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HIGH MELTING SILICIDES

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Introduction

In this paper a preliminary survey is made of the refractory properties of silicides of groups III through VII, and evidence is presented to establish the existence and composition of one tungsten, two molybdenum, and three tantalum silicides besides the MSi_2 compounds already proved to exist.

The compounds of metals with silicon have received insufficient attention in the chemical and metallurgical literatures. In Table I are listed all the silicides of groups III - VII whose structures were reported up to January, 1949, including Mo_3Si whose existence and structure are first reported in this work. A number of additional silicides of these metals have been reported, but must often be considered unproved as to composition because of the impurity of materials employed and the difficulty usually present of separating several substances of very imperfectly known properties before analysis could be made for composition.

In the direct investigations of metallic silicides that have been so far reported there is little to indicate that any metallic silicides are stable, high melting compounds. Only two compounds in the silicon-metal phase diagrams given in Hansen[7] show melting points higher than that of silicon itself. VSi_2 has a melting point of 1927°K.[8] Moissan and Holt[9] report that V_2Si has a still higher melting point.

From extrapolating his experimental points, Vogel[10] predicted a CeSi with a melting point of about 1800°K. However, $CeSi_2$ has since been proved to exist by the identification of its crystal structure[4]. Since all Vogel's data were taken at higher silicon concentrations than that of $CeSi_2$, they should be reinterpreted as indicating a melting point for $CeSi_2$ of about 1710°K. No conclusions as to the existence or stability of CeSi can be made from his work.

Table I

Crystal Structures for Silicides of Groups III - IV

Compound	Symetry	Reference
MnSi	Cubic (T^4)	(1)
Cr_3Si	Cubic (O_h^3)	(1)
V_3Si		(2)
Mo_3Si		This work
Mn_3Si	Cubic (O_h^9)	(1)
$ThSi_2$	Tetragonal (D_{4h}^{19})	(3)
$CeSi_2$		(4)
α-USi_2		(4)
$PuSi_2$		(4)
$NpSi_2$		(4)
$MoSi_2$	Tetragonal (D_{4h}^{17})	(1)
WSi_2		(1)
$ReSi_2$		(5)
$ZrSi_2$	Tetragonal (D_{2h}^{17})	(1)
U_3Si_2	Tetragonal (D_{4h}^5)	(4)
$MnSi_2$	Tetragonal	
$CrSi_2$	Hexagonal (D_6^4)	(1)
VSi_2		(5)
$CbSi_2$		(5)
$TaSi_2$		(5)

Table I (Continued)

Compound	Symetry	Reference
β-USi_2	Hexagonal (D_{6h}^{1})	(4)
Mn_5Si_3	Hexagonal (D_{6h}^{3})	(1)
$TiSi_2$	Orthorhombic (D_{2}^{24})	(6)

Despite the absence of direct evidence that stable, high melting silicides can be prepared, we felt, from a comparative study of halides, oxides, sulfides, nitrides and carbides, that markedly stable silicides might be found in the region between Zr and Ta.[11] Accordingly, we restricted our study to silicides of Ti, Zr, Cb, Ta, Mo, and W, placing major emphasis on the last three of these silicon-metal systems because of the ready availability of these metals in pure powder form.

All preparations were by direct synthesis from the elements. The silicon used analyzed 99.87% pure. The principal impurities were carbon and aluminum. The purity of the metals used was verified by examination of their X-ray diffraction and spectroscopic lines. The X-ray analysis indicated pure metals and the spectroscopic examinations revealed no major impurities.

The samples were mixed together as 100 to 400 mesh powders and heated to the desired temperature in the induction furnace described by Brewer, Bromley, Gilles, and Lofgren[14]. Approximately 3/4 atmospheres of argon was used to inhibit silicon volatilization during reaction. The crucibles and samples were weighed before and after heating. The weight changes observed were usually less than one percent of the weight of the samples. Metal to silicon ratios in the reaction products then were calculated on the assumption that all the weight losses were due to silicon volatilization, except for a few molybdenum-silicon heatings in non-degassed Al_2O_3 crucibles. In the latter heatings the silicon loss was assumed to be slightly less than the total weight loss.

The heatings were made in molybdenum, in Al_2O_3 and in $TaSi_x$ containers. It does not appear, from comparison of the results of similar heatings in different containers, that composition of the samples mixed can have been changed more than two or three percent by reaction with either molybdenum or alumina containers as long as the silicon to metal ratio was less than 2.

