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# Synthesis of a hexagonal hydride phase of $\text{ZrCr}_2\text{H}_x$ ( $x = 5.75$ ) under high hydrogen pressure

M Dorogova<sup>1</sup>, T Hirata<sup>1</sup>, S M Filipek<sup>1</sup> and H Bala<sup>2</sup>

<sup>1</sup> Institute of Physical Chemistry, Polish Academy of Sciences, ul. Kasprzaka 44/52, 01-224 Warsaw, Poland

<sup>2</sup> Czestochowa Polytechnical University, Czestochowa, Poland

E-mail: hirata@ichf.edu.pl

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## Abstract

A hexagonal hydride of  $\text{ZrCr}_2\text{H}_x$  with a hydrogen concentration of  $x = 5.75$  was synthesized using high hydrogen pressure (5 kbar) at 100 °C for 72 h. The synthesized hydride is well characterized as regards structure and/or stability, as compared with cubic or hexagonal  $\text{ZrCr}_2$  hydrides that are formed under conventional hydrogenation conditions.

## 1. Introduction

It is known that high-hydrogen-pressure techniques are helpful for preparing new hydride phases in metal and alloy compounds, as exemplified by novel hydride phases being synthesized in several  $\text{AB}_2$  Laves compounds [1, 2]. As regards  $\text{ZrCr}_2$ , so far, the cubic or hexagonal hydrides of  $\text{ZrCr}_2$  and related compounds with a low hydrogen concentration have only been synthesized under conventional hydrogenation conditions [3–5]. However, it would be intriguing/challenging to further extend the solubility of hydrogen in  $\text{ZrCr}_2$  by means of high-hydrogen-pressure techniques, and to characterize the structure and/or stability of the synthesized hydride in comparison with cubic or hexagonal  $\text{ZrCr}_2$  hydrides that are formed under conventional hydrogenation conditions.

## 2. Experimental details

The starting compound of  $\text{ZrCr}_2$  was prepared by fusing a batch of Zr and electrolytic Cr in an electric arc furnace, repeating the melting several times to ensure homogeneity of the compound. X-ray diffractometry confirmed that the starting compound is of single phase (hexagonal) with lattice parameters  $a = 5.0923 \text{ \AA}$  and  $c = 8.2881 \text{ \AA}$ , which agree with the literature data ( $a = 5.102 \text{ \AA}$  and  $c = 8.294 \text{ \AA}$ ) [3]. Hydrogenation was performed under 5 kbar  $\text{H}_2$  at 100 °C for 72 h; the hydrogen content of  $\text{ZrCr}_2\text{H}_x$  was determined to be  $x = 5.75$

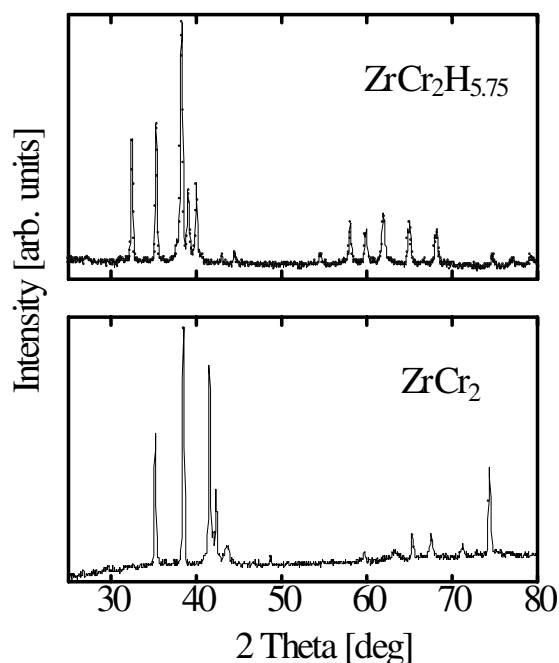


Figure 1. A comparison of the x-ray diffraction patterns of  $\text{ZrCr}_2$  and  $\text{ZrCr}_2\text{H}_{5.75}$ .

