Monatshefte für Chemie 117, 1271—1278 (1986)

Monatshefte für Chemie
Chemical Monthly

Studies on Hydrolyzable Carbides. XXII: The Carbothermal Reduction of Scandium Oxide Sc_2O_3

Bohumil Hájek *, **Pavel Karen**, and **Vlastimil Brožek**

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

(Received 23 August 1985. Revised 18 December 1985. Accepted 13 January 1986)

The composition of the products of carbothermal reduction of Sc_2O_3 is examined by X-ray diffraction and chemical analysis and by the hydrolysis method. At pressures of 10^{-2}–1 Pa, the reaction starts in the temperature region of 1 000–1 200 °C. The first product is Sc_2OC of NaCl type; at 1 Pa and 1 400–1 500 °C this substance is formed quantitatively (according to stoichiometry) within 50–100 h, repeated homogenization, however, is necessary, or else Sc_2OC reacts locally with Sc_2O_3 giving $Sc_2O_{1+x}C_{1-x}$. The lattice parameter of Sc_2OC in the presence of $Sc_{15}C_{19}$ is 457.6_3 pm. At temperatures above 1 500 °C, $Sc_{15}C_{19}$ is incompletely formed by subsequent reaction with carbon. The product melts at cca. 1 800 °C; carbon dissolves and the final composition approaches ScC_2. Carbon separates during solidification. The phase fractions in the products are affected by evaporation, the vapour pressures above both Sc_2OC and $Sc_{15}C_{19}$ being comparable with the pressure requisite for the carboreduction process. The results are discussed with respect to the often ambiguous published data.

[Keywords: Scandium(III)oxide carboreduction; Sc_2OC; $Sc_{15}C_{19}$*]*

Untersuchung hydrolysierbarer Carbide, XXII. Die karbothermische Reduktion von Scandiumoxid

Zur Untersuchung von Produkten der karbothermischen Reduktion von Scandiumoxid wurden sowohl röntgenographische und chemische Analyse als auch die hydrolytische Methode verwendet. Bei 10^{-2} bis 1 Pa beginnt die Reaktion im Temperaturintervall von 1 000–1 200 °C. Das erste Reaktionsprodukt ist das Scandiumoxidcarbid Sc_2OC von NaCl-Typ, das quantitativ (der Stöchiometrie entsprechend) bei 1 400–1 500 °C und 1 Pa in 50—100 Stunden entsteht. Eine wiederholte Homogenisierung ist allerdings notwendig, damit es zu keiner lokalen Reaktion zwischen Sc_2OC und Sc_2O_3 kommt, bei der dann die Phase $Sc_2O_{1+x}C_{1-x}$ entsteht. In Gegenwart von $Sc_{15}C_{19}$ ist der Gitterparameter von Sc_2OC $a = 457.6_3$ pm. Über 1 500 °C führt eine weitere Reaktion mit Kohlenstoff zu einer nicht ganz vollendeten Bildung von $Sc_{15}C_{19}$. Bei cca. 1 800 °C schmilzt das Reaktionsprodukt bei gleichzeitiger Auflösung von weiterem Kohlenstoff und die Zusammensetzung nähert sich der Formel ScC_2, beim Erstarren fällt der

Kohlenstoff wieder aus. Die Verteilung der Phasen im Produkt wird von der Verdampfung beeinflußt, da die Dampfdrucke von Sc_2OC und $Sc_{15}C_{19}$ mit dem zum Karboreduktionverlauf notwendigen Druck vergleichbar sind. Die erhaltenen Ergebnisse werden in Relation mit den nicht eindeutigen Angaben in der Literatur diskutiert.

Introduction

Carbothermal reduction of metal oxides is a conventional method of synthesis of metal carbides. Carbides of scandium are prepared nearly exclusively by this method because of the rare availability of scandium metal. With respect to the position of scandium within the periodic system of elements the carbothermal reduction of scandium oxide was expected to result in products similar to those of the neighbouring elements: the dicarbide [1] ScC_2 and the higher carbide of similar composition [2–5] were signalized as analogues of CaC_2 and YC_2; the monocarbide [6–9] ScC_{1-x} and carbide-oxide [6, 10] Sc(C, O) seemed to be structure analogues of TiC_{1-x} and Ti(C, O), respectively; and Sc_4C_3 was looked upon as an analogue [11] of Al_4C_3.

