Chemistry of
Metals and Alloys

Chem. Met. Alloys 10 (2017) 45-49
Ivan Franko National University of Lviv
www.chemetal-journal.org

Decarbonization of the $Ce_2Mn_{17}C_{1.77}$ compound upon lithiation

Mykola HEMBARA[1]*, Vasyl KORDAN[1], Volodymyr PAVLYUK[1], Bogdan KOTUR[1]

[1] *Department of Inorganic Chemistry, Ivan Franko National University of Lviv,*
Kyryla i Mefodiya St. 6, 79005 Lviv, Ukraine
* *Corresponding author. Tel.:* +380-96-4179192*; e-mail: hembaramukola@gmail.com*

Received April 27, 2017; accepted June 27, 2017; available on-line April 1, 2018

The ternary compound $Ce_2Mn_{17}C_{1.77}$ was investigated by means of X-ray powder diffraction, scanning electron microscopy and energy-dispersive X-ray analysis. The structure type $Pr_2Mn_{17}C_{1.77}$ was confirmed using the Rietveld method. Electrochemical lithiation of $Ce_2Mn_{17}C_{1.77}$ was carried out in Swagelok-type cells with a positive electrode containing $LiCoO_2$ over 30 cycles. Decarbonization of the $Ce_2Mn_{17}C_{1.77}$ ternary carbide upon lithiation was accompanied by a decrease of the cell volume (from 847.9(2) Å^3 to 842.7(5) Å^3) and formation of α-Li_2C_2, Li_xC_y carbides, and amorphization of the Ce_2Mn_{17} subcell. The morphology of the anode surface underwent changes and the grain size of the material decreased.

Carbides / Crystal structure / Isostructural compounds / Electrochemical lithiation

Introduction

Electrode materials on the basis of intermetallic compounds are widely used in the production of modern energy sources. Some intermetallic compounds containing *d*- and *p*-elements have the ability to intercalate lithium atoms in their structures, thanks to the availability of large octahedral voids in their crystal structures [1,2]. Therefore, they are potential candidates for production of negative electrodes in electrochemical reactions.

Three ternary carbides, $Ce_2Mn_{17}C_{1.77}$ [3], $CeMn_{11}C_{2-x}$ [4] and $Ce_{3.67}MnC_6$ [5], are known to occur in the Ce–Mn–C system. Among these, $Ce_2Mn_{17}C_{1.77}$ has the lowest carbon content, 8.5 at.%, and is stable in air. It crystallizes in a $Pr_2Mn_{17}C_{1.77}$-type structure (Pearson symbol *hR*66, space group *R*-3*m*; $a = 8.785$ Å, $c = 12.683$ Å, $V = 847.7$ Å^3), which is a derivative of the Th_2Zn_{17}-type structure [3]. There are large octahedral voids in the structure of the intermetallic, which are partially (~59 %) occupied by carbon atoms. This compound could be interesting for the investigation of electrochemical lithiation with the purpose to search for structures suitable for electrochemical intercalation of lithium. The electrochemical lithiation and its mechanism for carbides have not yet been investigated.

In this work we present results on the synthesis, crystal structure investigation and electrochemical lithiation of the ternary carbide $Ce_2Mn_{17}C_{1.77}$.

Experimental

An 1.5 g alloy of composition $Ce_{10}Mn_{80}C_{10}$ was prepared by arc-melting a cold-pressed pellet of powders of the initial elements cerium, manganese and carbon with a purity not less than 99.9 wt.% (Alfa Aesar, A. Johnson Matthey Company) under an argon atmosphere purified with Ti getter on a water-cooled copper hearth, using a non-consumable tungsten electrode. During the melting procedure the weight loss was < 5.0 wt.% of the total mass of the ingot. The alloy was annealed in an evacuated quartz glass ampoule at 600°C for 45 days.

The phase analysis of the alloy and the crystal structure refinement were performed with the help of the WinXPOW [6] and WinCSD program packages [7], using powder X-ray diffraction (XRD) data obtained with a DRON-2.0M (Fe*K*α) powder diffractometer. Metallographic studies and qualitative and quantitative composition analyses of powders were performed by energy-dispersive X-ray spectroscopy (EDX) with a scanning electron microscope REMMA-102-02.