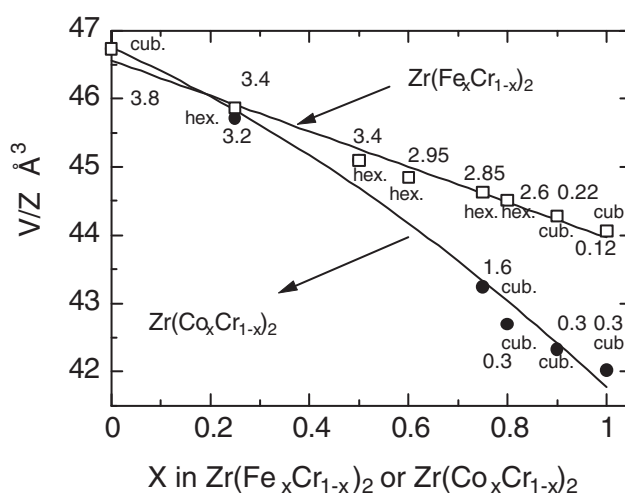
by a Perkin–Elmer type 240 elementary analyser. Meanwhile, an attempt was made to form  $\text{ZrCr}_2$  deuteride, and we were able to obtain  $\text{ZrCr}_2\text{D}_x$  ( $x \sim 6.0$ ). The structure and/or stability of  $\text{ZrCr}_2\text{D}_6$  were almost the same as those of  $\text{ZrCr}_2\text{H}_{5.75}$ .

### 3. Results and discussion

It turned out that the x-ray diffraction pattern of  $\text{ZrCr}_2\text{H}_{5.75}$  resembles that of hexagonal  $\text{Zr}(\text{Cr}_{0.6}\text{Fe}_{0.4})_2\text{D}_{2.813}$  ( $a = 5.340 \text{ \AA}$  and  $c = 8.709 \text{ \AA}$ ) [5] rather than that of cubic  $\text{ZrCr}_2\text{D}_{3.51}$  ( $a = 7.680 \text{ \AA}$ ) [3]. A careful analysis using the program Dicvo191 [6] revealed that all of the x-ray diffraction lines observed for  $\text{ZrCr}_2\text{H}_{5.75}$  can be identified with those of hexagonal  $\text{ZrCr}_2\text{H}_{5.75}$  ( $a = 5.4841 \text{ \AA}$  and  $c = 8.9892 \text{ \AA}$ ) and hexagonal  $\text{ZrCr}_2\text{H}_x$  expanded by some hydrogen incorporation (table 1).

It should be noted that the lattice parameters of hexagonal  $\text{ZrCr}_2\text{H}_{5.75}$  are larger than those of  $\text{Zr}(\text{Cr}_{0.6}\text{Fe}_{0.4})_2\text{D}_{2.83}$ , because of a large hydrogen content in  $\text{ZrCr}_2\text{H}_{5.75}$ , while the replacement of Cr by Fe contracts the lattice of  $\text{ZrCr}_2$ . The volume expansion upon hydrogenation amounts to about 25% for  $\text{ZrCr}_2\text{H}_{5.75}$ . On the other hand, the hexagonal phase of  $\text{ZrCr}_2$  with slightly larger lattice parameters relative to the starting compound is attributed to hydrogen incorporation in  $\text{ZrCr}_2$ . Thus, hydrogenation of  $\text{ZrCr}_2$  under high hydrogen pressure gives rise to the formation of hexagonal  $\text{ZrCr}_2$  hydride and hydrogen-incorporated  $\text{ZrCr}_2$  (hexagonal), which could coexist with each other.

The hexagonal phase of  $\text{ZrCr}_2$  corresponds to a low-temperature phase, whereas cubic  $\text{ZrCr}_2$  is stable at high temperatures, and transition to the high-temperature phase takes place at 900–944 °C. While it is most probable that the initial structure of  $\text{ZrCr}_2$  dominates the hydride structure formed upon hydrogenation, it is still interesting whether the hexagonal-to-cubic phase transition of  $\text{ZrCr}_2$  hydride is induced by any change in hydrogen concentration,



**Figure 2.** Scattering angles of the x-ray diffraction lines observed and calculated for  $ZrCr_2H_{5.75}$ , along with their intensity and index.

**Table 1.** Scattering angles of the diffraction lines observed in  $ZrCr_2H_{5.75}$ , along with the intensity, index, and comparison with calculations.

