INVESTIGATION OF THE PRODUCTS OF REACTION OF (Sc, Y)$_2$O$_3$ AND (Sc, Dy)$_2$O$_3$ MIXED CRYSTALS WITH CARBON IN PROPORTIONS CORRESPONDING TO THE FORMATION OF M$_{15}$C$_{19}$ PHASE*

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Scandium, yttrium, and dysprosium formates were subjected to reaction with carbon in a stoichiometric ratio of $M_2O_3 : C = 1 : (83/15)$ at 1 650°C and 1 Pa for 40 h to give products containing typical phases of Sc_2OC and $Sc_{15}C_{19}$, Y_2OC and YC_2, and Dy_2OC and DyC_2, respectively (Y_2OC and Dy_2OC *Fm3m*, $a = 494{\cdot}7 \pm 0{\cdot}2$ and $495{\cdot}0 \pm 0{\cdot}2$ pm, respectively). The mixed scandium-yttrium or scandium-dysprosium carbides prepared under the same conditions did not exhibit diffraction patterns of the $M_{15}C_{19}$ carbides, and were constituted by mixed dicarbide and mixed oxide-carbide crystals. Yttrium and, to a greater extent, dysprosium are preferentially located in the dicarbide structure, whereas scandium occupies more the oxide-carbide structure. The mixed scandium-dysprosium carbide $(Sc_{0,94}Dy_{0,06})_{15}C_{19}$ ($P\bar{4}2_1c$, $a = 753 \pm 1$ pm, $c = 1\,506 \pm 3$ pm) starts to form at temperatures above the melting temperature of the mixture (1 750—1 800°C). The composition of the gaseous products of hydrolysis is consistent with the phase composition of the samples. The method of quantitative phase analysis based on the GLC analysis of the gases evolved on the hydrolysis is employed for the analysis of complex phase systems. In addition to chemical and X-ray diffraction analysis, the hydrolysis method is also applied to the determination of additional products.

Studying the products of carbothermal reduction of scandium oxide we were able to demonstrate[1] that while the oxide-carbide Sc_2OC and the carbide $Sc_{15}C_{19}$ are formed in the reaction, the dicarbide ScC_2 is not. Yttrium oxide[2-4], on the other hand, yields the dicarbide YC_2 and a smaller amount of oxide-carbide Y_2OC. Dysprosium and other lanthanides also afford dicarbides. As the ionic radii of Sc^{3+} and Y^{3+} or Dy^{3+} (81, 90, and 90 pm, respectively), are favourable for their mutual isomorphic substitution such as in the mixed crystals formed from the Sc_2O_3–Y_2O_3 system[5], the present work is devoted to the study of the products of carbothermal reduction of (Sc, Y)$_2$O$_3$ and (Sc, Dy)$_2$O$_3$ mixed crystals, using the respective formates for their preparation. Since the main problem pursued was that of the existence of mixed crystals of the $M_{15}C_{19}$ carbide type[6], the oxides were combined with carbon invariably in the stoichiometric ratio of 1 : (83/15).

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EXPERIMENTAL

Carbothermal reduction. Scandium oxide 99% (Lachema; impurities, as determined by spectral analysis, were on the levels of 10^{-1}% Si, 10^{-1}% Th, 10^{-2}% Fe, 10^{-2}% Y) and yttrium oxide of 5N purity (for electronics) or dysprosium oxide 99·9% (USSR) were dissolved in 50% formic acid of reagent grade purity under boil. The solutions were mixed with colloidal graphite (Acheson Colloiden, The Netherlands) in the stoichiometric ratio of $(Sc_xM_y)_2O_3 : C = 1 : (83/15)$ (M = Y or Dy), and vacuum evaporated to dryness at 40°C. The obtained mixture of formates with carbon were preliminarily decomposed in a vacuum of 1 kPa at 600°C to the oxides, which feature en enhanced reactivity[7]. The samples were pelletized and sintered at 1 650°C in a vacuum of 1 to 10 Pa for 40 h in the furnace of an Exhalograph EA-1 instrument (Balzers, Liechtenstein); the tantalum crucible used was coated with a layer of TaC.

X-ray diffraction measurements. The techniques and procedures were as described previously[4]. The lattice parameters of the phases were evaluated by statistical treatment according to Burnham[8].

Gas chromatographic analysis. The operation procedure using a HP 5830 A chromatograph has been described[9].

