Effect of Substitution on Hydrogen Storage Properties of Ti-V-Fe System

Ti-V based alloys are considered as promising third generation hydrogen storage materials, as they have a great potential to replace the AB₅ alloys in the hydrogen compressor systems [25-38, 131]. V can form both monohydride (VH₁) and dihydride (VH₂). Though the modynamical parameters for the conversion of the monohydride to dihydride are appropriate for room temperature hydrogen storage, but the stability of the monohydride is higher for the practical fuel cell application. As a result the reversible hydrogen storage capacity of V remains well below the theoretical value. Again the activation of the pure body centered cubic (bcc) V phase remains a problem. So by alloying with suitable materials, the bcc phase solid solution can be designed as an appropriate material for hydrogen storage. The most effective alloying element is found to be Ti, as both Ti & V can absorb large amount of hydrogen. The maximum hydrogen content of Ti and V are found to be 3.78 and 3.54 wt. % respectively. Though Ti has an hcp structure at room temperature, it can form bcc structure by the addition of small amount of bcc forming elements, such as, V, Fe or Mn. Ti and V can form solid solutions at all proportions. The physical factors for formation of substitutonal solid solution are guided by Hume –Rothery rule [132]. According to that, the atomic size of
the two elements should not differ more than 15% and they should have similar crystal structure. Their electro negativity difference should not be very high, because it is likely that in such cases they prefer to form a stable structure than continuous solid solution. The most advantageous factor of V based solid solution is that in almost all the cases the solid solutions react with hydrogen without disproportionation [27] and after reaction with hydrogen they form single phase face centered cubic (fcc) lattice structure.

The different hydrogen absorption sites of bcc phase solid solutions can be explained from the crystal structure. When hydrogen interacts, then three types of hydrides, with three different structures, can be formed. When the H/M ratio is less than 0.5 then the hydride shows bcc structure with slightly extended lattice parameter than the parent alloy. But with increase in the amount of hydrogen the structure of the hydride changes. The mono hydrides form pseudo face centered cubic (fcc) lattice, where the metal atoms occupy the fcc sites and the hydrogen atoms occupy the octahedral holes. The saturated dihydride shows a fluorite type of structure, where the metal atoms occupy the fcc sites and the hydrogen atoms occupy the tetrahedral holes. Fig. 3.1 shows the crystal structures of the mono hydride and the dihydride indicating different tetrahedral and octahedral holes.

The transformation of the bcc alloy towards the fcc hydride [Fig. 3.2] can be explained assuming that the arrangement of metals does not changed during hydrogenation even though anisotropic volume expansion there. As shown in the figure the direction of [100] in bcc crystal corresponds to the direction [110] of the fcc crystal.
Fig. 3.1 The structure of (a) the monohydride (hydrogen atoms occupying the octahedral sites) and (b) the dihydride (hydrogen atoms occupying the tetrahedral sites). The larger spheres represent the metal atoms and the smaller spheres represent the hydrogen atom.

Fig. 3.2 Transformation of the bcc alloy structure towards the fcc hydride structure.

Due to large number of available interstitial sites, the hydrogen absorption capacity of the bcc phase alloys are usually better than the conventional AB$_2$ types of Laves phase alloy. Though they show quite high hydrogen absorption capacities, but Ti-V based bcc solid solution suffer from certain disadvantages towards practical application. The alloys need rigorous activation prior to hydrogen absorption, the kinetics of hydrogen absorption is not
satisfactory, and they need high desorption temperature for the complete desorption of the stored hydrogen. As both the Ti and V hydrides are quite stable, the enthalpy of dihydride formation has relatively high values compared to those of LaNi$_5$ hydrides. As a result, the alloys have flexibility in the choice of their thermodynamic properties through modification of the alloy composition. Substitution of a small amount of a transition element like Fe, Co, Ni, Mn or Cr changes the hydrogen absorption characteristics of Ti-V system very drastically [25-38, 131-151]. Nomura et. al. has reported the hydrogen absorbing properties of the Ti-V-Fe system, and found that a bcc alloy with a composition of Ti$_{0.435}$V$_{0.490}$Fe$_{0.075}$ absorbed a large amount of hydrogen (3.9 wt. % at 252 K) indicating that that proper amount of Fe substitution for part of Ti can improve the hydrogen storage properties and the kinetics of hydrogen absorption [27]. One of the highest value of the hydrogen storage capacity reported so far at room temperature is 4.2 wt. % in the bcc single phase Ti-40V-10Cr-10Mn alloy [137]. The hydrogen storage capacity of Ti-V-Cr was found to improve with the substitution of Ti by Zr, though it increases the slope of the P-C isotherm [135]. From the hydrogen absorption studies in Ti-V-M (M = Fe, Mn, Co, Cr, Ni) alloys it was found that Laves phase related bcc solid solutions show a flat plateau, fast kinetics and easiness in activation [5]. Ti$_{0.70}$V$_{0.30}$-10 at. %M (M = Fe, Mn, Co, Cr, Ni) alloys react with hydrogen at room temperature without any heat treatment can absorb hydrogen just after evacuation in the apparatus consisting of glass components [148]. The results from the studies gives a new way to find a novel hydrogen absorbing phase by studying the constituent phases in multiphase alloys which desorbs hydrogen under ambient conditions. In general, substitution leads to an easy activation of the material, while the hydrogen storage capacity is reduced. Substitution of Ti or V with elements like Zr, Cr, Fe or Mn often results in the formation of a secondary phase, which is identified to be a C14 Laves phase and the coexistence of Laves phase makes the activation procedure easier as compared to pure bcc phase [138]. Zr substitution is
reported to improve the hydrogen absorption properties of Ti-V alloys by improving the grain boundary network of C14 Laves phase [131]. Hang et al. [34] has found for Ti$_{10}$V$_{84-x}$Fe$_x$Zr$_x$ (x = ¼ 1, 2, 4, 6, 8) alloys, the ratio of the secondary phase (C14 laves phase) increases with increasing Zr content. They also found that, as the Zr content in the alloy increases, the activation behavior is improved, but the hydrogen absorption and desorption capacities decrease gradually.

In the present chapter we report our systematic approach towards the improvement of hydrogen storage properties of Ti-V solid solution. In the first section we will discuss the experimental parameters for the preparation of alloys, hydrides and the characterizations. The hydrogenation and dehydrogenation conditions also will be discussed for the particular experiments. In the next section we will give the interesting results we got during our present study and will discuss our results accordingly. In the last section of the chapter we will conclude our experimental findings.

### 3.1 Experimental Details

The alloys were prepared by arc melting the high purity elements (99.9%) in a water-cooled copper hearth under argon atmosphere. The buttons were remelted several times to ensure homogeneity. The crystal structures of the alloys were examined by X-ray diffraction (XRD) using monochromatic CuK$_\alpha$ radiation.

X-ray Microanalyses of the representative alloys were done using Electron Probe Micro-Analyzer (EPMA, CAMECA SX-100 model). For analysis, the alloys were mounted in resin, ground with different grades of emery paper and polished on lapping wheel with diamond paste of 0.25 μm grain size. An acceleration voltage of 20 kV and stabilized beam current of 4 nA and 20 nA were used for ‘back scattered electron (BSE)’ and quantitative/qualitative analysis, respectively. The beam size was kept at < 1 μm to reduce
the convolution effect so as to arrive at good compositional estimates. Raw intensity data were corrected for atomic numbers, absorption and fluorescence using the PAP (Pouchou and Pichoir) procedure [152].

Hydriding was carried out using a standard Sieverts type set up discussed in Chapter II. The activation procedure involved heating the sample under diffusion vacuum ($10^{-6}$ mbar) for 2 hours at 673 K. After activation, the sample was cooled to the working temperature under vacuum, followed by introduction of hydrogen gas into the reaction chamber. Pressure-composition isotherms were studied in the temperature range 298-523 K and up to a hydrogen pressure of 2 MPa, using freshly crushed samples. The surface poisoning of the hydride samples were done by air exposure at liquid nitrogen temperature. The deuterides of selected alloys were prepared following the same procedure as described above.

