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Preparation, Identification and Chemical Properties of the Thorium Silicides[1a]

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An X-ray diffraction investigation of the thorium–silicon system establishes the existence of "β-$ThSi_2$," ThSi and Th_3Si_2 in addition to α-$ThSi_2$ which has been previously reported. "β-$ThSi_2$" is hexagonal, space group D^1_{6h} – P6/mmm, with $a_0 = 3.985 \pm 0.002$ Å. and $c_0 = 4.220 \pm 0.002$ A. The phase contains a higher ratio of thorium to silicon atoms than does α-$ThSi_2$ and apparently has a real composition of about $ThSi_{1.5 \pm 0.2}$. ThSi is orthorhombic, space group D^{16}_{2h} – Pbnm, with $a_0 = 5.89$Å., $b_0 = 7.88$ Å., and $c_0 = 4.15$ Å. Th_3Si_2 is primitive tetragonal, space group D^5_{4h} – P4/mbm, with $a_0 = 7.835 \pm 0.003$ and $c_0 = 4.154 \pm 0.005$ Å. These phases are isomorphous with corresponding uranium silicides. Reactivities of the thorium silicides with twelve common chemical reagents are reported.

A study of thorium–silicon compounds was undertaken because, although thorium and uranium usually form similar compounds with metalloids, only one silicide of thorium, α-$ThSi_2$,[2] was known compared to six silicides of uranium.[3] The known uranium silicides are USi_3,[4,5] α-USi_2,[4,6] β-USi_2,[4,6] USi,[4,6] U_3Si_2[4,6] and U_3Si.[4,6] Another phase, γ-USi_2, has been reported,[7] but the cell constants and reported structure are so nearly identical with those for USi_3 that the existence of γ-USi_2 is questionable.

Experimental

Mixtures of powdered thorium and silicon in the desired atomic ratios were heated in graphite, tungsten or aluminum oxide containers *in vacuo* to temperatures of 1000–1700° for varying periods of time. Weights of samples varied from 0.5 to 4.0 g. Crucible reaction was not noted unless the Si:Th atomic ratio was greater than 3:1 or less than 0.33:1.

The thorium powder which was available at the commencement of our investigations contained considerable thorium dioxide. Samples with initial compositions in the range $ThSi_{4.0}$ to $ThSi_{1.22}$ (neglecting oxide content) when heated to 1400–1700° for about one hour showed only faint diffraction patterns of thorium dioxide. Lower temperatures or higher thorium contents always gave preparations containing considerable oxide contaminant. It is apparent that in high silicon content samples heated to high temperatures, oxygen was removed by reactions of the type $(n + 2)Si + ThO_2 = ThSi_n + 2SiO(g)$. To eliminate oxygen from high silicon content samples prepared at lower temperatures a few preparations were made using the aluminum solvent technique of Brauer and Mitius.[2] These preparations, after dissolution of the aluminum by hydrochloric acid, yielded thorium dioxide-free platelets of α-$ThSi_2$ which if heated to 1460° for one hour or more were converted to a phase isostructural with β-USi_2 and hence designated "β-$ThSi_2$." When thorium of lower oxide content became available, samples of all desired compositions were prepared successfully by direct synthesis from the elements.

Analysis of each preparation was made by standard X-ray powder diffraction techniques. Diffraction patterns were obtained on 114.6 mm. cameras using nickel-filtered copper Kα radiation. The samples were mounted on silica fibers.

The "β-$ThSi_2$" Phase.—When samples of α-$ThSi_2$ were heated above 1400° and cooled to room temperature a new phase was found. Diffraction data, which are given in Table I for the first 21 planes of this phase, correspond to a hexagonal unit cell with $a_0 = 3.985 \pm 0.002$ Å. and $c_0 = 4.220 \pm 0.002$ Å. Comparison of the spacings and intensities with those for β-USi_2 showed the phases to be isostructural and the new phase was accordingly named β-$ThSi_2$. Intensities for each reflection were calculated by using the relationship

$$I = (F^2)\frac{1 + \cos^2 2\theta}{\sin^2\theta \cos\theta}\,p$$

with the symbols having their usual meaning. The space group is D^1_{6h}-P6/mmm with one thorium in (0, 0, 0) and two silicon in $\pm(^1/_3, {}^2/_3, z)$ with $z = {}^1/_2$. The calculated X-ray density is 8.23 g. cm.$^{-3}$.

TABLE I

CRYSTALLOGRAPHIC DATA FOR "β-$ThSi_2$"

hkl	$\sin^2\theta$ Obsd.	$\sin^2\theta$ Calcd.	I^a Obsd.	I^a Calcd.
001	0.0334	0.0334	m	177
100	.0499	.0499	s	752
101	.0835	.0833	vs	2480
002	.1336	.1335	w$^+$	346
110	.1492	.1497	s$^-$	744
102	.1836	.1834	s	257
111		.1833		77
200	.2000	.1996	w$^+$	112
201	.2329	.2330	s$^-$	481
112	.2834	.2832	s$^-$	506
202	.3323	.3331	w$^+$	20
103	.3502	.3502	s$^-$	246
210		.3493		90
211	.3826	.3827	s$^-$	430
300	.4494	.4491	m$^-$	121
113		.4500		28
212	.4826	.4828	m$^+$	112
301		.4825		26
203	.4996	.4999	m$^-$	148
302	.5836	.5826	m	188
104		.5838		49

[a] vs, very strong; s, strong; m, medium; w, weak.

