

Structure and hydrogen desorption studies of $(\text{Ti}_{0.16}\text{Zr}_{0.05}\text{Cr}_{0.22}\text{V}_{0.57})_{1-x}\text{M}_x$ (M: Cu, Mm) alloys

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ABSTRACT: BCC based alloys represent a large and versatile group of hydrogen storage materials. Systematic studies to find out the most appropriate elemental substitution which can turn the material readily activated have been taken. Alloy systems $(\text{Ti}_{0.16}\text{Zr}_{0.05}\text{Cr}_{0.22}\text{V}_{0.57})_{1-x}\text{M}_x$, (M: Cu and Mm, $x = 0.0 - 0.10$) were synthesized by arc-melting in a water-cooled Cu mold in argon atmosphere and investigated for their hydrogen storage behaviour. Phase analysis and structural studies were carried out using powder X-ray diffraction (XRD) and transmission electron microscopy (TEM). These analyses indicate the retention of the parent BCC phase on Cu and Mm addition. Though the alloys have less hydrogen storage than the parent BCC phase, the desorption temperature of residual hydrogen is lowered.

Keywords: Hydrogen storage alloy, BCC structure, Transition metal alloys

1. INTRODUCTION

Hydrogen storage in metal hydrides has received considerable attention as it is an inherently safe and effective mode over compressed cylinders and cryogenic tanks. Investigations on solid hydrogen absorption materials e.g. LaNi_5 , TiFe , and TiMn_2 reveal that the gravimetric storage capacity in these traditional metal hydride (MH) systems is not more than 2 wt%, which is not satisfactory for practical applications [1-3]. Ti-V based BCC alloys found significance as their storage capacity is higher compared to AB and AB_5 type alloys [4-6]. However, the high material cost and poor activation characteristics restrict the potential use of BCC alloys. These issues have been taken

up by researchers by substituting appropriate and cost effective transition elements. It has been observed that the activation of BCC alloys would be easier if they contain Laves phase [6-8]. However, the presence of Laves phase in BCC alloys would decrease the storage capacity. Ferrovandium alloy, which is cheaper than pure V, was introduced into Ti-based BCC alloys. The hydrogen storage capacity of the alloy Ti-Zr-Cr-V decreased on addition of small quantity of Fe [9, 10]. It has been reported that the hydrogen storage capacity of $\text{V}_{55}\text{Ti}_{22.5}\text{Cr}_{16.1}\text{Fe}_{6.4}$ alloy improved on addition of small quantity of rare-earth metals [11]. But the pure rare-earth based alloys are expensive and so there is a need to search for new materials with good

hydrogen storage properties and economic viability. Misch-metal (Mm), a mixture of low cost light rare-earth elements (La, Ce, Pr, Nd etc.), can be used instead of individual rare-earth elements. Earlier good hydrogen storage properties such as activation, hydrogen storage capacity and kinetics were reported for Mm based AB, AB₂ and AB₅ alloys [2, 12, 13]. But there is no systematic study on the effect of Mm content on hydrogen storage properties of Ti-Zr-Cr-V alloy.

Therefore in the present investigation, it was planned to study the effect of the nature of M on structural and hydrogenation properties of (Ti_{0.16}Zr_{0.05}Cr_{0.22}V_{0.57})_{1-x}M_x (M: Cu, Mm and X= 0.0 to 0.10).

2. EXPERIMENTAL DETAILS

Alloys with the composition (Ti_{0.16}Zr_{0.05}Cr_{0.22}V_{0.57})_{1-x}M_x (M: Cu, Mm and X= 0.0, 0.03, 0.05, 0.07, 0.10) were prepared by arc-melting in a water-cooled Cu mold under high purity argon atmosphere. To achieve compositional homogeneity, the ingot was turned over and re-melted 3-4 times. The ingots were mechanically ground in air to make the powder sample. P-C isotherm was measured using 1g of powder in ~200 μm size with a Sievert's type apparatus at 293 K. The phase and micro structure of the samples were

investigated by powder X-ray diffraction (XRD) using a Rigaku X-ray diffractometer with CuKα radiation ($\lambda = 1.54178 \text{ \AA}$) and transmission electron microscopy (JEM-2000FXII). The general structure analysis system (GSAS) program was used to perform the Rietveld refinement [14, 15]. To determine the temperature where the leftover hydrogen was desorbed, differential thermal gravimetric analysis measurements (TA 2960 TGA/DTA) were carried out up to 600 °C at a heating rate of 10 °C/min. Highly pure N₂ (99.999 %) was used as a purging gas in DTA and TG experiments.