ScC_{1-x} was first assumed to be present in the products of reaction of scandium metal with carbon [12]. It was shown later, however, that scandium and carbon form together three solid compounds: a vacant carbide [13–15] $Sc_{2-3}C$ with a disordered structure of NaCl type or an ordered superstructure of trigonal symmetry (S.G. $R\bar{3}m$); the carbide [14] Sc_4C_3 with a structure of Pu_2C_3 (S.G. $I\bar{4}3d$) and the carbide [10] $Sc_{15}C_{19}$, of a novel structure type (S.G. $P\bar{4}2_1c$).

We have recently studied the Sc—O—C phase system, particularly with the aim to offer an interpretation of the literature data concerning the carbides of scandium. In a preliminary communication [16] we have shown that the carbothermal reduction of scandium oxide gives rise to the carbide-oxide Sc_2OC which in turn reacts with carbon to give the carbide $Sc_{15}C_{19}$. Relations between the structure and the hydrolysis behaviour of $Sc_{15}C_{19}$ were the concern of our paper [17] and some properties of the novel carbide-oxide Sc_2OC were reported by us in papers [18, 19]. Recently we confirmed [20] the occurrence of a wide homogeneity region for the $Sc_1(O, C, \square)_1$ phase of NaCl type, involving both Sc_2OC and $Sc_{2-3}C$.

The aim of the present paper was to describe in detail the effect of the reaction conditions on the composition of the products of carboreduction of Sc_2O_3 so as to supplement the recent studies [4, 7, 21, 22].

Experimental

Scandium oxide (96% Sc_2O_3, 2% ThO_2; spectral analysis: Si 10^{-1}%, Mn 10^{-2}%, Mg, Bi 10^{-3}%) was purified [23] to obtain 99.8% oxide, which was dissolved in 50% formic acid p. a. to give scandium formate. Isolated from the solution, this compound was subjected to triple vacuum crystallization at 60 °C from redistilled water acidified with formic acid. Scandium oxide (10^{-2}% Si, 10^{-3}% Mn, 10^{-4}% Fe) was obtained by thermal decomposition of scandium formate crystals at 600 °C. The substance was homogenized with granulated carbon black of 99.99% purity (Pramet, Šumperk) in an agate mortar to a uniform dark-black colour, pressed into pellets, and heated in a graphite crucible in the Exhalograph EA-1 (Balzers, Liechtenstein). Occasionally, the partly reacted pellets were re-homogenized and sintered. Temperatures used for the carbothermal reduction were 1 000–2 100 °C, pressures 10^{-2}–1 Pa, and scandium oxide-to-carbon molar ratios 1 : 2 to 1 : 7.

The solid phase evaporation was examined by analyzing layers deposited on a graphite target placed above the crucible bottom in a distance such that the target temperature was 200–300 °C lower than the temperature of the pellets in the crucible. In some cases, the scandium oxide contaminated by ThO_2 was used for continual X-ray determination of the evaporation losses; thorium dioxide served as a convenient internal standard whose amount remained constant in the conditions used (1 530 °C, $Sc_2O_3 + 3\,C$). The phase contents were determined by comparison of the theoretical and observed intensities of selected reflections in the diffraction patterns.

The product composition was determined by chemical and powder X-ray diffraction analysis as described previously [18]. Some samples were also characterized by analysis of the gaseous products from sample decomposed with 50% H_2SO_4 in an evacuated ampoule, fitted with a silicone rubber stopper. The decomposition was allowed to proceed at 80 °C for several days. The gases evolved were analyzed on a Hewlett-Packard 5840A gas chromatograph, with carrier gases either hydrogen or argon, according to [17].

