HEPTAMANGANESE TRICARBIDE Mn_7C_3*

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A procedure was examined for the preparation of Mn_7C_3 by reaction of manganese dust with n-pentane at 850°C and a reduced pressure. The identity of the product was confirmed by chemical and X-ray diffraction analysis; no other carbide was found to be present. The powder X-ray diffraction patterns were investigated in terms of the structure assignment either to the hexagonal *$P6_3mc$* or the orthorhombic *Pnma* symmetry. The reflection intensities fit better the latter structure, but the possibility of hexagonal indexing indicates that the octahedral structural elements do not arrange coherently during the synthesis. The composition of the products of hydrolysis is also consistent with the formula Mn_7C_3. The gaseous products contain hydrogen, methane, and a number of other hydrocarbons, mostly saturated, whose concentration decreases with increasing number of carbon atoms in the molecule. The concentration distribution of the hydrocarbons is discussed in terms of the radical mechanism of the hydrolysis; the data are borne out indicating that in Mn_7C_3 the covalent nature of the bonds is more pronounced than in salt type carbides.

The hydrolyzability of carbides is in a relation to their structure. Easily hydrolyzed are particularly stoichiometric ionic carbides[1,2] such as CaC_2 or LaC_2, or high-molecular structures of ionic nature such as Al_4C_3. Some interstitial carbides are also hydrolyzed; data of their hydrolysis, however, are insufficient and do not lead to unique concepts of the process. In the present work, which is meant as a model study of hydrolysis of interstitial carbides, we are concerned with the hydrolysis of heptamanganese tricarbide, and in this connection, also with its synthesis and structure.

The Mn–C system can occur[3,4] in six phases, *viz.* Mn_3C_{1-x} $Mn_{23}C_6$, $Mn_{15}C_4$, Mn_3C, Mn_5C_2, and Mn_7C_3. The phases can be prepared by reacting the metal with the corresponding amount of carbon. In view of the low thermal stability of carbides of manganese, the products obtained in this manner at temperatures below 1 000°C may contain some oxygen or other components of the reaction system[3,5].

Heptamanganese tricarbide was first prepared by Westgren and Phragmen[6]. Initially its structure was thought hexagonal, but this view was revised later by West-

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gren[7], who suggests that the compound possesses a trigonal superstructure similar to that in Cr_7C_3. Nevertheless, both the trigonal[3,8] and the hexagonal[9] structures were considered in more recent study. According to Bouchaud and Fruchart[5,10], neither of them is quite correct; the authors refined the results and suggest that the substance has an orthorhombic symmetry, apparent especially on well-crystallized samples. Bouchaud[5] rejects the trigonal superstructure both for Mn_7C_3 and Fe_7C_3, and so do Rouault, Herpin and Fruchart[11] for Cr_7C_3, which is presumably isomorphous with the orthorhombic Mn_7C_3. Still, in some papers[4,12] only the hexagonal structure is regarded for Mn_7C_3, no discussion being devoted to this problem. As an illustration of the complexity of the problem, it is worth mentioning that the diffraction patterns of heptamanganese tricarbide are not included in the JCPDS (formerly ASTM) catalogue.

Carbides of manganese are hydrolyzed by water or dilute acids[13-16]. Published data indicate the formation of methane and hydrogen[13], and also of additional saturated as well as unsaturated hydrocarbons[14,15]; in paper[16] the gaseous hydrolysis products are specified for the various carbide phases.

When testing for the agreement between the stoichiometric and the structure results one should choose a single phase preparation with a known, well-defined structure. This requirement in best met by Mn_7C_3, the thermally most stable (up to 1 113°C, ref.[4]) and carbon-richest carbide of manganese. In order to prevent the formation of oxygen-stabilized phases, use was made of a novel approach starting from the metal and n-pentane. For the above reasons attention was paid also to the problem of the actual structure of the Mn_7C_3 samples prepared.

EXPERIMENTAL

The samples were prepared by reacting manganese dust of 4N purity, grain size below 0·06 mm, with n-pentane (99·9%, Carlo Erba) in the apparatus described previously[17]. The conditions were as follows: flow rate of n-pentane vapour at its saturated vapour pressure (20°C) 10—20 $l\,h^{-1}$ temperature 840—850°C, reaction period 1·5 h.