3. RESULTS AND DISCUSSIONS

3.1 (Ti_{0.16}Zr_{0.05}Cr_{0.22}V_{0.57})_{1-x}M_x (M=Cu)

3.1.1. Structural Characterization: XRD and Rietveld refinement

The representative powder XRD patterns for copper addition are shown in Fig.1. The XRD patterns represent the parent BCC as a main phase. With increasing Cu content, the main peak positions were shifted gradually to higher angle. The lattice parameters decreased from 3.033 to 3.013 Å as the Cu content increased from 0 to 10 at%. In Fig.1 some less intense extra peaks are also present. The quantitative analysis on formation of the phase was done using Rietveld refinement program. Fig.2 (a) shows the result of the Rietveld refinement

Table 1 Refined parameters obtained from the Rietveld refinement using X-ray powder diffraction data at room temperature of (Ti_{0.16}Zr_{0.05}Cr_{0.22}V_{0.57})_{1-x}Cu_x alloys.

Sample	phase	a (Å)	b(Å)	c(Å)	α	β	γ	Phase (%)
Original								
$R_{wp}=9.56$	ZrO ₂	4.934(2)	5.320 (2)	5.63 (1)	90	100.3(3)	90	2.39
$R_p=6.41$	ZrCr ₂	5.226 (4)	5.226 (4)	8.704 (2)	90	90	120	27.70
$S=1.23$	BCC	3.03362(6)	3.03362(6)	3.03362(6)	90	90	90	69.91
Cu 0.05								
$R_{wp}=9.16$	ZrO ₂	5.155(3)	5.179(4)	5.322(6)	90	99.4(2)	90	1.32
$R_p=7.25$	ZrCr ₂	5.202(2)	5.202(2)	8.522(5)	90	90	120	39.55

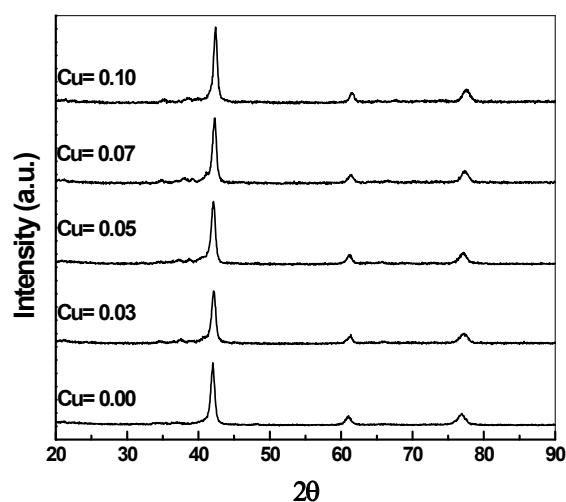


Fig.1. X-ray diffraction patterns for $(\text{Ti}_{0.16}\text{Zr}_{0.05}\text{Cr}_{0.22}\text{V}_{0.57})_{1-x}\text{Cu}_x$ ($x = 0$ to 0.10) alloys.