Chemical analysis. The procedure for the determination of the total and free carbon, oxygen, and nitrogen was as reported previously[4]. The total content of scandium and yttrium or dysprosium was determined by a backtitration procedure as follows. To a sample dissolved in 50% HNO_3 of reagent grade purity was added a known amount of Chelaton III and the excess of the latter was titrated with $Zn(NO_3)_2$ of reagent grade purity using Eriochrome Black T as indicator; pyridine was added in a solution buffered with ammoniacal buffer to pH 10—11. The concentration of the titrant solution of $Zn(NO_3)_2$ was determined also by back titration using identical aamounts of the reagents and adhering to the same conditions as applied to the analysis. Though, not substantially, the scandium chelate is more stable than the chelates of yttrium and dysprosium and so scandium was determined by direct titration. In order to eliminate interferences from yttrium or dysprosium, the titration of scandium with Chelaton III was conducted at the limiting acidity, pH max. 3. Just before the end point the pH was adjusted by dilution with redistilled water for achieving a permanent colour change, instead of adding urotropine as usual. The titre of Chelaton III was determined by titration of a known amount of scandium trichloride obtained by reduction chlorination of the oxide. The weighing bottles were filled with scandium trichloride directly in the dry box connected with the condensation space of the reduction chlorination apparatus. The $ScCl_3$ standards were sampled from the place where the refined product with the the highest albedo condensed.

RESULTS AND DISCUSSION

As follows from the data of Table I, the reaction of the oxides with carbon resulted invariably in the formation of a multiphase product. While Sc_2O_3 yielded a mixture of Sc_2OC with $Sc_{15}C_{19}$, the mixed systems transformed into the oxide-carbides and dicarbides; $M_{15}C_{19}$ type phases ($P\bar{4}2_1c$) in amounts detectable by X-ray diffraction measurement did not appear even if the ratio of scandium to the other metal was as high as 2 : 1. Only when the product containing Sc and Dy in this molar ratio was remelted at nearly 1 800°C, the sample obtained exhibited complex diffraction patterns aming which the reflections of the $M_{15}C_{19}$ structure could be traced.

The mass contents of the phases in the products were calculated by balance based on the metal content in the sample and the total and free carbon data. The content of scandium and the other metal in the mixed oxide-carbide was determined by Vegard's rule, using the parameters of a = 456·2, 494·7, and 495·0 pm for Sc_2OC,[10] Y_2OC, and Dy_2OC, respectively. The remaining data were obtained by balance. Since the product contained, according to the X-ray diffraction measurements, only two phases, the determination of the third variable, *viz.* the metal ratio in the mixed dicarbide, required independent determination of three elements; the two metals concerned and bonded carbon were chosen for this purpose. Oxygen appears least convenient for the analysis from the point of view of the error involved, and moreover, the value from the analysis is always somewhat higher than as corresponds to the balance for the two-phase system. Probably, then, the samples contained unreacted oxides or mixed oxides, although in amounts below the limit of detection

TABLE I

Phase analysis of the carbides prepared

Starting components correspond to	Phase identified	Content[a] wt.%	Lattice parameters, pm	
			a	c
$Sc_{15}C_{19}$	Sc_2OC	55·5	457·73 ± 0·08	
	$Sc_{15}C_{19}$	44·5	748·3 ± 0·3	1 496 ± 3
$Sc_{10}Y_5C_{19}$	$(Sc_{0.37}Y_{0.63})C_2$	66·5	362·1 ± 0·6	607 ± 6
	$(Sc_{0.96}Y_{0.04})_2OC$	33·5	457·5 ± 0·2	
$Sc_{10}Y_5C_{19}$	$(Sc_{0.19}Y_{0.81})C_2$	56·1	363·5 ± 0·4	609 ± 1
	$(Sc_{0.95}Y_{0.05})_2OC$	43·9	458 ± 0·3	
$Sc_5Y_{10}C_{19}$	$(Sc_{0.00}Y_{1.00})C_2$	65	364·4 ± 0·3	609 ± 1
	$(Sc_{0.72}Y_{0.28})_2OC$	35	467 ± 1	
$Y_{15}C_{19}$	YC_2	64·3	365·7 ± 0·2	611·4 ± 0·9
	Y_2OC	35·7	494·7 ± 0·2	
$Sc_{10}Dy_5C_{19}$ re-melted	$(Sc_{0.20}Dy_{0.80})C_2$	(1/3)	361·5 ± 0·3	610 ± 2
	$(Sc_{0.92}Dy_{0.08})_2OC$	(1/3)	459·0 ± 0·4	
	$(Sc_{0.94}Dy_{0.06})_{15}C_{19}$	(1/3)	753 ± 1	1 506 ± 3
$Sc_5Dy_{10}C_{19}$	$(Sc_{0.41}Dy_{0.59})C_2$	86	358·1 ± 0·1	598·6 ± 0·2
	$(Sc_{0.41}Dy_{0.59})_2O_3$	14	1 024 ± 1	
$Dy_{15}C_{19}$	DyC_2	78	368 ± 1	619 ± 4
	Dy_2OC	22	495 ± 0·2	