Powder X-Ray Diffraction

The diffraction patterns were obtained on a Geigerflex instrument (Rigaku-Denki) equipped with a goniometer: filtered CrK_α radiation was used, the anodic current was 10 mA, voltage 40kV. The flat samples were protected against humidity by a layer of petrolatum and paraffin oil.

The theoretical diffraction patterns were calculated by the Lazy Pulverix program[18] based on the entered coordinates of the atoms of the asymmetric group in the elementary cell and the corresponding lattice parameter. The lattice parameters of our samples were obtained by statistical processing using the program by Burnham[19]. The density of the samples was measured by means of a manostatic densimeter with tensometric recording[20].

Chemical Analysis

The carbide samples were dissolved in concentrated hydrochloric acid of reagent grade purity, the free carbon was separated by filtration on a Gooch crucible and determined, similarly as the total carbon, on a Coulomat Strohlein apparatus, type KEHR, by ignition in a stream of oxygen. In the filtrate stabilized with hydroxylammonium chloride, manganese was determined chelatometrically at pH 10—11 in the presence of triethanolamine using Eriochrome Black T as indicator. The content of bonded oxygen was determined on an EAO-202 Exhalograph Balzers. Nitrogen was detected, after dissolving the sample in hydrochloric acid, by reaction with Nessler's reagent in alkaline solution.

Gas Chromatographic Analysis

Carbide powder was freed from gases by evacuation in an ampoule, and decomposed in it with water at 80°C. After the decomposition, the gas was sampled and analyzed on a Hewlett–Packard 5840A gas chromatograph interfaced to a 18850 A terminal. The following program was used: a 2 m column of 30% DC 200 on Chromosorb P (C_3—C_5 hydrocarbons), back flushing of the column (hydrocarbons C_6 and higher), 2 m column of Porapak Q (CO_2, C_2 hydrocarbons), and a 5A molecular sieve (H_2, O_2, N_2, CO, CH_4). The temperature was held at 70°C, the flow rate of helium as the carrier gas was 20 ml min^{-1}; a thermal conductivity detector (TCD) was used.

Qualitatively, the records were evaluated by using standards (Linde). The substance-specific correction factors for our TCD were established based on the analysis of a standard mixture of hydrogen, carbon dioxide, and C_1—C_4 saturated hydrocarbons. As a result, the content of these compounds could be read directly in per cent values by volume, the content of additional components, if present, was calculated as the balance by means of molar correction factors[21] with respect to the factor of methane established experimentally for our TCD.

Mass Spectrometric Analysis

Higher hydrocarbons emerging from the hydrolysis were analyzed on a 8000 A mass spectrometer (LKB, Stockholm). The injection temperature was 150°C, ionization energy 15 and 70 eV.

RESULTS AND DISCUSSION

Synthesis of Mn_7C_3

The reaction of manganese with n-pentane at 850°C, similarly as that with methane[14], gives rise to the carbide richest in carbon, hence, Mn_7C_3. (The highest stability of this carbide was also confirmed by a model thermodynamic calculation for the reactions of manganese with methane[22]). The reaction temperature is lower and the time shorter than in the conventional reaction of manganese with carbon. By chemical analysis, the preparations contained 90·6% Mn and 8·15% bonded carbon; the residue (1·6%) was free carbon. No oxygen or nitrogen was observed, which agrees with the results obtained by Fisher and Bangert[15] for carbide prepared by reacting methane with the oxide, Mn_3O_4.

Structure

The structure of the Mn_7C_3 samples prepared is to an extent disordered as far as the orientation of the manganese atoms octahedra is concerned: the powder diffraction patterns exhibit reflections corresponding to the hexagonal as well as the orthorhombic structure, and also reflections which the hexagonal symmetry fails to account for. The difference between the hexagonal arrangement ($P6_3mc$, the Ru_7B_3 type[23]) and the arrangeent in the orthombic symmetry is very small[5,10].

