INVESTIGATION OF THE PRODUCTS OF CARBOTHERMAL REDUCTION OF YTTRIUM OXIDE BY THE HYDROLYSIS METHOD*

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For the investigation of the products of reaction of yttrium oxide with carbon mixed in various proportions, the chemical and X-ray diffraction methods of analysis were combined with the gas chromatographic analysis of the mixture of hydrocarbons and hydrogen formed on the sample decomposition with water. The carboreduction of Y_2O_3 was examined at relatively low temperatures, convenient for obtaining the reaction intermediates in higher yields. At 1 600°C and pressures of 10^{-3} Pa the reduction of a mixture of Y_2O_3 with carbon in a stoichiometric ratio of 1 : 7 yields YC_2 in equilibrium with 20% of Y_2OC phase. At lower carbon contents (down to the Y_2O_3 : : C ratio of 1 : 2) the fraction of the Y_2OC phase increases up to approximately 30%. In addition to Y_2O_3, the reaction mixture contains also Y_2C, Y_2OC and a phase giving propyne on hydrolysis. The presence of traces of C_3 hydrocarbons and small amounts of methane in the product of hydrolysis of the carbide sample prepared by the carbothermal reduction of the oxide can be explained in terms of the occurrence of the $Y_{15}C_{19}$ phase, probably substituted in part by oxygen, and of the Y_2OC phase. The results are compared with those obtained previously for the Sc_2O_3 + + C system.

Since its introduction by Moissan[1] in 1896, carbothermal reduction of yttrium oxide has become a routine method for the preparation of yttrium dicarbide. In addition to the expected even hydrocarbons, however, the gaseous product of hydrolysis of the dicarbide contains also methane and traces of C_3 hydrocarbons .The content of methane is of the order of 0·01 – 1%; the values found in literature[2-5] are higer the lower temperatures and/or less perfect vacuum are used in the synthesis of YC_2. In our previous papers[2,5] we have shown that hydrolysis of salt type dicarbides can never result in the formation of methane or odd hydrocarbons *via* the thermal scission of the primarily created ethyne, and so their occurrence among the products of hydrolysis of YC_2 is indicative of the presence of some phase impurities in the sample. In the investigation of the carbothermal reduction we directed our attention to the identification of the methanide, or propyne-yielding, hydrolyzable phase co-existing with the dicarbide in the Y—C—O system which has to be considered.

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According to Samsonov and coworkers[6], the reduction of yttrium oxide can result in the formation of the YC, Y_2C_3, and YC_2 phases; the authors, however, were unable to identify these products by X-ray diffraction measurements. The composition of the gaseous product of hydrolysis is not reported.

A complex study was therefore undertaken by us in which the X-ray diffraction analysis of the solid is combined with the gas chromatographic analysis of the hydrocarbons evolved during the hydrolysis. Mixtures of the starting substances in various proportions were employed and treated at a relatively low temperature of 1 600°C, which enabled us, as expected, to obtain yttrium dicarbide and additional phases in amounts sufficient for their identification.

EXPERIMENTAL

Carbothermal reduction of yttrium oxide. Yttrium oxide of 5N purity (for electronics) and granulated carbon black of 4N purity (Pramet, Šumperk) were mixed in stoichiometric proportions of 1 : 7 (samples *A*), 1 : 5·53 (samples *B*), and 1 : 2 (samples *C*), and the mixtures were pressed into pellets and sintered in the graphite crucible of an Exhalograph EA-1 instrument (Balzers, Liechtenstein). Temperature 1 600°C, final pressure above the reaction mixture $1{\cdot}3 \cdot 10^{-3}$ Pa, reaction time 43 h.

X-ray diffraction measurements. The X-ray diffractograms were obtained on a Mikrometa II instrument (Chirana, Prague) equipped with a goniometer and a GM tube and working with filtered CuK_α radiation. The planar samples were protected against humidity by means of a layer of paraffin oil with vaseline. The lattice parameters of the phases were determined by a statistical treatment employing the program[7], the theoretical diffraction patterns were calculated by the "Lazy Pulverix" program[8] on an IBM 370/135 computer.

