ROENTGENOGRAPHIC AND THERMODYNAMIC STUDY OF THE EXISTENCE OF MIXED CRYSTALS IN THE LaC$_2$-YC$_2$ SYSTEM*

Bohumil Hájek, Vladimír Kohout and Vratislav Flemr

*Department of Inorganic Chemistry,
Prague Institute of Chemical Technology, 166 28 Prague 6*

The reaction heats for the mixed crystal formation in the LaC$_2$-YC$_2$ system were obtained from the equilibrium gas pressures measured during the carboreduction. The low positive values of the reaction heats are consistent with the X-ray diffraction study of the carbothermal reduction products of the oxides, where the formation of the (La, Y)C$_2$ dicarbide mixed crystals was only observed in the two side regions up to 25 mol.% of each of the minority components. The composition of the gaseous hydrolysis products of the (La, Y)C$_2$ mixed crystals corresponds to the hydrolysis products of the dicarbide. No methane was detected for samples with low yttrium contents.

Dicarbides of rare earth elements, MC$_2$, are all dimorphic; the low-temperature tetragonal modifications of CaC$_2$-I type are transformed into the cubic modification at higher temperatures. The transformation temperatures increase with decreasing metal atom size[1], because the smaller the atom in size, the greater strain can be expected in the cubic structure containing the bulky C$_2$ groups. For LaC$_2$ and YC$_2$ the transformation temperatures are 1 060 and 1 320°C, respectively[2].

The strain in the cubic structure can be also relieved by partly substituting the metal atoms by atoms of another rare earth element. For mixed dicarbides of rare earth elements present in the equimolar ratio the transformation temperature is lowered, and if the cations do not differ in size too much (the relative difference in the cation radii $(M_1^{3+} - M_2^{3+})/M_1^{3+}$ should not exceed[5−7] 14−18%), the cubic phase is even steady at room temperature. This condition is met for the LaC$_2$-YC$_2$ system $(r_{La^{3+}} = 106 \cdot 1$ pm, ref.[8], and $r_{Y^{3+}} = 88$ pm, ref.[9]), for which Adachi and coworkers[3,4] found tetragonal mixed crystals within the side regions only, up to 30 mol% of the minority component; in the equimolar composition range the face centered cubic phase was observed.

In the La$_2$O$_3$-Y$_2$O$_3$ system, mixed crystals are also formed in the side regions

---

only, up to about 30 mol % of each of the minority components; the Y_2O_3-based mixed crystals are cubic and the La_2O_3-based crystals are hexagonal. At the 1 : 1 molar ratio a rhombic perovskite phase[10] of $LaYO_2$ is formed.

Since the carbide samples were prepared by us with an Exhalograph EA-1 instrument which can be adapted for monitoring the equilibrium pressures during the carboreduction, we aimed to supplement the X-ray diffraction study of Adachi and coworkers[3,4] with a thermodynamic study of the reaction heats in the LaC_2–YC_2 system. Another objective of this work was to investigate the hydrolysis of $(La,Y)C_2$ in view of the fact that in contrast to the LaC_2 dicarbide[11-15], the hydrolysis products of YC_2 prepared by carbothermal reduction of the oxide invariably contained some amounts of methane[11,13] which indicates that irremovable residual carbide--oxide intermediates of the carbothermal reduction were probably present.

EXPERIMENTAL

Preparation of Starting Mixtures for Carboreduction

Mixtures of Y_2O_3 of 99·9% purity (Reakhim, USSR) and La_2O_3 of 99·8% purity (Lachema, Brno), whose purity was checked by spectral analysis, were dissolved in minimal amounts of nitric acid of reagent grade purity (Lachema, Brno) and diluted. The hydroxides were precipitated with 10% ammonia, filtered out, and heated in a platinum crucible at 1 000°C for 10 h. The products were analyzed for La and Y and characterized by their X-ray diffraction patterns. The reaction mixtures for the carboreduction were prepared by mixing the mixed oxide crystals with granulated carbon black of 99·999% purity (Pramet, Šumperk) in a ratio such as to comply with the equation

$$a\,La_2O_3 + b\,Y_2O_3 + 7\,(a+b)\,C \rightarrow 2a\,LaC_2.2b\,YC_2 + 3(a+b)\,CO\,, \qquad (A)$$
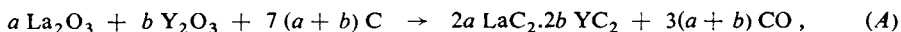
homogenizing in an agate mortar, pressing into pellets in a hand press.

