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**CONTAMINATION BY OXYGEN AND NITROGEN DURING  
THE HIGH-TEMPERATURE SYNTHESIS OF RARE EARTH  
ELEMENT CARBIDES AND THE HYDROCARBON CONTENTS  
OF THEIR HYDROLYSIS PRODUCTS\***

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Contamination of reaction mixtures of rare earth elements and carbon by air oxygen and nitrogen at high temperatures results in changes in the phase composition of the products, which in turn lead to changes in the composition of the hydrolysis gas. La, Ce, Pr, and Nd give carbide-oxides  $Ln_2O_2C_2$  of acetylide nature, in concentrations increasing with increasing extent of contamination. For the "smaller" rare earth elements from Dy, Ho to Lu, the contamination leads to methanide-type carbide-oxides (or nitrides)  $M(C, N, O, \square)$ . A slight contamination of mixtures of the metals with carbon which are somewhat carbon-deficient with respect to the 1 : 2 composition gives rise to a phase which evolves a gas containing  $C_3$  hydrocarbons in a high concentration (nearly 50%), while its methane content is very low. The stability of this allylenide phase, which is not the  $M_{15}C_{19}$  carbide, increases in the direction towards Lu to an extent such that the phase forms even besides higher amounts of the carbide-oxide-nitride, *i.e.*, also on extensive contamination.

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Formulation of unique relations between the presence of  $C_1$ ,  $C_2$  or  $C_3$  groups in the structures of rare earth element carbides and the nature of the corresponding gaseous hydrolysis products in the form of natural, even or  $C_{3n}$  ( $n = 1, 2, \dots$ ) hydrocarbon sequences, respectively, is complicated by the fact that for dicarbides or sesquicarbides of rare earth elements having atomic radii smaller than gadolinium, the even hydrocarbons are accompanied by odd ones (particularly methane) irrespective of whether the carbides were prepared by carbothermal reduction of the oxides<sup>1-6</sup> or by reaction of the metals with carbon<sup>7,8</sup>.

We have studied this problem<sup>6,9-14</sup> on dicarbides prepared by carboreduction of the oxides and were able to demonstrate that the presence of the odd hydrocarbons in the hydrolysis products are to be ascribed to phase impurities rather than thermal or radical splitting of the  $C_2$  groups in the dicarbides. The carboreduction conditions were modified (carbon deficit, lower temperature, higher CO pressure) to obtain samples richer in the methanide-type impurity, and the latter was identified as the intermediate product in the carboreduction of sesquioxides of rare earth elements

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with smaller atomic radii, *viz.*, the carbide-oxide  $M_2OC$  (refs<sup>13-15</sup>). The composition of the hydrolysis product, characterized by a  $C_3$  hydrocarbon content, was determined<sup>16</sup> for the  $Sc_{1.5}C_{1.9}$  phase. This phase then was found<sup>17</sup> to be the ultimate carboreduction product just for scandium; in this respect scandium differs from the other rare earth elements.

In the present work, this topic is studied for carbides prepared by reaction of the metals with carbon, particularly with respect to the problem of whether the composition of the hydrolysis product gas varies with increasing contamination of the reaction mixture by air at high temperatures and whether this change is associated with an adequate change in the phase composition of the sample, with a view to making use of this fact for the identification of the hydrolyzable phase impurity of the carbide-oxide(-nitride). This assumed phase impurity could not be detected by X-ray diffraction measurements<sup>7,8</sup>, and its presence can only be inferred from the reported composition of the hydrolysis products.

## EXPERIMENTAL

*High-temperature contamination by air.* The compact metals, *viz.* yttrium 99.9% (BDH, England), lanthanum 99% and lutetium 99% (both Soyuzkhimeksport, Moscow) were filed under cetane to obtain particles about 0.07 mm in size. A holmium wire (99%, Metals Res., England) was disintegrated in a tungsten carbide mortar. Dysprosium dust 99% (Schuchard, Munich) was used as received. The batches of the metals were mixed with granulated carbon black of purity better than 99.999% (Pramet, Šumperk), homogenized under *n*-heptane in a tungsten carbide vibration mill, pressed into pellets about 1 g weight, and heated in an Exhalograph EA-1 instrument (Balzers, Liechtenstein) at 1400–1700°C in zirconium diboride (La, Y) or tantalum metal (others) crucibles. During the sintering of the yttrium or lanthanum-containing samples, the 2 l furnace space was evacuated to  $1.3 \cdot 10^{-2}$  Pa pressure, attained at 1000°C. Air was then admitted to a pressure of 6–200 Pa, which was held constant during the high-temperature reaction by means of a rotary pump. Samples with Dy, Ho or Lu were heated under argon containing 2 wt. % air at a total pressure of 0.4–50 kPa. The reaction conditions are given in detail in Tables I, II, and IV.