Results

The idealized pathway of the carbothermal reduction of scandium oxide can be written as

$$Sc_2O_3 + 3\,C = Sc_2OC + 2\,CO \qquad (1)$$

$$Sc_2O_3 + 5.5\overline{3}\,C = 2\,ScC_{19/15} + 3\,CO \qquad (2)$$

the overall reaction (2) being a sum of the process (1) and a consecutive reaction where the carbide-oxide Sc_2OC transforms into the carbide $Sc_{15}C_{19}$,

$$Sc_2OC + 1.2\overline{6}\,C = 2\,ScC_{19/15} + CO \qquad (3)$$

A pause in the evolution of carbon monoxide during the carboreduction, corresponding to the liberation of 2 moles of CO per mole of Sc_2O_3, was observed under certain circumstances [21].

Carboreduction at Carbon Contents Higher than Corresponding to Formation of Sc_2OC

Independent of the extent of carbon excess, the start of the carboreduction was observed at 1 000–1 050 °C for a pressure of 10^{-2} Pa or at

1 130–1 180 °C for a pressure of 1 Pa; several percent carbide-oxide appeared in the product in 100 h of reaction. At temperatures above 1 500 °C, reaction (3) starts to proceed. The reacted sample is silver-grey in colour and contains, according to conditions, a residue of 20–50 %wt. carbide-oxide phase. The product melts on increasing the temperature to 1 800 °C, no appreciable loss of carbide-oxide taking place because the sample evaporation starts to compete. At 10^{-2} Pa and 1 530 °C, rectangular truncated bipyramids of $Sc_{15}C_{19}$ appear on the cooler graphite target; these grow into spherical aggregates about 50 μm in diameter, with large surfaces of metallic lustre. At 1 800 °C, a compact layer of $Sc_{15}C_{19}$ forms on the target in several hours even at a pressure of 1 Pa; the sample evaporates completely on increasing the temperature to 2 100 °C.

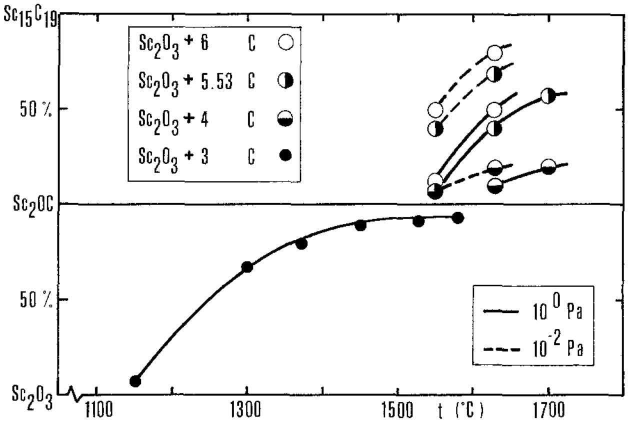

Fig. 1. Composition of the products of carboreduction of Sc_2O_3 (wt. %) after 50 ± 5 h of reaction under various conditions

For the $Sc_{15}C_{19}$ phase in a layer obtained by evaporation at 1 530 °C, the lattice parameter for a pseudocubic cell, calculated from 19 reflections within the diffraction angle region of 40–60°, is $a = 1.49967 \pm 27$ nm. A layer nearly 1 mm thick, whose X-ray patterns indicated pure $Sc_{15}C_{19}$, was separated from the substrate and subjected to hydrolysis. The hydrocarbon fractions were practically identical with those obtained previously [17] from $Sc_{15}C_{19}$ sample "F" prepared by carboreduction of the oxide. Again, the methane content and the [H]/[C] ratio gave evidence of the occurrence of Sc_2OC in the layer treated; actually it was present in the bottom layer, as was found on removing $Sc_{15}C_{19}$ by hydrolysis by air humidity.

The products of carboreduction of Sc_2O_3 never contained the sesquicarbide Sc_2C_3 or dicarbide ScC_2. At temperatures above the melting temperature of $Sc_{15}C_{19}$ (1 780 °C), carbon dissolves in the melt which is very aggressive even to the graphite of the crucible. During solidification, this carbon separates as hexagonal flakes observable on a metallographic sample of the solid silvery-lustrous melt or after hydrolytic decomposition of $Sc_{15}C_{19}$. The flake graphite content corresponded to the presence of 80% $ScC_{1.9 \pm 0.2}$ + 20% Sc_2OC in the melt at 1 900 °C.