Carbothermal Reduction

The carboreduction was conducted in an adapted steady-state vacuum furnace of an Exhalograph EA-1 instrument (Balzers, Liechtenstein). The temperature was slowly increased to the preselected value so that the pressure inside the furnace was constantly $1·3332 . 10^{-2}$ Pa. The carboreduction was carried out at 1 880°C, the time of heating was 6 h. The mixed crystals obtained were gold-yellow in colour and showed a metallic lustre.

X-Ray Diffraction Measurements

A Geigerflex diffractograph (Rigaku Denki) working with CoK_α radiation was used; Fe filter, GM tube detector, scanning region 2—70°. Undergoing rapidly hydrolysis, the carbides had to be ground quickly in a mortar with Canada balsam, and the X-ray diffraction measurements had to be performed immediately.

Hydrolysis Study

Samples of the mixed dicarbides were hydrolyzed with water at ambient temperature and the gaseous hydrolysis products were analyzed gas chromatographically on a Chrom 41 instrument (Laboratorní přístroje, Prague) equipped with a flame ionization detector for hydrocarbons and a thermal conductivity detector for hydrogen.

The components were identified by the internal standard method and quantitated by calibration with standards. The chromatographic peak areas were measured planimetrically and the component concentrations were obtained by means of calibration graphs for the standards, by multiplication by Onkiehong's factor[16] and conversion to percentage volumes.

Equilibrium Gas Pressures During Carbothermal Reduction

The measurements were performed on the Exhalograph apparatus. After a perfect degassing of the furnace, at 600°C the rotary and diffusion air pumps were disengaged and the furnace was closed, the temperature was raised, the equilibrium was allowed to establish, and the pressure inside the furnace was read on a pointer pressure gauge. Each measurement was repeated five times and the average value was used. The oxide of carbon formed primarily during the carbothermal reduction was carbon monoxide; however, since between the reaction zone and the pressure gauge the CO formed passed through regions of decreasing temperature where it came in contact with large areas of the graphite components of the apparatus, the disproportionation reaction

$$2\,CO \;\rightleftharpoons\; CO_2 + C \tag{B}$$

took place to a great extent and the gas actually measured was carbon dioxide.

RESULTS AND DISCUSSION

The X-ray diffraction analysis of the samples prepared confirmed the results of Adachi and coworkers concerning the LaC_2–YC_2 system where smooth series of mixed dicarbide crystals are formed in the two side regions up to minimally 25 mol % of the minority component (Fig. 1). The chemical composition of the solid dicarbide
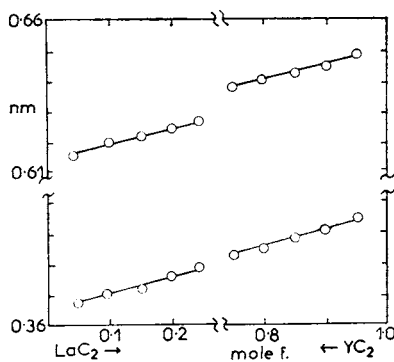
FIG. 1

Dependence of the lattice parameters of mixed dicarbides in the La–Y–C system system on composition

solutions is given in Table I. In the middle region, however, a mixture of the two tetragonal mixed crystals was observed by us rather than the cubic $LaC_2.YC_2$ phase.

The hydrocarbon contents of the gaseous hydrolysis products (Table II) agree well with those for the hydrolysis of pure LaC_2 (refs[11−15]) and YC_2 (refs[11−13]). The major hydrolysis products are acetylene (60−70 vol.%) and C_2 hydrocarbon (20−25 vol.%); higher saturated and unsaturated C_4 hydrocarbons and hydrogen (∼2 vol.%) are also present. The hydrolysis products of samples with higher yttrium contents contained also methane, which is always present in the gaseous hydrolysis products of YC_2.
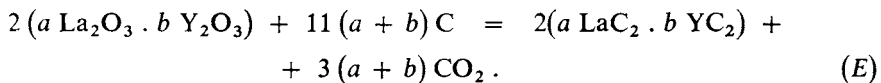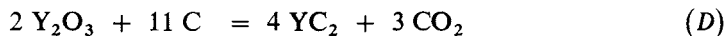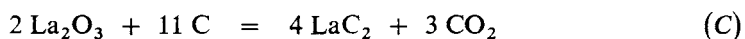
The temperature dependence of the equilibrium pressures above the reaction mixture can be evaluated to obtain the reaction heats for the carboreduction of the mixed crystals or the pure dicarbides, and these, in conjunction with the heats of mixing of the oxides evaluated by analysis of the phase diagram, can be used to estimate the heat of mixing for the formation of mixed crystals for the two dicarbides and thus to assess the tendency to the formation of new phases in the system. In view of the fact that no phase diagrams or other equilibrium data are available for mixture of the two dicarbides in question or for other dicarbide mixtures, this information is of importance for estimating the phase stability in the LaC_2–YC_2 system.