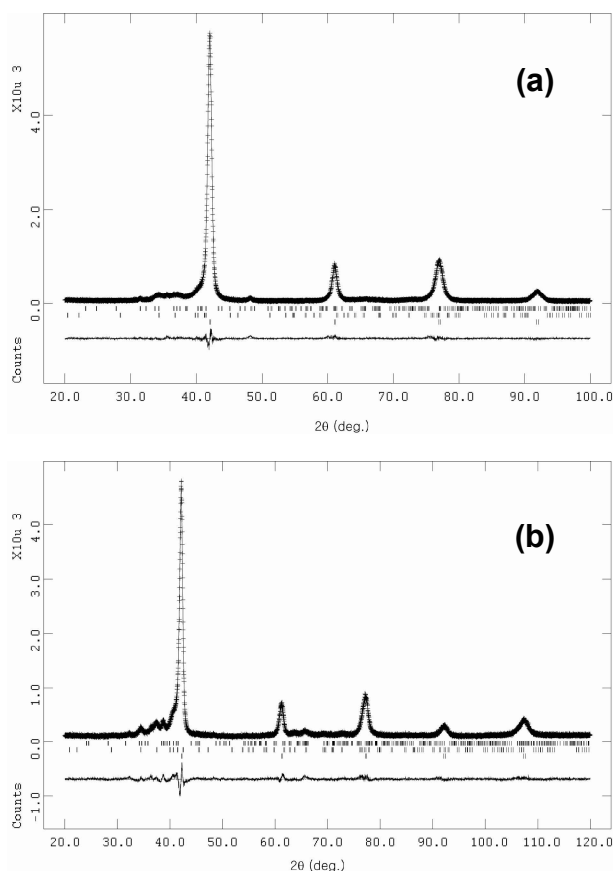


Fig. 2. Rietveld analysis for the alloy $\text{Ti}_{0.16}\text{Zr}_{0.05}\text{Cr}_{0.22}\text{V}_{0.57}$ and $(\text{Ti}_{0.16}\text{Zr}_{0.05}\text{Cr}_{0.22}\text{V}_{0.57})_{0.95}\text{Cu}_{0.05}$.

for the original alloy $\text{Ti}_{0.16}\text{Zr}_{0.05}\text{Cr}_{0.22}\text{V}_{0.57}$. The Rietveld refinement pattern was obtained using the model containing matrix

with BCC, ZrCr_2 , and ZrO_2 phases. The percentage of BCC, ZrCr_2 , and ZrO_2 phases based on the refined scale factors was 69.91%, 27.70% and 2.39% respectively. The Rietveld refinement of $(\text{Ti}_{0.16}\text{Zr}_{0.05}\text{Cr}_{0.22}\text{V}_{0.57})_{0.95}\text{Cu}_{0.05}$ consisting of three phases, namely BCC, ZrCr_2 and ZrO_2 , is shown in Fig.2(b). The parameters refined for both these alloys are given in Table 1. The XRD study is well supported by transmission electron microscopic study of the synthesized alloys (Fig. not show here).

3.1.2 Hydrogenation / dehydrogenation characteristics

Fig.3 shows the P-C isotherms of the $(\text{Ti}_{0.16}\text{Zr}_{0.05}\text{Cr}_{0.22}\text{V}_{0.57})_{1-x}\text{Cu}_x$ alloys at 293 K. It is observed that the substitution of Cu does not enhance the overall gravimetric hydrogen density of the alloy. The decrease in the hydrogen storage capacity with increasing Cu content can be explained by the increase in ZrCr_2 phase and decrease in the BCC phase. The BCC phase absorbs more hydrogen than ZrCr_2 phase. Fig 3 also shows that the Cu substitution raises the plateau pressure and shortens plateau regions, which suggests a significant change in the hydride stability. The shortened plateau pressure indicates decrease of the hydrogen desorption capacity. The 5 at% Cu alloy behaves differently in P-C isotherm, compared to other Cu substituted alloys. However, this has no bearing on overall hydrogen desorption capacity of the alloy.

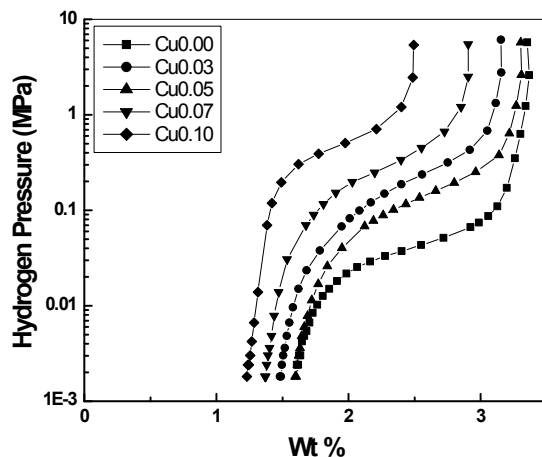
3.2. $(\text{Ti}_{0.16}\text{Zr}_{0.05}\text{Cr}_{0.22}\text{V}_{0.57})_{1-x}\text{M}_x$ ($\text{M} = \text{Mm}$)