Attempts to electrochemically insert lithium into the ternary phase $Ce_2Mn_{17}C_{1.77}$ were carried out in Swagelok-type cells that consisted of a negative electrode containing 0.3 g of the alloy and a positive electrode containing $LiCoO_2$. A separator, soaked in electrolyte (1 M solution of $Li[PF_6]$ in ethylenecarbonate / dimethylcarbonate 1:1), was placed between the electrodes. Testing of the batteries was carried out in the galvanostatic regime (charging at 0.5 mA to 4.0 V *vs.* $LiCoO_2$, discharging at 0.1 mA to 0.7 V *vs.* $LiCoO_2$) over 30 cycles. A galvanostat MTech G410-2 [8] was used to measure the electrochemical properties of the alloy.

Results and discussion

Crystal structure data (structure type $Pr_2Mn_{17}C_{1.77}$) and cell parameters for $Ce_2Mn_{17}C_{1.77}$ were reported in [3], however, the atomic and isotropic displacement parameters had not been studied earlier. We refined the cell parameters, atomic and isotropic displacement parameters for this ternary compound by means of the Rietveld method. These data are listed in Table 1. In the refinement process the site occupation factor for the carbon site was fixed to the value (G = 0.59) found for the $Pr_2Mn_{17}C_{1.77}$ prototype. The refined XRD profiles of the $Ce_{10}Mn_{80}C_{10}$ alloy annealed at 600°C are presented in Fig. 1. Details of the refinement are presented in Table 2. The sample contained minor (no more than 2 wt.%) impurities in the form of α-CeC_2 binary carbide. The calculated interatomic distances for the ternary carbide are listed in Table 3. The crystal structure of the carbide and the coordination polyhedra of the C atoms are shown in Fig. 2. There are no contacts between carbon atoms in the structure, resulting in stability in air. The interatomic distances d_{Ce-Ce} (3.944(8) Å) and d_{Ce-Mn} (3.149(7)-3.390(8) Å) are almost equal to the sum of the atomic radii of the elements (r_{Ce} = 1.83 Å, r_{Mn} = 1.30 Å [9]). However, the interatomic distances d_{Ce-C} (2.5393(4) Å), d_{Mn2-C} (1.917(9) Å), and d_{Mn3-C} (1.931(3) Å) are shorter, indicating some covalent bonding between these atoms (r_{Ce} = 1.83 Å, r_{Mn} = 1.3 Å, r_C = 0.92 Å for atomic radius, r_C = 0.77 Å for covalent radius [9]). It appears that this bonding stabilizes the ternary carbide, since the binary compound Ce_2Mn_{17} does not exist. In fact, no binary compound occurs in the Ce–Mn system [10,11].

Experimental XRD patterns of the sample before and after electrochemical lithiation are shown in Fig. 3. The cell parameters of $Ce_2Mn_{17}C_{1.77}$ before and after electrochemical lithiation are listed in Table 4. The cell volume of the main phase was reduced and the binary lithium carbide α-Li_2C_2 was formed: space group *Immm*, structure type Rb_2O_2, a = 3.6438(6) Å, b = 4.828(1) Å, c = 5.452(1) Å, V = 95.93(3) Å^3. Traces of an unknown phase were also observed (see Fig. 3). This phase, formed during the electrochemical reaction, probably contains Li and C and will be referred to as Li_xC_z.

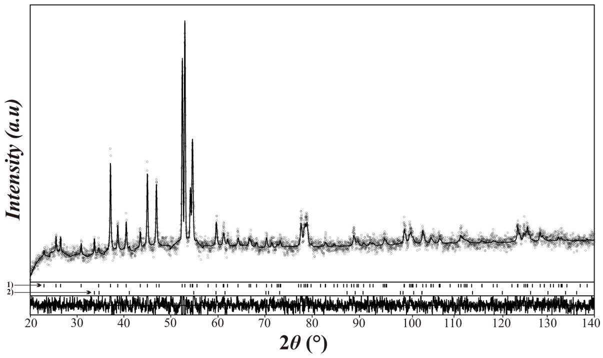


Fig. 1 Observed (dots) and calculated (line) profiles and their difference (bottom) for the XRD pattern of the $Ce_{10}Mn_{80}C_{10}$ sample annealed at 800°C for 45 days. The Bragg positions are marked by vertical bars: 1 – $Ce_2Mn_{17}C_{1.77}$; 2 – α-CeC_2.