The carboreduction thus does not suit for complete removal of oxygen from the reaction mixture and preparation of pure $Sc_{15}C_{19}$.

Carboreduction at Carbon Contents Corresponding to Formation of Sc_2OC

In contrast to $Sc_{15}C_{19}$, for Sc_2OC the reaction conditions can be established such that a diffractographically pure phase emerges. For a quantitative course of reaction (1), the reaction mixture has to be heated at 1 400–1 500 °C and 1–2 Pa for 50–100 h; after about 2/3 of the reaction time the mixture has to be re-homogenized. The product is Sc_2OC of virtually stoichiometric composition, with a lattice parameter $a = 457.5$–457.6 pm, identical with that for the carbide-oxide in equilibrium with $Sc_{15}C_{19}$. If the re-homogenization is omitted, unreacted grains of Sc_2O_3 remain and give with the Sc_2OC formed a carbide-oxide slightly richer in oxygen on the expense of carbon, $Sc_2O_{1+x}C_{1-x}$, with a lattice parameter near 456 pm ($x \cong 0.06$). Pressure lowering down to 10^{-2} Pa brings about sample evaporation even at temperatures near 1 500 °C, a layer of $Sc_{15}C_{19}$ crystals growing on the graphite target. When a higher pressure (1–2 Pa) was used at 1 530 °C, a thin, first velvet-black and later (200 hours) silvery crystalline layer of Sc_2OC deposited on the target. The lattice parameter of the carbide-oxide in the layer (in the presence of $Sc_{15}C_{19}$) lay in the narrow region of 457.59 ± 0.01 to 457.63 ± 0.02 pm. The Sc_2OC crystals were square platelets about 10 μm in size. The kind of the deposit appears to be in a relation to the carbon surface of the target; if a target coated by a titanium nitride layer is used, only traces of a NaCl type phase with the lattice parameter of $a = 450$ pm are formed even in a long vapourization time.

The sample evaporation at temperatures above 1 500 °C and pressures below 1 Pa indicates appreciable changes in the composition of the carboreduction product. Due to the loss of $Sc_{15}C_{19}$ or Sc_2OC, volume redistribution of the components takes place, local or absolute excess of scandium oxide forms, and a carbide-oxide richer in oxygen with a lattice parameter lower than for Sc_2OC is created. The initially sharp X-ray reflections of the carbide-oxide grow broader, which is related with inhomogeneities in the phase grains.

Table 1. *Course of evaporation of* Sc_2OC *from the product of carboreduction of* $Sc_2O_3 + 3\,C$ *at 1530 °C and 1.5* Pa

	Time of annealing		
	70 hours	140 hours	440 hours
Weight fraction left	1	3/4	2/3
Sc_2O_3 content, wt. %	8	9	13
Carbide-oxide content, wt. %	92	91	87
a, pm	456.2 ± 0.1	456.0 ± 0.2	454.7 ± 0.7

Data of Table 1 demonstrate that within 440 h of heating at 1 530 °C and 1.5 Pa, the pellet lost 1/3 its weight and a carbide whose lattice parameter corresponded approximately to $ScO_{0.6}C_{0.4}$ was formed. The methane and hydrogen contents of the gas evolved by hydrolysis, expressed by the [H]/[C] ratio of 4.40, corresponded to a composition of the hydrolyzed phase of $ScO_{0.58}C_{0.42}$ (hydrolytic decomposition of a $ScO_{0.5}C_{0.5}$ phase results in the formation of pure methane).

Discussion

Carboreduction of sesquioxide involving formation of an intermediate carbide-oxide, M_2OC, of NaCl type has been observed for several elements: yttrium [24, 25], dysprosium [26], ytterbium [27], and perhaps also some other heavy rare earth elements, as well as for titanium [28] where the carboreduction of TiO_2 gives rise, among others, to Ti_2O_3 which transforms immediately into $TiO_{0.5}C_{0.5}$. The oxide PuO_2 behaves similarly [29].