[a] From chemical analysis or X-ray diffraction data.

by the powder X-ray diffraction method. If the oxides are present, the carbon balance requires a lowering of the assumed content of the oxide-carbide. This fact can account for the content of methane in the hydrolysis product being below the calculated value (Tables II and III).

The error of the phase analysis based on the balance approach can be well illustrated on the "$Sc_{10}Y_5C_{19}$" samples. The reproducibility of the lattice parameter of the mixed carbide-oxide formed is ±0·5 pm, which leads to an error of ±0·005 in the value of x in the formula $(Sc_{1-x}Y_x)_2OC$. The lattice parameter of the pure component, discandium carbide-oxide, prepared under similar conditions (1 500 – 1 700°C,

TABLE II

Analytical data of the carbides prepared

Starting mixture corresponds to	Elemental composition[a] of the phase mixture, wt.%						Content of hydrocarbon precursors[b] mol.%		
	Sc	Y	Dy	C_{bond}	C_{free}	O	C_1	C_2	C_3
$Sc_{15}C_{19}$	67·4	—	—	15·1	12·2	6·7	75	9	16
	64·7			14·8	12·2	8·6			
$Sc_{10}Y_5C_{19}$	35·5	40·2	—	19·9	—	4·4	29	71	—
	34·9	39·5	—	19·5	—	6·2			
$Sc_{10}Y_5C_{19}$	35·3	41·8	—	17·2	—	5·8	40	60	—
	35·0	41·5	—	17·1	—	6·4			
$Sc_5Y_{10}C_{19}$	15·9	63·4	—	16·8	—	3·9	30	70	—
	16·0	63·7	—	16·9	—	3·4			
$Y_{15}C_{19}$	—	81·5	—	15·8	—	2·8	23	77	—
	—	80·8	—	15·6	—	3·6			
$Sc_5Dy_{10}C_{19}$	13·2	—	69·5	15·0	—	2·4	—	100	—
	13·2	—	69·5	15·0	—	2·5			
$Dy_{15}C_{19}$	—	—	88·2	10·8	—	1·0	13	87	—
	—	—	88·5	10·8	—	0·7			

[a] Upper figures: calculated values; bottom figures: found values; [b] values corresponding to the calculated phase composition; the hydrocarbon precursors mixture is understood as the mixture after the carbide hydrolysis in which the consecutive addition reactions of unsaturated hydrocarbons (acetylenes in particular), associated with their hydrogenation, have not yet taken place. Such reactions occur during the hydrolysis as well as in the gas mixture above the decomposed carbide until the depletion of the hydrogen present.