Gas chromatographic analysis. Samples of the *A* and *B* series were decomposed with excess distilled water in an evacuated ampoule until the reaction was complete (5 min and 1 h for samples *A* and *B*, respectively). Samples of series *C* were treated with excess 50% sulphuric acid at 60°C; the reaction was complete in 2 days. The gas sampled was injected into a HP 5830 A gas chromatograph equipped with a 18850 A terminal (Hewlett–Packard). A thermal conductivity detector was used. The operation and data evaluation procedures were as reported previously[9].

Chemical analysis. The content of yttrium was determined chelometrically. The sample was dissolved in nitric acid, residues of yttrium oxide, if present, were dissolved at elevated temperatures. Carbon residues were filtered off, the acidity of filtrate was adjusted to pH 3—4 with urotropine, several drops of pyridine were added, and the solution was titrated with Chelaton III until the colour of xylenol orange indicator changed from violet to pure yellow. A back change of colour, if any, was corrected for with an additional portion of pyridine, and the solution was titrated further to the ultimate end point.

The content of the total and free carbon was determined, on the ignition of the sample or of an asbestos filter retaining the free carbon (after the dissolution of the sample in hot 50% H_2SO_4), on a Kehr Coulomat Ströhlein apparatus. The content of oxygen was determined on a Balzers EAO-202 Exhalograph. Nitrogen was detected by reaction with Nessler's reagent in the filtrate after filtering free carbon off.

RESULTS AND DISCUSSION

The products of the carbothermal reduction of yttrium oxide with carbon added in different proportions had different appearance. The pellets of series *A* had golden colour and contained gray inclusions.The samples of series *B* had surface of golden colour whereas in fracture the pellets were silver-gray. Samples of series *C* had golden-colour surface, a black core, and a gray interlayer. By X-ray diffraction analysis, samples *A* contained approximately 85% *bct* YC_2 phase ($a = 367{\cdot}0 \pm 0{\cdot}2$ pm, $c = 617 \pm 3$ pm) and 15% *fcc* phase ($a = 495{\cdot}9 \pm 0{\cdot}3$ pm). Samples *B* contained about 50% YC_2, 40% *fcc* phase ($a = 494{\cdot}7$ pm), and 10% Y_2O_3. Samples with the lowest starting content of carbon, *viz.* series *C*, contained only about 10% YC_2 and 90% *bcc* Y_2O_3 ($a = 1\,059{\cdot}6 \pm 0{\cdot}1$ pm). The lattice parameter of the starting yttrium oxide was $a = 1\,060{\cdot}1 \pm 0{\cdot}2$ pm.

The chemical analysis data indicate that the *fcc* phase composition corresponds roughly to the formula Y_2OC; the formula Y_4C_3O is less consistent with the chemical analysis for samples *A* and *B* .The reflection intensities for the *fcc* phase are in agreement with the calculated values for a mixed crystal of the hypothetical YO and YC structures of the NaCl type with an approximately equimolar ratio of these components (Fig. 1).

As indicated by the gas chromatography data, the occurrence of methane in the gaseous product of hydrolysis is associated with the presence of the *fcc* phase of Y_2OC in the sample. In order to facilitate the interpretation of the results, the values of the hydrocarbon product composition were converted to the fractions of gases formed on the hydrolysis of the components in the assumed ratios. Pure YC_2, containing C_2 groups, yields primarily ethyne and hydrogen, which react to give a series of even hydrocarbons. Methane arises from the hydrolysis of Y_2OC, as follows, *e.g.*, from the analogy with the carbide-oxide of scandium[10], Sc_2OC. However, neither YC_2