Some of the compositions were hydrogenated without any activation treatment. This procedure involved degassing of the freshly crushed alloy particles under high vacuum ($10^{-6}$ mbar) for 1 hour followed by introduction of hydrogen gas into the chamber.

The kinetic study was done at room temperature and a hydrogen pressure of 20 atm. after one absorption-desorption cycle.

$^{57}$Fe Mössbauer spectra were recorded using $^{57}$Co(Rh) source in a conventional spectrometer working in constant acceleration mode. The spectrometer was calibrated with $\alpha$-Fe and the isomer shift values given in this work are with respect to $\alpha$-Fe. The experimental data were fitted by least square curve-fitting program.

The amount of total hydrogen/deuterium in the hydrides was estimated by monitoring the change in the hydrogen/deuterium pressure during the absorption process. The saturation composition was also determined by complete decomposition of a small amount of the hydride sample in an evacuated and calibrated chamber as discussed in Chapter II.
The temperature programmed desorption (TPD) measurements were done using an automated TPD instrument up to 1073 K, at a constant heating rate of 10 K/min. High purity argon was used as the carrier gas.

Electrochemical measurements were carried out using Potentiostat/galvanostat (PGSTAT20, Echochemie, Netherlands) attached with frequency response analyzer (FRA). The alloy button cut into plate shape was used as working electrode, Ag/AgCl as the reference electrode and platinum wire mesh as the counter electrode. 6 M KOH solution was used as electrolyte. Impedance measurements were carried out using a sinusoidal ac excitation signal with peak to peak amplitude of 10 mV and frequency in the range 0.1 Hz to 100 kHz.

3.2 Results and Discussion

The section deals with the results & discussion part of the Ti-V-Fe alloys which has been studied during the present thesis. Based on the alloys composition this section has been divided in three parts and discussed separately. This part of the work is organized as follows. In the first part the findings on Ti$_{1-x}$VFe$_x$ (x = 0.1, 0.15, 0.2, 0.4) and Ti-V-Fe-Cr alloys are discussed. Here the effect of different amounts of Fe substitution on Ti-V alloy is depicted. The effect of Cr substitution on selected Ti-V-Fe alloys is presented also. In the second part the hydrogen storage characteristics of Zr Substituted Ti$_{0.85}$VFe$_{0.15}$ alloy is discussed and the effect of Zr on the structural and hydrogen storage properties has been reported. In the third part of the effect of Ce substitution on the hydrogen storage and electrochemical properties of the Ti$_{0.85}$VFe$_{0.15}$ alloy has been presented. In the remaining portion of the section will be discussed separately with the exact work plan.
3.2.1 Hydrogen storage properties of Ti$_{1-x}$VFe$_x$ ($x = 0.1, 0.15, 0.2, 0.4$) and Ti-V-Fe-Cr alloys

In this part of the work, we report the hydrogen absorption properties of Ti-V alloys with 10, 15, 20 and 40 at. % of Fe substitution for Ti. The alloys have been characterized for the crystal structure and the pressure composition isotherm, kinetics of hydrogen absorption, hydrogen storage properties and the hydrogen desorption are studied in detail. Again, the expansive vanadium metal is partially substituted with less expensive Cr metal, in order to study the effect of Cr substitution on the hydrogen absorption properties and the activation treatment. The following two compositions, Ti$_{0.85}$VFe$_{0.15}$ and Ti$_{0.8}$VFe$_{0.2}$ have been substituted with Cr (60 at. %) in place of V forming two new compositions, Ti$_{0.85}$V$_{0.4}$Fe$_{0.15}$Cr$_{0.6}$ and Ti$_{0.8}$V$_{0.4}$Fe$_{0.2}$Cr$_{0.6}$ respectively.

3.2.1.1 The structural aspects of the alloys and the hydrides

3.2.1.1.1 X-ray diffraction

The XRD patterns of the compositions Ti$_{0.9}$VFe$_{0.1}$ and Ti$_{0.85}$VFe$_{0.15}$ and their corresponding hydrides are shown in Fig 3.3. From the XRD data we found that, except Ti$_{0.85}$VFe$_{0.15}$, all the other Ti-V-Fe compositions show a mixed structure composed of a body centered cubic (bcc) phase and a secondary C14 Laves phase, with bcc as the major phase. The nature of the secondary phase has been examined by the earlier researchers also using XRD and scanning electron microscope techniques [138, 139]. The lattice parameters of the secondary phase for Ti$_{0.9}$VFe$_{0.1}$ alloy in the present study are found to be $a = 5.10$ Å and $c = 7.78$ Å. The composition, Ti$_{0.85}$VFe$_{0.15}$ contains mainly the bcc phase. The X-ray diffraction studies have been done on Ti$_{0.85}$V$_{0.4}$Fe$_{0.15}$Cr$_{0.6}$ and Ti$_{0.8}$V$_{0.4}$Fe$_{0.2}$Cr$_{0.6}$ shows the presence of a secondary C14 hexagonal Laves phase along with the bcc phase. The secondary phase is indexed on the basis of C14 Laves phase for Ti$_{0.85}$V$_{0.4}$Fe$_{0.15}$Cr$_{0.6}$ alloy and the corresponding
lattice parameters are found to be \(a = 6.850 \text{ Å}\) and \(c = 7.616 \text{ Å}\). To see the effect on annealing on the secondary phase we have annealed \(\text{Ti}_{0.9}\text{VFe}_{0.1}\) alloy for 9 days at 900°C in vacuum sealed quartz tube. It has been observed that after annealing the bcc phase increases for \(\text{Ti}_{0.9}\text{VFe}_{0.1}\) alloy. Though in case of Cr containing samples, there is not much effect of annealing on the secondary phase. The lattice parameters for the various \(\text{Ti}_{1-x}\text{VFe}_x\) alloys are listed in Table 3.1.

![X-ray diffraction patterns](image)

**Fig. 3.3** X-ray diffraction patterns for (a) \(\text{Ti}_{0.9}\text{VFe}_{0.1}\) (b) \(\text{Ti}_{0.9}\text{VFe}_{0.1}\text{H}_{3.65}\) (c) \(\text{Ti}_{0.85}\text{VFe}_{0.15}\) and (d) \(\text{Ti}_{0.85}\text{VFe}_{0.15}\text{H}_{3.83}\). (The lines corresponding to the secondary phase are marked by ‘*’.)**
Table 3.1 Lattice parameters and the total hydrogen storage capacities of $\text{Ti}_{1-x}\text{VFe}_x$ alloys

<table>
<thead>
<tr>
<th>Alloy composition</th>
<th>Bcc phase lattice parameter (Å)</th>
<th>Hydrogen/Formula unit</th>
<th>Total hydrogen storage capacity (wt. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiV</td>
<td>3.12</td>
<td>2.92</td>
<td>2.86</td>
</tr>
<tr>
<td>$\text{Ti}<em>{0.9}\text{VFe}</em>{0.1}$</td>
<td>3.10</td>
<td>3.65</td>
<td>3.53</td>
</tr>
<tr>
<td>$\text{Ti}<em>{0.85}\text{VFe}</em>{0.15}$</td>
<td>3.09</td>
<td>3.83</td>
<td>3.7</td>
</tr>
<tr>
<td>$\text{Ti}<em>{0.8}\text{VFe}</em>{0.2}$</td>
<td>3.01</td>
<td>2.5</td>
<td>2.42</td>
</tr>
<tr>
<td>$\text{Ti}<em>{0.6}\text{VFe}</em>{0.4}$</td>
<td>3.00</td>
<td>2.26</td>
<td>2.01</td>
</tr>
</tbody>
</table>

From the table it can be stated that the lattice parameter of the bcc phase decreases with increasing Fe content. This due to the smaller atomic radius of Fe as compared to that of Ti and V (Ti: 1.47 Å, V: 1.34 Å, Fe: 1.26 Å). Similar trend has been observed by other experimentalists also [27, 28]. In the present case, the lattice parameter decreases from 3.098 Å to 3.086 Å as the Fe content increases from 10 at. % to 15 at. %. This change is in accordance with the Vegard’s law which states that for substitutional solid solution the change in unit cell dimension is be linear with the change in composition. The structure of the corresponding hydrides are found to be face centered cubic (fcc) and the lines corresponding to the secondary phase are not seen in the X-ray diffraction patterns of the hydrides. After the hydrogenation all the metals go in the powder form due to fact that bcc structure of the alloy transforms into a new fcc structure with an increase in the internal stress. As the hydriding takes place at room temperature so it can not reveal the internal stress so crack formation occurs and eventually with cycling the hydride goes into powder form.