As will be clear from Fig. 1, the tetrahedral arrangement of the manganese atoms in the two structures is the same. However, in the hexagonal arrangement the columns of the octahedral groupings of manganese atoms, connected by their triangular faces, are oriented so that their three-fold axis lies in the z direction always in one sense, whereas in the orthorhombic arrangement the same inclination with respect to the three-fold axis is only preserved in the diagonals of the imaginary hexagonal network. The difference in the orientation of the octahedral columns is $\pi/3$. Furthermore, the orthorhombic cell is somewhat distorted with respect to the reference hexagonal cell. As a result of the distortion of the pseudo-hexagonal orthorhombic structure, the diffraction reflections are split into a number of closely lying lines. It is this splitting of reflections, together with the existence of a reflection for $d = 223{\cdot}3$ pm which disagrees with the hexagonal symmetry, that brought Bouchaud[5] to consider the orthorhombic symmetry. However, according to our calculations based on the atomic positions reported by Bouchaud[5], the theoretical intensity of the reflection for $d = 223{\cdot}3$ pm ($hkl_{\text{o-rh}}$ 201) is negligible as compared with the intensity observed by Bouchaud for Mn_7C_3 or with the analogous reflection for carbide of iron[24]. For the subsequent calculations we employed therefore the more

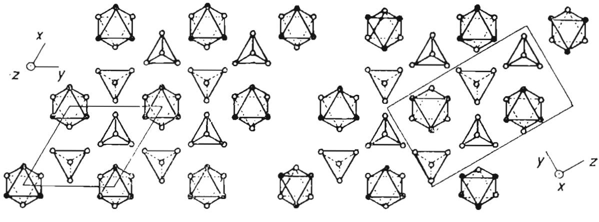

FIG. 1

Arrangement of the metal atoms in the hexagonal structure of the type[23] Ru_7B_3 and in the orthorhombic structure of the type[11] Cr_7C_3. ○ fractional coordinate 0 and fractional coordinate 1; ● fractional coordinate 1/2 in the direction perpendicular to the drawing plane

a $P6_3mc$ type Ru_7B_3, *b* Pnma type Cr_7C_3

recently published[11] coordinates of atoms in the structure of Cr_7C_3 belonging to the space group *Pmcn*, transformed into the *Pnma* orientation as given in Table I.

The calculation of the diffraction patterns for orthorhombic Mn_7C_3, based on these new coordinates, yields for the intensity of the 201 reflection a higher value, approaching better the intensity observed for our sample (Table II) as well as for the sample of Bouchaud[5].

Table II gives the *hkl* indices for the hexagonal and for the corresponding orthorhombic structures so as to make apparent the genesis of the orthorhombic reflections from the hexagonal ones. The observed reflections are indexed for the two alternatives. The parameters for the hexagonal lattice are slightly more correct than those for the orthorhombic lattice, where, however, the index assignment is questionable with regard to the insufficiently clear splitting of the hexagonal 002 and 210 doublet into five orthorhombic reflections. The observed intensities, on the other hand, agree appreciably better with the calculated values for the orthorhombic structure. For in-

TABLE I

Atom positions used for the calculation of the theoretical diffraction patterns of Mn_7C_3 of hexagonal and orthorhombic structure types

Hexagonal Mn_7C_3 ($P6_3mc$)		Positions for Ru_7B_3 type (ref.[23])		Modification for Mn_7C_3 (ref.[5])
position		x/a	y/b	z/c
6c	Mn_I	0·4563	−0·4563	1/3
6c	Mn_{II}	0·1219	−0·1219	0
2b	Mn_{III}	1/3	2/3	5/6
6c	C_I	0·187	−0·187	0·580
Orthorhombic Mn_7C_3 (*Pnma*)		Transformed coordinates (ref.[11])		
position		x/a	y/b	z/c
8d	Mn_I	0·2509	0·0657	0·0218
8d	Mn_{II}	0·0565	0·0642	0·8119
4c	Mn_{III}	0·2501	0·250	0·2063
4c	Mn_{IV}	0·2619	0·250	0·4165
4c	Mn_V	0·0579	0·250	0·6261
8d	C_I	0·0288	0·0291	0·3428
8d	C_{II}	0·4594	0·2500	0·5629