The $M_{15}C_{19}$ carbide phase is the final carboreduction product for Sc_2O_3 only; although it emerges also in the Y–C system [30] and in systems of carbon with heavier rare earth elements starting from holmium [31–34], but only from the reaction of carbon with the metal.

These phenomena are associated, among other things, with the atomic size of the metal element and with the possibility for the bulky C_2 group to be embedded in the MC_2 dicarbide structure. Scandium is the only rare earth element to possess an ionic radius whose value is below the limit of stability [35] of the CaC_2—I type dicarbide structure (S.G. P 4/mm). The next nearest carbide of scandium might be the carbide Sc_2C_3. For Y and Tm to Lu rare earth elements, however, this structure must be stabilized by using high pressures for the synthesis [36, 37]; scandium does not form Sc_2C_3 even under such conditions. According to Refs. [38–40], more than

80% of the scandium atoms have to be substituted by the bulkier atoms of thorium for a substitution-mixed crystal of this type to form during the high-pressure synthesis. Thus, the carbide $Sc_{15}C_{19}$ is the highest carbide of scandium with respect to the carbon content.

For a long time the carbide of scandium had been written in the literature as ScC; actually, the initial suggestion of this formula was not based on experimental data, but it followed from the concept of building-up of the so-called "interstitial" compounds, in analogy with VC or TiC [41–43]. *Hume-Rothery* [44], *Chupka* et al. [1] and *Nowotny* and *Neckel* [45], however, demonstrated later that scandium, with its three valency electrons, cannot form ScC.

Where an X-ray-pure phase of NaCl type was identified [6, 7, 9] as the product of carbothermal reduction of Sc_2O_3, its lattice parameter was about 451 pm. This lowering in the lattice parameter can be explained with regard to the high temperatures used (about 2000 °C), so that $Sc_{15}C_{19}$ carbide evaporated from the $Sc_2O_3 + 4\,C$ reaction mixture, the latter grew poorer in carbon, and grains of the excess Sc_2O_3 reacted with the carbide-oxide, evolving carbon monoxide and making it richer in oxygen. If the reaction was conducted under atmospheric pressure, the partial pressure of the nitrogen traces in contact with the sample was possibly sufficient for reduction nitridation giving rise to a Sc(O, C, N) phase.

It should be kept in mind that during the carboreduction of scandium oxide, the vapour pressure of the carboreduction products and the pressure of CO making their formation possible are comparable in magnitude. This is one of the major factors that can alter the phase composition of the resulting mixture of the carbide and carbide-oxide and also affects the composition of the carbide-oxide. The observed region of shift of the carbide-oxide phase composition, $Sc_1(O, C)_1$, however, is considerably narrower than the region of homogeneity of the $Sc_1(O, C, \square)_1$ phase [20] at 900 °C. We have demonstrated [20] that a prerequisite for the formation of a $Sc_1\,(O, C, \square)_1$ phase is the presence of scandium metal in the reaction mixture of Sc_2O_3 and C, which indicates that the carboreduction proceeds invariably via the carbide-oxide rather than the free metal.

References

[1] *Chupka WA, Berkowitz I, Giese CF, Ingram MG* (1958) J Phys Chem 62: 611
[2] *Wagner S* (1968) Dissertation, University of Vienna
[3] *Petrů F, Brožek V, Hájek B, Dufek V* (1969) Z Chem 9: 71
[4] *Petrů F, Brožek V, Hájek B* (1970) Rév Chim Miner 7: 515
[5] *Hájek B, Brožek V, Mostecký J* (1971) Monatsh Chem 102: 1387
[6] *Auer-Welsbach H, Nowotny H* (1961) Monatsh Chem 92: 198
[7] *Samsonov GV, Makarenko GI, Kosolapova TYa* (1962) Dokl Akad Nauk SSSR 144: 1062

