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Abstract

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On Scandium Carbides and Complex Scandium-Titanium Carbides

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The natural interest in the properties and conditions for obtaining scandium carbides is due to the position of this element in the periodic system, where it is located next to titanium, which forms the very hard and refractory carbide TiC (1); moreover, the high degree of incompleteness of the *d*-electron shell of the scandium atom (the highest among the transition metals) makes it possible to expect still higher physical properties for its carbide than for titanium carbide. On the other hand, scandium heads subgroup III A, which should impart to its compounds special features characteristic of compounds of the rare-earth metals.

The literature data on methods of preparation and properties of scandium carbides are extremely limited. Scandium carbide was first obtained in the work of Friedrich and Sittig (2), who assigned to it the composition Sc_4C_3; later, in work (3), scandium carbide ScC with a cubic structure of the NaCl type was reported, and the existence of Sc_2C carbide with a hexagonal structure analogous to that of V_2C was proposed. Vickery and co-workers (4), using specimens obtained by reduction of scandium oxide with carbon at high temperatures, showed that scandium monocarbide ScC exists, but that it possesses not a cubic but a hexagonal structure with 10 atoms in the unit cell (the preparation studied by him contained 78% Sc as against 78.92% Sc in ScC), despite the fact that the ratio of the radius of the carbon atom to the radius of the scandium atom is sufficiently small (0.48) for formation of the usual cubic interstitial phase; at the same time scandium mononitride possesses a cubic structure of the NaCl type. The reason for this might lie in the formation of covalent bonds between carbon atoms, which have lower ionization potentials than nitrogen atoms. According to Hume-Rothery (5), formation of the cubic structure in the case of ScC is suppressed by a deficiency of electrons, and the carbide is characterized by the hybrid electronic configuration d^2sp^3, corresponding to octahedral coordination.

In the work of Novotny and Auer-Welsbach (6), doubt was expressed concerning the correctness of Vickery's results on the structure of ScC, as well as concerning the validity of the assumption that a cubic phase of the NaCl type cannot form between scandium and carbon. In this connection they investigated the conditions for obtaining ScC carbide by reducing scandium oxide with carbon at 2000° (6) and by synthesis from the elements (7). As a result, a phase with a cubic structure and lattice period $a = 4.48$ kX was obtained, which, in Novotny' s opinion, corresponds either to a carbide with a deficiency of carbon atoms, ScC_{1-x}, or to an oxycarbide $Sc(C,O)$, but which in general, in its lattice parameter, agrees satisfactorily with the lattice periods of neighboring analogous phases—CeC, TiC, etc.

In the present work, attempts were repeated to obtain scandium carbide phases by reduction of scandium oxide with carbon, assuming the occurrence of the following reactions:

$$Sc_2O_3 + 5C = 2ScC + 3CO; \quad Sc_2O_3 + 6C = 2Sc_2C_3 + 3CO; \quad Sc_2O_3 + 7C = 2ScC_2 + 3CO$$

however, unlike previous works, heating of the corresponding charges was carried out in vacuum with continuous removal of the gaseous reaction products.

The results of studying the course of the reaction calculated for the production of the monocarbide are shown in Fig. 1, from which it follows that the reduction and carbide-formation reaction begins at a temperature of 1300-1400°; with increasing temperature the content of combined carbon in the reduction products increases, without, however, reaching the calculated content (21.08%) up to 1900°. The attainment of a carbon content close to the calculated value, with the sum of the contents Sc + C_{total} approaching 100%, pertains to the temperature range of about 1900-2000°, when the reaction mass is completely molten. In this case the content of C_{combined} is somewhat higher than the calculated content in ScC, which can be explained either by considerable dissolution of carbon in this carbide or by formation of another, carbon-richer carbide. An attempt to vary the heating time of the charge at a temperature of 1800°, i.e., up to the beginning of melting of the reaction mass, from 1 to 5 hours did not give satisfactory results, since the content of C_{combined} did not exceed 13-15% at a high content of C_{free}. In this connection the soot content in the charge was reduced from 95 to 80% of the calculated amount. Under these conditions, at a temperature of 1850° the content of combined carbon fluctuates within the range from 11 to 14%, with the sum of the contents Sc + C_{total} not exceeding 92%; at 1900° the content of C_{combined} reaches 22.1-22.3% (with a soot content in the charge of 80-85% of the calculated amount), but the content of C_{free} does not fall below 6%, and the sum Sc + C_{total} amounts to only 93-95%. Thus, under the indicated conditions, it is not possible to obtain ScC of the calculated composition.

Fig. 1. Temperature dependence of the chemical composition of the products of the reaction:

$$Sc_2O_3 + 5C = 2ScC + 3CO$$

(in vacuum, 1 h)

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The carbon content C_{combined} in samples obtained at temperatures above 1900°, increased relative to that calculated for ScC, made it possible, as already indicated, to suppose the existence of carbides higher in carbon content—Sc_2C_3 or ScC_2. Carrying out the second of the above reactions, calculated for the production of Sc_2C_3, gave results from which it follows that the full content of C_{combined} is not reached under any conditions; the same also applies to the results of studying the course of the reaction calculated for the production of ScC_2.

A more detailed study of the mechanism of the reaction calculated for the production of the monocarbide leads to the preliminary conclusion that this reaction proceeds, under certain conditions, through a stage of formation of metallic scandium. Thus, when the reaction is carried out in an alumina crucible at 1800°, the composition of the reduction product is as follows: 78.8% Sc; 22.0% C_{total}; 7.6% C_{free} (the sum Sc + C_{total} = 100.8%). Recalculation to the phase composition, on the assumption of formation of ScC, gives, respectively, contents of Sc and carbon not included in ScC almost the same as in ScC.