3.2.1.1.2 Electron probe micro analysis

Fig. 3.4 shows the electron probe X-ray micrographs of $\text{Ti}_{0.9}\text{VFe}_{0.1}$, $\text{Ti}_{0.85}\text{VFe}_{0.15}$, $\text{Ti}_{0.8}\text{VFe}_{0.2}$ and $\text{Ti}_{0.6}\text{VFe}_{0.4}$ alloys. $\text{Ti}_{0.85}\text{VFe}_{0.15}$ alloy shows a single phase bcc structure in the
EPMA analysis. For all the other alloys the X-ray micrographs clearly indicate a mixed phase structure and the proportion of the secondary phase varies with the alloy composition.

**Fig. 3.4** Electron micrographs for (a) Ti$_{0.9}$VFe$_{0.1}$ and (b) Ti$_{0.85}$VFe$_{0.15}$ (c) Ti$_{0.8}$VFe$_{0.2}$ and (d) Ti$_{0.6}$VFe$_{0.4}$ alloys

The composition of two phases analyzed by EPMA shows that the Fe substitutes some of the Ti atoms forming the Fe substituted Ti-V alloys. This becomes apparent from the Ti Kα and Fe Kα X-ray line profiles [Fig. 3.5]. Wave-length dispersed X-ray line spectra obtained from each of the phases indicate that both the bright phase and light phases are essentially constituted of Ti, V and Fe where as the Fe content of the secondary phase is
larger than that of the bcc phase. This can also be confirmed by the micro elemental analysis of Ti$_{0.9}$VFe$_{0.1}$ alloy which clearly shows larger concentration of Fe in the secondary phase.

Fig. 3.5 (a) Ti Ka and Fe Ka X-ray line profiles of Ti$_{0.9}$VFe$_{0.1}$ alloys (b) Electron micrographs for Ti$_{0.9}$VFe$_{0.1}$ alloys showing the relative concentrations of Fe metal in the bcc and secondary phase.
3.2.1.2 The hydrogen absorption behavior of Ti-V-Fe alloys

Hydrogen absorption desorption behavior of any alloy is characterized by the pressure composition isotherm (PCT) diagram. The pressure-composition absorption curves for Ti$_{1-x}$VFe$_x$ (x = 0.0, 0.1, 0.15, 0.20 and 0.40) alloys at room temperature are shown in Fig. 3.6.

![PCT diagram for Ti$_{1-x}$VFe$_x$ alloys](image)

**Fig. 3.6** Pressure-composition absorption curves for Ti$_{1-x}$VFe$_x$ (x = 0, 0.1, 0.15, 0.2 and 0.4) alloys at room temperature

For all the above compositions, the plateau regions are found to be flat with a plateau pressure <0.02 atm., which is the lowest detection limit in our set up. The two-plateau regions observed in some earlier studies on Ti-V-Cr-Mn systems [138, 139], are not observed for any of our systems within the pressure ranges studied. The pressure composition isotherms of all the alloys have been studied at different temperature as shown in Fig. 3.7. With increase in temperature, the plateau region decreases for all the alloys, but the increase in the absorption plateau pressure is still lower than the detection limit of our instrument.
Fig. 3.7 Pressure-composition absorption curves for Ti$_{1-x}$VFe$_x$ (x = 0, 0.1, 0.15, 0.2 and 0.4) alloys at different temperatures.

It may be seen from the figure that with increase in temperature, the plateau region decreases and the absorption/desorption plateau pressure is quite low even at 523 K. The hydrogen absorption kinetics of all the alloys was studied at room temperature and 20 atm. hydrogen pressure after one hydrogen absorption desorption cycle. It has been found that the
kinetics of hydrogen absorption is quite fast and the equilibrium is reached within 5 minutes in each step.

The hydrogen storage capacities of Ti$_{1-x}$VFe$_x$ alloys as a function of Fe content, x, are plotted in Fig. 3.8.

![Graph](image)

**Fig. 3.8** Variation of hydrogen absorption capacity with respect to the Fe content in Ti$_{1-x}$VFe$_x$ alloys ($x = 0.0, 0.1, 0.15, 0.2$ and $0.4$).

From the figure it can be found that the hydrogen storage capacity of Ti$_{1-x}$VFe$_x$ increases steadily with Fe content up to $x = 0.15$. Further increase in the Fe content brings down the hydrogen storage capacity drastically. The hydrogen storage capacity of the Ti-V-Fe series under investigation can be strongly correlated with the structures of the parent alloys. At higher Fe concentrations, the bcc phase is found to coexist with the secondary phase. The bcc phase in Ti-V system is reported to absorb more hydrogen than the secondary phase [12] due to less packing density of bcc phase. The composition Ti$_{0.85}$VFe$_{0.15}$ is found to have only the bcc structure for the as cast alloy, and it has the maximum storage capacity of 3.7 wt. % among the various Ti-V-Fe compositions studied in this work.
It is interesting to note that with increasing Fe content the process of activation becomes easier. The alloys Ti$_{0.8}$VFe$_{0.2}$ and Ti$_{0.6}$VFe$_{0.4}$ absorb hydrogen without any high temperature activation treatment, involving the heating of the samples at 673 K for 2 hours under high vacuum. It may be noted at this point that, due to the presence of secondary phase the crack formation at the surface becomes easier. As a result, before hydrogen absorption these samples require lesser activation. The bcc phase alloys are much harder and more hardly pulverized than the C14 Laves phase alloys. In Laves phase alloys, the cracking occurs easily resulting in the exposure of new fresh surface in the hydrogen atmosphere. As a result more hydrogen can penetrate into the alloy through the newly formed alloy surface and the lattice expansion due to hydrogenation of the alloy enhances further cracking. In this way the alloys get activate quite easily. However, in our case for Ti$_{0.8}$VFe$_{0.2}$ and Ti$_{0.6}$VFe$_{0.4}$ alloys the absorption requires the application of a higher H$_2$ pressure ~ 0.8 MPa and an incubation time of 1 hour is observed. Their storage capacities are found to be 2.42 wt. % and 2.01 wt. %, respectively. We also found that the annealed samples have a relatively slow hydrogen pick up as compared to the as cast material, which directly prove the positive effect of secondary phase on the activation treatment of the alloy before hydrogen absorption. Various works in the literature also have shown that the presence of a secondary phase makes hydriding of this system easier [34].