3.2.1. Structural Characterization: XRD and Rietveld refinement

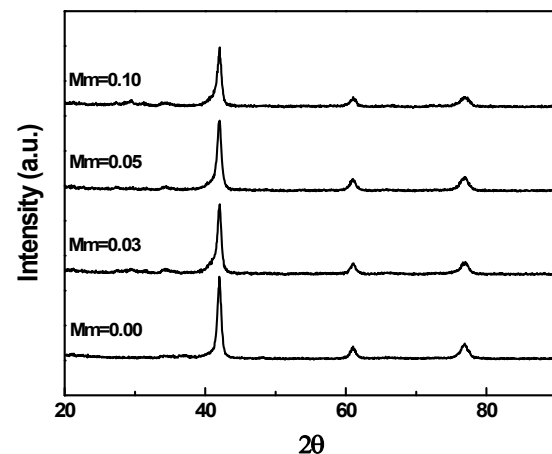
The representative powder XRD patterns for Mm addition are shown in Fig.4. The XRD patterns represent the parent BCC as a main phase. With increase in Mm content, small amount of Ce and Ce_7O_{12} phases were also observed. The atomic radius of Ce is much higher than Ti, Zr and therefore its total substitution for Ti, Zr does not become compatible for structural stability of the matrix alloy. It is therefore, not surprising

Table 2 Refined parameters obtained from the Rietveld refinement using X-ray powder diffraction data at room temperature of $(\text{Ti}_{0.16}\text{Zr}_{0.05}\text{Cr}_{0.22}\text{V}_{0.57})_{1-x}\text{Mm}_x$ alloys.

Sample	phase	a (Å)	b(Å)	c(Å)	α	β	γ	Phase (%)
Original								
$R_{\text{wp}}=9.56$	ZrO ₂	4.934(2)	5.320 (2)	5.63 (1)	90	100.3(3)	90	2.39
$R_{\text{p}}=6.41$	ZrCr ₂	5.226 (4)	5.226 (4)	8.704 (2)	90	90	120	27.70
$S=1.23$	BCC	3.03362(6)	3.03362(6)	3.03362(6)	90	90	90	69.91
Mn0.05								
$R_{\text{wp}}=6.97$	La	5.255(6)	5.255(6)	5.255(6)	90	90	90	2.05
$R_{\text{p}}=5.41$	Ce ₇ O ₁₂	10.522(4)	10.522(4)	9.916(1)	90	90	120	1.93
$S=1.41$	Ce	2.727(2)	2.727(2)	4.960(5)	90	90	90	7.45
	ZrCr ₂	5.203(2)	6.037(3)	8.242(9)	90	90	120	23.84
	BCC	3.03728(7)	3.03728(7)	3.03728(7)	90	90	90	64.73

**Fig.3.** Desorption P-C isotherms at 293 K for $(\text{Ti}_{0.16}\text{Zr}_{0.05}\text{Cr}_{0.22}\text{V}_{0.57})_{1-x}\text{Cu}_x$ ($x= 0$ to 0.10) alloys.

that Ce is thrown out of the lattice as a separate phase. Ce gets oxidized easily in air during the powder preparation; therefore the presence of Ce₇O₁₂ phase in the matrix along with Mm compositions was found. Ce might be partly getting accommodated in the lattice which thus supporting the change of lattice parameter from 3.033 to 3.037 Å as the Mm content increases from 0 to 10 at %. The XRD study is well supported by transmission electron microscopic study of

**Fig.4.** X-ray diffraction patterns for $(\text{Ti}_{0.16}\text{Zr}_{0.05}\text{Cr}_{0.22}\text{V}_{0.57})_{1-x}\text{Mm}_x$ ($x= 0$ to 0.10) alloys.

