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The Ternary Systems: Cr–Al–C, V–Al–C, and Ti–Al–C and the Behavior of H-Phases (M_2AlC)

J. C. SCHUSTER, H. NOWOTNY,* AND C. VACCARO

Institute of Materials Science, The University of Connecticut, Storrs, Connecticut 06268

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Phase relationships in the ternary systems Cr–Al–C, V–Al–C, and Ti–Al–C have been investigated. All previously reported ternary H-phase Me_2AlC (Me = Cr, V, Ti) and the perovskite phase Ti_3AlC are confirmed. No new ternary phase was found. At 1000°C Ti_2AlC and Ti_3AlC are coexistent. In addition, the H-phase was found in equilibrium with TiC_{1-x}, $TiAl_3$, and TiAl; the perovskite with TiC_{1-x}, Ti_3Al, and Ti (solid solution with Al). TiC_{1-x} coexists with Al(l) at temperatures above 800°C. V_2AlC coexists at 1000°C with Al_4C_3, Al(l), Al_3V, V_7Al_8, V (solid solution with Al), V_2C, ζ-VC_{1-x}, and VC_{1-x} (including V_8C_7). At 1000°C Cr_2AlC is in equilibrium with Al_4C_3, γ-Cr_5Al_8, Cr (solid solution with Al), Cr_7C_3, and Cr_3C_2. At 800°C Cr_2AlC coexists also with graphite and β-Cr_2Al. V_2AlC forms a complete series of solid solutions with Cr_2AlC and Ti_2AlC. At about 1000°C the solid solution series Ti_2AlC–Cr_2AlC exhibits a miscibility gap.

Introduction

Among so-called complex carbides (*1*) formed by two metals and carbon, the ternary combinations involving transition element (M)–B–group element (metametal) (M')–carbon, carbides of formula $M_3M'C$ (perovskite carbides) and $M_2M'C$ (H-phase) display a surprisingly wide occurrence. This reflects somewhat the simple geometry of crystal structure in both these types of phases and the filling mode by an interstitial stabilizer (carbon). The filling mode can clearly be seen from the fact that other nonmetal stabilizers such as nitrogen (and oxygen) also form numerous perovskite or H-phases. Furthermore carbon deficiency, which is very typical for interstitial alloys, has been found for perovskite carbides, but substoichiometric compositions or appreciable homogeneous domains have also been detected in H-phases, for example, Nb_2SC_{1-x} (x = 0–0.6), where sulfur replaces the metametal.

It is noteworthy that the structural array of the perovskite-type carbide represents an antitype of the nonmetallic perovskite ($CaTiO_3$). The correspondence of metallic structure types and nonmetallic (saltlike) structure types or vice versa has been widely observed (*2*) and quite recently the crystal structure of $LiNbO_2$ (*3*) has been recognized as an anti-H-phase type structure (or vice versa). The parent lattice consists of, e.g., Ti_2Al and NbO_2, respectively, and the interstitials are carbon atom and Li^+ ion, respectively. The titanium resp. oxygen atoms occupy the 4f positions (in the $P6_3/mmc$ space group), which has a free parameter in the z direction. The small difference for the free parameter z is due to the preferentially

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* To whom correspondence should be addressed.

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ionic bonding in $LiNbO_2$, while in the metallic H-phase a mixed bonding state dominates.

One has to mention furthermore the relatively high stability of these complex carbides considering the competition with the extremely stable binary carbides such as TiC_{1-x}, VC_{1-x}, or Cr_3C_2.

Complex carbides and corresponding nitrides, such as Ti_3AlC, Ti_2AlC, and Ti_2AlN, were recently reported to be of considerable interest because of their outstanding properties as abrasives. It is claimed (*4*) that these ternary compounds are far superior for glass polishing to the common strong abrasives such as silicon carbide, fused alumina, borides, and carbonitrides of transition elements.

No detailed study of the ternary system Ti–Al–C has been made so far and the same is true for the related systems V–Al–C and Cr–Al–C. These combinations are also attractive insofar as metallic and nonmetallic carbides compete, e.g., TiC_{1-x} and Al_4C_3. As a first approach, isothermal sections at 700, 800, and 1000°C have been investigated. Furthermore, the mutual exchange of the transition element within the H-phase was studied. The results are presented here.