We have substituted less expensive Cr in place of V for Ti$_{0.8}$VFe$_{0.2}$ and Ti$_{0.6}$VFe$_{0.4}$ and established its effect on the hydrogen absorption capacities and the activation treatment. The hydrogen storage capacities for Ti$_{0.85}$V$_{0.4}$Fe$_{0.15}$Cr$_{0.6}$ and Ti$_{0.8}$V$_{0.4}$Fe$_{0.2}$Cr$_{0.6}$ are found to be 2.01 wt. % and 1.51 wt. %, respectively. The pressure composition diagrams are shown in Fig. 3.9.
We find that the storage capacity decreases with increasing Cr concentration but there is no observable change in the absorption plateau pressure up to 423 K. Among the two compositions, Ti\(_{0.85}\)V\(_{0.4}\)Fe\(_{0.15}\)Cr\(_{0.6}\) is found to absorb hydrogen without any prior activation. In this case, the freshly crushed coarse alloy powder is degassed for one hour to remove the adsorbed gases and then hydrogen is introduced into the reaction chamber. The absorption of
hydrogen without activation takes place at a hydrogen pressure as low as 0.02 MPa, unlike the Cr free composition Ti$_{0.8}$VFe$_{0.2}$, which requires the application of a higher hydrogen pressure of 0.8 MPa. The initial absorption is quite fast for Cr substituted sample and within one hour it reaches its maximum hydrogen storage capacity of 1.51 wt. %.

### 3.2.1.3 Desorption characteristics of the alloys

To compare the stabilities of different hydride temperature programmed desorption profile has been studied in an automated TPD instrument. The experiments were carried out with the air poisoned hydride because of the limitations of the home made Sievert’s setup. Though the air poisoned hydrides show some what higher desorption temperature due to the oxide layer on the surface, still it gives quite good comparison about the stability of the hydrides from the desorption peak temperature. In temperature programmed desorption more than one peak can be obtained due to different reasons. If the alloy shows multiphase structure, then depending upon the relative stabilities of the different hydride phases, hydrogen can desorb at different temperatures. Again in a single phase alloys also, the absorbed hydrogen atoms can occupy different interstitial sites with different potential energies, which again results in the multiple peak in the TPD profile. It can be mentioned at this point that, with increase in the heating rate the peak position shifts. Subsequently always it is more fundamental to compare between the desorption onset temperatures than the peak temperatures for different hydrides. But in the present case the heating rate is kept constant, so we can compare between the desorption peak temperature of different hydrides. As an example, a comparison between the TPD profiles of Ti$_{0.9}$VFe$_{0.1}$H$_{3.65}$ and Ti$_{0.8}$VFe$_{0.2}$H$_{2.5}$ reveal that, with increasing Fe concentration, the hydrogen desorption temperature decreases as shown in Fig. 3.10, which in turns reflects the relative stabilities of the hydrides. This may be attributed to the fact that with increasing Fe concentration the relative stability of the hydride decreases and hence the hydrogen desorption takes place at a lower temperature. As Fe is
more electronegative element than the Ti and V so it forms much unstable hydrides and as a result with the doping of Fe in the Ti-V system the relative stability of the hydride decreases. It may be recalled that FeTi is a reversible hydride at room temperature.

![Fig. 3.10](image)

**Fig. 3.10** Thermal desorption profiles of (a) $Ti_{0.8}VFe_{0.2}H_{2.5}$ (b) $Ti_{0.9}VFe_{0.1}H_{3.65}$.

Most of the metal hydride systems exhibit normal isotope effect at room temperature, where the protide is more stable than their corresponding deuteride. As a rule, at sufficiently low temperatures, a deuteride will be more stable than the corresponding hydride [13, 153]. After a certain cross over temperature, the hydride becomes more stable. If for a certain alloy, the cross over temperature is higher than the room temperature then at the room temperature it shows inverse isotope effect. In the case of commercial V metal, the crossover point is calculated to be 410 K [153] and because of this fact many of the Vanadium based alloys are reported to exhibit inverse isotope effect at lower temperature [153], where the deuteride and tritide form more stable compound (i.e. compound having lower dissociation pressure at room temperature) than the corresponding hydride. In general, the isotopic effect is indicated by the ratio of the dissociation pressure of the deuteride to that of the hydride. In the present work, in order to compare the stability of the hydride vis-à-vis. the deuteride, TPD studies
have been carried out on the hydride as well as the deuteride of Ti$_{0.9}$VFe$_{0.1}$ alloy. The TPD profiles for Ti$_{0.9}$VFe$_{0.1}$H$_{3.65}$ and the corresponding deuteride Ti$_{0.9}$VFe$_{0.1}$D$_{3.65}$ are shown in Fig. 3.11.

![Fig. 3.11 Thermal desorption profiles of (a) Ti$_{0.9}$VFe$_{0.1}$H$_{3.65}$ (b) Ti$_{0.9}$VFe$_{0.1}$D$_{3.65}$.](image)

The desorption profiles show two peaks for the hydride as well as the deuteride. From the TPD data it can be seen that the desorption onset temperature shifts to higher temperature for the deuteride as compared to that of the hydride. The onset of desorption is seen at 660 K and the peak temperatures of the deuteride are 763 K and 863 K, respectively. The desorption onset temperature of the hydride is 629 K and the peak temperatures are 724 K and 822 K, respectively. Thus, from this observation we conclude that the deuteride is more stable than the corresponding hydride of Ti$_{0.9}$VFe$_{0.1}$ alloy, which means that the system shows reverse isotope effect. This type of reverse isotope effect has been reported earlier also for the Ti-V based solid solution. Cho et. al. [150] has reported lower plateau pressure for deuterium in Ti$_{1.0}$Cr$_{1.5}$V$_{1.7}$ alloy indicating higher stability of the deuteride which can be explained by the
differences between the standard enthalpy and entropy of formation for the deuteride and the hydride.

TPD profiles are recorded for the Cr free Ti$_{0.8}$VFe$_{0.2}$ hydride and Cr containing Ti$_{0.8}$V$_{0.4}$Fe$_{0.2}$Cr$_{0.6}$ hydride and are shown in Fig. 3.12. From the TPD data of Ti$_{0.8}$V$_{0.4}$Fe$_{0.2}$Cr$_{0.6}$H$_{1.55}$ it can be seen that desorption starts at 570 K and the peak temperature is 685 K. The desorption profile for the Cr substituted sample Ti$_{0.8}$V$_{0.4}$Fe$_{0.2}$Cr$_{0.6}$H$_{1.55}$ is less broad as compared to the Cr free system though the peak temperature is almost the same. This implies that all the stored hydrogen can be desorbed over a narrower temperature range, starting from 560 K up to 800 K as compared to the Cr-free sample.

![Graph showing TPD profiles](image)

Fig. 3.12 Thermal desorption profiles of Ti$_{0.8}$V$_{0.4}$Fe$_{0.2}$Cr$_{0.6}$H$_{1.55}$, Ti$_{0.8}$V$_{0.4}$Fe$_{0.2}$Cr$_{0.6}$D$_{1.55}$ and Ti$_{0.8}$VFe$_{0.2}$H$_{2.5}$.

Fig. 3.12 also shows the TPD of the hydride as well as the deuteride of Ti$_{0.8}$V$_{0.4}$Fe$_{0.2}$Cr$_{0.6}$. The onset temperature for desorption of the deuteride is slightly higher
than that of the hydride showing a small signature of inverse isotope effect. The desorption peak temperature is almost the same for both the hydride and the deuteride. Since the Cr substituted Ti\(_{0.8}V_{0.4}Fe_{0.2}Cr_{0.6}\) absorbs hydrogen without any prior activation and hydrogen can be recovered at a reasonable temperature range, this system can be a good getter material for hydrogen and its isotopes, as compared to the conventional material like U which is radioactive and highly pyrophoric in nature.