TABLE I

Results of chemical analysis of $(La_xY_{1-x})C_2$ mixed dicarbides

Carbide	Molecular weight (theor.)	Calculated/Found				Δ^a %
		% La	% Y	% C_{bond}	C_{free}	
$La_{0.90}Y_{0.10}C_2$	157·9	79·16	5·63	15·21	—	—
		75·3	4·9	14·1	3·6	2·1
$La_{0.85}Y_{0.15}C_2$	155·4	75·97	8·58	15·45	—	—
		73·3	7·3	13·8	2·5	3·1
$La_{0.75}Y_{0.25}C_2$	150·4	69·26	14·77	15·97	—	—
		68·6	13·1	14·2	1·5	2·6
$La_{0.25}Y_{0.75}C_2$	124·5	27·69	53·16	19·15	—	—
		25·9	50·1	17·9	2·9	3·2
$La_{0.15}Y_{0.85}C_2$	120·4	17·30	62·75	19·95	—	—
		16·5	61·2	19·7	1·1	1·5
$La_{0.10}Y_{0.90}C_2$	117·9	11·78	67·85	20·37	—	—
		10·2	64·3	18·1	3·9	3·5

[a] Balance to 100%, includes inaccuracy of analysis and bonded nitrogen and oxygen (carbide-oxides and carbide-nitrides), which were not determined.

With regard to the fact that the gas measured was carbon dioxide, the overall process of the carbothermal reduction of the oxides and their mixed crystals should be written as

$$2 La_2O_3 + 11 C = 4 LaC_2 + 3 CO_2 \qquad (C)$$

$$2 Y_2O_3 + 11 C = 4 YC_2 + 3 CO_2 \qquad (D)$$

$$2 (a\ La_2O_3 . b\ Y_2O_3) + 11 (a + b) C = 2(a\ LaC_2 . b\ YC_2) +$$
$$+ 3 (a + b) CO_2 . \qquad (E)$$

Choosing the pure component at the temperature of the system and at normal pressure as the standard state, the equilibrium constant of carboreduction is

$$K_3, K_4 = P_{CO_2}^{*3}$$

where
$$K_5 = P_{CO_2}^{*3(a+b)}$$

$$P_{CO_2}^* = P_{CO_2}/P_{normal}$$

The reaction heat of the carboreduction can be evaluated based on the Van't Hoff reaction isobar for (i),

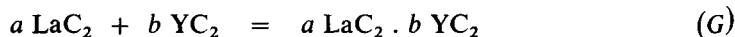$$[\partial \ln K_i/\partial T]_P = \Delta H_i/RT^2 .$$

TABLE II

Composition of products obtained by hydrolysis of $La_xY_{1-x}C_2$ mixed dicarbides with water at 25°C

Product	Content, %, for x value of					
	0·90	0·85	0·75	0·10	0·15	0·25
Hydrogen	0·79	1·15	0·82	2·16	10·77	2·35
Methane	—	—	—	0·49	3·87	7·46
Ethane + ethene	17·88	25·64	23·05	23·09	21·65	27·04
Ethyne	76·17	67·83	72·02	68·9	60·07	57·31
n-Butane	0·23	0·31	0·26	0·07	0·39	0·12
n-Butene	2·67	2·23	1·91	2·90	1·49	2·65
trans-2-Butene	0·62	0·62	0·64	0·72	0·37	0·70
cis-2-Butene	0·56	0·56	0·29	0·58	0·19	0·64
1,3-Butadiene	0·13	0·21	—	0·07	0·12	0·39
1,2-Butadiene	—	0·02	—	—	—	—
1-Butyne	0·95	1·43	1·01	1·02	1·08	1·34