the synthesized alloys (Fig. not show here). The partial accommodation of Ce is also reflected in the quantitative analysis on formation of the phase using Rietveld refinement program. Fig.5 shows the results of the Rietveld refinement for the alloy $(\text{Ti}_{0.16}\text{Zr}_{0.05}\text{Cr}_{0.22}\text{V}_{0.57})_{0.95}\text{Mm}_{0.05}$, which consists of five phases. The five phases are assigned to original matrix phase with parent BCC, ZrCr₂, Ce, Ce₇O₁₂ and La

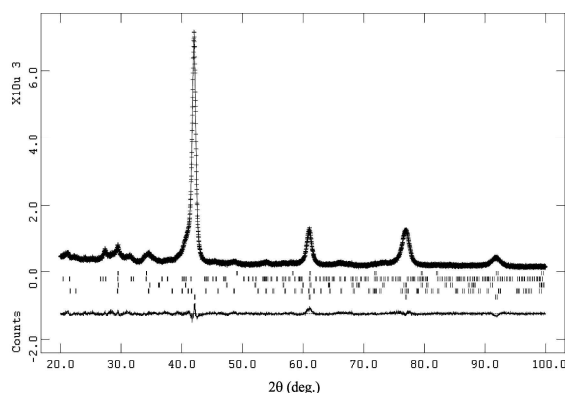


Fig. 5. Rietveld analysis for the alloy $(\text{Ti}_{0.16}\text{Zr}_{0.05}\text{Cr}_{0.22}\text{V}_{0.57})_{0.95}\text{Mm}_{0.05}$.

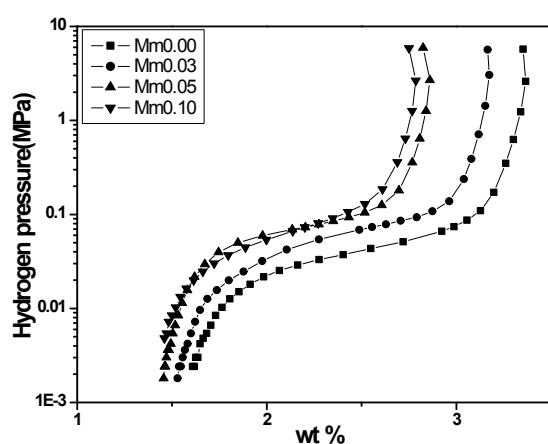


Fig. 6. Desorption P-C isotherms at 293 K for $(\text{Ti}_{0.16}\text{Zr}_{0.05}\text{Cr}_{0.22}\text{V}_{0.57})_{1-x}\text{Mm}_x$ ($x = 0$ to 0.10) alloys.

wherein the relative percentage of BCC phase decreases on Mm substitution. The parameters refined for this alloy are given in Table 2.

3.2.2 Hydrogenation / dehydrogenation characteristics

Fig. 6 shows the P-C isotherms of the $(\text{Ti}_{0.16}\text{Zr}_{0.05}\text{Cr}_{0.22}\text{V}_{0.57})_{1-x}\text{Mm}_x$ alloys at 293 K. The hydrogen storage capacity of the alloy decreases and plateau pressure increases with Mm content. One of the reasons for the drop in hydrogen storage capacity of the Mm substituted alloy may be due to high atomic weight fraction of misch metal (Mm) and other elements like Ti, Zr, Cr and V. Fig. 6 shows that the Mm addition slightly improves the plateau pressure and reduces the width of plateau pressure. It

suggests that beside BCC phase, the plateau pressure might be affected by secondary phases. Thus, total hydrogen storage capacity and effective hydrogen storage capacity decreases which reduced the width of plateau pressure.