TABLE III

Composition of gases evolved on the hydrolysis of the carbides prepared

Hydrocarbon	Content, vol.%, in the gas evolved from the carbide prepared from a mixture whose composition corresponded to							
	$Sc_{15}C_{19}$	$Sc_{10}Y_5C_{19}$	$Sc_{10}Y_5C_{19}$[a]	$Sc_5Y_{10}C_{19}$	$Y_{15}C_{19}$	$Sc_{10}Dy_5C_{19}$	$Sc_5Dy_{10}C_{19}$	$Dy_{15}C_{19}$
Hydrogen	4·45	1·87	0·95	3·19	2·04	1·54	1·18	1·24
Methane	62·5	15·8	27·8	27·4	21·5	54·3	6·14	9·9
Ethane	2·00	8·44	6·24	6·60	7·79	3·77	8·57	8·73
Ethene, ethyne	3·70	64·2	58·5	55·3	64·7	22·8	71·4	76·0
Propane	7·46	1·08	0·25	0·35	0·10	4·44	0·33	0·07
Propene	6·90	0·90	0·39	0·26	0·06	4·52	0·36	0·05
Propyne, propadiene	6·82	0·47	0·54	0·20	0·19	4·94	0·38	0·03
2-Methylpropane	0·27	0·03	—	—	—	0·07	—	—
1-Butene	0·49	2·91	2·04	3·55	1·69	0·91	3·18	1·70
Butane	1·15	0·91	0·87	0·90	0·43	1·02	1·81	0·52
1,3-Butadiene	—	0·19	0·23	0·19	0·09	0·10	0·35	0·09
2-Methylpropene	0·49	0·04	—	—	—	0·14	—	—
cis-2-Butene	0·13	0·37	0·47	0·24	0·23	0·27	0·64	0·25
trans-2-Butene	0·03	0·54	0·24	0·06	0·12	0·07	0·43	0·14
1-Butyne	—	0·75	0·53	0·70	0·43	—	0·76	0·61
2,2-Dimethylpropane	0·19	—	—	—	—	—	—	—
2-Methyl-3-butene	0·24	—	—	—	—	0·11	—	—
2-Methylbutane	0·13	0·04	—	—	—	0·05	—	—
C_4 Unspecified	0·05	0·21	0·13	0·06	0·23	0·07	0·16	0·04
C_5 Unspecified	0·76	0·15	0·07	0·09	—	0·29	0·11	0·03
C_6 and higher	2·22	1·00	0·84	0·96	0·42	1·26	1·26	0·60
H/C ratio[b]	2·81	1·75	1·87	1·92	1·77	2·45	1·61	1·58

[a] A different sample; [b] the ethene–ethyne mixture is approximated by the formula $CH_{2.4}$, the unspecified higher hydrocarbons, by the formula C_nH_{2n}.

30 – 120 h, 0·01 – 1 Pa, Sc_2O_3 : C ratio 1 : 3) is $a = 456{\cdot}2 \pm 0{\cdot}1$ pm (number of measurements[10,11] $n = 4$), whereupon the error in x increases up to $\pm 0{\cdot}008$. The carbide-oxide phase can contain, in the nonmetal sublattice, as much as 4% vacancies at the expense of carbon; these can be occupied by oxygen[10]. This fact is disregarded in this work when setting up the formulae because it cannot be accounted for quantitatively. In addition to the excess carbon and $Sc_{15}C_{19}$, the Sc_2OC phase is also formed; its lattice parameter is about 457·6 pm as determined within the present study[11].

Now, consider the errors in the chemical analysis. The standard deviation of the determination of the metals by the chelometric titration was $\delta_M = \pm 0{\cdot}2$ (% metal) and the reproducibility of the determination of carbon was $\delta_C = \pm 0{\cdot}1$ (% carbon) ($n = 5$ and 3, respectively). Taking into account the errors of determination and inaccuracy in the estimate of the mixed crystal composition as provided by Vegard's rule, the resulting composition can lie within the region of 43·5 wt.% $(Sc_{0.942}Y_{0.058})_2 . OC$ and 56·5 wt.% $Sc_{0.218}Y_{0.782}C_2$ to 44·5 wt.% $(Sc_{0.958}Y_{0.042})_2OC$ and 55·5 wt.% $Sc_{0.166}Y_{0.834}C_2$. If the carbide-oxide phase is assumed to contain 4% vacancies in the carbon positions, then – for the most unfavourable case of summation of all the associate errors – the limit of this region shifts to 45·5 wt.% $(Sc_{0.942}Y_{0.058})_2 . OC_{0.96}$ with 54·5 wt.% $Sc_{0.23}Y_{0.77}C_2$. The overall relative errors in the mole fractions of Sc and Y in the cation part of the mixed carbide-oxide thus are about 1% and 16%, respectively, the errors in the mole fractions of the two metals in the mixed dicarbide are about 16% and 4%, respectively. The absolute error of determination of the metal content in the other mixed dicarbides prepared should be on the same level, hence, about $\pm 0{\cdot}03$.

The presence of C_3 hydrocarbons in the products of hydrolysis of the mixed phases (Table III), in amounts of about 1 – 2 vol.%, gives evidence of the occurrence of 6 – 12 wt.% $M_{15}C_{19}$ phases. The fact that the content of these hydrocarbons approaches the upper limit of the above region if scandium is present in the sample in a higher quantity supports the idea that the $M_{15}C_{19}$ phase formation is particularly typical of systems containing scandium. The lattice parameters of the $(Sc, Dy)_{15}C_{19}$ mixed crystal approach those of pure $Sc_{15}C_{19}$ and indicate that the possibility of substitution of scandium by the bulkier atoms of other rare earth elements is rather limited. While in the starting mixture the scandium to dysprosium molar ratio was 2 : 1, in the $(Sc, Dy)_{15}C_{19}$ mixed crystal it attained values as high as 24 : 1.