TABLE II

Comparison of the calculated diffraction patterns of Mn_7C_3 in the hexagonal and the orthorhombic symmetries with the observed data (CrK_α radiation). The determined lattice parameters for the two structures (pm) are: $a = 693{\cdot}0 \pm 0{\cdot}2$, $c = 454{\cdot}1 \pm 0{\cdot}2$; $a = 454{\cdot}1 \pm 0{\cdot}4$, $b = 694{\cdot}5 \pm \pm 0{\cdot}6$, $c = 1\,198{\cdot}8 \pm 1{\cdot}2$, the parameters used for the calculation are: $a = 694{\cdot}4$ $c = 454{\cdot}2$ (ref.[4]); $a = 454{\cdot}6$, $b = 695{\cdot}9$, $c = 1\,197{\cdot}6$ (ref.[5])

Hexagonal symmetry ($P6_3mc$)				Orthorhombic symmetry ($Pnma$)					
hkl	I_{calc}^{rel}	θ_{obs} deg	$d_{obs} - d_{calc}$ pm	hkl	I_{calc}^{rel}	$I_{calc}^{rel\,a}$	I_{obs}^{rel}	θ_{obs} deg	$d_{obs} - d_{calc}$ pm
100	2·7			011	16·3				
				002	7·6				
				101	2·1				
101	1·5			111	0·0				
				102	0·3				
110	1·6			020	0·6				
				013	1·1				
				112	30·7				
				103	27·3				
200	14·4			022	60·1				
				004	14·3				
				113	0·0				
				121	126·9				
201	124·4			122	1·6				
				104	0·7				
				114	72·2				
002	112·2			200	318·3			30·21	0·60
				123	56·4				
				031	408·0	472·0	367	30·29	−0·18
210	254·5	30·33	−0·005	024	313·9			30·33	−0·04
				015	309·2			30·41	−0·33
				201	196·9	66·1	150	30·97	−0·49
				210	61·4				
102	361·3	32·63	−0·05	211	918·1			32·63	0·04
				202	464·8	563·7	433	32·68	−0·19
				105	286·3				
				212	31·4				
				131	1 000	1 000	1 000	34·35	0·05
211	1 000	34·35	0·075	124	965·3				
				115	982·0				
300	92·1	34·90	0·152	033	229·2	115·1	133	34·90	−0·10
				006	113·6				
				203	0·0				
				132	508·0	172·4	58	35·80	0·8

TABLE II
(*Continued*)

Hexagonal symmetry ($P6_3mc$)				Orthorhombic symmetry ($Pnma$)					
hkl	I^{rel}_{calc}	θ_{obs} deg	$d_{obs} - d_{calc}$ pm	hkl	I^{rel}_{calc}	$I^{rel\,a}_{calc}$	I^{rel}_{obs}	θ_{obs} deg	$d_{obs} - d_{calc}$ pm
112	35·8	37·12	−0·118	213	54·0	51·3	50	37·07	0·14
				220	98·7		67	37·15	−0·36
				221	4·2				
301	230·0	38·76	−0·114	133	219·8	110·5	67	38·65	0·14
				106	109·2		83	38·76	0·09
202	191·4	39·22	0·083	222	536·1	278·4	242	39·22	0·01
				204	263·4				
				125	29·8				
				116	175·1				
				214	25·4				
220	123·8	41·40	−0·040	040	173·9	175·6	116	41·39	−0·23
				026	343·7		133	41·42	−0·03
				223	52·5				
				134	258·4				

[a] Recalculated with respect to the total intensities of reflections that for the hexagonal indexing were regarded as coinciding, and intensities of the observed, in the hexagonal symmetry non-indexable reflections with the presumed orthorhombic indices (hkl) 201 and 132.

stance, the 201_{hex} reflection, whose relative intensity should be $I_{201} = 0·1244I_{211}$, was not in fact observed. The intensity ratio for the 301_{hex} and 202_{hex} lines was reverse as compared with the predicted value. Both facts can be well explained in terms of the orthorhombic symmetry. Of the purely orthorhombic reflections whose theoretical intensity is so high that the lines should be observable, the above-discussed $201_{o\text{-}rh}$ reflection and the $132_{o\text{-}rh}$ reflection were recorded; their intensities, however, differ somewhat from the predicted values and the differences between the calculated and the observed interplanar distances are here also highest.

