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ABSTRACT

Tables are presented in which are listed the phases which have been reported for the silicides of Ti, Zr, V, Nb, Ta, Cr, Mo, and W. Their ideal structure type, lattice constants, space groups, parameters of one of the type, and references are tabulated.

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Recently there has been a great interest in the compounds of silicon with the transition metals. Many new compounds have been prepared and their properties studied. In some cases, where the ideal composition was unknown, the phases were given incorrect names, and there has been some confusion as to which phases were being referred to.

In the following tables an attempt has been made to list the phases which have been reported in each system, their ideal structure type, lattice constants, parameters of one of the type and adequate references. The compositions given are the ideal compositions, but in many cases the actual compositions can deviate widely. For some compounds there are wide homogeneity ranges with varying lattice constants. In this table no attempt has been made to give the range of lattice parameters, for often this is not accurately known. Instead, lattice constants are given for a typical composition. For the case where compounds had been reported with the incorrect ideal composition, a note has been added in square brackets, stating what the true ideal composition is. All early data which had been given in kX units have been converted to Angstroms. The space group notation and positions of the atoms are listed as given in the International Tables.[1]

For references to early work in this field, and to properties of these compounds see "Refractory Hard Metals," Schwarzkopf and Kieffer,[2] and for more recent work the review paper by Nowotny and Parthé.[3] It is hoped that these tables will be of use to future workers in this field.

I should like to thank Professors L. Brewer and D. H. Templeton for their assistance in the preparation of this paper.

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Table I

Structure types of transition metal silicides

Nominal Composition	Ti	Zr	V	Nb	Ta	Cr	Mo	W
MSi_2	orth.-$TiSi_2$[4]*	orth.-$ZrSi_2$[7,8]	hex.-$CrSi_2$[14]	hex.-$CrSi_2$[14]	hex.-$CrSi_2$[14]	hex.-$CrSi_2$[14,26]	tetr.-CaC_2[29]	tetr.-CaC_2[29]
MSi	structure unknown[5]	orth.-FeB[7]				cubic-FeSi[26]		
M_6Si_5		structure unknown; not found by ref.(7); may be part of ZrSi phase region.[9,10]						
M_3Si_2		tetr.-U_3Si_2[11] called Zr_4Si_3 by ref. (9).		[Nb_3Si_2 reported in ref.(21) is Nb_5Si_3 - Cr_5Si_3 type.]		[Cr_3Si_2 reported in refs. (21) and (27) is Cr_5Si_3.]	[Mo_3Si_2 reported in ref. (21) is Mo_5Si_3.]	[W_3Si_2 reported in ref. (21) is W_5Si_3.]
M_5Si_3	hex.-Mn_5Si_3[6]	hex.-Mn_5Si_3[12] called Zr_5Si_2 by ref. (9).	[hex.-Mn_5Si_3 type reported in ref. (15) is ternary compound requiring C or B.[16]]	[hex.-Mn_5Si_3 type reported in ref. (12) is ternary compound requiring C or B.[16]]	[hex.-Mn_5Si_3 type reported in ref. (24) is ternary compound requiring C, B or N.[16]]		[hex.-Mn_5Si_3 type reported in ref. (30) is ternary compound requiring C.[12,16]]	
M_5Si_3			tetr.-Cr_5Si_3[17,18]	tetr.-Cr_5Si_3[17,18]	tetr.-Cr_5Si_3[18]	tetr.-Cr_5Si_3[17,22,28]	tetr.-Cr_5Si_3[17,22,28,31]	tetr.-Cr_5Si_3[17,22,28,31]
M_5Si_3				tetr.-Cr_5B_3[22]	tetr.-Cr_5B_3			
M_2Si		tetr.-$CuAl_2$[11]	[V_2Si reported in earlier work does not exist.[19]]	[αNb_2Si reported in (23) is Cr_5B_3 type. βNb_2Si reported in (23) is Mn_5Si_3 type.]	tetr.-$CuAl_2$[24]	[Cr_2Si reported in refs. (26,27) is undoubtedly Cr_5Si_3]		
M_3Si			cubic - "β W"[20]			cubic - "β W"[26]	cubic - "β W"[32]	
M_4Si-M_5Si		probably more than 2 phases near this composition.[12]			hex.-$Ta_{4.5}Si$ ideal Ni_3Sn type.[24]			
		one form is isostructural with $TaSi_{0.2}$.[13]		structure unknown; isostructural with $TaSi_{0.2}$.[13] Not found by ref. (9).	$TaSi_{0.2}$ structure unknown.[25] Different from $Ta_{4.5}Si$.			