In each metal-silicon system, spectroscopic examinations were made for contamination by Al and by Mo of the containers. All examinations showed less than .01% container contamination except for a $W_{.87}Si_{.13}$ sample which showed between .01-.1% molybdenum after being heated 32 minutes near 2290°K. One would have expected little reaction of the metals or silicon with Al_2O_3; however, use of molybdenum containers is possible only because the silicon reacts rapidly with the metal powder with which it is mixed, and equilibrium is never established with the container because of the slowness of solid diffusion. Serious attack on the molybdenum containers should be expected whenever there is silicon present in excess of that in the highest silicide of the system being studied or whenever the sample reaches its melting temperature.

The only attempt to prepare compounds of higher silicon to metal ratio than 2/1 was made in the tantalum silicon system. The silicon there ate through the bottoms of the molybdenum crucibles used, giving a mixture of $TaSi_2$ with a weaker $MoSi_2$ phase. Probably silicon to metal ratios higher than 2 could be heated in alumina crucibles without crucible attack, but no attempt was made to do so, since any phases of higher silicon content than MSi_2 would doubtless be relatively low melting and have high silicon partial pressures.

Results

The data for the preparations carried out are summarized in Tables II, III, IV and V. The first columns of these tables list the notebook designations of samples heated. The second columns give the molal compositions of metal and silicon mixed and, when the samples are reheatings, give the designations of the samples being reheated. The third columns list the containers used. The fourth columns contain the highest temperatures read in degrees Kelvin during the runs and the fifth columns give the approximate time that the temperature of the samples were within 100° of the maximum temperatures. The sixth columns give the percentage weight loss of the samples assuming the weight losses of crucibles and samples are all due to volatilization of sample. The seventh columns contain the compositions which would be present after heating if all the weight losses were due to silicon volatilization alone, and if the containers did not react. The final columns contain the phase assignments made after X-ray and spectrographic study of the samples prepared. The samples in each table are given in order of decreasing silicon content. The phase giving the stronger X-ray pattern is underlined. It should be remembered that a phase with a simple structure will give a strong X-ray pattern even when a relatively small amount is present.

Table II reports the tantalum silicide preparations. Three phases besides the previously reported $TaSi_2$[12, 5] were found. The crystal structures have not yet been identified, but on the basis of the preparations completed the phase assignments $TaSi_{.60\pm.05}$, $TaSi_{.4\pm.1}$ and $TaSi_{.2\pm.05}$ seem reasonable. The only anomaly is the appearance of a phase in Sample 2S63b which could not be identified as one expected in the Ta-Si system from results of any of the other heatings.

Of the three molybdenum silicides reported in Table III, only $MoSi_2$ was

Table II

Ta-Si Preparations

Sample No.	Compositions Mixed	Container	Maximum T°K.	Time, in Minutes, within 100° of Maximum Temperature.	% Weight Lost	Probable Composition of Products	Phases Found
1S69g	$Ta_{.115}Si_{.885}$	Mo	1920	9(vac.=10^{-5}atm)	Attacked Crucible		$\underline{TaSi_2}$, $MoSi_2$
1S69h	$Ta_{.221}Si_{.779}$	Mo	1920	9(vac.=10^{-5}atm)	Attacked Crucible		$\underline{TaSi_2}$, $MoSi_2$
1S56a	$Ta_{.335}Si_{.665}$	Mo	1950	17	1.24	$Ta_{.35}Si_{.65}$	$TaSi_{.60}$, $\underline{TaSi_2}$
2S59a	$Ta_{.35}Si_{.65}$	Mo	2380	43	Attacked Crucible		--------
1S91d	$Ta_{.408}Si_{.592}$	Mo	1920	3	.75	$Ta_{.42}Si_{.58}$	$TaSi_{.60}$, $\underline{TaSi_2}$
1S93c	$Ta_{.42}Si_{.58}$ (1S91d)	Mo	2040	11	.14	$Ta_{.42}Si_{.58}$	$TaSi_{.60}$, $\underline{TaSi_2}$
1S54c	$Ta_{.496}Si_{.504}$	Mo	1930	12	.26	$Ta_{.50}Si_{.50}$	$\underline{TaSi}_{.60}$, $TaSi_2$
1S93a	$Ta_{.50}Si_{.50}$ (1S54c)	$TaSi_X$	2040°	11	---	$Ta_{.50}Si_{.50}$	$\underline{TaSi}_{.60}$, $TaSi_2$
1S91c	$Ta_{.574}Si_{.426}$	Mo	1920°	3	.16	$Ta_{.57}Si_{.43}$	$TaSi_{.60}$, $\underline{TaSi_2}$
1S93b	$Ta_{.57}Si_{.43}$ (1S91c)	Mo	2040°	11	.68	$Ta_{.59}Si_{.41}$	$\underline{TaSi}_{.60}$, $TaSi_2$
3S75a	$Ta_{.598}Si_{.402}$	Al_2O_3	1880°	35	.62	$Ta_{.62}Si_{.38}$	$\underline{TaSi}_{.60}$
3S75b	$Ta_{.633}Si_{.367}$	Al_2O_3	1880	35	.25	$Ta_{.64}Si_{.36}$	$TaSi_{.4}$ $\underline{TaSi}_{.60}$
1S54b	$Ta_{.666}Si_{.334}$	Mo	1930	12	.03	$Ta_{.67}Si_{.33}$	$\underline{TaSi_4}$
2S63b	$Ta_{.716}Si_{.284}$	$TaSi_X$	2300	19	-.22	---	$\underline{TaSi}_{.20}$, (?)
1S91b	$Ta_{.735}Si_{.265}$	Mo	1920	3	-.08	$Ta_{.73}Si_{.27}$	$\underline{TaSi}_{.4}$