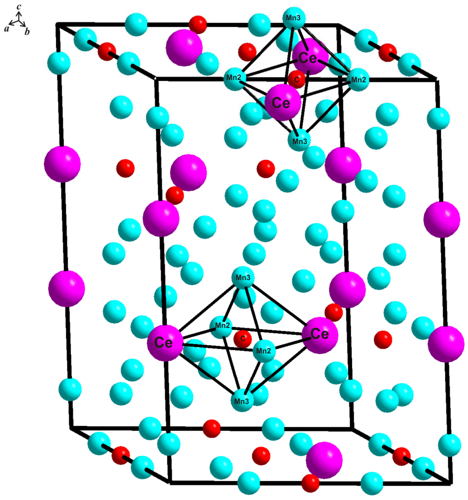


Fig. 2 Crystal structure of $Ce_2Mn_{17}C_{1.77}$. The coordination polyhedra of the carbon atoms are indicated.

Table 1 Atomic and isotropic displacement parameters for $Ce_2Mn_{17}C_{1.77}$.

Atom	Wyckoff position	Site occupation	*x*	*y*	*z*	B_{iso}, Å^2
Ce	6*c*	1	0	0	0.3447(5)	0.59(4)
Mn1	9*d*	1	½	0	½	0.5(3)
Mn2	18*f*	1	0.2801(8)	0	0	0.9(3)
Mn3	18*h*	1	0.5044(6)	-*x*	0.1509(7)	1.0(2)
Mn4	6*c*	1	0	0	0.0944(9)	0.6(1)
C	9*e*	0.59 [a]	½	0	0	1.0 [a]

[a] fixed during the refinement

Table 2 Details of the structure refinement of the $Ce_2Mn_{17}C_{1.77}$ ternary compound in the $Ce_{10}Mn_{80}C_{10}$ sample annealed for 45 days.

Phase	$Ce_2Mn_{17}C_{1.77}$
Content in the sample, wt.%	98.32±1.33
Space group	*R*-3*m*
Z	3
a, Å	8.7821(5)
c, Å	12.6949(9)
V, Å^3	847.9(2)
Calculated density, g cm^{-3}	7.308(2)
Radiation and wavelength, Å	X-rays, Fe*K*α; 1.54056
2θ (°) and sinθ/λ (Å^{-1})	20-140; 1
Zero shift, °(2θ)	0.003
Preferred orientation	0.94(3) [0 0 1]
R_B, %	5.26
R_p, %	1.99
GooF	1.11
Scale factor	0.216(1)

Table 3 Interatomic distances (*d*, Å) in the crystal structure of $Ce_2Mn_{17}C_{1.77}$.

Atoms	*d*	Atoms	*d*
Ce – 3C	2.5393(4)	Mn3 – 1C	1.917(9)
– 3Mn3	3.149(7)	– 2Mn1	2.510(5)
– 1Mn4	3.178(2)	– 2Mn3	2.633(7)
– 6Mn2	3.190(3)	– 2Mn2	2.643(8)
– 3Mn3	3.390(8)	– 1Mn4	2.709(8)
– 3Mn1	3.396(4)	– 2Mn2	2.721(8)
– 1Ce	3.944(8)	– 1Ce	3.149(7)
Mn1 – 4Mn2	2.481(2)	– 1Ce	3.390(8)
– 4Mn3	2.510(5)	Mn4 – 1Mn4	2.40(2)
– 2Mn4	2.696(4)	– 3Mn1	2.696(4)
– 2Ce	3.396(4)	– 3Mn3	2.709(8)
Mn2 – 1C	1.931(3)	– 6Mn2	2.736(6)
– 2Mn2	2.460(5)	– 1Ce	3.178(2)
– 2Mn1	2.481(2)	C – 2Mn3	1.917(9)
– 2Mn3	2.643(8)	– 2Mn2	1.931(3)
– 2Mn3	2.721(8)	– 2Ce	2.5393(4)
– 2Mn4	2.736(6)		
– 2Ce	3.190(3)		

Table 4 Results of the XRD phase analysis of the $Ce_{10}Mn_{80}C_{10}$ sample before (1) and after the 30-th cycle of electrochemical lithiation (2).