It can be thus deduced that the Mn_7C_3 sample prepared, constituting a conglomerate of crystallites, has neither a purely hexagonal nor a purely orthorhombic symmetry. This can be explained so that the octahedral columns of manganese atoms in the crystallites are not arranged coherently enough. The powder diffraction patterns then can be indexed in both symmetries. The occurrence of the $201_{o\text{-}rh}$ reflection for our sample with an imperfectly developed orthorhombic superstructure which is practically undisturbed with respect to the hexagonal structure indicates that this reflection is not associated with the distortion of the hexagonal lattice; its intensity only depends on the positions of the atoms in the orthorhombic cell. This is consistent with the data for the modified atomic coordinates used for our calculation of the theoretical diffraction patterns.

Based on the lattice parameters of Mn_7C_3, we calculated the theoretical densities for the hexagonal and the orthorhombic structures, *viz.* 7 393 and 7 388 kg m^{-1}, respectively. The densities, agree with the data of Bouchaud[5] and with our experimental values 7 240 ± 500 kg m^{-3}; the slight decrease against the theory is due to the presence of free carbon. The pycnometric density of Mn_7C_3 as found by the authors[16], 3 800 kg m^{-3}, was not confirmed; this erroneous value was obviously derived based on the incorrectly calculated X-ray density, 3 690 kg m^{-3}, when half of the formula units in a cell were considered.

Hydrolysis

The gaseous products of hydrolysis of Mn_7C_3 were found to contain hydrogen, methane, and additional hydrocarbons, particularly saturated ones. The samples being hydrolyzed in vacuum, the oxidation state of manganese transformed into II. Stoichiometrically the H/C ratio in the gaseous products should be 4·67; the experimental value is 4·75. The difference may be due to the presence of an impurity of manganese metal in the sample or to an inaccuracy in the gas chromatographic determination of hydrogen. The composition corresponding to the H/C ratio of 4·75 is $Mn_{7.125}C_3$. The H/C ratio calculated for the data reported in ref.[16] is 3·29, corresponding to the composition $Mn_{4.9}C_3$.

In agreement with the observations of Fisher and Bangert[15], the solid product formed on the decomposition of Mn_7C_3 with water in the absence of air is manganese(II) hydroxide, which is not oxidized even after a longer time of standing in the atmosphere of the products of hydrolysis. By reaction of Mn_7C_3 with atmospheric humidity, however, a brown product is formed; as indicated by the results of gravimetric analysis, the compound is manganese(III) oxide-hydroxide. This was confirmed also by the powder X-ray diffraction examination: the diffraction patterns corresponded to feitknechtite MnO(OH) as given in the ASTM cards[25].

The composition of the gaseous hydrolytic products of Mn_7C_3 (Table III) can be interpreted in terms of the mechanism of hydrolysis, analogous, *e.g.*, to the hydrolysis of uranium monocarbide[26,27]. The water molecules attack the Mn–Mn and Mn–C bonds on the surface, whereupon Mn^{2+} and OH^- ions and atomic hydrogen are formed. With the nearest partially naked, isolated carbon atoms the atomic hydrogen forms hydrocarbon radicals, which by additional recombination in the presence of excess hydrogen atoms give molecules of hydrogen, methane, and additional, particularly saturated, hydrocarbons. The concentration of the hydrocarbons decreases with increasing number of carbon atoms in their molecules, as does the probability of recombination of hydrocarbon radicals in the presence of atomic hydrogen. This radical mechanism should be limited to the extent to which the metal–carbon bond has a partly ionic nature. It is clear that if the ionic character of the metal–carbon bond is pronounced enough, the hydrolysis (in its true sense) will lead to the hydrocarbon corresponding to the carbide ion involved (C^{4-}, C_2^{2-}, C_3^{4-}); the mechanism will be the same as in the hydrolysis of other salts of weak acids and strong bases. For Mn_7C_3, a predominantly covalent nature of the Mn–C bonds is assumed by Novik and Taran[12], who, based on the asymmetric arrangement of the carbon atoms between the six manganese atoms of the trigonal coordination prisms, suppose that there is a covalent bonding relation between a carbon atom and four of the six surrounding manganese atoms.