3.2.1.4 Summary

In this work, the effect of Fe substitution on the hydrogen absorption properties and activation treatment of Ti-V system have been investigated. The activation of the alloy Ti-V for hydrogenation is facilitated by Fe substitution. The hydrogen storage capacity increases with Fe content up to 15 at. % and decrease drastically on further increase in the Fe content. A maximum storage capacity of 3.7 wt. % is obtained for the composition Ti\(_{0.85}VFe_{0.15}\). From the desorption temperatures of the hydride and the deuteride of Ti\(_{0.9}VFe_{0.1}\), it is seen that the deuteride is more stable than the corresponding hydride. Again with increase in the Fe substitution the desorption temperature increase due to the destabilization of the hydride. The ease of activation of Ti-V-Fe system is improved further by Cr substitution (60 at. %) in place of V. The composition Ti\(_{0.8}V_{0.4}Fe_{0.2}Cr_{0.6}\) absorbs hydrogen without any prior activation or any heat treatment. The total hydrogen content of the hydride is reduced on Cr substitution. Thermal desorption studies show a sharper desorption profile for the Cr containing hydride as compared to the Cr-free hydride.
3.2.2 Hydrogen absorption characteristics of Zr substituted Ti$_{0.85}$VFe$_{0.15}$ alloy

In the previous work on Ti-V-Fe system, we studied Fe substitution to improve the activation treatment of TiV alloy. As the Fe content increases, the maximum hydrogen absorption capacity improves slightly up to 15 at. % Fe substitution at Ti site and thereafter, it decreases. Ti$_{0.85}$VFe$_{0.15}$ alloy exhibited the maximum hydrogen storage capacity (3.7 wt. % at room temperature) within the studied Ti$_{1-x}$VFe$_x$ series. However, this alloy needed rigorous activation before hydrogen absorption. In the present study, Ti$_{0.85}$VFe$_{0.15}$ alloy is modified by 5 at. % Zr substitution in place of vanadium, to explore the possibility of improving the hydrogen absorbing properties without any significant reduction in the hydrogen storage capacity.

3.2.2.1 Crystal structure

The powder X-ray diffraction (XRD) patterns of Ti$_{0.85}$VFe$_{0.15}$ and the corresponding hydride Ti$_{0.85}$VFe$_{0.15}$H$_{3.83}$ are given in Fig. 3.13. From the XRD pattern it can be seen that Ti$_{0.85}$VFe$_{0.15}$ alloy shows bcc structure and the lattice parameter is found to be 3.08 Å. The structure changes to fcc on complete hydrogenation, which is in agreement with the earlier studies on Ti-V-Fe based systems [30]. The XRD pattern of the hydride Ti$_{0.85}$VFe$_{0.15}$H$_{3.83}$ could be indexed on the basis of fcc structure with a lattice parameter 4.29 Å.

Fig. 3.14 shows the XRD patterns of Ti$_{0.85}$V$_{0.95}$Fe$_{0.15}$Zr$_{0.05}$ and its hydrides with compositions Ti$_{0.85}$V$_{0.95}$Fe$_{0.15}$Zr$_{0.03}$H$_2$ and Ti$_{0.85}$V$_{0.95}$Fe$_{0.15}$Zr$_{0.05}$H$_{3.74}$, respectively. It is observed from the XRD pattern that 5 at. % Zr substitution in place of vanadium results in a multi phase structure consisting mainly C15 Laves phase along with some V based bcc solid solution [Fig. 3.14]. In some earlier works [131, 139], Zr substitution is reported to result in a secondary Laves phase formation. It may be noted that the C15 Laves phase structure
remains unchanged on hydrogenation of Ti$_{0.85}$V$_{0.95}$Fe$_{0.15}$Zr$_{0.05}$ alloy though there is appreciable shift in the peak positions to lower 2-theta values indicating volume expansion due to hydrogenation. The lattice parameter of the alloy is 7.36 Å, where as that of the saturated hydride is 7.85 Å.

**Fig. 3.13** XRD patterns of Ti$_{0.85}$VFe$_{0.15}$ alloy and the hydride Ti$_{0.85}$VFe$_{0.15}$H$_{3.83}$.

**Fig. 3.14** XRD patterns of Ti$_{0.85}$V$_{0.95}$Fe$_{0.15}$Zr$_{0.05}$, Ti$_{0.85}$V$_{0.95}$Fe$_{0.15}$Zr$_{0.05}$H$_2$ and Ti$_{0.85}$V$_{0.95}$Fe$_{0.15}$Zr$_{0.05}$H$_{3.74}$. (A C15 Laves phases, * V based bcc solid solution)
For comparison purpose, the XRD pattern of the intermediate hydride composition Ti$_{0.85}$V$_{0.95}$Fe$_{0.15}$Zr$_{0.05}$H$_2$ is shown along with that of the saturated hydride. The intermediate hydride has been prepared by exposing the activated alloy under calculated amount of hydrogen. The composition has been rechecked in the hydrogen estimation setup. The intermediate dihydride (Ti$_{0.85}$V$_{0.95}$Fe$_{0.15}$Zr$_{0.05}$H$_2$) and is found have the same structure as that of the saturated hydride (Ti$_{0.85}$V$_{0.95}$Fe$_{0.15}$Zr$_{0.05}$H$_{3.74}$), with smaller lattice parameter (7.73 Å).

3.2.2.2 Hydrogen absorption properties

The alloy Ti$_{0.85}$VFe$_{0.15}$ is found to absorb a maximum of 3.83 H atoms/formula unit (3.7 wt. %) to form a saturated hydride with a composition Ti$_{0.85}$VFe$_{0.15}$H$_{3.83}$ while Ti$_{0.85}$V$_{0.95}$Fe$_{0.15}$Zr$_{0.05}$ forms a saturated hydride with a composition Ti$_{0.85}$V$_{0.95}$Fe$_{0.15}$Zr$_{0.05}$H$_{3.74}$ (3.5 wt. %), at room temperature.

The maximum hydrogen absorption capacities of Ti$_{0.85}$VFe$_{0.15}$ and Ti$_{0.85}$V$_{0.95}$Fe$_{0.15}$Zr$_{0.05}$ alloys are found to be 3.7 wt. % (H/M = 3.83) and 3.5 wt. % (H/M = 3.74), respectively. This implies that the total hydrogen storage capacity of Ti-V-Fe alloy does not change appreciably by Zr substitution. While Ti$_{0.85}$VFe$_{0.15}$ requires activation treatment at 673 K for 2 hours prior to hydrogen absorption, Zr substituted alloy could absorb hydrogen without any prior activation treatment. Zr substituted system is found to absorb hydrogen without any heat treatment with an incubation time of 5 hours at a hydrogen pressure of 10 atm. Thus, by substituting a small amount of Zr, the activation of the alloy prior to hydrogen absorption becomes easier. This could be due to the fact that with Zr substitution, the C15 Laves phase increases and crack formation at the surface becomes easier, so that hydrogen can easily diffuse through the cracks. The rate of hydrogen absorption for both the alloy systems as a function of time after one absorption-desorption cycle is shown in
Fig. 3.15. It can be seen that the hydrogen absorption rate is quite fast and both the alloys reach the saturation composition in about 200 seconds.

Fig. 3.15  *Kinetic study of Ti$_{0.85}$VFe$_{0.15}$ and Ti$_{0.85}$V$_{0.95}$Fe$_{0.15}$Zr$_{0.05}$ alloys at room temperature and 20 atm. hydrogen pressure (Recorded after one absorption desorption cycle).*

The pressure composition isotherms (PCT) for the two alloys Ti$_{0.85}$VFe$_{0.15}$ and Ti$_{0.85}$V$_{0.95}$Fe$_{0.15}$Zr$_{0.05}$ are shown in Fig. 3.16 and Fig. 3.17, respectively. The pressure composition isotherms have been studied at room temperature and 373 K. It can be seen from the figures that the plateau region is flat for both the alloys at room temperature and the plateau pressure is less than 0.02 atm.