No.	Phases	Structure type	Pearson symbol	Space group	*a*, Å	*b*, Å	*c*, Å	*V*, Å^3
1	$Ce_2Mn_{17}C_{1.77}$	$Pr_2Mn_{17}C_{1.77}$	*hR*66	*R*-3*m*	8.7821(5)	–	12.6949(9)	847.9(2)
	α-CeC_2	CaC_2	*tI*6	*I*4/*mmm*	3.878(2)	–	6.487(2)	97.557(8)
2	$Ce_2Mn_{17}C_{1.77-y}$ (y = ?)	$Pr_2Mn_{17}C_{1.77}$	*hR*66	*R*-3*m*	8.765(2)	–	12.665(4)	842.7(5)
	α-Li_2C_2	Rb_2O_2	*oI*8	*Immm*	3.6438(6)	4.828(1)	5.452(1)	95.93(3)
	Li_xC_z (x = ?, z = ?)	[a]						

[a] unknown crystal structure

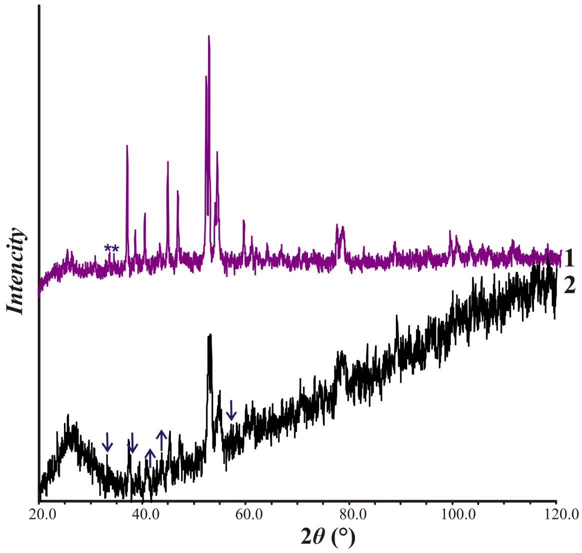


Fig. 3 Experimental XRD pattern of the $Ce_{10}Mn_{80}C_{10}$ sample before (**1**) and after the 30-th cycle of electrochemical lithiation (**2**). Impurities: * – α-CeC_2, ↓ – α-Li_2C_2, ↑ – Li_xC_z (x = ?, z = ?).

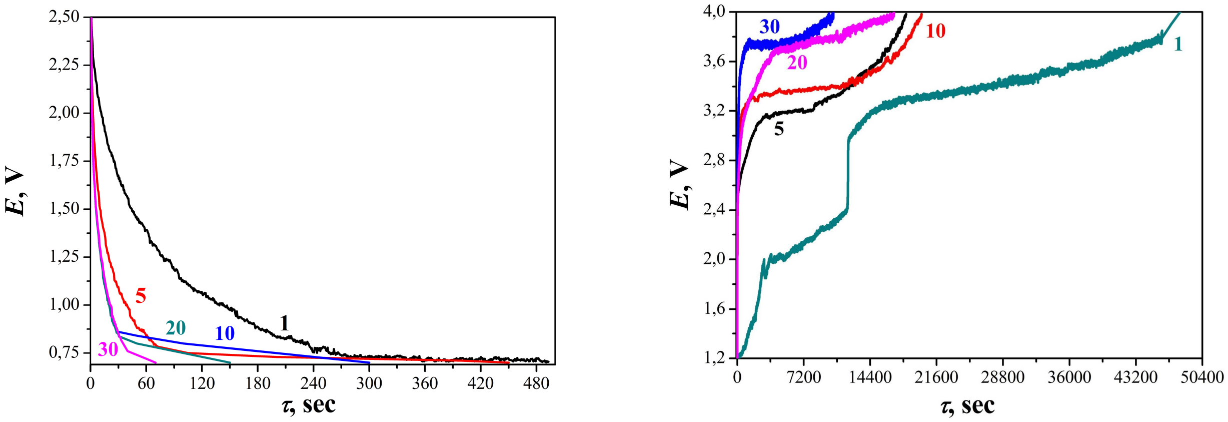
Electrochemical lithiation of $Ce_2Mn_{17}C_{1.77}$ caused decarbonization of the initial ternary carbide, due to the large difference in electronegativity between carbon and lithium. As a result, the binary lithium carbide α-Li_2C_2 was formed. This means that lithium extracted carbon from the initial ternary carbide during the electrochemical process. The decarbonization process is irreversible and the degree of removal of carbon probably depends on the size of the particles of the carbide and the amount of electricity that passed through the electrodes. The irreversibility of the process is clearly visible from the discharge curves, where the delithiation plateau is very small and constantly decreases from cycle to cycle, with decreasing carbon in the parent compound (Fig. 4). At the cathode electrochemical delithiation occurs. The Li-ions leave their positions through channels of the structure of $LiCoO_2$ and move to the surface of the alloy [12].

