

**HYDROLYSIS OF TERNARY CARBIDES OF MANGANESE Mn_3MC
(M = Al, Ga, In, Sn)***Pavel KAREN^a, Roman KRÁL^a, Jaroslav KUBÁT^b and Bohumil HÁJEK^a^a *Department of Inorganic Chemistry and*^b *Department of Coke and Gas and Air Protection,**Prague Institute of Chemical Technology, 166 28 Prague 6*

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Perovskite type ternary carbides of manganese Mn_3MC (M = Al, Ga, In, Sn) are hydrolyzable by acids, water and air moisture. Mn_3AlC is hydrolyzed most readily; its linear corrosion rate with liquid water is $0.3 \mu m h^{-1}$ at $60^\circ C$, whereas the value for Mn_3GaC is $0.06 \mu m h^{-1}$. The reactivity decreases with increasing nobleness of the nontransition metal involved. The hydrolysis process gives rise to a mixture of hydrogen and methane and a low amount of higher saturated and unsaturated hydrocarbons whose fractions are consistent with the concept of the radical mechanism of the hydrolysis reaction.

Carbides of transition metals possess some characteristic features in which they differ from carbides of nontransition metals. The chemical bonding in most of them has the character of a metallic bond, and this is related with the stability of structures of those transition metal carbides containing more metal than as corresponds to the conventional concept of valency of the element in question in its bonding to carbon. Subjected to hydrolysis, these carbides give hydrogen and a homologous hydrocarbon series, usually a natural or an even one according to the kind of carbon grouping in the carbide structure^{1,2}. In contrast to this, carbides of nontransition metals do not have a metallic character and their hydrolysis only results in the hydrocarbon corresponding to the anionic carbon grouping in the structure of the solid.

In this relation it appeared useful to gain information on the hydrolysis behaviour of ternary carbides comprising a transition and a nontransition metal. We elected carbides of manganese with the perovskite type structure, Mn_3MC , where the nontransition metals were aluminium, gallium, indium and tin, which themselves (save aluminium) do not form carbides. The formation, preparation and properties of these ternary carbides have been investigated by several authors³⁻¹², no data of their hydrolysis, however, are available although carbides of manganese themselves are readily hydrolyzed.

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EXPERIMENTAL

Preparation. The carbides were synthesized by a two-step procedure comprising the preparation of binary alloys of the two metals and their subsequent reaction with carbon. Granulated manganese powder of reagent grade purity (Lachema, Brno) was melted under argon in a corundum crucible with the appropriate amount of Al, Ga, In or Sn of 5N purity (Research Institute for Metals, Panenské Břežany). The alloy was analyzed for manganese, the deficient component was added if necessary, and the melting was repeated. The alloy was crushed and ground and homogenized for 48 h in a tungsten carbide vibrating mill with the corresponding amount of granulated carbon black of 5N purity (Pramet, Šumperk) under hexane. The resulting mixture consisting of particles about 3 μm size was compressed into pellets, placed in a glassy carbon boat, sealed in a quartz ampoule under 10 kPa argon, and sintered at 900°C. Samples were taken in 200 h and the remainder was additionally annealed in a molybdenum casing for another 500 h in the presence of a getter, which was a mixed metal accommodated in a corundum crucible near the sample.

Chemical analysis. Manganese was determined chelometrically¹³ after dissolving the sample in hot concentrated hydrochloric acid. The nontransition metals were determined, after diluting, by flame spectrophotometry on a Varian AA 775 instrument. Total carbon was determined on a Ströhlein CS-mat 900 instrument by combustion in oxygen. Free carbon, trapped on prepared asbestos filter after sample dissolution, was determined likewise.

Powder X-ray diffraction patterns. A focussing chamber 57.3 mm in diameter (State Research Institute for Materials, Prague-Běchovice) combined with a Mikrometa 2 (Chirana) source was employed for phase analysis. The diffraction patterns for the determination of the lattice parameters were obtained on a Rigaku Denki diffractometer. Filtered CrK_α radiation was invariably used.