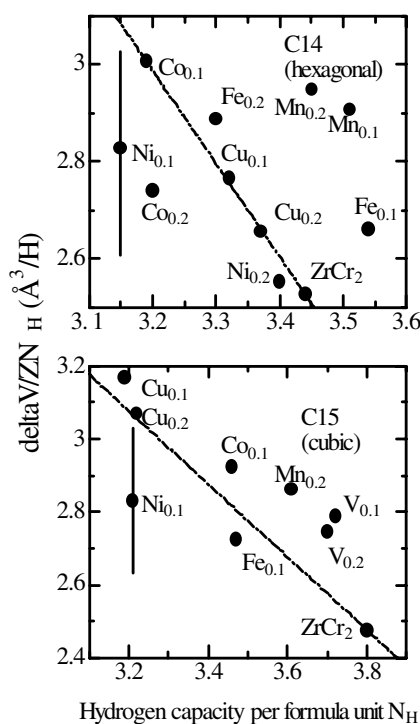
$2\theta$ (observation)	Intensity	$hkl$	$2\theta$ (calculation)	$2\theta$ (difference)
27.30	11	102	27.296	0.004
32.60	50	110	32.630	-0.030
35.35	58	103	35.391	-0.041
38.40	100	112	38.425	-0.025
39.18	26	201	39.207	-0.027
40.10	22	004	40.091	0.009
43.04	4	202	43.045	-0.005
44.64 <sup>a</sup>	5	202	44.640	0.000
58.24	17	300	58.231	0.009
60.06	20	213	60.030	0.030
61.65	14	115	61.639	0.011
62.18 <sup>a</sup>	20	213	62.139	0.041
65.12 <sup>a</sup>	18	302	65.126	-0.006
68.38	14	220	68.366	0.014
74.96 <sup>a</sup>	5	107	74.978	-0.018
76.70 <sup>a</sup>	3	311	76.721	-0.021
81.80 <sup>a</sup>	5	117	81.789	0.011

<sup>a</sup> The lines assigned to hexagonal  $ZrCr_2$  with hydrogen incorporated; other lines correspond to hexagonal  $ZrCr_2$  hydride.

temperature and pressure. No hexagonal-to-cubic phase transition of  $ZrCr_2$  hydride could be detected with a change in hydrogen concentration in the present work.

Nevertheless, it is noteworthy that either cubic or hexagonal hydride can be formed depending on  $x$  in the  $Zr(Fe_xCr_{1-x})_2$  and  $Zr(Co_xCr_{1-x})_2$  systems, as shown in figure 2.

The values of  $V/Z$  ( $\text{\AA}^3$ ) decrease with  $x$  and depend on the type of the substitution atoms as well as the hydrogen concentration, where  $V$  is the unit-cell volume and  $Z$  the molar number per formula unit ( $Z = 4$  and  $8$  for cubic and hexagonal hydrides respectively). Interestingly



**Figure 3.** The values of  $\Delta V = (V(\text{ZrCr}_2\text{H}_x) - V(\text{ZrCr}_2))/ZN_H$  as a function of  $N_H$  for cubic and hexagonal hydrides of  $\text{ZrCr}_2$  and related compounds.

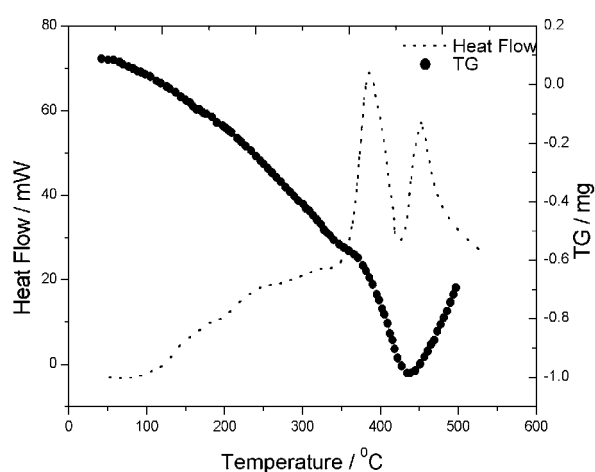
(This figure is in colour only in the electronic version)

figure 2 implies that the cubic-to-hexagonal phase transition or vice versa is probable in  $\text{ZrCr}_2$  hydride on application of pressure, which has a similar lattice contraction to the substitution-relevant volume change.

The most interesting aspect to address in the present work is that the hydrogenation-induced volume changes cannot remain constant, but tend to decrease with increase in hydrogen concentration for hexagonal and cubic  $\text{ZrCr}_2$  hydrides. Figure 3 presents the values of  $\Delta V = (V(\text{ZrCr}_2\text{H}_x) - V(\text{ZrCr}_2))/ZN_H$  against  $N_H$  for cubic and hexagonal hydrides of  $\text{ZrCr}_2$  and related compounds, where  $V(\text{ZrCr}_2\text{H}_x)$  and  $V(\text{ZrCr}_2)$  are the unit-cell volumes of  $\text{ZrCr}_2$  hydride and  $\text{ZrCr}_2$ , respectively, and  $Z$  has the same meaning as before. While the data are too scattered to ensure a good correlation, it is likely that the values of  $\Delta V$  never remain constant, but tend to decrease with  $N_H$  while the  $\Delta V$ s are comparable to  $\sim 2.8 \pm 0.2 \text{\AA}^3/\text{H}$  as shown for metals and intermetallic compounds [7].