3.3. DTA/TG tests

To investigate the leftover hydrogen of the alloys $\text{Ti}_{0.16}\text{Zr}_{0.05}\text{Cr}_{0.22}\text{V}_{0.57}$, $(\text{Ti}_{0.16}\text{Zr}_{0.05}\text{Cr}_{0.22}\text{V}_{0.57})_{0.95}\text{Cu}_{0.05}$ and $(\text{Ti}_{0.16}\text{Zr}_{0.05}\text{Cr}_{0.22}\text{V}_{0.57})_{0.95}\text{Mm}_{0.05}$, DTA and TG measurements were done and the results are shown in Fig. 7. Samples obtained after P-C isotherm measurements were used for these analyses. The number of endothermic peaks assignable to hydrogen desorption in the DTA curve may illustrate the kind of sites for hydrogen storage. Fig. 7 (a-b) shows the presence of only one endothermic peak for both the compositions $\text{Ti}_{0.16}\text{Zr}_{0.05}\text{Cr}_{0.22}\text{V}_{0.57}$ and $(\text{Ti}_{0.16}\text{Zr}_{0.05}\text{Cr}_{0.22}\text{V}_{0.57})_{0.95}\text{Cu}_{0.05}$. This indicates that there is only one kind of site available for hydrogen absorption in low pressure regime. The endothermic peaks are at 378°C and 333°C for $\text{Ti}_{0.16}\text{Zr}_{0.05}\text{Cr}_{0.22}\text{V}_{0.57}$ and $(\text{Ti}_{0.16}\text{Zr}_{0.05}\text{Cr}_{0.22}\text{V}_{0.57})_{0.95}\text{Cu}_{0.05}$ respectively. In Cu substituted hydride, hydrogen desorption takes place at much lower temperature than the original alloy. This observation suggests that the phase stability of hydride decreases with increasing Cu content. The TG graph shows an apparent weight loss of 0.97% and 0.91% for $\text{Ti}_{0.16}\text{Zr}_{0.05}\text{Cr}_{0.22}\text{V}_{0.57}$ and $(\text{Ti}_{0.16}\text{Zr}_{0.05}\text{Cr}_{0.22}\text{V}_{0.57})_{0.95}\text{Cu}_{0.05}$ alloys in the temperature range about 400°C and 380°C (Fig. 7 a, b).

However, in the Mm doped alloy, the weight loss assignable to hydrogen desorption takes place in two steps (TG, Fig. 7c) which keep up a correspondence with the two endothermic peaks in the DTA curve. Hence there might be two types of sites available for hydrogen absorption. Out of these two sites, one possesses lower stability of hydrogen storage as indicated by lower temperature (320°C) weight loss in