GLC analysis. The carbides were hydrolyzed with water in evacuated glass ampoules with silicone rubber stoppers fitted with a Teflon sealing foil; the hydrolysis time was from one (Mn_3AlC) to six (Mn_3InC) weeks, temperature 60°C. The gas evolved was analyzed on a Hewlett-Packard 5830A gas chromatograph using two arrangements. In the one, two columns were used: one, 1 m long, contained a 5 Å molecular sieve (H_2 , O_2 , N_2 , CH_4), the other, 2.5 m long, contained Porapak Q and T (CO_2 , C_2H_4 , C_2H_6); the detection was thermal conductivity, carrier gas helium fed at a flow rate of 20 ml min^{-1} . In the other arrangement, a column 2.1 m long packed with DC 200 on Chromosorb P (CH_4 , C_2 through C_6 hydrocarbons) was used; the detection was flame ionization, carrier gas was hydrogen at a flow rate of 15 ml min^{-1} . A natural gas standard was employed for both qualitative and quantitative analysis purposes, hydrogen content was determined by balance calculation.

Hydrolysis rate. The course of the hydrolysis reaction was monitored by measuring continuously the volume of the gas evolved at 27 and 60°C under argon. During the decomposition of approximately 0.1 g of Mn_3AlC sample with distilled water containing traces of a surfactant, the carbide powder was magnetically rotated. The linear corrosion rate of the carbide was calculated in terms of the model of contracting spheres in a particulate system of a known size distribution¹⁴.

RESULTS AND DISCUSSION

Carbide Synthesis and Characterization

The diffusion reaction of carbon with the manganese alloys (Table I) led invariably to products containing the perovskite type Mn_3MC ternary carbides. The results of qualitative X-ray phase analysis and chemical analysis are given in Table II. Only Mn_3AlC was phase pure, the remaining samples contained some amount of unreacted carbon, and Mn_3InC and Mn_3Sn , even some unreacted In and Sn, respectively. The amount of these impurities decreased only slightly on the additional 500 h annealing. The presence of less than 2% Mn_4N in the Mn–Ga alloy as well as the presence of MnO in the surface parts of the Mn_3GaC pellets observed after 200 h of annealing was due to contamination by air that took place during the melting of the Mn–Ga alloy. The Mn_4N content of the starting alloy corresponded to no more than 0.12 wt. % nitrogen in the ternary carbide, which in turn corresponds to 3% carbon for which nitrogen can completely substitute in the carbide structure¹⁰. For the remaining carbides, ammonium ions were not detected in the solution after acid decomposition.

The lattice parameter values (Table II) lie near the upper limits of published data (Mn_3AlC , refs^{5,11,12}; Mn_3GaC_x , refs^{10,11}; $Mn_3In_xC_x$, ref.⁷; Mn_3SnC_x , refs^{5,11}), and since the lattice parameters of Mn_3MC_x carbides increase as x approaches unity, it follows that the carbon content of our samples is near the maximum value attainable. For Mn_3GaC_x (Mn_3GaN_x), the dependence of the lattice parameter on x is available¹⁰, and it can be deduced from it that the composition of the ternary

TABLE I
Results of X-ray diffractometric analysis of starting manganese alloys

Alloy	Major phase	Content estimate	Lattice parameters pm	Minor phase	Content estimate	Lattice parameters pm
Mn_3Al	$\beta Mn-Al$	$\sim 2/3$	$a = 641$	$\beta Mn_{0.95}Al_{0.05}$ αMn	$\sim 1/3$ $\leq 2\%$	$a = 633$
Mn_3Ga	$\epsilon Ga-Mn$ (hex)	$< 100\%$	$a = 541$ $c = 436$	Mn_4N	$\leq 2\%$	
Mn_3In	$\beta Mn-In$	$2/3$	$a = 667$	In	$\sim 1/3$	$a = 325$ $c = 495$
Mn_3Sn	$Mn_{11}Sn_3$ (hex)	$< 100\%$	$a = 567$ $c = 453$			

carbide obtained on a 700 h annealing is $\text{Mn}_3\text{GaC}_{>0.95}\text{N}_{<0.03}$, taking into account the presence of nitrogen as discussed above.