Several data for cubic  $\text{ZrCr}_2$  hydride also revealed no constant volume changes upon hydrogenation, but a decreasing trend with increase in the hydrogen concentration. Meanwhile,  $d(\Delta V / Z N_H) / dN_H \sim 1.11$  for cubic hydride is smaller than the corresponding value of 1.93 for hexagonal hydride. This implies that hydrogen incorporation is more effective in the lattice distortion of  $\text{ZrCr}_2$  on the formation of hexagonal  $\text{ZrCr}_2$  hydride than for that of cubic  $\text{ZrCr}_2$  hydride, while the substitution-related lattice distortion needs to be taken into consideration.

To look into the stability of  $\text{ZrCr}_2\text{H}_{5.75}$  and/or  $\text{ZrCr}_2\text{D}_6$ , we have performed TG and DSC experiments and variable-temperature x-ray diffractometry. The following results should be noted. The weight loss, which is attributed to hydrogen release from  $\text{ZrCr}_2\text{H}_{5.75}$ , starts at  $50^\circ\text{C}$



**Figure 4.**  $T_g$  and the DSC curve obtained while  $\text{ZrCr}_2\text{H}_{5.75}$  was heated at  $10^\circ\text{C min}^{-1}$  under pure Ar gas.

**Table 2.** The ratio  $d_{hkl}(\text{after})/d_{hkl}(\text{before})$  of the interplanar spacings of the sample after and before heating. Underlines indicate the lattice parameters of the sample before heating, i.e.,  $\text{ZrCr}_2\text{H}_{5.75}$ .

$hkl$	Equation (1) <sup>a</sup>	Equation (2) <sup>b</sup>
110	0.93	0.92
103	0.92	0.92
112	0.92	0.92

$$^a d_{hkl}(\text{after})/d_{hkl}(\text{before}) = (\sin \theta)_{\text{before}}/(\sin \theta)_{\text{after}}$$

$$^b d_{hkl}(\text{after})/d_{hkl}(\text{before}) = [\sqrt{(4/3)a^2(h^2 + hk + k^2) + l^2/c^2}]/[\sqrt{(4/3)a^2(h^2 + hk + k^2) + l^2/c^2}]$$

and continues up to  $450^\circ\text{C}$ , and then weight gain takes place. We were able to estimate that the weight loss up to  $400^\circ\text{C}$  corresponds to the release of all hydrogen atoms from  $\text{ZrCr}_2\text{H}_{5.75}$ . On the other hand, the weight gain from  $400^\circ\text{C}$  is due to oxidation, revealing that the sample changes colour after heating; it is also shown that the DSC curves are characterized by complex features because of the intervention of oxidation during heating.

Variable-temperature x-ray diffractometry revealed upward shifts of the diffraction lines to occur during heating, which can be explained by the lattice contraction as hydrogen is released from  $\text{ZrCr}_2\text{H}_{5.75}$ . From several prominent x-ray diffraction lines, the ratio  $d_{hkl}(\text{after})/d_{hkl}(\text{before})$  of the interplanar spacings of the sample after and before heating was estimated to be 0.92, i.e., 8% contraction in the d-spacings when all the hydrogen atoms were desorbed. This value coincides well with the corresponding ratio, which was calculated using  $d_{hkl} = 1/\sqrt{(4/3)a^2(h^2 + hk + k^2) + l^2/c^2}$ , using the lattice parameters  $a$  and  $c$  determined for  $\text{ZrCr}_2$  and  $\text{ZrCr}_2\text{H}_{5.75}$  in the present work (table 2).

#### 4. Conclusions

A hexagonal hydride of  $\text{ZrCr}_2\text{H}_x$  with a large content of hydrogen ( $x = 5.75$ ) was synthesized under high hydrogen pressure. The synthesized hydride is well characterized as regards structure and/or stability, as compared with cubic and hexagonal  $\text{ZrCr}_2$  hydrides that are formed under conventional hydrogenation conditions. When hexagonal and cubic hydrides of  $\text{ZrCr}_2$  and related compounds are formed, it is pointed out that the volume changes per hydrogen

do not remain constant, but tend to decrease with increase in the hydrogen concentration, revealing a distinctive structure dependence. No hexagonal-to-cubic phase transition could be detected with a change in hydrogen concentration in the present work, but it is suggested that the hexagonal-to-cubic phase transition or vice versa can be induced by application of pressure.

### Acknowledgments

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