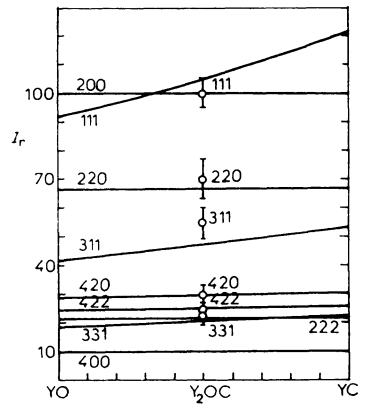

FIG. 1

Calculated relative intensities ($I_{200} = 100$) of the first nine reflections in the powder X-ray diffraction patterns of a series of YO and YC mixed crystals of the NaCl type (CuK_α radiation); a comparison with the observed reflection intensities of yttrium carbide-oxide

nor Y_2OC can account for the presence of C_3 hydrocarbons. We suggest that the phase responsible from them is $Y_{15}C_{19}$, although we were unable to detect this phase in the X-ray diffractograms because of its low concentration. We proceed from the assumption that the composition of the gaseous product of hydrolysis is the same as for the $Sc_{15}C_{19}$ phase:, *viz.* 55 vol.% CH_4, 10 vol.% C_2, 30 vol.% C_3, 3 vol.% C_4, 1 vol.% C_5, and 1 vol.% C_6 and higher hydrocarbons. The possible differences in the resulting phase composition due to the inaccurate estimate of the composition of the hydrolysis product of $Y_{15}C_{19}$ are discussed below.

The phase composition obtained based on the gas chromatographic analysis (Tables I–III) is in a good agreement with the chemical analysis data, particularly for samples *A*, and warrant the assumed approximate formula Y_2OC for the *fcc* phase The balance for samples *B* is affected to an extent by the presence of the unreacted Y_2O_3, which has been ignored. In fact, the elemental composition calculated based on the gas chromatographic analysis pertains to the hydrolyzable moiety, whereas the chemical analysis concerns the entire sample. The distribution of the mixture components in the sense of dehomogenization, leading to a simultaneous formation of YC_2 and Y_2OC besides Y_2O_3, seems to be due to a pressure gradient of CO in the pellet during the carbothermal reduction rather than an insufficient

TABLE I

Quantitative phase analysis of sample *A* based on the gas chromatographic analysis of the products of its hydrolysis. Elemental composition by GLC analysis and by chemical analysis, respectively (wt.%): yttrium 80·43, 80·37; bonded oxygen 1·47, 1·15; bonded carbon 18·10, 18·48

Hydrocarbons	Content, vol.%, from the phase			
	Y_2OC	YC_2	"$Y_{15}C_{19}$"	sample in total (phase mixture)
C_1	10·9	—	2·00	12·9
C_2	—	74·8	0·3	75·1
C_3	—	—	1·01	1·01
C_4	—	2·83	—	2·83
C_5	—	—	0·015	0·015
C_6	—	0·387	—	0·387
H_2				7·62
Phase content, mol.%	11·8	87·9	0·32	
wt.%	18·9	77·2	3·9	
H/C ratio[a]	4	1·5	45/19	

[a] H/C ratio corresponding to the calculated phase composition 1·68, H/C ratio in the gas mixture analyzed 1·69.

homogenization of the starting mixture. This is evident from the shall appearance of the pellets of series *C*. The hydrolyzable moiety of samples *C* constitutes as little as a quarter by weight of the pellet; the remaining part is Y_2O_3. For this reason, the balance for these samples was complemented by the elemental balance including Y_2O_3, based on the contents of yttrium and bonded carbon in the sample.

The balance calculations of the composition of the hydrocarbon gas evolved on the hydrolysis of carbides represent an extra means for the phase analysis of the solid concerned; in particular, it enables even trace amounts of the phases of hydrolyzable carbides, carbide-oxides, and the like to be detected and determined. The accuracy of the method is limited by the reproducibility of the hydrolytic decomposition and by the accuracy of the GLC analysis. In the particular case of sample *A*, the standard deviation for the determination of methane formed on the hydrolysis of various portions of the sample did not exceed ±0·25 (vol.% CH_4) even if the measurements were extended over a long time period (1 year); *n* was 2 + 2, so that the relative error was ±2%. Consider the inaccuracy in the estimate of the methane content in the product of hydrolysis of pure "$Y_{15}C_{19}$" to be as high as 15%; even then the error in the deterimation of the fraction of CH_4 formed from the Y_2OC phase will not ex-

TABLE II

Quantitative phase analysis of sample *B* based on the gas chromatographic analysis of the products of its hydrolysis. Elemental composition by GLC analysis and by chemical analysis, respectively (wt.%): yttrium 81·1, 80·6; bonded oxygen 2·44, 4·1; bonded carbon 16·5, 15·3

