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Structural studies of the deuterides of carbon containing yttrium alloys

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Abstract

The present work describes a structural characterization of the yttrium–carbon compounds, Y_2C and YCoC, and their corresponding deuterides using temperature desorption spectroscopy (TDS) and high-resolution powder X-ray and neutron diffraction. Carbon atoms orderly occupy 1/3 (YCoC) or 1/2 (Y_2C) of the available octahedra, Y_4Co_2 and Y_6, respectively. Strong Y–C interactions lead to the 'shrinking' of these C-filled sites, with the Y–C bond distances between 2.49 and 2.51 Å for the compounds studied. Deuterium atoms in $YCoCD_{0.5}$ and in $Y_2CD_{2.55}$ occupy two different types of octahedra, similar to those filled by C. The occupancy of D sites is related to the radii of the occupied interstices. Both the too small Y_4Co_2 and the too large Y_6 octahedra have reduced filling. In $Y_2CD_{2.0-2.55}$ deuterium also nearly completely occupies Y_4 tetrahedra. From TDS it is evident that D bonding weakens in the sequence Y_4–Y_6–Y_4Co_2.

Keywords: Hydrogen storage materials; Gas–solid reactions; Crystal structure and symmetry; X-ray diffraction; Neutron diffraction

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1. Introduction

During the last years carbon nanomaterials have attracted considerable interest as prospective materials for H storage [1]. In such a respect it is important to expand the knowledge concerning C–H interactions. Metal hydrides have been extensively studied during the last decades. However, the H-storage properties of C-containing intermetallic compounds have been reported for only a few compounds (e.g. Y_2C, $Y_5Si_3C_x$ [2–4]). In order to improve the understanding of the atomic environment of hydrogen in carbon-containing metal hydrides, structural characterisations of the yttrium–carbon compounds Y_2C and YCoC and their corresponding deuterides have been performed in the present work. In these systems, an interrelation between C- and H-sublattices and deuterium absorption–desorption properties can be revealed. The emphasis is put on comparative analysis of the data for the different systems.

2. Experimental details

The alloys YCoC and Y_2C were prepared by arc melting in argon atmosphere. To reduce incoherent scattering contributions during the powder neutron diffraction (PND) experiments, deuterium-loaded samples were studied rather than hydrides. Synchrotron powder X-ray diffraction (SRPXD) data were collected at the Swiss–Norwegian Beam Line at ESRF, Grenoble. PND data were collected with the PUS high-resolution two-axis diffractometer [5] at IFE, Kjeller, Norway. The diffraction data for the deuterides and the carbides were analysed with the Rietveld-type method [6] using the GSAS software [7]. Unit cell information derived from Rietveld-type refinements of the diffraction data and experimental details are given in Table 1. For $Y_2CD_{2.0}$ a combined SRPXD and PND Rietveld-type refinement was performed. A typical plot displaying the data of the Rietveld-type refinements ($Y_2CD_{2.0}$) is shown in Fig. 1. The crystal structure of the carbides YCoC and Y_2C were investigated with SRPXD after a complete deuterium absorption–desorption cycle. A model of hard spheres was used for the calculations of the sizes of the interstitials. Further experimental details are given in Ref. [2].

3. Results and discussion

Y_2C (space group $R\bar{3}m$; $a=3.6248(8)$ Å, $c=17.9640(5)$ Å) crystallizes in a close packed structure containing Y_4 tetrahedra connected to Y_6 octahedra. The sequence be-

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Table 1
Crystal structure data (unit cell parameters, atomic coordinates[a], fractional occupation numbers (*n*), radii of cavities (*r*) and summary of the diffraction data (298 K)) derived from Rietveld refinements of powder diffraction data for YCoC, $YCoCD_{0.5}$, Y_2C, $Y_2CD_{2.0}$ and $Y_2C_{2.55}$