Table II (Continued)

Ta-Si Preparations

Sample No.	Compositions Mixed	Container	Maximum T°K	Time, in Minutes, within 100° of Maximum Temperature.	% Weight Lost	Probable Composition of Products	Phases Found
2S59b	$Ta_{.74}Si_{.26}$ (1S91b)	Mo	2380	43	---	-----	Ta, $\underline{TaSi}_{.20}$
1S69b	$Ta_{.778}Si_{.222}$	Mo	2180	6	.01	$Ta_{.78}Si_{.22}$	$\underline{TaSi}_{.4}$, $TaSi_{.20}$
1S91a	$Ta_{.841}Si_{.159}$	Mo	1920	3	-.15	$Ta_{.84}Si_{.16}$	Ta, $TaSi_{.20}$, $\underline{TaSi}_{.4}$
2S59a	$Ta_{.84}Si_{.16}$ (1S91a)	Mo	2380	43	---	-----	$\underline{Ta}$, $TaSi_{.20}$
1S69a	$Ta_{.890}Si_{.110}$	Mo	2180	6	-.03	$Ta_{.89}Si_{.11}$	$\underline{Ta}$, $TaSi_{.20}$

Table III

Mo-Si Preparations

Sample No.	Compositions Mixed	Container	Maximum T°K	Time, in Minutes, within 100° of Maximum Temperature.	% Weight Lost	Probable Composition of Products	Phases Found
3S48c	$Mo_{.318}Si_{.682}$	Al_2O_3	2120	20	<6.46	$Mo_{.35}Si_{.65}$	$MoSi_2$
3S60c	$Mo_{.397}Si_{.603}$	Al_2O_3	1930	68	<1.21	$Mo_{.40}Si_{.60}$	$MoSi_{.65}$, $MoSi_2$
1S58a	$Mo_{.443}Si_{.557}$	Mo	1960	9	.77	$Mo_{.45}Si_{.55}$	(?), $MoSi_2$
3S48a	$Mo_{.516}Si_{.484}$	Al_2O_3	2120	20	< 2.17	$Mo_{.54}Si_{.46}$	$MoSi_{.65}$, $MoSi_2$
3S4c	$Mo_{.578}Si_{.422}$	Mo	1950	3	.35	$Mo_{.58}Si_{.42}$	$MoSi_{.65}$, $MoSi_2$
3S60b	$Mo_{.595}Si_{.405}$	Al_2O_3	1930	68	< .95	$Mo_{.60}Si_{.40}$	$MoSi_{.65}$
3S4b	$Mo_{.673}Si_{.327}$	Mo	1950	3	.21	$Mo_{.68}Si_{.32}$	Mo, Mo_3Si, $MoSi_{.65}$
3S48b	$Mo_{.676}Si_{.324}$	Al_2O_3	2120	20	< 1.15	$Mo_{.69}Si_{.31}$	Mo_3Si, $MoSi_{.65}$
3S60a	$Mo_{.69}Si_{.31}$ (3S48b)	Al_2O_3	1930	68	.16	$Mo_{.70}Si_{.30}$	Mo_3Si, $MoSi_{.65}$
3S4a	$Mo_{.745}Si_{.255}$	Mo	1950	3	.47	$Mo_{.75}Si_{.25}$	Mo, Mo_3Si, $MoSi_{.65}$
3S16d	$Mo_{.747}Si_{.253}$	Al_2O_3	2160	6	<1.19	$Mo_{.76}Si_{.24}$	Mo_3Si
3S1b	$Mo_{.751}Si_{.249}$	Mo	2430	3	1.11	$Mo_{.77}Si_{.23}$	Mo, Mo_3Si
3S42c	$Mo_{.77}Si_{.23}$ (3S16d)	Mo	2290	32	.98	$Mo_{.78}Si_{.22}$	Mo_3Si