Hydrolyzability

All of the ternary carbides synthesized are subject to hydrolysis, their reactivity, however, is different. They react with non-oxidizing mineral acids similarly as the metals themselves, and they also decompose on the action of air moisture, Mn_3AlC being most reactive and Mn_3InC and Mn_3SnC , least reactive. Exposed to air of 70% relative moisture at 20°C, a conventionally ground powder sample of Mn_3AlC , grain size about 10 μm , gets covered by a visible brown layer of manganese(IV) oxide-hydroxide in a time from several days to weeks, Mn_3InC , only in several months.

The linear corrosion losses for the reaction of Mn_3AlC with water at 27°C and 60°C are given in Table III. The hydrolysis rate of Mn_3GaC is appreciable only at 60°C, amounting to 0.06 $\mu\text{m h}^{-1}$. The decomposition of the remaining samples was too slow for reliable measurement.

Hydrolysis

The hydrolysis of the ternary carbides with water in the absence of oxygen resulted in the formation of a white inorganic residue containing manganese(II) and the

TABLE II
Results of diffractometric phase analysis and chemical analysis

Sample	Time h	Lattice parameter ^a pm	Minor phase wt. %	Chemical analysis, %				
				Mn	M	C _{bond}	C _{tot}	
Mn_3AlC	200	387.22 ± 0.01	—	calc.	80.87	13.24	5.89	
				found	81	11	5.4	5.4
Mn_3GaC	200	389.45 ± 0.04	$\text{MnO} \sim 2\%$	calc.	66.85	28.28	4.87	
				found	65	29	4.8	5.8
Mn_3GaC	700	389.57 ± 0.06		found	67	27	4.4	5.8
Mn_3InC	200	397.34 ± 0.02	$\text{In} \sim 10\%$	calc.	56.51	39.37	4.12	
				found	55	39	4.8	5
Mn_3InC	700	397.26 ± 0.01	$\text{In} \sim 5\%$	found	52	42	4	5
Mn_3SnC	200	397.92 ± 0.01	$\beta\text{Sn} \sim 2\%$	calc.	55.77	40.16	4.06	
				found	56	40	3.5	4.6

^a Parameter *a* for perovskite type carbide; mean error of statistical processing following ref.¹⁵.

trivalent (Al, Ga, In) or divalent (Sn) metal in the form of hydroxides or oxide-hydroxides. The gas evolved contained hydrogen, methane and a homologous series of saturated hydrocarbons, and traces of unsaturated hydrocarbons (Table IV). The concentration of each higher hydrocarbon in the series was lower than that of the preceding one, as is typical of hydrolysis of "metallic" carbides of transition elements for which a radical pathway of reactions proceeding from a primary mixture of methane and hydrogen has been suggested by us^{1,2}. It is clear from Table IV that the amount of higher hydrocarbons with respect to the amount of methane decreases with increasing fraction of hydrogen in the gas system. The extent of the radical

TABLE III

Linear corrosion loss during the reaction of Mn_3AlC powder with water at 27 and 60°C

Extent of carbide reaction	Corrosion loss, $\mu m h^{-1}$	
	27°C	60°C
0.2	0.09	0.32
0.5	0.08	0.28
0.8	0.07	0.26

TABLE IV

Composition of gaseous products of hydrolysis of ternary carbides

Sample	Hydrogen and hydrocarbon contents ^a , vol. %							S %	H/C
	H ₂	CH ₄	C ₂	C ₃	C ₄	C ₅	C ₆		
Mn ₃ AlC	74.7	22.4	2.5	0.35	0.038	0.005	n.d.	4.6	9.0
			0.02	n.s.	0.003	0	n.d.		
Mn ₃ GaC	77.7	21.6	0.6	0.05	0.003	0	0	0.9	10.7
			0.01	n.s.	0	0	0		
Mn ₃ InC	75.8	18.8	3.6	1.26	0.200	0.023	0.007	10.5	8.37
			0.2	n.s.	0.040	0.003	n.s.		
Mn ₃ SnC	88.5	9.6	0.44	0.60	0.035	0.009	0.04		15.5
			0.52	n.s.	0.160	0.017	n.s.		

