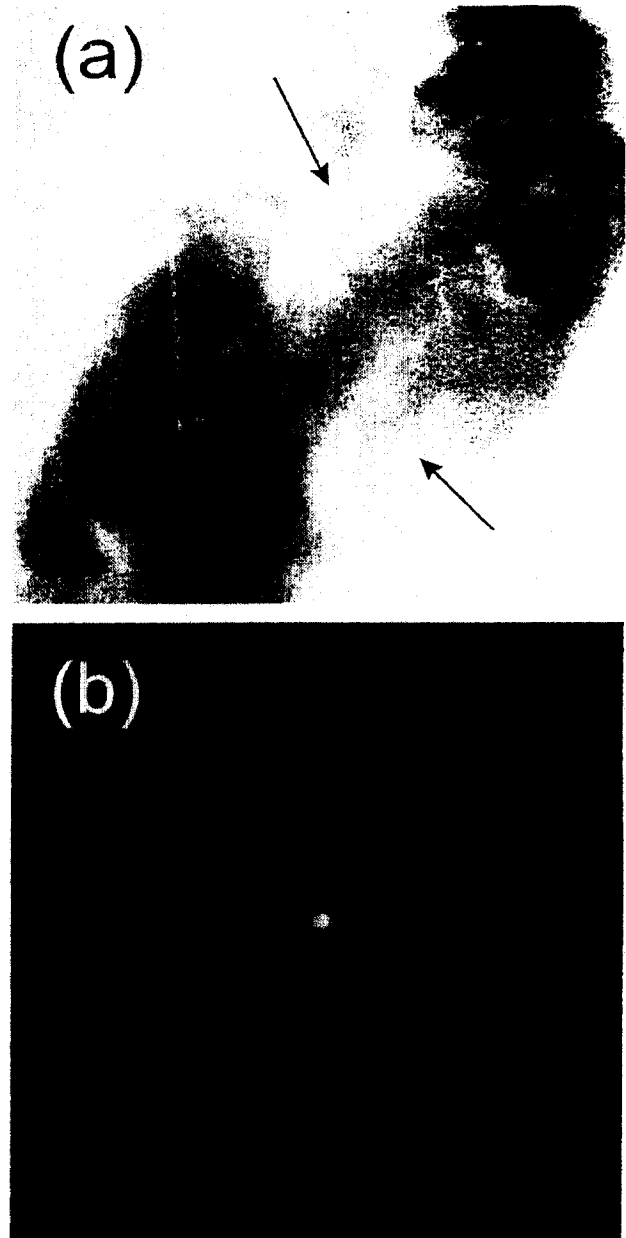

Fig. 8 (a) Bright field TEM image of degraded sample and (b) corresponding electron diffraction pattern

4. Conclusions

The $(V_{0.53}Ti_{0.47})_{0.925}Fe_{0.075}$ alloy which has two plateau region was thermally cycled between room temperature and 600℃ under a

hydrogen pressure of 10atm. About 40% of the hydrogen storage capacity was lost after 400cycles. BCT phase and amorphous phase were formed as degradation products. The phase transformation from BCC to BCT phase was caused only by thermal energy under hydrogen atmosphere. This phase transformation caused the degradation of low plateau region. The formation of amorphous phase in FCC matrix phase caused the degradation of high plateau region.

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