*Another structure has been reported for $TiSi_2$ - orthorhombic $ZrSi_2$ form[34]

Table II

Structural data for transition metal silicides
(in Angstroms)

$TiSi_2$ - orthorhombic[4] - D_{2h}^{24} - Fddd		Z = 8		
	a = 8.252	8 Ti in (a)		
	b = 4.782	16 Si in (c)	x = 1/3	
	c = 8.540			
$ZrSi_2$ type - orthorhombic - D_{2h}^{17} - Cmcm		Z = 4		
$ZrSi_2$	a = 3.721[8]	4 Zr in (c)	y = 0.109[7]	
	b = 14.68	4 Si_I in (c)	y = 0.449	
	c = 3.683	4 Si_{II} in (c)	y = 0.750	
$TiSi_2$	a = 3.62[34]			
	b = 13.76			
	c = 3.60_5			
$CrSi_2$ type - hexagonal		D_6^4 - P 6_2 22	Z = 3	
$CrSi_2$	a = 4.431[26]	3 Cr in (d)		
	c = 6.364	6 Si in (j)	x = 1/6	
VSi_2	a = 4.571[14]			
	c = 6.371			
$NbSi_2$	a = 4.794[14]			
	c = 6.589			
$TaSi_2$	a = 4.782[14]			
	c = 6.565			
CaC_2 type - tetragonal		D_{4h}^{17} - I 4/mmm	Z = 2	
$MoSi_2$	a = 3.206[29]	2 M in (a)		
	c = 7.877	4 Si in (e)	z = 0.333	
WSi_2	a = 3.218			
	c = 7.896			
FeB type - orthorhombic		D_{2h}^{16} - Pnma	Z = 4	
ZrSi	a = 6.98_2[7]	4 Zr in (c)	$x = 0.17_8$	$z = 0.125$
	b = 3.78_6	4 Si in (c)	$x = 0.03_2$	$z = 0.61_1$
	c = 5.30_1			

Table II

(2)

FeSi type - cubic	$T^4 - P2_13$			Z = 4	
CrSi	a = 4.629[26]			4 M in (a)	$x_{Fe} = 0.139$
				4 Si in (a)	$x_{Si} = 0.845$
U_3Si_2 type - tetragonal	D^5_{4h} - P4/mbm			Z = 2	
Zr_3Si_2	a = 7.081[33]			2 Zr in (a)	
	c = 3.701			4 Zr in (h)	x = 0.17[11]
				4 Si in (g)	x = 0.37
Mn_5Si_3 type - hexagonal	D^3_{6h} - P 6_3/mcm			Z = 2	
Ti_5Si_3	a = 7.465[6]			4 M_I in (d)	
	c = 5.162			4 M_{II} in (g)	$x_{Mn} = 0.23$
				4 Si in (g)	$x_{Si} = 0.60$
Zr_5Si_3	a = 7.958[33]				
	c = 5.564				
Cr_5Si_3 type - tetragonal	D^{18}_{4h} - I_4/mcm			Z = 4	
V_5Si_3	$a = 9.42_9$[18]				
	$c = 4.75_6$				
Nb_5Si_3	$a = 10.01_8$[18]				
	$c = 5.07_2$				
Ta_5Si_3	$a = 9.8_6$[18]				
	$c = 5.0_5$				
Cr_5Si_3	a = 9.170[28]				
	c = 4.636				
Mo_5Si_3	a = 9.642[28]	9.617[31]	9.66[21]		
	c = 4.905	4.899	4.99		
W_5Si_3	a = 9.605[28]	9.645[31]	9.56[21]		
	c = 4.964	4.969	4.94		

Table II

(3)

Cr_5B_3 type - tetragonal D_{4h}^{18} - I4/mcm Z = 4

Nb_5Si_3 a = 6.55_7 [22]

c = 11.86_0

4 M in (c)

16 M in (ℓ) $x_{Nb} = 0.166$ $z_{Nb} = 0.15$

4 Si in (a)

8 Si in (h) $x = 0.37_5$

Ta_5Si_3 a = 6.50_3

c = 11.84_9

$CuAl_2$ type - tetragonal D_{4h}^{18} - I4/mcm Z = 4

Zr_2Si a = 6.599 [11]

c = 5.298

8 M in (h) $x_{Ta} = 1/6$

4 Si in (a)

Ta_2Si a = 6.157 [24]

c = 5.03_9

"β - W" type - (W_3O) cubic O_h^3 - Pm3n

V_3Si a = 4.721 [20]