For an additional testing of the stability of the balance of the $Sc_{10}Y_5C_{19}$ sample composition by the chemical analysis, assume the existence of the $M_{15}C_{19}$ phase, in the most unfavourable case involving scandium solely. The content of $Sc_{15}C_{19}$ be 9 wt.%; them the remaining phases in the "$Sc_{10}Y_5C_{19}$" sample will be $(Sc_{0.942} . Y_{0.058})_2OC_{0.96}$ (40 wt.%) and $Sc_{0.06}Y_{0.94}C_2$ (51 wt.%), provided that the results of the chemical analysis from the less favourable part of the error interval are taken into account. The proportion of scandium in the mixed dicarbide is lowered appreciably owing to the presence of the $Sc_{15}C_{19}$ phase. Unreacted oxides will have an opposite effect, which, however, does not lend itself to quantitative treatment. Obviously, then, the results of the chemical and X-ray diffraction analysis, though by themselves fairly accurate, are on their own insufficient for a precise quantitative analysis of the mixed phase mixtures, and the balance obtained has to be considered with circumspection. Therefore, for the sample with the starting scandium to dysprosium ratio of 2 : 1, which, moreover, after the melting was sintered with the tantalum of the crucible, the phase analysis was carried out by employing the hydrolysis method. The composition of the gaseous products of hydrolysis is known for the carbides which are of the same structure types as the phases observed: $Sc_{15}C_{19}$ carbide[9]: 55 vol.% CH_4, 10% C_2, 30% C_3, 3% C_4, 1% C_5, 1% C_6; Sc_2OC carbide-oxide[10]: virtually 100% CH_4; YC_2 dicarbide[2]: C_2 and additional even hydrocarbons.

The composition of the hydrocarbon gas was divided into the fractions coming from the various phases (Table IV). The fraction from the $M_{15}C_{19}$ phase, given by the content of C_3 hydrocarbons (which are not formed from any of the other phases present) was subtracted from the total to give, by a simple stoichiometry, the corres-

TABLE IV

Quantitative phase analysis of the re-melted sample of the carbide prepared from the metal formates and carbon in a stoichiometry corresponding to the formula $Sc_{10}Dy_5C_{19}$; the analysis is based on the balance of the gaseous hydrolysis product

Hydrocarbon	Content, vol.%, from the phase			
	$M_{15}C_{19}$[a]	M_2OC[b]	MC_2[c]	Sample in total (phase mixture)
C_1	25·3	29·0	—	54·3
C_2	4·63	—	21·9	26·6
C_3	13·9	—	—	13·9
C_4	1·39	—	1·26	2·65
C_5	0·463	—	0	0·456
C_6	0·463	—	0·111	0·574
H_2				1·54
Weight of 1 mole phase, g	1 008 ± 14	136·7 ± 2·4	163 ± 7	
Phase content, mol.%	7·8 ± 2	49·7 ± 2	42·5 ± 2	
wt.%	36·6 ± 7	31·4 ± 5	32·0 ± 5	
H/C ratio[d]	45/19	4/1	3/2	

Elementary formula from the X-ray analysis according to Vegard's rule (for the error see text) [a] $(Sc_{0.94}Dy_{0.06})_{15}C_{19}$; [b] $(Sc_{0.92}Dy_{0.08})_2OC$; [c] $Sc_{0.20}Dy_{0.80}C_2$; [d] H/C ratio corresponding to the calculated phase composition 2·39 ± 0·02, H/C ratio in the gas mixture analyzed 2·45.

ponding amount of the $M_{15}C_{19}$ carbide. The remaining methane (after subtracting the above fraction) is a product of hydrolysis of the M_2OC phase, and its content was converted to the amount of the carbide-oxide. The gas left contained nearly exclusively even hydrocarbons, and as such was considered to be the product of hydrolysis of the MC_2phase. The amount-of-substance of the carbon atom pairs then was identical with that of the dicarbide.

The scandium and dysprosium fractions in the mixed crystal were determined by applying Vegard's rule; the lattice parameters of ScC_2 were estimated as described below, the parameters of $Dy_{15}C_{19}$ were considered identical with those of $Y_{15}C_{19}$, *viz.* $a = 749$ pm, $c = 1\,588$ pm (ref.[12]), in view of the fact that the parameters of dysprosium and yttrium dicarbides also differ to a minor extent only[13]. The error in the determination of the mole fraction of Dy in the $M_{15}C_{19}$ and M_2OC mixed crystals then was ±0·02 and ±0·01, respectively, and the error in the determination of the mole fraction of Sc in the dicarbide was ±0·06.