		YCoC	$YCoCD_{0.5}$	Y_2C	$Y_2CD_{2.0}$	$Y_2CD_{2.55}$
Space group		$P4_2/mmc$	$P4_2/mmc$	$R\bar{3}m$	$P\bar{3}m1$	$P\bar{3}1m$
a (Å)		3.65150(2)	3.6575(1)	3.62483(8)	3.6556(1)	6.3124(3)
c (Å)		6.86514(4)	6.8998(3)	17.9640(5)	5.9973(2)	5.9320(4)
$\Delta V/V$ (%)		–	0.84	–	1.86	0.14
D in 1b	*n*					0.19(3)
	r					0.97
D in 2d	*n*		0.38(1)		1.00(3)	0.79(1)
	r		0.54		0.60	0.83
D in 2f	*n*		0.116(7)			
	r		0.47			
D in 6k	*n*					0.977(8)
	r					0.54
Data collection		SRPXD	PND	SRPXD	SRPXD/ PND	PND
Wavelength, λ (Å)		0.49983	1.5554	0.50056	0.50095/ 1.5554	1.5554
Angle range (2θ)		3–30	10–130	3.5–34.1	4.0–26.3/ 10–130	10–130
Step lengths ($\Delta 2\theta$)		0.005	0.05	0.006	0.005/0.05	0.05
R_p (%)		6.6	4.8	4.5	12.6[b]	5.1
Rw_p (%)		8.3	5.21	6.1	17.6[b]	6.5

Calculated standard deviations in parentheses.

[a] Occupied positions are; for YCoC and $YCoCD_{0.5}$: 2 Y in 2e: (0,0,1/4), 2 Co in 2b: (1/2,1/2,0), 2 C in 2c: (0,1/2,0); for $YCoCD_{0.5}$: 0.76 D1 in 2d: (1/2,0,0), 0.23 D2 in 2f: (1/2,1/2,1/4); for Y_2C: 6 Y in 6c: (0,0,*z*), $z=0.25793(5)$, 3 C in 3a: (0,0,0); for $Y_2CD_{2.0}$: 2 Y in 2d: (1/3,2/3,*z*), $z=0.2265(3)$, 1 C in 1a: (0,0,0), 2 D in 2d, $z=0.607(1)$; for $Y_2CD_{2.55}$: 6 Y in 6k: (*x*,0,*z*), $x=0.3511(4)$, $z=0.2431(4)$, 1 C in 1a: (0,0,0), 2 C in 2c: (1/3,2/3,0), 0.19 D1 in 1b: (0,0,1/2), 1.58 D2 in 2d: (1/3,2/3,1/2) and 1.95 D3 in 6k: (*x*,0,*z*), $x=0.3077(4)$, $z=0.6254(4)$.

[b] Combined Rietveld refinements of SRPXD and PND data.

tween tetrahedra and octahedra is 2:1. Carbon occupies 1/2 of the available octahedra in an ordered way. These octahedra stack in a sequence CY_6–empty Y_6–CY_6, etc. Formation of the deuteride causes a structural phase transition with a collective shift of the neighbouring layers.

The crystal structure of YCoC (space group $P4_2/mmc$; $a=3.6515(2)$ Å, $c=6.86514(4)$ Å) is a derivative of the BCC lattice with one particular octahedral site orderly filled with C. Alteration of C-filled and empty octahedra and deformation of the originally equivalent Y_4Co_2 octahedra leads to the tetragonal lattice with $a_{tetr} \cong a_{cub}$; $c_{tetr} \cong 2\ a_{cub}$. The unit cell now contains three crystallographically different Y_4Co_2 octahedral sites: 2d (1/2, 0, 0), 2f (1/2, 1/2, 1/4) and 2c (0, 1/2, 0). The 2c site is completely occupied by C atoms while the other two octahedra are empty. The stacking of these Y_4Co_2-octahedra completely fills the structure.

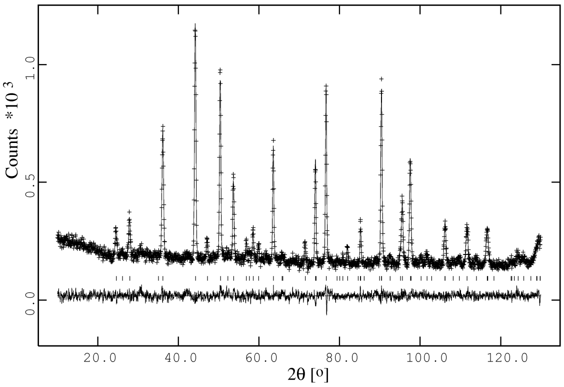

Fig. 1. Powder neutron diffraction pattern for $YCoCD_{0.5}$ showing observed (crosses), calculated (upper line) and difference (bottom line) plot. The positions of the Bragg peaks are shown as bars.