Table IV

W-Si Preparations

Sample No.	Compositions Mixed	Container	Maximum T°K.	Time in Minutes, within 100° of Maximum Temperature.	% Weight Lost	Probable Composition of Product	Phases Found
1S91f	$W_{.403}Si_{.597}$	Mo	1920	3	.12	$W_{.41}Si_{.59}$	$WSi_{.7}$, $\underline{WSi_2}$
3S16a	$W_{.41}Si_{.59}$(1S91f)	Mo	2160	6	.28	$W_{.41}Si_{.59}$	$WSi_{.7}$, $\underline{WSi_2}$
1S58c	$W_{.498}Si_{.502}$	Mo	1960	9	.17	$W_{.50}Si_{.50}$	$\underline{WSi}_{.7}$, WSi_2
3S15a	$W_{.50}Si_{.50}$ (1S58c)	Mo	2160	6	.22	$W_{.51}Si_{.49}$	$\underline{WSi}_{.7}$, WSi_2
3S75c	$W_{.582}Si_{.418}$	Al_2O_3	1890	35	.35	$W_{.59}Si_{.41}$	$\underline{WSi}_{.7}$
1S91h	$W_{.631}Si_{.369}$	Mo	1920	3	.13	$W_{.64}Si_{.36}$	$\underline{W}$, $WSi_{.7}$, WSi_2
3S16c	$W_{.64}Si_{.36}$ (1S91h)	Mo	2160	6	.09	$W_{.64}Si_{.36}$	W, $\underline{WSi}_{.7}$
3S42b	$W_{.64}Si_{.36}$ (1S91h)	Mo	2290	32	.19	$W_{.64}Si_{.36}$	$\underline{W}$, $WSi_{.7}$
1S91e	$W_{.754}Si_{.246}$	Mo	1920	3	.06	$W_{.76}Si_{.24}$	$\underline{W}$, $WSi_{.7}$
3S15b	$W_{.76}Si_{.24}$ (1S91e)	Mo	2160	6	.00	$W_{.76}Si_{.24}$	$\underline{W}$, $WSi_{.7}$
1S91g	$W_{.870}Si_{.130}$	Mo	1920	3	.10	$W_{.87}Si_{.13}$	$\underline{W}$, $WSi_{.7}$
3S16b	$W_{.87}Si_{.13}$ (1S91g)	Mo	2160	6	.29	$W_{.88}Si_{.12}$	$\underline{W}$, $WSi_{.7}$
3S42a	$W_{.87}Si_{.13}$(1S91g)	Mo	2290	32	.14	$W_{.88}Si_{.12}$	$\underline{W}$, $WSi_{.7}$

Table V

Miscellaneous Si Preparations

Sample No.	Compositions Mixed	Container	Maximum T°K	Time in Minutes within 100° of Maximum Temperature.	% Weight Lost
1S56b	$Zr_{.496}Si_{.504}$	Mo	1950	17	1.13
1S56c	$Ti_{.510}Si_{.490}$	Mo	1950	17	3.26
1S58b	$Zr_{.66}Si_{.34}$	Mo	1960	9	.61
1S69c	$Cb_{.543}Si_{.457}$	Mo	2180	6	1.46

previously known. It was reported independently by Honigschmid, by Defacqz, and by Watts (as reported by Hansen[7]), and was proved by the structural determination of Zachariasen[13]. Several investigators have reported Mo_2Si_3, but never with clear cut evidence and several others have tried, but failed to make this compound. We find no such phase, but cannot exclude the possibility that Mo_2Si_3 is stable below 1930°K. We do find a phase $MoSi_{.65\pm.05}$ and a phase which, from the compositions which show it, we would call $MoSi_{.35\pm.05}$. The structure of this last phase is primative cubic, a = 4.890±.002, space group O_h^3. There are six Mo and two Si atoms per unit cell. The X-ray density is 8.97±.01 and the experimental density is 8.4±.3. The phase then is Mo_3Si. It is isomorphous with Cr_3Si and V3Si. The formula Mo_3Si agrees well with the composition $MoSi_{.35\pm.05}$ found for the phase from our comparison of phases found with compositions prepared. An anomolous phase was found in an early heating which could be a phase of compositions around MoSi which is stable below 1960°K. The picture was poor.