The error of the phase analysis was assessed similarly as in paper[4] to find that the absolute error in the phase contents does not exceed ±2 mol.%. The error, in wt.%, including the inaccuracy in the application of Vegard's rule is given in Table IV.

The theoretical H/C ratio in the gas mixture from the hydrolysis of the phase system of the calculated composition is 2·39 ± 0·01, thus approaching the value of 2·45 calculated from the gas mixture composition obtained by analysis. The difference is apparently due to the indefinite amount of multiple bonds in the ethyne–ethene mixture and in the mixture of some higher hydrocarbons which were analyzed as a total.

The gas mixtures from the hydrolysis of the other mixed carbides prepared correspond to initial mixtures of dicarbide and oxide-carbide, occasionally with a small fraction of $M_{15}C_{19}$. The analogous calculations of the phase composition based on the hydrolysis of the samples in question give results which are consistent with those obtained by chemical analysis.

The major products of the carbothermal reduction of the mixed crystals of scandium and yttrium or scandium and dysprosium oxides are carbides and carbide-oxides. The formation of dicarbide is typical of the carbothermal reduction of yttrium and dysprosium oxides but not of the reduction of scandium oxide. For all the initial oxide ratios used the dicarbide phase formed contained less than 0·4 mol of scandium per mol of both metals in the mixed crystal.

The lattice parameters of the hypothetical scandium dicarbide as determined by Vegard's rule, $a = 348 \pm 5$ pm, $c = 582 \pm 10$ pm, exceed those calculated by extrapolating the dependence of the lattice parameters of rare earth elements dicarbides[13] on the parameters of the hexagonal lattice of the corresponding metals[14], which gives $a = 320$ pm, $c = 570$ pm.

Interpolation making use of Vegard's rule in the systems of mixed rare earth elements dicarbides is somewhat complicated by the fact that cubic dicarbide phases of the NaCl type, which are steady at room temperature[15–17], can appear in them. In the YC_2–ScC_2 system such a cubic phase was not observed, and the presence of a cubic DyC_2–ScC_2 mixed crystal cannot be established with certainty. For instance, for samples with the initial ratio corresponding to Sc_5Dy_{10} the most intense reflection, 111, of this assumed phase ($a = 512 \pm 2$ pm) coincides with the 222 reflection of the mixed oxide crystal ($I2_13$) or with the 110 reflection of the mixed dicarbide crystal with a tetragonal structure ($I4/mmm$). Only the occurrence of a diffraction line that can be attributed to the 420 reflection can be looked upon as an evidence of the presence of the cubic mixed dicarbide crystal in the DyC_2–ScC_2 system. As documented by the data by Adachi and coworkers[17], crystals of mixed (1 : 1) dicarbides of rare earth elements possess the *fcc* symmetry even at room temperature provided that the relative differences in the ionic radii of the metals concerned, $(r_1 - r_2)/r_1$, lie within the region of 14–18%. When the relative differences are lower, tetragonal dicarbides are formed, whereas when the differences are higher, no mixed crystals are formed at all for the 1 : 1 molar ratio.

In our system of DyC_2 and ScC_2 dicarbides, the approach based on the differences in the ionic radii is not quite appropriate because the ScC_2 phase is unknown and thus the effect of the bonding in it on the size of the scandium atom cannot be assessed. A comparison can be better made for DyN and ScN, whose lattice parameters are $a = 490$ (ref.[18]) and 450 pm (ref.[19]), respectively; thus the difference between the radii is $r_{Dy} - r_{Sc} \approx 20$ pm, so the relative difference certainly exceeds the limit[17] of 18%, the radius of dysprosium being surely lower than 111 pm.

So, yttrium and dysprosium dicarbides can form mixed crystals with scandium dicarbide only in a region near to YC_2 or DyC_2. This region encompasses the range of existence of tetragonal mixed crystals adjacent to pure YC_2 or DyC_2 component and the region of existence of cubic mixed crystals. Its limit, which does not reach the 1 : 1 ratio, is identical with that for the formation of mixed dicarbide phases altogether. Our results indicate that this limiting value is characterized approximately by the formula $Sc_{0.4}M_{0.6}C_2$ where M is yttrium or dysprosium.

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