For the Ti-V-Fe system within the pressure range of 0.02 to 20 atm., we have not observed two distinct plateau regions as reported in the earlier studies on Ti-V-Mn systems [37]. They studied the hydriding properties of Mn substituted Ti$_{0.9}$Zr$_{0.1}$V$_x$Mn$_y$ alloys which are similar in composition to our Ti-V-Fe-Zr system and reported that the first plateau pressure is very close to zero atmosphere. With increasing temperature the length of the plateau region is found to decrease as expected, though the increase in the plateau pressure is beyond the detection limit of our set-up.
For the Ti-V-Fe-Zr system, in order to check the presence of a second plateau, a hydride with a lower hydrogen content having the composition Ti$_{0.85}$V$_{0.95}$Fe$_{0.15}$Zr$_{0.05}$H$_2$ is
prepared. However, from the X-ray diffraction studies mentioned above, this dihydride is found to have the same structure as that of the saturated hydride. By comparing the pressure composition isotherms of Ti$_{0.85}$VFe$_{0.15}$ and Ti$_{0.85}$V$_{0.95}$Fe$_{0.15}$Zr$_{0.05}$ alloys, it can be seen that the Zr substituted system shows an improved PCT profile with low hysteresis loss and a flat desorption plateau which are very important for long cyclic stability.

We have observed that the effective hydrogen storage capacity of the Zr-substituted system is slightly higher than that of the unsubstituted Ti-V-Fe system. In the present study, we define the effective hydrogen storage capacity as the amount of hydrogen desorbed from the alloy at 373 K under rotary vacuum ($10^{-3}$ mbar) in one hour. The temperature 373 K has been chosen for the experiment due to the fact that, according to Japanese WE-NET project, 373 K is the ideal operating temperature of the hydrogen absorbing alloys for the vehicular applications [35]. It has been found that the effective hydrogen storage capacity of Ti$_{0.85}$VFe$_{0.15}$ is 1.8 wt. % where as that of Ti$_{0.85}$V$_{0.95}$Fe$_{0.15}$Zr$_{0.05}$ alloy is 2.1 wt. %. It could be due to the fact that the removal of hydrogen from bcc phase is relatively difficult than from Laves phase, which is present as a secondary phase in the Zr substituted system.

3.2.2.3 Mössbauer study

Fig. 3.18 and 3.19 show the Mössbauer spectra of Ti$_{0.85}$VFe$_{0.15}$ and Ti$_{0.85}$V$_{0.95}$Fe$_{0.15}$Zr$_{0.05}$ alloys and the corresponding saturated hydrides recorded at room temperature.

The alloy Ti$_{0.85}$VFe$_{0.15}$ shows a singlet with an isomer shift value of $-0.120$ mm/s. Upon hydrogenation, two not very well separated peaks are observed in the Mössbauer spectrum having isomer shift values of 0.010 and 0.567 mm/s and with relative areas of 1.000 and 0.200, respectively indicating the presence of two different Fe sites.
Fig. 3.18 Room temperature Mössbauer spectra of Ti$_{0.85}$VFe$_{0.15}$ and Ti$_{0.85}$VFe$_{0.15}$H$_{3.83}$.

Fig. 3.19 Room temperature Mössbauer spectra of Ti$_{0.85}$V$_{0.95}$Fe$_{0.15}$Zr$_{0.05}$ and Ti$_{0.85}$V$_{0.95}$Fe$_{0.15}$Zr$_{0.05}$H$_{3.74}$.

In the case of Ti$_{0.85}$V$_{0.95}$Fe$_{0.15}$Zr$_{0.05}$ alloy, Mössbauer spectrum shows a single peak with a negative isomer shift value of $-0.208$ mm/s. However, the hydride Ti$_{0.85}$V$_{0.95}$Fe$_{0.15}$Zr$_{0.05}$H$_{3.74}$ shows two distinct peaks with isomer shift values of 0.132 and 0.661 mm/s, respectively. The relative areas of the two peaks are found to be 1.000 and 0.598, respectively. The origin of the two peaks for the hydride can be attributed to the fact that
there are at least two nonequivalent hydrogen-absorbing sites with different isomer shift values. The large change in the isomer shift value observed for one of the peaks in the hydride samples suggests a possible interaction between the metal and hydrogen atoms.

### 3.2.2.4 Temperature programmed desorption study

Temperature programmed desorption (TPD) profiles of $\text{Ti}_{0.85}\text{VFe}_{0.15}\text{H}_{3.83}$ and $\text{Ti}_{0.85}\text{V}_{0.95}\text{Fe}_{0.15}\text{Zr}_{0.05}\text{H}_{3.74}$ are shown in Fig. 3.20. It can be seen from the figure that there are at least two hydrogen-desorbing sites for $\text{Ti}_{0.85}\text{VFe}_{0.15}\text{H}_{3.83}$ and three hydrogen desorbing sites for $\text{Ti}_{0.85}\text{V}_{0.95}\text{Fe}_{0.15}\text{Zr}_{0.05}\text{H}_{3.74}$. The hydride $\text{Ti}_{0.85}\text{VFe}_{0.15}\text{H}_{3.83}$ shows two peaks, at 723 and 935 K, respectively and the lower temperature peak is the major peak indicating the desorption of most of the hydrogen around this temperature.

![TPD profiles](image)

**Fig. 3.20** TPD profiles of the hydrides $\text{Ti}_{0.85}\text{VFe}_{0.15}\text{H}_{3.83}$ and $\text{Ti}_{0.85}\text{V}_{0.95}\text{Fe}_{0.15}\text{Zr}_{0.05}\text{H}_{3.74}$

For the Zr-substituted hydride $\text{Ti}_{0.85}\text{V}_{0.95}\text{Fe}_{0.15}\text{Zr}_{0.05}\text{H}_{3.74}$, these two peaks are observed around 723 and 935 K and an additional peak is observed at 473 K indicating the onset of hydrogen desorption at a lower temperature. Thus, in the case of the Zr Substituted hydride,
appreciable amount of hydrogen desorption takes place at low temperatures. This observation supports the fact that the reversible (effective) hydrogen storage capacity of the Zr substituted alloy is higher than that of the non-substituted alloy though their maximum hydrogen storage capacities are comparable.

3.2.2.5 Summary

The hydrogen absorption and desorption characteristics of Ti$_{0.85}$VFe$_{0.15}$ alloy is modified by substitution of 5 at. % Zr in place of V. The maximum hydrogen absorption capacities of Ti$_{0.85}$VFe$_{0.15}$ and Ti$_{0.85}$V$_{0.95}$Fe$_{0.15}$Zr$_{0.05}$ alloys are found to be 3.7 and 3.5 wt. %, respectively. Zr substitution results in the formation of a mixed phase structure and the activation of this material for hydrogen absorption is easier as compared to the unsubstituted Ti-V-Fe system. Zr substitution improves the hydrogen absorption-desorption characteristics of Ti$_{0.85}$VFe$_{0.15}$ alloy by decreasing the hysteresis loss without affecting the maximum hydrogen storage capacity considerably. The effective hydrogen storage capacity is found to improve by 5 at. % Zr substitution in place of V. The increase in the effective hydrogen storage capacity can be attributed to the fact that Zr substituted alloy has an additional site, which desorbs hydrogen at a lower temperature as compared to Ti-V-Fe system.

3.2.3 Hydrogen absorption studies on Ce substituted Ti$_{0.85}$VFe$_{0.15}$

In this study, we attempted to improve the hydrogen absorption characteristics of the bcc Ti$_{0.85}$VFe$_{0.15}$ alloy by substituting a small amount of Ce (2 and 5 at. %) for Ti. Since rare earths have strong affinity towards oxygen, they preferentially react with oxygen, thereby improving the homogeneity of the bcc phase [18-22]. The alloys Ti$_{0.85-x}$Ce$_{x}$VFe$_{0.15}$(x = 0 and 0.02 and 0.05) have been characterized by pressure-composition isotherms studies. The microstructures of the alloys have been characterized by electron probe microanalysis.
(EPMA) technique. Further, the electrochemical performance of Ce-free and Ce-substituted alloys has been studied.

3.2.3.1 Structural characterization

Fig. 3.21 shows the XRD patterns of Ti_{0.85-x}Ce_{x}VFe_{0.15}(x = 0, 0.02 and 0.05) alloys.