An exact calculation of the theoretical concentrations of the various members of the hydrocarbon series, as formed in the hydrolysis of Mn_7C_3, is a complex problem. It is worth mentioning that the distribution of carbon atoms among the members of the hydrocarbon series can be approximated fairly well by the series $a_1 = 1$, $a_n = 1/(k \cdot 2^{n-1})$, where $n = 2, 3, 4 \ldots$ is the number of carbon atoms in a molecule of the hydrocarbon and k is a constant, $k = 1{\cdot}1$ for Mn_7C_3. The fit is demonstrated by Table III.

TABLE III

Composition of the gas mixture of the products of hydrolysis of Mn_7C_3 as determined by gas-liquid chromatography and mass spectrometry, and a comparison of the observed distribution of the carbon atoms among the various hydrocarbons with the distribution approximated by an infinite series

Compound	Content % vol.	Number of carbon atoms in a molecule	Distribution of carbon atoms	
			observed	approximated
Hydrogen	47·6			
Methane	38·9	1	1	1
Ethane, ethene	9·12	2	0·47	0·45
Propane	2·78	3	0·21	0·23
Butanes	1·08	4	0·11	0·11
Pentanes	0·300	5	0·039	0·057
Hexanes[a]	0·100	6	0·015	0·028
Heptanones[a]	0·051	7	0·009	0·014
Octanes[a]	0·022	8	0·004	0·07

[a] Results of mass spectrometric analysis.

Under the assumption of formation of saturated hydrocarbons only, the recombination reactions of the radicals do not result in an increase in the number of moles in the gas evolved against the theoretical stoichiometric proportion of four mol of gas per mol of carbide. The experimentally observed volume (in standard conditions), 208 ml per g sample containing no free carbon, is consistent with the predicted volume for the hydrolysis of Mn_7C_3, 213 ml g^{-1}, taking into account that a small fraction of higher hydrocarbons could have remained in the condensed state. For the ionic mechanism of hydrolysis, the gas volume would consist of 75% methane and 25% hydrogen. The radical mechanism is responsible for the higher content of hydrogen in the gas mixture.

It can be concluded that the suggested model of hydrolysis is consistent with the structure involving isolated carbon atoms as well as with the nature of bonding within the carbide structure. The results of analysis of the gaseous products also agree with the presumed stoichiometry, Mn_7C_3. The composition Mn_8C_3 suggested by Picon and Flahaut[28,29] was not confirmed. The reported[16] composition of the gaseous hydrolytic products sampled 10 min after the initiation of the decomposition, characterized by a higher fraction of unsaturated hydrocarbons and of hydrocarbons in general with respect to hydrogen, may be regarded as an indication of adsorption or chemisorption of the forming hydrogen on the surface of the reacting carbide.

The carbide of manganese under study is fairly reactive with water as compared with carbides of other transition metals. As suggested by Payer and Steahle[30], the disposition of interstitial carbides to dissolution is given by the properties of the metal involved. The anodic as well as cathodic polarization curves of carbides and the corresponding metals are reported[30] to be similar in shape. Since the formation of the interstitial carbide from the metal brings about a lowering in the homogeneity and adhesion of the passivating layer on the surface, the corrosion potential is usually lower for the carbide than for the metal. Metals such as titanium and chromium, with a highly passivating nature, also form carbides with higher corrosion potentials than as would comply with the electropositive nature of the metal. With the low tendency of manganese to passivation, the hydrolyzability of its carbides is also in agreement with its electropositive character. By our subjective observation, the affinity of Mn_7C_3 for water corresponds roughly with that of the carbide ThC, the corrosion potential of which is[30] $-0{\cdot}9\ V_H$.

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