Sample Preparation

Sample preparation was made on a large scale by sintering as well as by arc melting. The materials used are specified as follows (concentrations in wt%):

Titanium powder (2 *N*, containing: Ca, 0.4%; Al, 0.35%; Fe, 0.1%; C, 0.015%; Si, 0.003%; Sn, 0.002%; other, 0.003%; from Alpha Div., Ventron Corp.).

Titanium carbide powder (2 *N*, containing: C_{total}, 18.90%; C_{free}, 0.25%; O, 0.26%; N, 0.33%; B, Ca, Mg, Ni, Nb, W, 0.02% each; from Alpha Div., Ventron Corp.).

Vanadium powder (2 *N*, containing: C, 0.09%; Si, 0.08%; Cr, 0.06%; Fe, 0.05% Al, 0.02%; other, <0.01%; from Alpha Div., Ventron Corp.).

Vanadium carbide powder (2 *N*, containing: C_{total}, 18.90%; C_{free}, 0.29%; O, 0.12%; N, 0.1%; W, 0.07%; Cr, 0.05%; Fe, 0.05%; Cu, Si, Zr, 0.02% each; from Alpha Div., Ventron Corp.).

Chromium powder (2 *N*, containing: Fe, 0.36%; C, 0.02%; Al, 0.02%; S, 0.02%; Si, 0.01%; from Koch–Light Lab. Ltd.).

Aluminium rods (5N5, from Koch–Light Lab. Ltd.).

Aluminium powder (3N8, containing: Fe, <0.1%; Si, 0.05%; other, <0.02%; from Alpha Div., Ventron Corp.).

Graphite rods (reactor grade).

Graphite powder (2N8, containing: Ca, 0.04%; Si, 0.04%; Fe, 0.02%; Al, 0.02%; Si, 0.015%; Ti, 0.01%; from Union Carbide Corp.).

As previously described (*5*), the preparation of samples was carried out by mixing of the corresponding powders in the proper ratio. As all room temperature operations (weighing, mixing, pressing) were carried out in air, some contamination of the powders by nitrogen or oxygen cannot be ruled out. However, the short exposure times and not-too-small particle sizes (typically 40 to 100 μm) should have limited this to a minimum. Some samples were prepared starting from master alloys and carbides. After arc melting all samples were sealed in an evacuated quartz tube, annealed at temperatures between 600 and 1200°C (170 to 500 hr), and quenched in water. As some samples showed a tendency to react with the quartz wall, these specimens were placed in a graphite crucible which was then encapsulated in an evacuated quartz tube.

On the basis of an average of 30 samples (5 g each) the isothermal sections have been worked out by means of X-ray analysis. All the binary phases were first corroborated and there was virtually no disagreement with literature data. Similarly the findings concerning the occurrence of the H-phases and Ti_3AlC have been confirmed, as can be seen from Tables I–III.

The Ternary System Ti–Al–C

In Fig. 1, the isothermal section for 1000°C displaying the phase equilibria is presented. β-Titanium has not been retained in the ternary alloy. This is explicable as aluminium and also carbon are α-stabilizers. Both the complex carbides Ti_3AlC and Ti_2AlC, which are the only ternary compounds, determine essentially the phase repartition. TiC_{1-x}, the most stable phase in addition to graphite, is in equilibrium with Al_4C_3, Al(l), $TiAl_3$, TiAl, H-phase, and perovskite phase, but is not in equilibrium with Ti_3Al at 1000°C. At this temperature, furthermore, the ternary carbides exhibit small homogeneous ranges which unambiguously show up in a variation of the lattice parameters. In particular, the parameter change for the perovskite carbide compared to that of TiC_{1-x}, however, appears to be due to carbon filling and Ti/Al substitution (see Fig. 1). Similarly for the H-phase, the Ti/Al

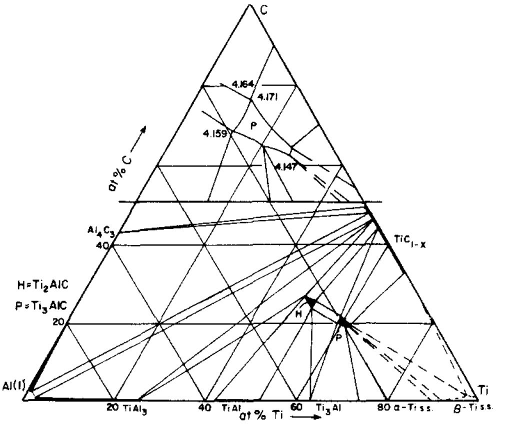

FIG. 1. Isothermal section (annealed at 1000°C) of the Ti–Al–C system; upper part represents the magnified area around the perovskite carbide Ti_3AlC. From thermochemical data it can be concluded that TiC_{1-x} and aluminium react, forming Al_4C_3 and $TiAl_3$ below 800°C.