The XRD pattern indicates that Ti_{0.85}VFe_{0.15} alloy crystallizes in bcc structure with a lattice parameter of 3.086 Å. It is observed from the XRD patterns that Ce substitution for Ti results in a small amount of CeO_{2} phase along with the main bcc phase. This observation is in agreement with the earlier works [140-143], wherein a small amount of Ce substitution in V_{55}Ti_{22.5}Cr_{16.1}Fe_{6.4} is reported to result in a secondary CeO_{2} phase formation. Since most of the Ce is getting converted into CeO_{2}, the change in lattice parameter is very small. For example, the lattice parameter changes from 3.086 Å for the Ce-free alloy to 3.095 Å for the
2 at. % Ce substituted alloy to 3.097 Å for the 5 at% Ce substituted alloy. We also find peaks due to an additional phase in the Ce substituted alloys, although the exact composition is not known. This phase is not matching with any of the reported phases such as Ti$_2$FeO$_x$, CeTiO$_x$ or Ce-Ti alloys. Yan et al [141] made similar observations in Ce substituted V$_{55}$Ti$_{22.5}$Cr$_{16.1}$Fe$_{6.4}$ wherein these peaks are attributed to unknown phase. Since the composition of our parent alloy Ti$_{0.85}$VFe$_{0.15}$ is different from the alloy V$_{55}$Ti$_{22.5}$Cr$_{16.1}$Fe$_{6.4}$ studied by Yan et al [140], the intensity of the X-ray peaks corresponding to unknown phase is at variance.

Fig. 3.22 shows the XRD patterns of the representative alloy Ti$_{0.83}$Ce$_{0.02}$VFe$_{0.15}$ and its hydride, Ti$_{0.83}$Ce$_{0.02}$VFe$_{0.15}$H$_{4.26}$, respectively.

![X-ray diffraction patterns of 2 at. % Ce substituted alloy Ti$_{0.83}$Ce$_{0.02}$VFe$_{0.15}$ and its hydride Ti$_{0.83}$Ce$_{0.02}$VFe$_{0.15}$H$_{4.26}$](image)

**Fig. 3.22** X-ray diffraction patterns of 2 at. % Ce substituted alloy Ti$_{0.83}$Ce$_{0.02}$VFe$_{0.15}$ and its hydride Ti$_{0.83}$Ce$_{0.02}$VFe$_{0.15}$H$_{4.26}$.
The structure changes from bcc to fcc on hydrogenation. The peaks corresponding to the unknown phase are not prominent in the XRD pattern of the hydride except the one at higher angle, 76.25°. This may be due to the partial overlapping of some of the peaks of the hydride of the unknown phase (shifted to the lower 2-theta value upon hydrogen absorption) with the peaks of the main fcc hydride phase. The XRD pattern of the hydride Ti$_{0.83}$Ce$_{0.02}$VFe$_{0.15}$H$_{4.26}$ could be indexed on the basis of fcc structure with lattice parameter 4.350 Å. Similarly, the hydrides Ti$_{0.85}$VFe$_{0.15}$H$_{3.83}$ and Ti$_{0.80}$Ce$_{0.05}$VFe$_{0.15}$H$_{4.27}$ are found to have fcc structure with lattice constants 4.292 and 4.350 Å, respectively.

3.2.3.2 Micro chemical analysis using EPMA

Detailed microchemical analyses of the alloys have been carried out using EPMA technique. The Ti$_{0.85}$VFe$_{0.15}$ alloy shows a single phase microstructure (Fig. 3.23(a)) whereas Ce-substituted Ti$_{0.83}$Ce$_{0.02}$VFe$_{0.15}$ and Ti$_{0.80}$Ce$_{0.05}$VFe$_{0.15}$ alloys exhibit three phase microstructure. Representative back scattered electron image for Ti$_{0.83}$Ce$_{0.02}$VFe$_{0.15}$ alloy is shown in Fig. 3.23(b).

It is apparent from the image that there are (i) large bright (roughly 10-15 micron size) and (ii) small bright (roughly 2-5 micron size) phases distributed within single phase matrix. It is noted that the large bright phases have a tendency to cluster at the triple point junctions and grain boundaries whereas small bright phases are more random in nature. Wave-length dispersed X-ray line spectra obtained from each of these different phases indicate that the large bright phase is essentially constituted of Ce and O whereas small bright phase contains significant amount of Ce together with Ti and V. This becomes apparent from the Ce La-, Ti Ka- and V Ka X-ray line profiles (3.24 (a)-(c)).
Fig. 3.23 Electron micrographs of (a) Ti$_{0.85}$VFe$_{0.15}$ and (b) Ti$_{0.83}$Ce$_{0.02}$VFe$_{0.15}$, respectively. Back scattered electron image is showing occurrence of large and small Ce precipitates within the matrix of Ti$_{0.83}$Ce$_{0.02}$VFe$_{0.15}$ alloy. Note that the bright big areas (marked as 1) are mostly occurring at the triple point junction (marked by black arrows) and less bright small areas (marked as 2) are defining the grain boundaries.

A comparative study of EPMA results with those obtained from XRD analysis show good correlation. Additionally, EPMA data identifies the third unidentified phase of XRD spectra as the one having significant amount of Ce, Ti and V. This may be the same in case of Yan et al [140] and Wu et al [141].
Fig. 3.24 (a) Ce La, (b) Ti Ka and (c) V Ka X-ray line scans showing compositional variations among different phases of Ti$_{0.83}$Ce$_{0.02}$VFe$_{0.15}$ alloy.

3.2.3.3 Hydrogen absorption characteristics

The alloys Ti$_{0.95}$VFe$_{0.15}$, Ti$_{0.83}$Ce$_{0.02}$VFe$_{0.15}$ and Ti$_{0.80}$Ce$_{0.05}$VFe$_{0.15}$ are found to have maximum hydrogen absorption capacities of 3.7 wt. % (H/M = 3.83), 4.02 (H/M = 4.26) and 3.92 wt. % (H/M = 4.27), respectively. The hydrogen storage capacities of Ti$_{0.85-x}$Ce$_x$VFe$_{0.15}$ alloys as a function of Ce content, x, are given in Table 3.2.

The activation of Ce containing alloys is found to be easier as compared to Ce-free alloy. This could be due to the fact that the Ce-containing alloys have a secondary phase with crack formation at the surface so that hydrogen can easily diffuse through the cracks. The rate of hydrogen absorption for all the alloys as a function of time after one absorption-desorption cycle is shown in Fig. 3.25.
Table 3.2 Lattice parameters before and after hydrogenation and the maximum storage capacities of the alloys

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Lattice parameter of BCC phase (Å)</th>
<th>Hydride Composition</th>
<th>Lattice parameter of FCC phase (Å)</th>
<th>Capacity (Wt. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti₀.₈₅VFe₀.₁₅</td>
<td>3.086</td>
<td>Ti₀.₈₅VFe₀.₁₅H₃.₈₃</td>
<td>4.292</td>
<td>3.7</td>
</tr>
<tr>
<td>Ti₀.₈₃Ce₀.₀₂VFe₀.₁₅</td>
<td>3.095</td>
<td>Ti₀.₈₃Ce₀.₀₂VFe₀.₁₅H₄.₂₆</td>
<td>4.350</td>
<td>4.02</td>
</tr>
<tr>
<td>Ti₀.₈₀Ce₀.₀₅VFe₀.₁₅</td>
<td>3.097</td>
<td>Ti₀.₈₀Ce₀.₀₅VFe₀.₁₅H₄.₂₇</td>
<td>4.350</td>
<td>3.92</td>
</tr>
</tbody>
</table>

Fig. 3.25 Kinetic study on Ti₀.₈₅VFe₀.₁₅, Ti₀.₈₃Ce₀.₀₂VFe₀.₁₅ and Ti₀.₈₀Ce₀.₀₅VFe₀.₁₅ alloys.