The scheme of the electrochemical reactions can be presented as:

$$Ce_2Mn_{17}C_{1.77} + x\mathrm{Li}^+ + x\bar{e} \xrightarrow{\text{decarboniz ation}}$$
$$Ce_2Mn_{17}C_{1.77\text{-}z} + \mathrm{Li}_x\mathrm{C}_z\,(\alpha - \mathrm{Li_2C_2})$$

$$\mathrm{LiCoO_2} - x\bar{e} \xleftrightarrow{\text{charge}-\text{discharge}}$$
$$\mathrm{Li}_{1-x}\mathrm{CoO_2} + x\mathrm{Li}^+$$

The EDX analysis of the alloy after the electrochemical process showed almost the same quantitative Ce/Mn ratio as in the initial sample ($Ce_{10.93}Mn_{89.07}$ before, $Ce_{10.73}Mn_{89.27}$ after). The SEM-images that are presented in Fig. 5 show considerable changes of the morphology of the surface of the alloy. Partial amorphization of the electrode material and reduced grain size are also seen.



a *b*

Fig. 4 Selected charge (*a*) and discharge (*b*) curves (cycle 1, 5, 10, 20, 30) for $Ce_2Mn_{17}C_{1.77}$ *vs*. $LiCoO_2$.

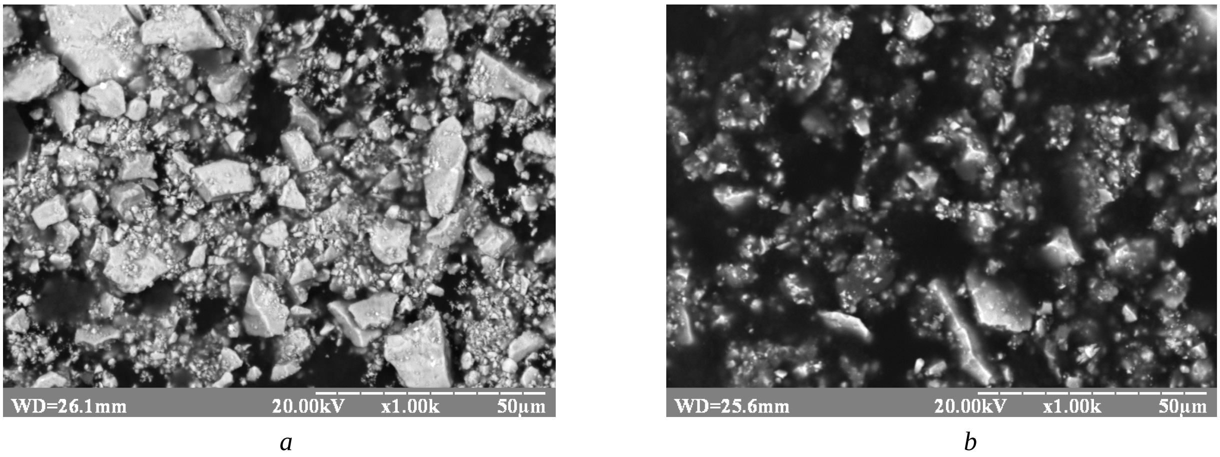


Fig. 5 SEM-images of the studied alloy before (*a*) and after (*b*) the 30-th cycle of electrochemical lithiation. Quantitative composition from EDX analysis of the samples $Ce_{10.93}Mn_{89.07}$ (*a*) and $Ce_{10.73}Mn_{89.27}$ (*b*).