TABLE I

PHASES AND LATTICE PARAMETERS IN THE TITANIUM–ALUMINIUM–CARBON SYSTEM

			Literature values (6) (average)	
Phases	a (nm)	c (nm)	a (nm)	c (nm)
Binary[a]				
α-Ti (10% at% Al)	0.2934_8	0.4691_5	0.2934	0.4700
Solid solution (ss)	0.2938_0[b]	0.4700_3[b]		
Ti_3Al	0.5788_3	0.463_7	0.5765	0.4625
	0.5791_4[b]	0.4657_2[b]		
TiAl (50 at% Al)	0.3930	0.4074	(49 at% Al) 0.3998	0.4076
$TiAl_3$	0.5440_4	0.8585_3	0.5446	0.8608
Al_4C_3	0.3333_8[b]	2.502_6[b]	0.3331	2.499
Ternary				
Ti_2AlC[c]	0.3056_0[b]	1.362_3[b]	0.304	1.360
Ti_3AlC[c]	0.4162_2[b]		0.415_6	

[a] Arc melted, annealed at 700°C, 340 hr.

[b] Arc melted, annealed at 1000°C, 170 hr.

[c] In composition for perovskite.

substitution is more significant than the carbon deficiency. At 700°C no homogeneous range can be detected for the H-phase and very little change of the lattice parameter is observed for the perovskite carbide.

In agreement with the observed lattice parameter change for samples quenched from 1000°C, Ti/Al substitution decreases the lattice parameter while additional carbon content increases the lattice parameter of the perovskite phase. The variation of the H-phase parameters at this temperature has been observed to be between $a = 0.3045$, $c = 1.363_6$, and $a = 0.3065_4$, $c = 1.376_1$ nm. The tie lines characterizing equilibria with the TiC_{1-x} carbide were found taking into account the parameter variation from 0.4333_2 ($TiC_{1-x} + Al_4C_3$) down to 0.430_5 nm (TiC_{1-x} + perovskite + α-Ti).

There has been no solubility found for the third component within the binary phases, e.g., carbon in the Ti–Al phases or aluminium in TiC_{1-x}. Furthermore, even the solubility of TiC_{1-x} in liquid aluminium seems to be small for the temperature region investigated. The ternary carbides form well above 1000°C by peritectic reactions out of TiC_{1-x} + l. In this context it should be mentioned that a more recent development of high-strength aluminium is based on hardening by finely dispersed TiC (*7*). Investigating Al–TiC alloys Taiichiro (*8*) has observed at 650°C partial decomposition of TiC, forming Al_4C_3 and $TiAl_3$ and leading to considerable hardening of aluminium. It should be mentioned furthermore that shock treatment of an Al–TiC composite by explosive techniques yields $TiAl_3$ and graphite (H. Nowotny, unpublished).

The Ternary System V–Al–C

An isothermal section at 1000°C reveals the high stability of the H-phase (Fig. 2). The H-phase coexists with V solid solution, Al(l), and all binary compounds, but not with graphite. It is interesting to mention the coexistence of the H-phase with aluminium. Virtually no homogeneity region was found for the H-phase and the same is true for the participating binary phases with respect to the third component. In particular no influence of aluminium on the vanadium carbides can be detected so far. For the 1000°C anneal the monocarbide showed up in the disordered state VC_{1-x} and in the ordered state V_8C_7 as well. Similarly the ordered subcarbide phase V_2C having ζ-Fe_2N-type structure has been found unchanged in the ternary system. The equilibrium concentration of the V solid solution with H-phase + V_2C can be determined from lattice parameter measurements to be about 23 at% Al. The newly obtained parameters for the occurring phases are listed with some literature data in Table II.