We find two phases at high temperatures in the tungsten-silicon system. WSi_2, which was discovered by Defacqz and Honigschmid (as reported by Hansen[7]) and confirmed by the structure determination of Zachariasen[13], and a previously unknown phase, $WSi_{.7\pm.1}$. The W_2Si_3 phase, whose existence has been claimed by some experimenters and denied by others[7] was found not to exist at the temperatures studied, that is above 1920°K.

The prediction that molybdenum, tantalum, and tungsten silicides would be high melting is verified by our experimental results. In none of our heatings in these three systems was melting observed, though crucible attack by a mixture of $TaSi_2$ and $TaSi_{.60}$ heated to 2380 is probably evidence for melting below that temperature. In Table VI we have listed lower limits to the lowest temperatures of liquid existence between each pair of adjacent

Table VI

Phase Region	Lower Limits to Eutectic Temperatures
$TaSi_2$ - $TaSi_{.60}$	2040°K
$TaSi_{.60}$ - $TaSi_{.4}$	1880°K
$TaSi_{.4}$ - $TaSi_{.20}$	2180°K
$Ta_{.20}$ - Ta	2380°K
$MoSi_2$ - $MoSi_{65}$	2120°K
$MoSi_{.65}$ - Mo_3Si	2120°K
Mo_3Si - Mo	2430°K
WSi_2 - $WSi_{.7}$	2160°K
$WSi_{.7}$ - W	2290°K

phases. Of course liquid perhaps may not appear till several hundred degrees above the temperatures given in Table VI.

One sample between W and $WSi_{.7}$ in composition when heated to 2720°K in a W crucible fused into the crucible. But in that heating three phases were found and the lattice constant of the tungsten was shifted. Both these things indicate some impurity from the shields or furnace atmosphere was present which may have lowered the melting point.

A sample of composition $Ti_{.51}Si_{.49}$ partially fused below 1950°K, and a sample of $Cb_{.54}Si_{.46}$ partially fused below 2180°K. We have already quoted a melting point of 1927°K for VSi_2 and estimated a melting point of 1710°K for $CeSi_2$, with presumably lower temperatures of melting for compositions between phases. All but two of the tantalum, molybdenum, and tungsten silicide system eutectic temperatures have been shown to be higher than 2120°, with at least one eutectic above 2430°K. It appears that the highest melting silicides are those formed by the heavier metals of groups III - VII, though the evidence is incomplete.

Most of the silicides we prepared were grey or blue-grey powders, but the columbium and titanium samples which partially fused had silver blue metallic appearances. The $Ti_{.53}Si_{.47}$ sample was very porous which, coupled with its relatively high weight loss during preparation, suggests that the Ti-Si system has higher silicon partial pressures than those of the other systems we investigated. When silicon powder was heated rapidly to 2120°K in a tantalum crucible the heat of reaction was great enough to fuse the crucible and the three molybdenum plates immediately below it. The product was a mixture of Ta and $TaSi_{.20}$ and one of Mo and Mo_3Si. Both mixtures had silver, metallic appearances.

The weight losses observed during our heatings were low, and it appears that some, at least, of these silicides will have low silicon partial pressures. Vapor pressure determinations will be made soon.

The X-ray diffraction pictures of this work were taken by Mrs. Lee Jackson and the spectroscopic analyses were made by John Conway and M. Moore.

Summary

The tantalum silicon, molybdenum-silicon, and tungsten-silicon systems have been investigated for solid phases stable above 1900°K. Three new tantalum silicide phases, two new molybdenum silicide phases, and one new tungsten silicide phase, are reported besides the MSi_2 phases previously known. The crystal structure of Mo_3Si is described. Lower limits for eutectic temperatures are given for the tantalum-silicon molybdenum-silicon, and tungsten-silicon systems, and the relative stabilities of the group III through VII metallic silicides are discussed.

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