It may be noted that the hydrogen absorption rate is quite fast and the hydrides reach near saturation value in about 120 seconds. Kinetic studies show that the hydrogen absorption is quite fast for all the three alloys. Fig. 3.26 shows the pressure-composition isotherms of Ti₀.₈₅₋ₓCeₓVFe₀.₁₅ (x = 0.0, 0.02 and 0.05) alloys at room temperature.
For all compositions, the plateau region is found to be <0.02 atm., which is the lowest detection limit of our set up. In general, V based bcc alloys form monohydride and dihydride phases, exhibiting two plateau regions in the P-C isotherms [131, 134, 146]. The plateau corresponding to monohydride exists in the region of low pressure of the order of $10^{-2}$ mbar, at room temperature. The two plateau region was not observed in the pressure range of this study, as resolving the two plateau region needs pressure measurements in the low pressure region [131, 134, 146]. As can be seen from the pressure-composition isotherm study, the length of the plateau region increases for the Ce substituted alloys as compared to that of Ce-free alloy, Ti$_{0.85}$VFe$_{0.15}$. The hydrogen storage capacity of Ti$_{0.85-x}$Ce$_x$VFe$_{0.15}$ increases with the increase in Ce content up to $x = 0.02$. Further increase in the Ce content to $x = 0.05$, reduces the hydrogen storage capacity of the alloy marginally.

![Absorption and Desorption Isotherms](image)

**Fig. 3.26** *Pressure-composition isotherms of Ti$_{0.85-x}$Ce$_x$VFe$_{0.15}$ (x = 0, 0.02 and 0.05) alloys at room temperature.*

As seen from EPMA studies, the formation of CeO$_2$ phase in the bcc phase plays a crucial role in improving the hydrogen storage capacity of Ce substituted alloys. Due to the
strong affinity of Ce to oxygen, Ce preferentially reacts with trace oxygen during melting, thereby, reducing the reaction of Ti with oxygen. This is likely to lead to improved homogeneity of the bcc phase with higher Ti content as mentioned in ref. [140-144].

3.2.3.4 Electrochemical characterization

Electrochemical characterization of the two representative alloys Ti$_{0.85}$VFe$_{0.15}$ and Ti$_{0.83}$Ce$_{0.02}$VFe$_{0.15}$ are presented in this section. From the polarization measurements carried out at small over-potentials (-6 to +4 mV vs. ref. electrode) at a scan rate of 1.5 mV/s for Ti$_{0.85}$VFe$_{0.15}$ and Ti$_{0.83}$Ce$_{0.02}$VFe$_{0.15}$ alloys, the estimated polarization resistance values are 264 and 253 mΩ, respectively. Corresponding exchange current densities calculated are 98 and 108.52 mA/g. The increased exchange current density of Ce doped alloy indicates improved electrocatalytic activity for the hydrogen electrode reactions. The exchange current density is dependent both on the construction of MH electrode plate and the additives in the electrode plate. An increase in the exchange current density for a battery electrode leads to an increase in the high-rate discharge capability [146].

Fig. 3.27 shows the current density versus time of Ti$_{0.85}$VFe$_{0.15}$ and Ti$_{0.83}$Ce$_{0.02}$VFe$_{0.15}$ alloys (un-charged) measured in KOH electrolyte at a DC voltage of 0.25 V.

The initial current density obtained is 538 and 783 mA/g for Ti$_{0.85}$VFe$_{0.15}$ and Ti$_{0.83}$Ce$_{0.02}$VFe$_{0.15}$ alloys studied with a broad and stable plateau region of ~175-100 mA/g for both the alloys. It may be noted that the Ce-containing alloy has higher initial current density as compared to that of Ce-free alloy.
**Fig. 3.27** Current versus time characteristics of Ti$_{0.85}$VFe$_{0.15}$ and Ti$_{0.83}$Ce$_{0.02}$VFe$_{0.15}$ alloys.

Fig. 3.28 shows the impedance spectra of Ti$_{0.85}$VFe$_{0.15}$ and Ti$_{0.83}$Ce$_{0.02}$VFe$_{0.15}$ (uncharged).

**Fig. 3.28** Measured impedance data plots of Ti$_{0.85}$VFe$_{0.15}$ and Ti$_{0.83}$Ce$_{0.02}$VFe$_{0.15}$ alloys. Inset shows the equivalent circuit used for fitting the data. $R_1$ is the contact resistance, $L_1$ is the $R_2/Q_1$ represent the charge transfer resistance at the electrode electrolyte interface.
The impedance spectra were recorded for Ti$_{0.85}$VFe$_{0.15}$ and Ti$_{0.83}$Ce$_{0.02}$VFe$_{0.15}$ in the frequency range of 0.1 Hz to 100 kHz. Impedance data fitted using a complex non linear least square program shows that contributions for electrode reactions are both from the charge transfer resistance and the diffusion resistance (W). $(R_2 \parallel Q_1)$ represents the charge transfer resistance at the electrode/electrolyte interface. $R_1$ accounts for the contact resistance. The equivalent circuit used for fitting the data is shown in the inset of Fig. 3.28. Both the samples studied required an inductance element ($L_1$) for an optimized fit. Diffusion resistance was higher for Ti$_{0.83}$Ce$_{0.02}$VFe$_{0.15}$ compared to that of Ti$_{0.85}$VFe$_{0.15}$. The anodic oxidation peaks of hydrogen in the cyclic voltammograms were observed at -0.59 V and -0.55 V vs. Ag/AgCl reference electrode respectively, for Ti$_{0.83}$Ce$_{0.02}$VFe$_{0.15}$ and Ti$_{0.85}$VFe$_{0.15}$. The shift of anodic peak potential results from the change of hydrogen diffusivity [147]. The diffusion resistance values of the fitted impedance data also agree with the negative anodic peak shift of the Ce doped sample.

3.2.3.5 Summary

In this work, the effect of Ce substitution on the microstructure, hydrogen absorption properties, peak current of hydrogen absorption and electrochemical behaviour of Ti$_{0.85}$VFe$_{0.15}$ system have been investigated. Substitution of Ce (2 and 5 at. %) for Ti is found to improve the hydrogen absorption capacity of Ti$_{0.85}$VFe$_{0.15}$ alloy. The maximum storage capacity of Ti$_{0.85}$VFe$_{0.15}$, Ti$_{0.83}$Ce$_{0.02}$VFe$_{0.15}$ and Ti$_{0.80}$Ce$_{0.05}$VFe$_{0.15}$ alloys are found to be 3.7, 4.02 and 3.92 wt. %, respectively. The plateau pressure is found to be <0.02 atm. for all compositions. The ease of activation of Ti-V-Fe system is found to improve by Ce substitution. EPMA studies showed the presence of CeO$_2$ phase in Ce-substituted alloys along with a third phase. Electrochemical studies showed increased exchange current density for Ce doped alloy indicating improved electrocatalytic activity for the hydrogen electrode reactions.
3.4 Conclusion

From the hydrogen storage studies on Ti$_{1-x}$VFe$_x$ series we could conclude that, by varying the concentration of Fe, the hydrogen storage properties of the alloys can be modified drastically. Ti$_{0.85}$VFe$_{0.15}$ shows the maximum hydrogen storage capacity of 3.7 wt. % within this series. Cr substitution in place of V does not increase the hydrogen storage capacity but improves the activation properties. Both Zr and Ce substitutions in Ti$_{0.85}$VFe$_{0.15}$ alloy provide positive effect on the hydrogen absorption properties. Zr substitution improves the hydrogen absorption-desorption characteristics of Ti$_{0.85}$VFe$_{0.15}$ alloy by decreasing the hysteresis loss without affecting the maximum hydrogen storage capacity considerably. The hydrogen storage capacity and the ease of activation of Ti-V-Fe system are found to improve by small amount of Ce substitution.