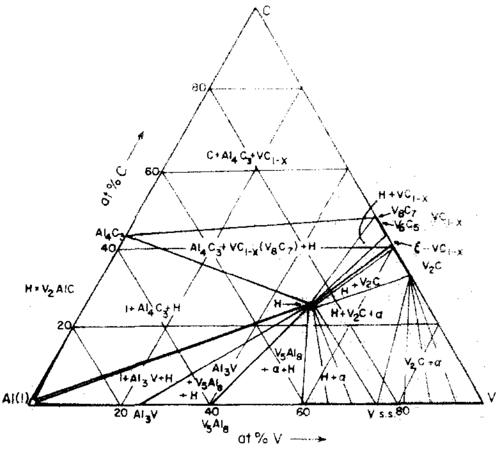

FIG. 2. Isothermal section (annealed at 1000°C) of the V–Al–C system.

The Ternary System Cr–Al–C

The equilibria are shown in Figs. 3a and b for isothermal sections at 800 and 1000°C. The major feature again is the existence of only one ternary carbide which is the H-phase. At 800°C, in the presence of graphite,

TABLE II

PHASES AND LATTICE PARAMETERS IN THE VANADIUM–ALUMINIUM–ALUMINIUM–CARBON SYSTEM

				Literature data (*6*)	
Phases	*a* (nm)	*b* (nm)	*c* (nm)	*a* (nm)	*c* (nm)
Binary					
V ss (50 at% Al) arc melted, annealed at 1000°C, 170 hr	0.30708			0.3075_5	
Two-phase				0.3068	
V_5Al_8 (59.5 at% Al)	0.9218_6			0.9205 (Two-phase, at 50 at% Al)	
VAl_3, arc melted, annealed at 700°C, 320 hr	0.533_5		0.8288	0.5345	0.8322
V_2C, arc melted, annealed at 1000°C, 170 hr	0.457_7–0.4602	0.5742–0.575_1	0.5037–0.5025_5[a]		
ζ-VC	0.4127			0.4129	
V_8C_7	0.8038–0.8313_3			0.8333	
VC_{1-x}	0.4154–0.4158_4			0.4150_6–0.4162	
Ternary					
V_2AlC	0.2911_6		1.3140	0.291_3	0.131_4

[a] V-rich to C-rich.

the ternary carbide is more stable than the binary carbides Cr_3C_2 and Al_4C_3. At the higher temperature, the H-phase was found to be less stable as compared to Cr_3C_2 and Al_4C_3; therefore, the reaction H + graphite = $Cr_3C_2 + Al_4C_3$ near 1000°C has to be assumed. No significant solubility region has been detected for the H-phase and no solubility has been found within the binary compounds for the third component either. As shown in Table III, the observed lattice parameters of the various participating phases are consistent with literature data for the binary systems.

For both the temperature sections, there is no coexistence between H and $Cr_{23}C_6$ on the one side and H and the Al-rich phases, θ, η, and ε, on the other, thus differing considerably from the former system.

The Partial Systems Ti_2AlC–V_2AlC–Cr_2AlC

Mutual substitution of the transition element in H-phases has been shown to occur for (Zr, Nb)$_2$AlC (*9*) or for (Ti, V)$_2$SC (*10*) but no systematic approach has been made so far. Therefore, a study was carried out for the neighboring elements, Ti, V, and Cr.

First, the corresponding H-phases were prepared and checked for homogeneity. A series of powder mixtures in proportions of 25, 50, and 75 mole% was then heated up for reaction at 1000°C for 170 hr in evacuated, sealed quartz tubes.

X-Ray powder diagrams of the obtained products revealed already a strong tendency for forming solid solutions, but the equilibrium state had not always been reached after this reaction time.

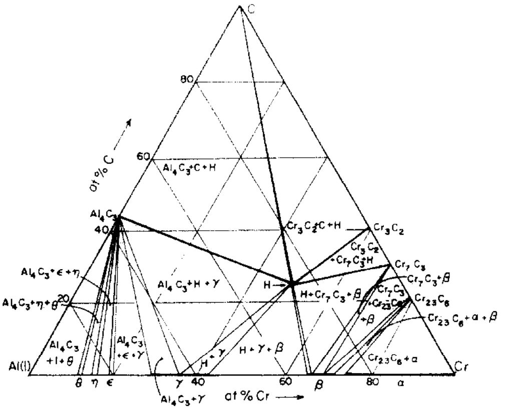

FIG. 3a. Isothermal section (annealed at 800°C) of the Cr–Al–C system.