*Hydrolysis and gas chromatographic analysis of the products.* The samples were hydrolyzed with water at 20°C to a complete decomposition. The hydrolysis products were analyzed on a Hewlett-Packard 5840A gas chromatograph as previously<sup>16</sup>.

*Chemical analysis of the solid samples.* The samples were dissolved in concentrated  $HNO_3$  of reagent grade purity and the metals were determined chelometrically using xylenol orange as the indicator<sup>18,19</sup>. Total carbon was determined by combustion in an oxygen stream using a KEHR type Coulomat Ströhlein instrument. Free carbon was determined likewise after dissolving the sample in concentrated HCl of reagent grade purity and filtering the carbon out on a prepared asbestos filter.

*X-ray diffraction analysis.* The X-ray diffraction patterns were obtained<sup>16</sup> and evaluated by employing published and calculated diffractograms of the corresponding carbides, oxides, nitrides, and carbide-oxides.

## RESULTS AND DISCUSSION

The contamination during the reaction of lanthanum metal with carbon gave rise to the carbide-oxide  $\text{La}_2\text{O}_2\text{C}_2$ . Its amount, as determined by X-ray diffraction, is higher after a longer time of contamination and for a more pronounced carbon deficit of the starting mixture. The largest amounts of  $\text{La}_2\text{O}_2\text{C}_2$  are found in the dust portion of the sample, which also affects considerably the composition of the hydrolysis product. Containing  $\text{C}_2$  carbon groups in its structure<sup>20</sup>,  $\text{La}_2\text{O}_2\text{C}_2$  hydrolyzes<sup>21</sup> to give  $\text{C}_2\text{H}_2$ . Thus, the composition of the hydrolysis product given in Table I is a sum of the sequence of even hydrocarbons from  $\text{LaC}_2$  and ethyne from  $\text{La}_2\text{O}_2\text{C}_2$ . The trace quantities of methane and  $\text{C}_3$  hydrocarbons can be attributed to impurities (Y and heavier rare earth elements) in the starting lanthanum.

TABLE I

Conditions of reaction of lanthanum with carbon accompanied by atmospheric contamination and results of analysis of the reaction and hydrolysis products

	La : C sample				
	2 : 3	15 : 19 A	15 : 19 B	15 : 19 C	15 : 19 dust
Reaction conditions					
Temperature, °C	1 500	1 400	1 400	1 400	
Reaction time, h	63	43	43	24	
Pressure in furnace, Pa	66	6·6	33	200	
X-ray phase analysis					
Major phase	$\text{LaC}_2^a$	$\text{LaC}_2$	$\text{LaC}_2$	$\text{LaC}_2$	$\text{La}_2\text{O}_2\text{C}_2$
Minor phase		$\text{La}_2\text{O}_2\text{C}_2$	$\text{La}_2\text{O}_2\text{C}_2$	$\text{La}_2\text{O}_2\text{C}_2$	
GLC analysis of hydrolysis products (mole %)					
$\text{H}_2$	4·8	4·0	3·7	5·0	2·6
$\text{CH}_4$	0·07	—	—	—	0·2
$\text{C}_2$ hydrocarbons	92	94·1	94·4	92·3	96·3
$\text{C}_3$ hydrocarbons	0·14	0·04	0·04	0·04	0·09
$\text{C}_4$ hydrocarbons	2·4	1·5	1·6	2·0	0·52
$\text{C}_5$ hydrocarbons	—	—	—	—	—
$\text{C}_6$ hydrocarbons	0·57	0·21	0·37	0·49	0·23
H/C molar ratio	1·5	<i>b</i>	<i>b</i>	<i>b</i>	1·09

<sup>a</sup> A fraction of lanthanum evaporated; <sup>b</sup> the fractions of  $\text{C}_2\text{H}_2$  and  $\text{C}_2\text{H}_4$  in the  $\text{C}_2$  hydrocarbon mixture were not determined.