^a Upper data: saturated hydrocarbons, lower data: unsaturated hydrocarbons; 0 — below the threshold concentration of 0.0005 vol. %; n.d. — not determined, n.s. — not separated.

reactions, leading to the hydrocarbon mixtures, decreases, as is expressed by the parameter s which is the fraction of H radicals, formed besides CH_4 , that has reacted with hydrocarbons to give H_2 and hydrocarbon radicals, recombining consecutively to hydrocarbons^{2,14}. A similar behaviour has been observed for carbides of manganese¹⁴ in dependence on the stoichiometry of the hydrolysis reaction.

A measure of the stoichiometry of the hydrolysis reaction of a carbide is the H/C molar ratio in the resulting hydrogen-hydrocarbon mixture. The difference between the H/C ratios for Mn_3AlC , Mn_3GaC and Mn_3InC is small and is given by the defectivity of the preparations. Mn_3AlC gave rise to a mixture with H/C = 9, which is the theoretical value, s was approximately 5%. Because of the carbon deficiency, Mn_3GaC gave a mixture with H/C about 11, s was as low as about 1%. The H/C = 8.37 ratio for Mn_3InC is consistent with the indium deficiency with respect to the ideal formula, which seems to be a characteristic feature of this system⁷ and agrees with the observed presence of the unreacted metal in the preparation (Table II). In accordance with the lower H/C ratio, s was 10% for this system.

The composition of the product of hydrolysis of Mn_3SnC (Table IV) differed from the products of the remaining carbides in the presence of unsaturated hydrocarbons in quantities which were even higher than those of the corresponding saturated hydrocarbons, particularly C_2 and C_4 , although the hydrogen content was highest of all the samples studied. The value of H/C = 15.5 (the theoretical value for Mn_3SnC is 8) corresponds to the bonded carbon content of the hydrolyzable fraction of the sample expressed by the formula $\text{Mn}_3\text{SnC}_{\sim 0.5}$. The formation of the unsaturated hydrocarbons in the observed concentrations can only be explained in terms of the assumption of the presence of C_2 groups in the ternary carbide structure, although binary carbides with C_2 groups are formed neither by manganese nor, particularly, by tin. It is noteworthy that a similar effect has been observed by McCollm and coworkers¹⁶ for $\text{La}_3\text{SnC}_{\sim 0.5}$; the authors relate the defect of catenation of C_1 groups to the large size of the tin atoms, allowing for location of C_2 defects in a fraction of the free octahedral sites of the structure.

It can be summed up that ternary carbides containing a transition element and a nontransition element hydrolyze in a manner corresponding to their "metallic" nature, or to the presence of "free" electrons in the structure with a fraction of metallic bonding. The presence of "free" electrons in the carbide structure is a prerequisite for the radical hydrolysis pathway, irrespective of whether the transition metal is present alone or together with a nontransition metal. The situation is well illustrated by the logically reverse experiment performed by Anderson and coworkers¹⁷, who prepared acetylides of divalent europium and ytterbium, respectively, by feeding ethyne into solutions of the elements in liquid ammonia. The EuC_2 and YbC_2 carbides formed did not possess a metallic nature, they did not contain free electrons and therefore their hydrolysis resulted in pure C_2H_2 although the starting compounds were ones of transition metals. In their trivalent state, the two elements form

dicarbides of the same formulae, EuC_2 and YbC_2 , which, however, are metallic in appearance and hydrolyze to give a rich mixture of even hydrocarbons and hydrogen.

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