Hydrocarbons	Content, vol.%, from the phase			
	Y_2OC	YC_2	"$Y_{15}C_{19}$"	sample in total (phase mixture)
C_1	20·5	—	0·55	21·05
C_2	—	72·4	0·1	72·5
C_3	—	—	0·352	0·352
C_4	—	3·24	—	3·24
C_5	—	—	—	—
C_6	—	0·421	—	0·421
H_2				2·04
Phase content, mol.%	20·35	79·55	0·094	
wt.%	31·45	67·45	1·1	
H/C ratio[a]	4	1·5	45/19	

[a] H/C ratio corresponding to the calculated phase composition 1·79, H/C ratio in the gas mixture analyzed 1·77.

ceed ±4%. In this less favourable case the content of Y_2OC will only be 11·8 ± ± 0·6 mol.%, and the content of YC_2, 87·9 ± 0·6 mol.%. The elemental composition of sample calculated from the phase analysis data obtained by the hydrolysis method is also at least comparable with the chemical analysis data as far as the accuracy is concerned; the absolute error in the yttrium, oxygen, and carbon contents calculated from the hydrolysis product balance is 0·03, 0·04, and 0·07 mol.%, respectively. The values obtained can involve systematic errors, due, in particular, to the incompleteness of the reaction of the sample hydrolyzed or to detection errors if the TCD has not been calibrated duly using reliable standards. An error which is difficult to eliminate is that arising from the retention of higher hydrocarbons in the reaction mixture during the hydrolysis, either by condensation or by adsorption on the voluminous inorganic residue (unless acid is used for the hydrolysis). The only method available for following this error consists in the decomposition of the carbide with

TABLE III

Quantitative phase analysis of sample *C* based on the gas chromatographic analysis of the products of its hydrolysis and the balance of the elemental composition as found by chemical analysis. Elemental composition by the balance of chemical and GLC analysis and by chemical analysis, respectively (wt.%): yttrium 79·7, 78·9; bonded oxygen 14·9, 15·7; bonded carbon 5.48, 5·42

Hydrocarbons	Content, vol.%, from the phase			
	Y_2OC	YC_2	"$Y_{15}C_{19}$"	sample in total (phase mixture)
C_1	3·54	—	21·0	24·5
C_2	—	55·1	3·5	58·6
C_3	—	—	10·5	10·5
C_4	—	3·45	[a]	3·45
C_5	—	—	0·022	0·022
C_6	—	0·587	[a]	0·587
H_2				0·82
CO_2				0·68
Phase content[b], mol.%	5·03	90·5	4·45	
wt.%	5·68	56·1	38·2	
Phase content[c], mol.%	1·78	32·1	1·58	
wt.%	1·35	13·3	9·08	
H/C ratio[d]	4	1·5	45/19	

[a] Unspecified because of the indefinite composition of the product of hydrolysis of this carbide given by the indefiniteness of its analogy with $Sc_{15}C_{19}$; [b] disregarding the Y_2O_3 present; [c] with respect to the content of Y_2O_3, *viz.* 64·53 mol.%, or 76·22 wt.%; [d] H/C ratio corresponding to the calculated phase composition 1·82, H/C ratio in the gas mixture analyzed 1·81.

a solution of ^3H_2O in water under radioanalytical monitoring[11]. The extent of this error has been examined by us[12] in the hydrolysis of ^{14}C labelled LaC_2. The activity of the retained – adsorbed and condensed – hydrocarbons was as high as 8·5% of the total activity of the hydrocarbons, hence, 8·5% of all of the C_2 groups of the carbide structure may not be present in the gas mixture analyzed. Thus, the determined content of YC_2 (in mol.%) may cover 91·5% only of the true content, which for sample *A* thus can lie near the upper limit of the range of 87·9–88·8%, and the content of Y_2OC can approach the lower limit of the range of 11·8–10·9 mol.%. The overall error of determination of the phase composition by the hydrolysis method, for sample *A*, is then ±1·2% for YC_2 and ±10% for Y_2OC if an error of 15% in the determination of the $Y_{15}C_{19}$ phase (given by the inaccuracy in the estimate of the composition of its hydrolysis product) and retention of 8·5% carbon in the reaction mixture are assumed. The elemental composition of sample *A*, with the phase contents of 88·8% YC_2, 10·9% Y_2OC, and 0·32% $Y_{15}C_{19}$, will be 80·35 wt.% Y, 1·36 wt.% O, and 18·3 wt.% C. These values approach those obtained by chemical analysis (Table I) better than if the hydrocarbon retention is disregarded.