On a transition from Y_2C to $Y_2CD_{2.0}$ (space group $P\bar{3}m1$; $a=3.6556(1)$ Å, $c=5.9973(2)$ Å), D fills one of the two available Y_4 tetrahedral sites. The metal sublattice transforms from CCP to HCP, which results in a shift of the C-filled Y_6 octahedra away from the D-filled tetrahedra. By further increase of the D-content, two types of Y_6 octahedra start filling with deuterium. This increases the number of different D-occupied sites to three. The respective fractional occupation numbers are 0.19 (D1), 0.79 (D2) and 0.977 (D3). The resulting compound is $Y_2CD_{2.55}$ (space group $P\bar{3}1m$; $a=6.3124(3)$ Å, $c=5.9320(4)$ Å). A volume contraction is observed on the transformation from $Y_2CD_{2.0}$ to $Y_2CD_{2.55}$. Relevant interatomic distances are given in Tables 2 and 3. The crystal structures of $Y_2CD_{2.55}$ and $YCoCD_{0.5}$ are shown in Fig. 2. The interstitial sites are presented in Fig. 3.

A relatively small volume expansion of 0.8% is observed on the transformation from YCoC to $YCoCD_{0.5}$ (space group $P4_2/mmc$; $a=3.6575$ Å, $c=6.8998$ Å, see Fig. 2). The *c*-axis increases slightly more than the *a*-axis

Table 2
Selected data for the different D-occupied positions in the compounds $YCoCD_{0.5}$, $Y_2CD_{2.0}$ and $Y_2CD_{2.55}$

Compound	D/Y	Site	T_{des} (°C)	Y–D (Å)	D–D (Å)	C–D (Å)	Co–D (Å)
$YCoCD_{0.5}$	0.5	$D1Y_4Co_2$	145	2.51393(7)	2.51393(7)	2.58625(9)	1.82876(6)
		$D2Y_4Co_2$		2.58625(9)		2.51393(7)	1.72494(8)
$Y_2CD_{2.55}$	1.28	$D1Y_6$	280	2.690(3)	2.080(5)	2.966(5)	–
		$D2Y_6$		2.555(2)	2.313(5)	2.966(5)	–
		$D3Y_4$	510	2.234(3)	2.080(5)	2.951(5)	–
$Y_2CD_{2.0}$	1.0	DY_4	510	2.283(6)	2.471(5)	3.162(1)	–

Table 3
Selected interatomic distances (Å) in $YCoCD_{0.5}$, YCoC, $Y_2CD_{2.55}$, $Y_2CD_{2.0}$, Y_2C and YD_3

Atoms	YCoC	$YCoCD_{0.5}$	Y_2C	$Y_2CD_{2.0}$	$Y_2CD_{2.55}$	YD_3 [a]
Y–Y	3.43257(2)– 3.65150(2)	3.4499(2)– 3.6575(1)	3.423(1)– 3.890(1)	3.441(3)– 3.901(3)	3.442(5)– 3.839(5)	3.637(2)– 3.935(2)
Y–C	2.50579(1)	2.51392(7)	2.4929(5)	2.510(1)	2.507(2)– 2.644(3)	–
Y–Co	3.10038(1)	3.10872(9)	–	–	–	–
Co–C	1.82575(1)	1.82876(6)	–	–	–	–
Y–D	–	2.51393(7)	–	2.283(6)– 2.334(3)	2.234(3)– 2.690(5)	2.105(2)– 2.518(3)

Calculated standard deviations in parentheses.

[a] Data from Ref. [12], $T=295$ K.

($c/a=1.886$ in $YCoCD_{0.5}$ compared to 1.880 in YCoC). This is associated with occupation by D-atoms in the two remaining Y_4Co_2 octahedra with a significant difference in fractional occupation numbers for these sites, 0.38(1) (D1) and 0.116(7) (D2) (see Fig. 3).