Substracting the heats of reactions (C) and (D) from the heat of reaction (E) and adding the heat of reaction

$$2a \, La_2O_3 \; + \; 2b \, Y_2O_3 \;\; = \;\; 2 \, (a \, La_2O_3 \, . \, b \, Y_2O_3) \qquad\qquad (F)$$
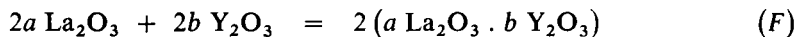
the reaction heat of the carbide formation

$$a \, LaC_2 \; + \; b \, YC_2 \;\; = \;\; a \, LaC_2 \, . \, b \, YC_2 \qquad\qquad (G)$$

is obtained, hence,

$$\Delta H_7 = \Delta H_5 + \Delta H_6 - a \, \Delta H_3 - b \, \Delta H_4 \, . \qquad\qquad (1)$$

High negative ΔH_7 values indicate a tendency to the formation of new phases whereas positive values are indicative of the occurrence of solid solutions in the dicarbides over a limited concentration region.

The heats of mixing for the oxides, *i.e.*, the reaction heats ΔH_6, are not experimentally available; approximate values, however, can be derived from the phase diagrams. Assuming the simplest nonideal, *viz.* the so-called regular, thermodynamic behaviour in the La_2O_3–Y_2O_3 system, the chemical potentials of the components can be expressed as

$$\mu_i = \mu_i^0 + RT \ln x_i + ART(1 - x_i)^2 \, , \qquad\qquad (2)$$

where x_i is the mole fraction of component i and A is a constant characteristic of the system.

The phase diagram of the La_2O_3–Y_2O_3 system shows that the two components are mutually sparingly soluble. For component i in the coexisting phases we have

$$\ln \left(x_i(\alpha) \right) + A(1 - x_i((\alpha))^2 = \ln \left(x_i(\beta) \right) + A(1 - x_i(\beta))^2 \, , \qquad\qquad (3)$$

where α and β denote the two solid solutions.

Parameter A thus can be evaluated by substituting for the concentrations of the two coexisting phases,

$$A = \left[\ln x_i(\beta)/x_i(\alpha) \right]/\left[(1 - x_i(\alpha))^2 - (1 - x_i(\beta))^2 \right] \, . \qquad\qquad (4)$$

The phase diagram for the La_2O_3–Y_2O_3 system[17] was analyzed and the regular model was found to suit well over a wide temperature region near 1 500°C; the A value is about 2·5. Hence, the heat of mixing in this system obeys the relation

$$\Delta H_6 = 2{\cdot}5RT \, ab/(a + b)^2 \, . \qquad\qquad (5)$$

The values obtained by pressure measurements in the reaction space during the reduction of La_2O_3 and Y_2O_3 are given in Table III, those for the reduction of the mixed oxide crystals $(La_xY_{1-x})_2O_3$, are given in Table IV. These were processed by the least squares method to fit the equation

$$\ln P^*_{CO_2} = A(1/T) + B, \qquad (6)$$

and the reaction heats of carboreductions $(C)-(E)$ were obtained. For La_2O_3

TABLE III

Carbon dioxide pressures observed during the carboreduction of La_2O_3 and Y_2O_3

T, K	$P^*_{CO_2}$, Pa	
	La_2O_3	Y_2O_3
1 800	$5\cdot9 . 10^{-4}$	$7 . 10^{-6}$
1 900	$2\cdot6 . 10^{-4}$	$6\cdot5 . 10^{-5}$
2 000	$1\cdot97 . 10^{-3}$	$3\cdot9 . 10^{-4}$
2 100	$5\cdot26 . 10^{-3}$	$1\cdot97 . 10^{-3}$
2 200	$1\cdot84 . 10^{-2}$	$9\cdot21 . 10^{-3}$
2 300	$6\cdot97 . 10^{-2}$	$3\cdot36 . 10^{-2}$
2 400	$2\cdot11 . 10^{-1}$	$1\cdot12 . 10^{-1}$
2 500	$5\cdot26 . 10^{-1}$	$4\cdot47 . 10^{-1}$

TABLE IV

Carbon dioxide pressure observed during the carboreduction of $(La_xY_{1-x})_2O_3$ mixed oxides