Apparently, diffusion of carbon into scandium, especially through an already formed ScC film, is very difficult and requires a long time; and when the reaction is carried out in vacuum with long holding times, evaporation of scandium through the carbide film and formation in the product of a considerable excess of free carbon are possible. Similar data are also obtained when the reaction is carried out in crucibles made of boron nitride and nitrided boron carbide. In this case the maximum amount of combined carbon, equal to 18-19%, is obtained when using a charge with a 10% excess of soot relative to the stoichiometric composition; the samples contain up to 6% free carbon. X-ray examination in such samples reveals—

a carbide phase with a cubic face-centered lattice of the NaCl type and a period $a = 4.53$ kX is detected.

Thus, the existence may be considered proven of cubic scandium carbide, close in composition to the formula ScC and possessing a tendency to add oxygen with the formation of oxycarbides, to dissolve carbon, and to similar effects, evidently connected with the exceptionally high degree of vacancy of the d-electron shell. This ability evidently should also manifest itself in the formation by scandium carbide of solid solutions with other isomorphous carbides with corresponding stabilization of the structure of scandium carbide. To test this assumption, we prepared solid solutions of scandium and titanium carbides by joint reduction of mixtures of the oxides $Sc_2O_3 + TiO_2$ with carbon in vacuum, calculated to obtain alloys of the ScC—TiC system with a composition step of 20 mol. %. The reduction—carburization products were subjected to hot pressing in order to obtain compact specimens. Metallographic analysis of the latter showed that all alloys are two-phase; moreover, the phase based on TiC, the content of which increases with the general increase in the titanium carbide content in the alloy (Fig. 2), has a hardness on the microhardness scale of about 5000 kg/mm^2, which considerably exceeds the microhardness of titanium carbide (3000 kg/mm^2); the hardness of the second phase, based on ScC, is about 2000 kg/mm^2, whereas the hardness of scandium carbide itself is 2700 kg/mm^2 (Table 1 and Fig. 3).

Fig. 3. Dependence of the microhardness of phases based on TiC (1) and ScC (2) on the composition of ScC—TiC alloys

Fig. 4. Concentration dependence of the specific electrical resistivity of ScC—TiC alloys

Table 1

Properties of alloys of the ScC—TiC system

ScC, mol. %	TiC, mol. %	Pycnometric density, g/cm^3	Microhardness, kg/mm^2: phase based on TiC	Microhardness, kg/mm^2: phase based on ScC	Specific electrical resistivity, μΩ · cm	Coefficient of thermal expansion $\alpha \cdot 10^{-6}$ deg^{-1}
100	0	3.06	–	2720	274.0	11.4
80	20	3.54	5170	2180	229.7	9.5
60	40	3.64	5270	1870	131.6	8.9
40	60	3.82	5530	2100	112.8	–
20	80	4.26	5680	1940	69.9	8.1
0	100	4.93	3000	–	52.5	8.3

The sharp increase in hardness upon dissolution of scandium carbide in titanium carbide is apparently connected with the high degree of vacancy of the 3*d*-electron level of the scandium atom; this also causes the decrease in the hardness of scandium carbide when titanium carbide is dissolved in it. Judging from the data obtained, there is a certain optimum concentration of solid solutions of these carbides in one another, corresponding to a strictly definite distribution of electron density in the lattice of the solid solutions and to the degree of overlap of the 3*d*-levels of titanium and scandium. It is possible

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Fig. 2

Figure 2: Fig. 2

Fig. 3

Figure 3: Fig. 3

Fig. 2. Microsections of alloys of the ScC—TiC system: *a*—ScC, *b*—80 mol. % ScC + 20 mol. % TiC; *v*—60 mol. % ScC + 40 mol. % TiC; *g*—40 mol. % ScC + 60 mol. % TiC; *d*—20 mol. % ScC + 80 mol. % TiC; *e*—TiC ($×$440)

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Fig. 3. Loosening of a silver electrode after polarization in 1 N NaOH, a—$\phi = -1.1$ (N.H.E.), b—$\phi = -1.5$ (N.H.E.). 30,000×

it may be assumed that, upon dissolution in scandium carbide of other cubic carbides (zirconium, hafnium, vanadium, niobium, tantalum), the limiting concentration of solutions of these carbides in ScC will be higher than that of titanium carbide; moreover, this increase should be inversely proportional to the degree of incompleteness of the *d*-shells of the metal atoms entering into them, expressed by the criterion $1/Nn$ (7), which is subject to further experimental verification. The limiting hardness of a solid solution of any of the cubic carbides in scandium carbide should in this case remain the same, or at least be of the same level.

The overlap of *d*-levels in the formation of solid solutions is also indicated by the decrease in specific electrical resistivity from scandium carbide to titanium carbide (Fig. 4). Judging from the data of metallographic analysis (Fig. 2), the region of solubility of scandium carbide in titanium carbide is greater than the region of solubility of titanium carbide in scandium carbide. Thus, the solid solution and the corresponding single-phase structure exist at least up to 20% ScC in the alloys (Fig. 2d), whereas upon dissolution of 20% TiC in ScC (Fig. 2b), the separation of a second phase on the polished section is clearly observed.

The coefficient of thermal expansion of ScC is $11.4 \cdot 10^{-6}$ and decreases sharply when 20 mol.% TiC is dissolved in ScC, remaining, with a further increase in the TiC content of the alloys, practically constant and close to the coefficient of thermal expansion of TiC.

The results obtained open broad prospects for the use of scandium carbide as a compound capable of sharply increasing the hardness of carbides of other transition metals, in particular titanium carbide, which may find numerous useful practical applications.

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