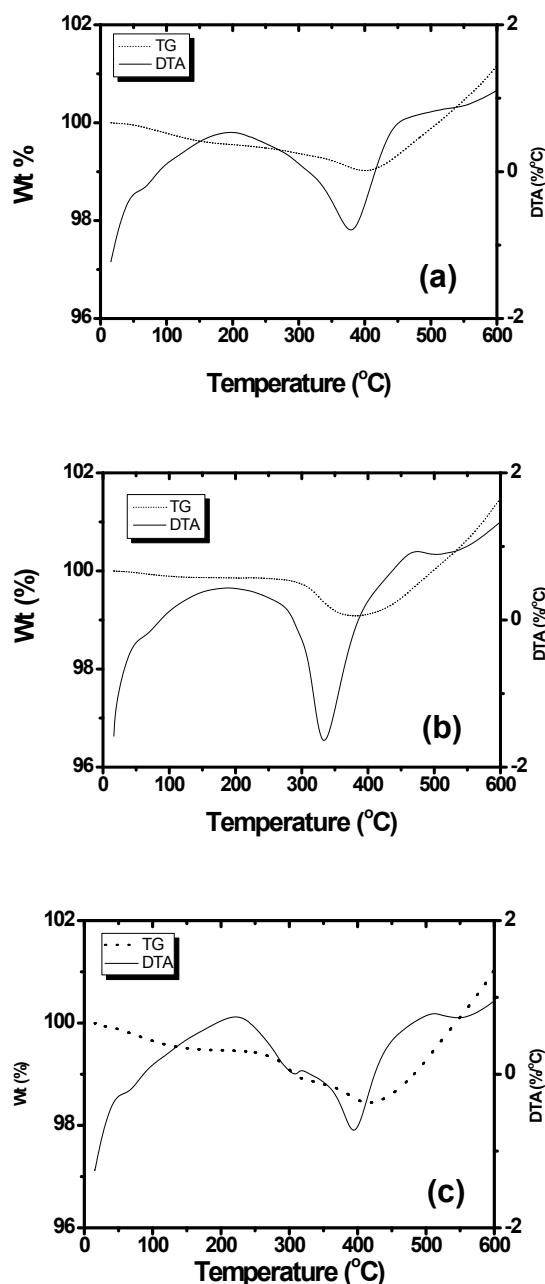


Fig.7. DTA-TG curves for the alloy (a) $\text{Ti}_{0.16}\text{Zr}_{0.05}\text{Cr}_{0.22}\text{V}_{0.57}$ (b) $(\text{Ti}_{0.16}\text{Zr}_{0.05}\text{Cr}_{0.22}\text{V}_{0.57})_{0.95}\text{Cu}_{0.05}$ (c) $(\text{Ti}_{0.16}\text{Zr}_{0.05}\text{Cr}_{0.22}\text{V}_{0.57})_{0.95}\text{Mm}_{0.05}$.

TG and the corresponding endothermic peak in DTA. The other site, forms more stable hydride as indicated by a weight loss in TG at 420 °C which is higher than that observed in TG of the original alloy. The endothermic peak in low-temperature region suggests the hydrogen desorption from the zirconium

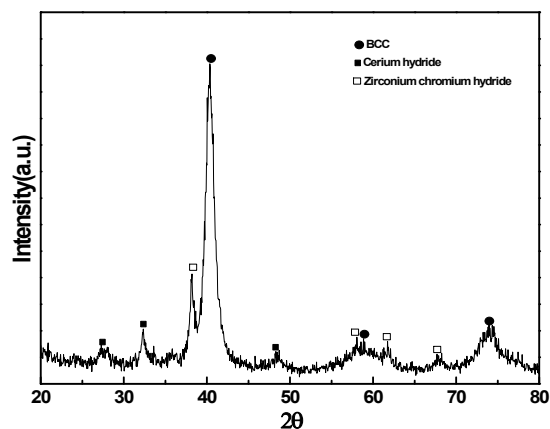


Fig.8. X-ray diffraction pattern of the $(\text{Ti}_{0.16}\text{Zr}_{0.05}\text{Cr}_{0.22}\text{V}_{0.57})_{0.97}\text{Mm}_{0.03}$ alloy obtained after the P-C isotherm measurements.

chromium hydride, while that in high temperature regions corresponds to the hydrogen desorption from BCC phase. The endothermic peak corresponding to cerium hydride could not appear because of higher value of heat of formation (ΔH) [16]. These observations are consistent with those in XRD results (Fig.8).

4. CONCLUSION

BCC based hydrogen storage materials $(\text{Ti}_{0.16}\text{Zr}_{0.05}\text{Cr}_{0.22}\text{V}_{0.57})_{1-x}\text{M}_x$ ($\text{M} = \text{Cu}$ and Mm) were synthesized by arc melting technique. The XRD and TEM results confirm that both Cu and Mm added alloys retain the parent BCC structure. The Rietveld refinement for Cu added samples show the presence of ZrCr_2 phase and oxide phase apart from the parent BCC phase. The amount and lattice parameter of BCC phase decreases, which results in decrease in hydrogen storage capacity of the alloy.

While in Mm added samples the main phase is BCC and other phases are Ce and Ce_7O_{12} . The lattice parameter of original alloy changes slightly from 3.033 to 3.037 Å. Reitveld analysis shows that the relative amount of BCC phase decreases from 69.9% to 64.7% on Mm addition. This

decrease in the quantity of BCC phase results in decrease in hydrogen storage capacity of the alloy. The residual hydrogen in the Cu substituted alloys was released at lower temperatures compared to the original alloy. But in the Mn added part of the absorbed hydrogen was released advantageously at lower temperatures. The remaining hydrogen is converted into the stable hydride, which is not suitable for hydrogen storage.

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