T, K	$P^*_{CO_2}$, Pa		
	$x = 0\cdot5$	$x = 0\cdot25$	$x = 0\cdot75$
1 800	$2\cdot0 . 10^{-5}$	$1\cdot5 . 10^{-5}$	$2\cdot6 . 10^{-5}$
1 900	$1\cdot3 . 10^{-4}$	$1\cdot0 . 10^{-4}$	$1\cdot8 . 10^{-4}$
2 000	$7\cdot4 . 10^{-4}$	$5\cdot9 . 10^{-4}$	$9\cdot5 . 10^{-4}$
2 100	$3\cdot5 . 10^{-3}$	$2\cdot88 . 10^{-3}$	$4\cdot2 . 10^{-3}$
2 200	$1\cdot4 . 10^{-2}$	$1\cdot22 . 10^{-2}$	$1\cdot64 . 10^{-2}$
2 300	$5\cdot0 . 10^{-2}$	$4\cdot54 . 10^{-2}$	$5\cdot66 . 10^{-2}$
2 400	$1\cdot62 . 10^{-1}$	$1\cdot52 . 10^{-1}$	$1\cdot76 . 10^{-1}$
2 500	$4\cdot74 . 10^{-1}$	$4\cdot61 . 10^{-1}$	$5\cdot0 . 10^{-1}$

Y_2O_3, $(La_{0.75}Y_{0.25})_2O_3$, $(La_{0.50}Y_{0.50})_2O_3$, and $(La_{0.25}Y_{0.75})_2O_3$, the reaction heats of carboreduction are ΔH_{red} = 1 470, 1 760, 1 570, 1 620, and 1 670 kJ mol^{-1}, respectively. The heats of formation of the mixed dicarbide crystals were calculated by substituting in Eq. (1); for $La_{0.75}O_{0.25}C_2$, $La_{0.5}Y_{0.5}C_2$, and $La_{0.25}Y_{0.75}C_2$, the values of ΔH_7 = 13, 20, and 11 kJ mol^{-1} were obtained.

Lying in the range of small positive values, the ΔH_7 heats indicate that in the LaC_2–YC_2 system at temperatures above 1 500°C the occurrence of new intermediate phases is improbable and the mixed crystal formation should take place in the side concentration regions only. This is consistent with the X-ray diffraction data giving evidence that in the equimolar composition range, a mixture of the two mixed dicarbide crystals occurs at low temperaturs.

REFERENCES

1. McColm T. J., Quigley T. A., Clark N. J.: Inorg. Nucl. Chem. *35*, 1931 (1973).
2. Bowman A. L., Krikorian N. H., Arnold G. P., Wallace T. C., Nereson N. G.: US At. Energy Comm. La-DC-8451, CESTI (1967).
3. Adachi G., Kotoni H., Yoshida N., Shiokawa I.: J. Less-Common Metals *22*, 517 (1970).
4. Adachi G., Nishihata I., Shiokawa I.: J. Less-Common Met. *32*, 301 (1973).
5. Adachi G., Tonomura F., Shiokawa I.: *Proc. 12th Rare Earth Res. Conference*, Vol. 1, 512 (1976).
6. Adachi G., Shibata Y., Ueno K., Shiokawa I.: Inorg. Nucl. Chem. *38*, 1023 (1976).
7. Loe I. R., McColm I. J., Quingley T. A.: J. Less-Common Met. *46*, 217 (1976).
8. Templeton D. H., Dauben C. H.: J. Amer. Chem. Soc. *76*, 5237 (1954).
9. Zachariasen W. H., Seaborg V. G. T., Katz J. J.: *The Actinide Elements*, p. 18. Mc Graw-Hill, New York 1954.
10. Padurow N. N., Schusterius C.: Ber. Deut. Keram. Ges. *32*, 292 (1955).
11. Hájek B., Brožek V., Popl M., Mostecký J.: This Journal *36*, 3236 (1971).
12. Kosolapova T. J., Makarenko G. N., Domashevich L. T.: Zh. Prikl. Khim. *44*, 953 (1971).
13. Pollard F. H., Nickless G., Evered S.: J. Chromatogr. *15*, 211 (1964).
14. Greenwood N. N., Osborn A. J.: J. Chem. Soc. *2*, 1775 (1961).
15. Svec H. J., Capellen J., Saafeld F. E.: J. Inorg. Nucl. Chem. *26*, 721 (1964).
16. Onkiehong L.: *Thesis.* Technical University, Eindhoven 1960.
17. Cassedane J., Forestier H.: C. R. Acad. Sci. *253*, 2953 (1961).

Translated by P. Adámek.