During the reaction of yttrium metal with carbon, the extensive contamination by the "vacuum" air of the rotary pump leads to oxidation of a part of the sample as far as the oxide,  $Y_2O_3$ . Subject to oxidation is mainly the free metal, unreacted carbon remaining in the mixture after a shorter time of reaction (Table II, last column). The reaction of the forming  $Y_2O_3$ , remaining metal, carbon, and, possibly,  $YC_2$ , gives rise – particularly at reduced carbon contents of the starting mixture (15Y : 19C) and at lower temperatures – to a product which contains the carbide-oxide ( $NH_4^+$  detection after hydrolysis is negative) and whose hydrolysis gives as

TABLE II

Conditions of reaction of yttrium with carbon accompanied by atmospheric contamination and results of analysis of the reaction and hydrolysis products

	Y : C sample				
	15 : 19 A	15 : 19 B	2 : 3 A	2 : 3 B	2 : 3 C
Reaction conditions					
Temperature, °C	1 450	1 500	1 500	1 500	1 500
Reaction time, h	24	41	48	85	23
Pressure in furnace, Pa	200	200	200	20	200
X-ray diffraction analysis					
Major phase	X	$YC_2$	$YC_2$	$YC_2$	$Y_2O_3$
Minor phase	$YC_2$	$Y_2O_3$ (40%)	X	$Y_2O_3$ (20%)	$YC_2$ YN
Chemical analysis (wt. %)					
Free carbon	0.5	—	—	—	10
Total carbon	15	16	17	17	18
Yttrium	76.3	79.6	76.3	80	71
Balance deficit	~8	~4	~6	~3	~11
GLC analysis of hydrolysis products (mole %)					
$H_2$	2.4	1.5	2.9	2.0	7.7
$CH_4$	1.2	4.0	2.7	4.4	3.7
$C_2$ hydrocarbons	53	84	73	82	68
$C_3$ hydrocarbons	40	3.6	19	6.7	18
$C_4$ hydrocarbons	2.6	3.2	2.5	3.7	2.9
$C_5$ hydrocarbons	0.03	—	—	0.14	0.04
$C_6$ hydrocarbons	0.7	0.4	0.4	1.2	0.4
H/C molar ratio	1.46	1.45	1.47	1.51	1.53

much as 40 vol.%  $C_3$  hydrocarbons ( $C_3H_4$  in particular). This is 15 times more than the amount observed in ref.<sup>7</sup> on the hydrolysis of an "yttrium sesquicarbide" sample. The methane content, comparable to that in ref.<sup>7</sup>, only indicates a possible presence of a small amount of the  $Y_1(O, C)_{1-x}$  cubic phase, which was not detected by X-ray diffraction. The qualitative X-ray analysis of the 15 : 19 A sample (Table II) did not give evidence of the presence of any of the phases of the Y-O-C system reported in the literature, viz. NaCl type  $Y(O, C, \square)$ ,  $YC_2$ ,  $Y_2C_3$ ,  $Y_{15}C_{19}$ , Y,  $Y_2O_3$ ;  $\delta$ -phase<sup>22</sup>;  $\alpha$ - $Y_5C_6$  or  $\alpha$ - $Y_2C_3$  (ref.<sup>23</sup>); or solid hydrolysis products. The diffraction patterns only resemble those of  $Y_{15}C_{19}$  (Table III); attempted indexing, however, failed. That the substance is not  $Y_{15}C_{19}$  is also evidenced by the hydrolysis product of 15 : 19 A sample where the H/C ratio is 1.46, in contrast to the 2.37 expected for  $Y_{15}C_{19}$ . The balance of data in Table II, viz., the elemental composition of the 15 : 19 A and 2 : 3 A samples established by chemical analysis and the composition of the hydrolysis product gas, indicates that the composition of the unknown phase, present besides  $YC_2$ , is about  $YO_{0.5+x}C_{1.4-y}$ , where x and y are between 0 and 0.1.

At higher carbon contents of the batches and somewhat higher temperatures (Y 2 : 3 A, C samples), the X-ray diffraction patterns exhibit reflections of yttrium dicarbide. The concentration of  $C_3$  hydrocarbons in the gas hydrolysis products decreases accordingly. Higher temperatures, longer reaction times or lower pressures apparently favour the reaction of the oxygen, bonded by yttrium, and carbon in the sense of carboreduction, and the stability of the unknown carbide-oxide phase with respect to  $YC_2$  and  $Y_2O_3$  decreases.

TABLE III

The first 15 observed powder X-ray diffraction data ( $CuK_\alpha$  radiation) of Y 15 : 19 A sample, giving 40%  $C_3$  hydrocarbons on hydrolysis

$1\theta$ Diffraction angle, deg	Relative intensity	$1\theta$ Diffraction angle, deg	Relative intensity
12.89	14	22.19	12
14.05	100	23.78	15
14.62	35	24.21	20
15.18	17	25.12	21
16.81	55	26.12	37
17.60	36	29.24	21
17.90	33	30.24	14
19.51	10		

Dysprosium, holmium, and lutetium metals subjected to reaction with carbon in argon atmosphere contaminated by air afford NaCl type cubic phases of the carbide-oxides(-nitrides) of methanide nature. A comparison of the lattice parameters  $a$  of these phases with the lattice parameter diagram for rare earth metal mono-nitrides, carbide-oxides  $M_2OC$  and carbides  $M_2C$  (ref.<sup>15</sup>) indicates that the nitrogen content of the cubic phase in question is low, particularly for dysprosium. The forma-