In the carbide Y_2C, the CY_6 octahedra are considerably smaller ($r=0.78$ Å) than the empty Y_6 octahedra ($r=0.95$ Å). This indicates a strong bonding between yttrium and carbon. This is also the case for $Y_2CD_{2.0}$. The filling of the initially empty Y_6 octahedra with D to $Y_2CD_{2.55}$ gives two crystallographically non-equivalent C-containing Y_6-octahedra (with radii $r=0.92$ Å (C1) and $r=0.79$ Å (C2)). However, the differences in the sizes between C-filled and D-filled octahedra become smaller compared to the differences between CY_6 and empty Y_6-octahedra in Y_2C (see Table 1). This is mainly due to the rebuilding of the metal lattice induced by deuterium insertion, and the corresponding shrinking of the Y_6 octahedron on insertion of D2 caused by the Y–D attractive bonding. The significantly different occupation numbers of the two different

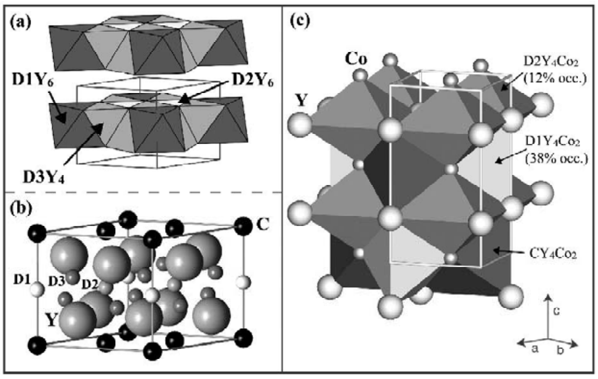

Fig. 2. The crystal structures of $Y_2CD_{2.55}$ and $YCoCD_{0.5}$ showing (a) the packing of Y_4 tetrahedra and Y_6 octahedra and (b) the unit cell content in the structure $Y_2CD_{2.55}$, and (c) packing of the Y_4Co_2 octahedra in $YCoCD_{0.5}$.

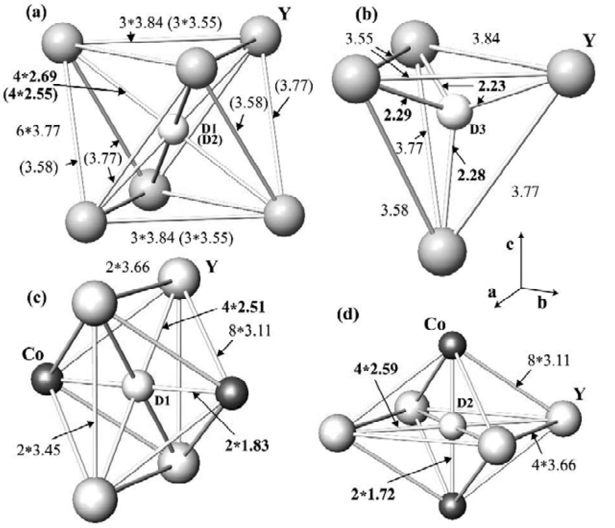

Fig. 3. (a) The D1 (D2)-filled Y_6 octahedra (fractional occupancy 0.19 (0.79)), (b) D3-filled Y_4 tetrahedron (fractional occupancy 0.98) in the structure of $Y_2CD_{2.55}$, and (c) the octahedrally coordinated 2d site (D1-site, fractional occupancy 0.38), (d) octahedrally coordinated 2f site (D2-site, fractional occupancy 0.116) in the structure of $YCoCD_{0.5}$. Selected interatomic distances are shown. Note that despite significant distortion of the Y_4 tetrahedron, all Y–D distances are close to each other indicating that D occupies a position near the ideal centre of the tetrahedron.

deuterium sites ($n_{D1}/n_{D2}=0.19/0.79$) can be attributed to the differences in size of the Y_6 octahedra. The reduced occupancy is characteristic for a too large site ($r=0.97$ Å). Similar regularities have been observed earlier for $Tb_3Ni_6Al_2$- and Zr_3Fe-based deuterides [8–11].

The D and C sites in the structure of $YCoCD_{0.5}$ are Y_4Co_2-type octahedra. They are all considerably smaller than the Y_6 octahedra in the Y_2C–D system, with radii of the cavity of the same order as for the $D3Y_4$ sites in $Y_2CD_{2.55}$. According to the PND-experiment, the D1, D2 and C atoms occupy the positions in the centres of the octahedra. The C-containing Y_4Co_2-octahedron is similar to one out of two D-containing Y_4Co_2-octahedra ($D1Y_4Co_2$), the latter being contracted in the axial direction Co–D–Co. For the $D2Y_4Co_2$ octahedron, an interstitial atom with a maximum radius 0.47 Å can be fitted in the central position. This is a relatively small site for deuterium occupation, and is the site in the structure with smallest occupation number.