6 M in (c)

2 Si in (a)

Cr_3Si a = 4.564 [26]

Mo_3Si a = 4.890 [32]

$Ta_{4.5}Si$ - hexagonal, ideal Ni_3Sn type. $Ta_3(Ta_{0.28}Si_{0.72})$ [24]

a = 6.10_5 for Ni_3Sn type - D_{6h}^4 - P $6_3/mmc$ Z = 2

c = 4.91_8

2 Sn in (c)

6 Ni in (h) $x_{Ta} = 0.826$

References

1. International Tables for X-ray Crystallography, Vol. I, Kynoch Press, Birmingham (1952).
2. P. Schwarzkopf and R. Kieffer, "Refractory Hard Metals," MacMillan Co., New York (1953).
3. H. Nowotny and E. Parthé, Planseeberichte fur pulvermetallurgie 2, 34 (1954).
4. F. Laves and H. J. Wallbaum, Z. Krist. 101, 89 (1939).
5. M. Hansen, H. D. Kessler, and D. J. McPherson, Trans. Am. Soc. Metals 44, 518 (1951).
6. P. Pietrowsky and P. Duwez, J. Metals 3, 772 (1951).
7. H. Schachner, H. Nowotny, and H. Kudielka, Monats. Chem. 85, 1140 (1954).
8. P. A. Vaughan and A. Bracuti, abstract of a paper presented at meeting of the American Crystallographic Association, June 27, 1955, Pasadena, California.
9. C. E. Lundin, D. J. McPherson, and M. Hansen, Trans. Am. Soc. Metals 45, 901 (1953).
10. D. A. Robins and I. Jenkins, Acta Met. 3, 598 (1955).
11. P. Pietrowsky, private communication.
12. O. Krikorian and L. Brewer, J. Electrochem. Soc. 103, 38 (1956).
13. G. A. Geach and A. G. Knapton, private communication.
14. H. J. Wallbaum, Z. Metallkunde 33, 378 (1941).
15. H. Schachner, E. Cerwenka and H. Nowotny, Monats. Chem. 85, 245 (1954).
16. H. Nowotny, B. Lux, and H. Kudielka, Monats. Chem. 87, 447 (1956).
17. A. G. Knapton, Nature 175, 730 (1955).
18. E. Parthé, H. Nowotny, and H. Schmid, Monats. Chem. 86, 385 (1955).
19. R. Kieffer, F. Benesovsky, and H. Schmid, Z. Metallkunde 47, 247 (1956).
20. H. J. Wallbaum, Z. Metallkunde 31, 362 (1939).
21. E. Parthé, H. Schachner, and H. Nowotny, Monats. Chem. 86, 182 (1955).
22. E. Parthé, B. Lux, and H. Nowotny, Monats. Chem. 86, 859 (1955).
23. G. Brauer and W. Scheele, Anorg. Chemie, edited by W. Klemm, Vol. 24, Part II, Dietrich Verlangsbuchdlg., Wiesbaden (1948).
24. H. Nowotny, H. Schachner, R. Kieffer, and R. Benesovsky, Monats. Chem. 84, 1 (1953).
25. L. Brewer, A. W. Searcy, D. H. Templeton and C. H. Dauben, J. Amer. Ceram. Soc. 33, 291 (1950).
26. B. Borén, Arkiv Kemi, Mineral., Geol., 11A, No. 10 (1933).
27. N. Kurnakov, Compt. rend. acad. sci., U.R.S.S. 34, 110 (1942).
28. C. H. Dauben, D. H. Templeton, and C. E. Myers, J. Phys. Chem. 60, 443 (1956).
29. W. H. Zachariasen, Z. Physik. Chem. 128B, 39 (1927).
30. H. Nowotny, E. Parthé, R. Kieffer, and F. Benesovsky, Monats. Chem. 85, 225 (1954).
31. B. Aronsson, Acta Chem. Scand. 9, 1107 (1955).
32. D. H. Templeton and C. H. Dauben, Acta Cryst. 3, 261 (1950).
33. McPherson's sample[5] measured at this laboratory.
34. P. G. Cotter, J. A. Kohn, and R. A. Potter, J. Amer. Ceram. Soc. 39, 11 (1956).