TABLE IV

Conditions of reactions of dysprosium, holmium, and lutetium with carbon accompanied by atmospheric contamination and results of analysis of the reaction and hydrolysis products

	M : C sample				
	Dy 15 : 19	Dy 1 : 1 A	Dy 1 : 1 B	Ho 15 : 19	Lu 15 : 19
Reaction conditions					
Temperature, °C	1 560	1 620	1 560	1 620	1 720
Reaction time, h	6	6	6	6	6
Pressure in furnace, kPa <sup>a</sup>	0.47	0.47	0.5–50	0.47	13
X-ray phase analysis					
Major phase	DyC <sub>2</sub>	Dy (C, N, O)	Dy (C, N, O) <sup>b</sup>	Ho (C, N, O) <sup>c</sup>	Lu <sub>2</sub> O <sub>3</sub>
Minor phase		?	DyC <sub>2</sub>	?	Lu(C, N, O) <sup>d</sup>
		DyC <sub>2</sub>			?
Chemical analysis (wt. %)					
Free carbon			0.3	—	3.3
Total carbon			6.3	7.7	8.3
Metal			91.6	91.1	89
Balance deficit			~2	~1	~3
GLC analysis of hydrolysis products (mole %)					
H <sub>2</sub>	14	11	18	11	1.0
CH <sub>4</sub>	2.5	23	54	36	50
C <sub>2</sub> hydrocarbons	80	40	19	46	3
C <sub>3</sub> hydrocarbons	1.1	20	5.4	3.3	46
C <sub>4</sub> hydrocarbons	1.8	4.5	2.8	3.1	0.07
C <sub>5</sub> hydrocarbons	0.02	0.2	0.4	0.2	0.02
C <sub>6</sub> hydrocarbons	0.7	1.1	0.5	0.5	0.6
H/C molar ratio	1.49	1.93	3.01	2.22	2.24

<sup>a</sup> Argon + air; <sup>b</sup>  $a = 497$  pm; <sup>c</sup>  $a = 492$  pm; <sup>d</sup>  $a = 480.8$  pm (NaCl type).

tion and composition of the  $M_1(O, C, N)_1$  phase in the products (Table IV) correspond to the carbon content of the starting mixture and to the stability of these phases in the metal–oxygen–carbon system, which increases with decreasing metal atom size, as was demonstrated by us<sup>14</sup> on the Y–Sc–O, C and Dy–Sc–O, C systems. Table IV also shows that appreciable amounts of  $C_3$  hydrocarbons in the hydrolysis products were found for the reaction of dysprosium with carbon at a low pressure of the argon–air atmosphere, *i.e.*, for Dy 1 : 1 A sample, and for Lu 15 : 19 sample even at an extensive contamination (large amounts of Lu(C, N, O) and  $Lu_2O_3$ ). The concentration of 46 vol.%  $C_3$  hydrocarbons (of this, 60%  $C_3H_4$ , 32%  $C_3H_6$ , and 8%  $C_3H_8$ ), besides methane (of which a fraction, at least, arises from the Lu (C, N, O) phase) and a negligible amount of other hydrocarbons, is considerably higher than as obtained by hydrolysis of  $Sc_{15}C_{19}$ . Thus, in the direction towards lutetium, also the stability of the allylenide-type carbide-oxide phase increases, the low concentration of  $C_2$  hydrocarbons and absence of higher branched hydrocarbons in the hydrolysis product of the Lu 15 : 19 sample suggesting that in the structure of this phase,  $C_3$  groups are also present, in contrast to  $Sc_{15}C_{19}$ , where only  $C_1$  and  $C_2$  groups in a mutual contact occur. The fact that in the presence of oxygen (and nitrogen), the  $M_{15}C_{19}$  phase did not appear even at the corresponding proportions of the starting components, indicates that this carbide possesses a narrow homogeneity region in the metal–oxygen–carbon ternary system.

The results of the X-ray phase analysis of model contaminated samples in conjunction with the gas chromatographic data of their hydrolysis products confirm the suggested concept of contamination of a metal–carbon mixture by air at high temperatures making possible the formation of the carbide-oxides(-nitrides) as intermediate products in the total oxidation to the sesquioxide (or nitride).

As a consequence of the increasing amount of the carbide-oxide phase besides the carbide, found by X-ray phase analysis, the hydrolysis product contains hydrocarbons, or exhibit other characteristics, as are not peculiar to the major phase of the carbide. The results also demonstrate how the gas chromatographic analysis of the hydrolysis product can be of assistance in detecting trace quantities of impurities in the major carbide phase.

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