Differently from the electrochemical lithiation process used here, lithium metal has sometimes been used as flux for the preparation of ternary rare-earth *d*-element carbides from the initial elements under an argon atmosphere at $T > 800°C$ in iron tubes. Among the carbides synthesized this way are $Dy_{10.14}Mn_{12.86}C_{18}$ and $Yb_{10.09}Mn_{12.91}C_{18}$ [13], $Gd_{10.34}Mn_{12.66}C_{18}$ [14], $Ln_{12}Mn_5C_{15}$ (Ln = Y, Pr, Nd, Sm, Gd-Tm, Lu) [15], $Yb_2Cr_2C_3$ [16], YbCoC [17], $Ln_4Ni_2C_5$ (Ln = Er, Tm, Yb, Lu) [18].

4. Conclusions

The cell parameters and the atomic and isotropic displacement parameters for the ternary compound $Ce_2Mn_{17}C_{1.77}$ were refined using the XRD Rietveld method. Electrochemical lithiation of $Ce_2Mn_{17}C_{1.77}$ was carried out over 30 cycles in Swagelok-type cells with a positive electrode containing $LiCoO_2$. Decarbonization of the ternary carbide was observed, accompanied by a decrease of the cell volume and formation of α-Li_2C_2, Li_xC_y carbides and amorphization of the Ce_2Mn_{17} alloy.

Acknowledgments

The authors are thankful to R.Ya. Serkiz (Scientific-Technical and Educational Center of Low-Temperature Studies, Ivan Franko National University of Lviv) for the SEM and EDX analyses of the samples.

References

[1] J.O. Besenhard, *Handbook of Battery Materials*, Wiley-VCH, Weinheim, 1999.
[2] C.A. Vincent, B. Scrosati, *Modern Batteries: an Introduction to Electrochemical Power Sources*, 2nd edition, Arnold, London, 1997.
[3] G. Block, W. Jeitschko, *Inorg. Chem.* 25 (1986) 279-282.
[4] G. Block, W. Jeitschko, *J. Solid State Chem.* 70 (1987) 271-280.
[5] A.M. Witte, W. Jeitschko, *Z. Naturforsch. B* 51 (1996) 249-256.
[6] Stoe & Cie, STOE Win XPOW (Version 2.10), 2004.
[7] L. Akselrud, Y. Grin, *J. Appl. Crystallogr.* 47 (2014) 803-805.
[8] http://chem.lnu.edu.ua/mtech/mtech.htm.
[9] G.B. Bokyy, *Crystal Chemistry*, Nauka, Moscow, 1970 (in Russian).
[10] A. Iandelli, *Atti Accad. Naz. Lincei, Cl. Sci. Fis. Mat. Nat., Rend.* 13 (1952) 265-269.
[11] K.A. Gschneidner, Jr., M.E. Verkade, *IS-RIC-7*, Rare Earth Information Center, Iowa State Univ., Ames, IA, Vol. 26, 1974.
[12] V. Kordan, O. Zelinska, V. Pavlyuk, I. Oshchapovsky, R. Serkiz, *Chem. Met. Alloys* 9 (2016) 84-91.
[13] G.E. Kahnert, W. Jeitschko, *J. Alloys Compd.* 196 (1993) 199-205.
[14] U.A. Böcker, W. Jeitschko, *J. Alloys Compd.* 243 (1996) L8-L10.
[15] U.A. Böcker, W. Jeitschko, G. Block, *J. Alloys Compd.* 236 (1996) 58-62.
[16] K. Zeppenfeld, R. Pöttgen, M Reehuis, W. Jeitschko, R.K. Behrens, *J. Phys. Chem. Solids* 54 (1993) 257-261.
[17] M.E. Danebrock, W. Jeitschko, A.M. White, R. Pöttgen, *J. Phys. Chem. Solids* 56 (1995) 807-811.
[18] U.E. Musanke, W. Jeitschko, M.E. Danebrock, *Z. Anorg. Allg. Chem.* 619 (1993) 321-326.