[8] *Zhurakovski EA, Dzeganovski VP* (1963) Dokl Akad Nauk SSSR 150: 1260
[9] *Petrů F, Hájek B, Brožek V* (1966) Z Chem 6: 32
[10] *Jedlicka H, Nowotny H, Benesovsky F* (1971) Monatsh Chem 102: 389
[11] *Fridrich E, Sittig L* (1925) Z Anorg Allg Chem 143: 293
[12] *Nowotny H, Auer-Welsbach H* (1961) Monatsh Chem 92: 789
[13] *Rassaerts H, Nowotny H, Vinek G, Benesovsky F* (1967) Monatsh Chem 98: 460
[14] *Krikorian NH, Bowman AL, Krupka MC, Arnold GP* (1969) High Temp Sci 1: 360
[15] *Atoji M, Kukuchi M* (1969) J Chem Phys 51: 3863
[16] *Hájek B, Karen P, Brožek V* (1982) Proc. 38th Conf Czech Chem Soc, Prague, Czechoslovakia, July 6–9, p 64
[17] *Hájek B, Karen P, Brožek V* (1984) J Less-Common Met 96: 35
[18] *Hájek B, Karen P, Brožek V* (1984) J Less-Common Met 98: 245
[19] *Karen P, Brožek V, Hájek B* (1985) Sci Pap Inst Prague Chem-Technol. B 30: 31
[20] *Karen P, Brožek V, Hájek B* (1985) Extended Abstracts of VIII. Int. Conf. of Solid Compds of Trans. Elements, Vienna, Austria, April 9–13, p P2 A7
[21] *Řehák B, Brožek V* (1972) Sci Pap Prague Inst Chem-Technol. B 14: 113
[22] *Brožek V* (1976) Sci Pap Inst Prague Chem-Technol B 21: 7
[23] *Petrů F, Koloč J, Brožek V, Mrňák L, Pešek J* (1969) Czech. Pat. No. 144116 (16. 1. 1969)
[24] *Hájek B, Karen P, Brožek V* (1984) Collect Czech Chem Commun 49: 936
[25] *Holcombe CE, Carpenter DA* (1981) J Amer Ceram Soc 64: C-82
[26] *Hájek B, Karen P, Brožek V* (1984) Collect Czech Chem Commun 49: 944
[27] *Haschke JM, Eick HA* (1970) Inorg Chem 9, 851
[28] *Lubimov VD, Alamovskii SI, Shveikin GP* (1981) Zh. Neorg. Khim. 26: 2314
[29] *Potter PE* (1972) J Nucl Matter 42: 1
[30] *Bauer J, Nowotny H* (1971) Monatsh Chem 102: 1129
[31] *Bauer J, Ansel D* (1985) J Less-Common Met 109: 345
[32] *Bauer J* (1974) J Less-Common Met 37: 161
[33] *Haschke JM, Eick HA* (1970) J Amer Chem Soc 92: 1526
[34] *Bauer J, Bienvenu H* (1980) CR Acad Sci Ser C 290: 387
[35] *Vannerberg N-G* (1962) Acta Chem Scand 16: 1212
[36] *Krupka MC, Giorgi AL, Krikorian NH, Sklarz EG* (1969) J Less-Common Met 17: 91
[37] *Novokshonov VI* (1980) Zh Neorg Khim 25: 684
[38] *Krupka MC, Giorgi AL, Szklarz EG* (1973) J Less-Common Met 30: 217
[39] *Krupka MC, Giorgi AL, Krikorian NH, Szklarz EG* (1969) J Less-Common Met 19: 113
[40] *Giorgi AL, Szklarz EG, Krikorian NH, Krupka MC* (1970) J Less-Common Met 22: 131
[41] *Hägg G* (1929) Z Phys Chem Abt B 6: 221
[42] *Hägg G* (1931) Z Phys Chem Abt B 12: 33
[43] *Jacobsen B, Westgren A* (1933) Z Phys Chem Abt B 20: 361
[44] *Hume-Rothery W* (1953) Phil Mag 44: 1154
[45] *Nowotny H, Neckel A* (1969) J Inst Metals 97: 2519