A volume contraction is observed on the transition $Y_2CD_{2.0} \rightarrow Y_2CD_{2.55}$. During the transition D starts to occupy rather big Y_6 octahedra. The Y–D bonding contracts these octahedra in the same way as the Y–C bonds contract the C containing Y_6 octahedra in Y_2C and $Y_2CD_{2.0}$. This is the main reason for the observed volume contraction of the saturated deuteride compared to the lower deuteride $Y_2CD_{2.0}$. The contraction going from the lower to the saturated deuteride is a well known phenomena for the hydrides formed by the rare earth metals (e.g. the La–D system, Ce–D system) [13–16]. The deuterides of the yttrium carbide can be viewed as layered compounds, where one layer contains yttrium–deuterium–yttrium and the other layer contains yttrium–carbon–yttrium slabs. Therefore, locally around the deuterium atoms, the compound resembles a rare earth deuteride.

In the Y_2C–D system, with a rather high D content (1.28 at. D/Y), it is evident that deuterium atoms avoid the neighbourhood of C-atoms. This is not so clear in the YCoC-structure where the D content is much smaller (0.5 at. D/Y) and no structural rearrangement of the metal atoms accompanies the introduction of deuterium into the system. Even though, the interstitial site with the largest D–C interatomic distances is the preferred site. The occupation of this site is also highly influenced by its size. In both Y_2C–D and $YCoCD_{0.5}$ the shortest C–Y interatomic distances are nearly constant, ranging from 2.507 to 2.514 Å. The Y–D distances for the deuterium located in octahedral positions are also rather similar, ranging from 2.51 to 2.69 Å. The preferred octahedral sites in the systems have Y–D distances ranging from 2.55 Å (in $Y_2CD_{2.55}$) to 2.59 Å (in $YCoCD_{0.5}$).

The most strongly bound deuterium site in $Y_2CD_{2.55}$ is the Y_4 tetrahedron (D3) and a temperature of 510 °C is needed for D evolution under dynamical vacuum conditions (see Fig. 4 and Table 2). A considerably lower temperature is required to remove the Y_6 octahedrally coordinated deuterium atoms (peak at 280 °C). Comparing the octahedral D-sites in $Y_2CD_{2.55}$ and $YCoCD_{0.5}$, a substitution of 1/3 part of Y by Co leads to the development of the octahedra Y_4Co_2. These show the less stable D-bonding (desorption peak at 145 °C).

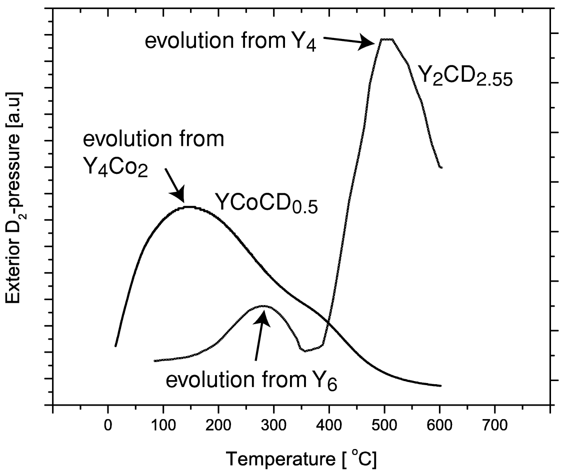

Fig. 4. Deuterium desorption traces from $YCoCD_{0.5}$ and $Y_2CD_{2.55}$ under dynamic vacuum conditions (heating rate 5 °C/min).

4. Conclusions

The structural chemistry of the Y_2C- and YCoC-based deuterides is governed by an interplay of Y–Y, Y–C, C–H(D) and H–H (D–D) atomic interactions. In the Y_2C–D system, strong repulsions between C and H(D) are manifested by a rebuilding of the Y sublattice in order to avoid simultaneous occupation of the neighbouring CY_6 octahedra and DY_4 tetrahedra. A differentiation in the occupancy of the available tetrahedral Y_4 and octahedral Y_6 and Y_4Co_2 sites by H(D) is related to their size and surroundings. Hydrogen bonding in the interstices weakens in the sequence Y_4–Y_6 –Y_4Co_2.

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