Thus the accuracy of the hydrolysis method of phase analysis method of phase analysis is undoubtely better than that of other methods such as powder X-ray diffraction or metallography. The method is also more convenient than other equally accurate methods such as the electron microprobe analysis requiring a special sample treatment and pure phase standards, *etc.* The fact that the hydrolysis method concerns the entire sample, whereas in the other methods only a definite, usually not very deep planar sections are treated, can often be also of advantage.

Our experiments give evidence that if subjected to carbothermal reduction with a sufficient amount of carbon, yttrium oxide yields YC_2 by a reaction in which the carbide-oxide Y_2OC is an intermediate product. While in a sample prepared at 2 100°C and $6·67 . 10^{-4}$ Pa the content of Y_2OC is only several hundredths per cent[2], an $Y_2O_3 : C = 1 : 7$ mixture treated at 1 600°C and $1 . 10^{-3}$ Pa yields nearly 20% of this intermediate. If the content of carbon is lowered so that $Y_2O_3 : C = 1 : 5·53$, the $Y_{15}C_{19}$ carbide does not form as would correspond to the stoichiometry. The $Y_2O_3 : C = 1 : 2$ mixture does not give Y_4O_3C. The hydrolyzable moiety contains Y_2OC methanide, YC_2 acetylide, and an allylene type carbide in approximately equal proportions. Thus, the content of the allylene type carbide is higher than in the samples obtained from carbon-richer mixtures. From this viewpoint, the allylene type carbide is also to be regarded as an intermediate product of the yttrium oxide carboreduction. Probably, rather than $Y_{15}C_{19}$ this phase is its partly oxygen-substituted analogue, $Y_{15}(O, C)_{19}$.

The carbothermal reduction of Y_2O_3 as observed by Samsonov and coworkers[6] then can be looked upon as a synthesis of a mixture of Y_2O_3, Y_2OC, and YC_2. The total content of bonded and free carbon and of yttrium in the resulting sample obtained at 1 600°C is reported to be 91–96%, in dependence on the starting ratio

of the components. The remainder is oxygen bonded in Y_2OC and in the unreacted Y_2O_3. The formation of the product referred to[13] as Y_2C_2O can be interpreted similarly.

If compared with the carbothermal reduction of scandium oxide[14], the carbothermal reduction of yttrium oxide exhibits some differences. First, while the reduction of scandium oxide gives the carbon-richest carbide $Sc_{15}C_{19}$ (to a limited extent only), the yttrium analogue is characteristic by the formation of YC_2 over a wide region of the component proportions. Second, the stability of the carbide-oxide intermediate, Y_2OC, in the Y_2O_3–C system is considerably lower than the stability of the Sc_2OC phase in the Sc_2O_3–C system; Y_2OC is not formed in a predominating quantity besides yttrium oxide. And third, the allylene type phase, probably $Y_{15}C_{19}$, appears during the carbothermal reduction of Y_2O_3 only if the starting mixture is highly deficient in carbon, whereas the $Sc_{15}C_{19}$ carbide is the final product of the reaction. In conclusion, the phase types that in the carbothermal reduction of scandium oxide are the main products, *viz.* Sc_2OC ($Fm3m$) and $Sc_{15}C_{19}$ ($P\bar{4}2_1c$) are only minority products in the reaction of yttrium oxide.

In view of the present study the fact is of crucial importance that the presence of the Y_2OC carbide-oxide in the dicarbide can account for the observed presence of traces of methane in the product of hydrolysis, which was a complicating factor in the treatment of the relation between the nature of the carbon groups in the dicarbide and the composition of the hydrocarbon mixture evolved during its hydrolysis.

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