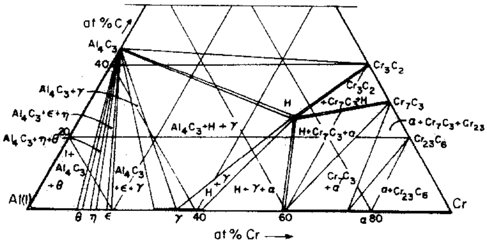

FIG. 3b. Isothermal section (annealed at 1000°C) of the Cr–Al–C system.

Ti_2AlC–V_2AlC

As can be seen from Table IV, there is a complete solid solution observed between these H-phases. The cell parameters change almost linearly, although the *a* parameter undergoes a slightly negative deviation (compression).

V_2AlC–Cr_2AlC

The results for V_2AlC–Cr_2AlC differ somewhat, inasfar as the reaction after 170 hr was obviously incomplete. The powder diagrams for 25 and 50 mol% Cr_2AlC still reveal the existence of two H-phases, the lattice parameters of one H-phase still corresponding to those of V_2AlC. The nonequilibrium state furthermore is clearly indicated by the diffuse lines of the other H-phase in the powder pattern. Prolonged reaction time leads again to complete formation of a continuous solid solution $(V, Cr)_2AlC$ (see Table IV).

Ti_2AlC–Cr_2AlC

No continuous transition of these H-phases has been observed even after a very

TABLE III

PHASES AND LATTICE PARAMETERS IN THE CHROMIUM–ALUMINIUM–CARBON SYSTEM

				Literature data (*6*)		
Phases	*a* (nm)	*b* (nm)	*c* (nm)	*a* (nm)	*b* (nm)	*c* (nm)
Binary						
Cr ss						
(25 at% Al)	0.2939			0.294_5 (24 at% Al)		
Cr_2Al						
(30 at% Al)	0.2974_5		0.8697	0.2990		0.8659 (29.3 at% Al)
(40 at% Al)	0.2996_5		0.8655	0.3001		0.8637 (34 at% Al)
$Cr_{23}C_6$	1.0655			1.0659		
Cr_7C_3	1.4031		0.4528	1.401		0.4532
Cr_3C_2	1.1466	0.5524	0.2828	1.148	0.553	0.2827
Ternary						
Cr_2AlC	0.286_6		1.282_5	0.286_0		1.28_2

TABLE IV

LATTICE PARAMETERS OF H-PHASE SOLID SOLUTIONS (ANNEALED AT 1000°C)

Partial system	*a* (nm)	*c* (nm)	Notes
Ti_2AlC–V_2AlC			
Ti_2AlC	0.3052	1.364	Starting material
$Ti_{1.5}V_{0.5}AlC$	0.3011	1.351_0	Anneal, 1 week
Ti V AlC	0.2975	1.339_3	Anneal, 1 week
$Ti_{0.5}V_{1.5}AlC$	0.2927	1.327_7	Anneal, 1 week
V_2AlC	0.2909	1.312_7	Starting material
V_2AlC–Cr_2AlC			
$V_{1.5}Cr_{0.5}AlC$	0.2903	1.305_4	Anneal, 2 weeks
V CrAlC	0.2893	1.297_0	Anneal, 5 weeks
$V_{0.5}Cr_{1.5}AlC$	0.2873	1.292_8	Anneal, 2 weeks
Cr_2AlC	0.2854	1.282	Starting material
CR_2AlC—Ti_2AlC			
$Cr_{1.5}Ti_{0.5}AlC$	0.2901	1.310_5	Anneal, 3 weeks
CrTiAlC	—	—	No H-phase
$Cr_{0.5}Ti_{1.5}AlC$	0.3041	1.3593	Minor amount of H-phase

long reaction time. Only a limited mutual solubility, which goes up on the chromium side to 25 mole% Ti_2AlC, and on the titanium side to about 6 mol% Cr_2AlC, has been detected (see Table IV). There is, however, no simple miscibility gap (pseudobinary section) between these H-phase solid solutions, because in addition to TiC_{1-x} other nonidentified phases occur. This may be due to the relatively high solubility of Cr_3C_2 in TiC_{1-x}, competing with the H-phase stability. Furthermore, the size difference of the metal atoms is largest for this partial system.

From this point of view, the substitution tendency is expected to be strongest for vanadium and chromium. On the other hand, as can be seen from the carbide behavior of TiC_{1-x} and VC_{1-x}, the easy formation of $(Ti, V)C_{1-x}$ solid solutions certainly is a hint of the fast reaction of the corresponding H-phases.

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