The X-ray structure determination and the formation of β-$ThSi_2$ by heating α-$ThSi_2$ suggested β-$ThSi_2$ to be a high temperature modification of $ThSi_2$. More thorough investigation, however, showed that α-$ThSi_2$ resulted from heating samples with Si:Th atom ratios 2:1 or higher at any temperature in the range 1000 to 1670°, while samples of lower silicon content heated in the same range yielded β-$ThSi_2$. A series of experiments was accordingly devised to prove whether or not the elemental compositions of the α and β phases are identical.

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[1] (a) Work supported by the Office of Naval Research. Contains material from the M.S. thesis of E. L. Jacobson, Purdue University, June, 1952. (b) Author to whom inquiries should be addressed.

[2] G. Brauer and A. Mitius, *Z. anorg. allgem. Chem.*, **249**, 325 (1942).

[3] In a paper that came to our attention after structure assignments were completed, G. F. Hardy and J. K. Hulm, *Phys. Rev.*, **93**, 1004 (1954), it is stated Zachariasen has found a β-$ThSi_2$ phase and a Th_3Si_2 phase and has made the same space group assignments as we find for two of the phases reported here.

[4] P. Gordon, B. Cullity, M. Cohen, G. Bitsianes, A. R. Kaufmann and R. B. Bostian, quoted by J. J. Katz and E. Rabinowitch in "The Chemistry of Uranium," McGraw-Hill Book Co., Inc., New York, N. Y., 1951, pp. 226–228.

[5] B. R. T. Frost and J. T. Mackrey, *J. Inst. Metals*, **82**, 177 (1953).

[6] W. H. Zachariasen, *Acta Cryst.*, **2**, 94 (1949).

[7] G. Brauer and H. Haag, *Z. anorg. allgem. Chem.*, **259**, 197 (1949).

Samples of initial composition $ThSi_{3.0}$ and $ThSi_{2.0}$ were heated simultaneously at 1520°. After heating, the diffraction patterns were those of pure α-$ThSi_{2.0}$ and of pure β-$ThSi_{2.0}$, respectively. These samples were crushed to fine powders, and enough silicon was added to the β-$ThSi_2$ to raise the silicon–thorium ratio to 3:1. Both samples were then reheated to 1670° for one hour and cooled to room temperature. Diffraction analysis showed that the α-$ThSi_2$ had been converted to β-$ThSi_2$, and that the β-$ThSi_2$ had reacted with the excess silicon to yield α-$ThSi_2$. A sample of β-$ThSi_2$ heated at 1000° for three days was not converted to α-$ThSi_2$.

These results are consistent with the conclusion that β-$ThSi_2$ contains a lower concentration of silicon than does α-$ThSi_2$ and that α-$ThSi_2$ is converted to β-$ThSi_2$ at high temperatures by silicon vaporization, perhaps partly as SiO. Comparison of diffraction patterns with compositions, after allowance for ThO_2 impurity, fixes the composition of α-$ThSi_2$ at about the ideal composition for $ThSi_2$. The actual composition of the β-$ThSi_2$ phase appears to be $ThSi_{1.5 \pm 0.2}$. Both β-USi_2[4] and β-$PuSi_2$[8] have been assigned compositions of $MSi_{1.5}$ from composition studies, although Zachariasen[6] discounted the uranium–silicon composition studies because of his structure results.

The ideal β-phase structure consists of close packed sheets of metal atoms placed directly over each other with an intermediate sheet of silicon atoms in each of the two holes per metal atom. A hexagonal close packed lattice of uniform spheres differs from this structure in that in packing of uniform spheres only half the holes between the top and bottom layers are filled. All positions in the intermediate layer can be filled without distortion only if the atoms of the intermediate layer are much smaller than those of the top and bottom layers. It is probable that silicon vacancies occur in the ideal β-MSi_2 lattices because of crowding. The silicon–silicon atoms in β-$ThSi_2$ are 0.10 Å. closer together than in α-$ThSi_2$.

The ThSi Phase.—Samples of composition near $ThSi_{1.0}$ when heated to 1500–1700° gave, in addition to β-$ThSi_2$, strong diffraction patterns of another phase. The phase was also obtained by prolonged heating of a sample of β-$ThSi_2$ *in vacuo* at 1450°.

The X-ray data for the first 23 reflections of this phase are shown in Table II. The $\sin^2\theta$ values can be fitted to an orthorhombic unit cell with a_0 = 5.89 Å., b_0 = 7.88 Å. and c_0 = 4.15 Å. Comparison of the lattice spacings and intensities for this phase and USi indicated that they are isostructural. The only other Group IVb element that has been shown to form a monosilicide of this structure is zirconium.[9] ThSi, along with USi and ZrSi, contains four molecules per unit cell. Four thorium atoms are located in $\pm (x, y, 1/4), (1/2 - x, y + 1/2, 1/4)$ and four silicon atoms are located in $\pm (u, v, 1/4), (1/2 - u, v + 1/2, 1/4)$. The parameters assigned to x and y are 0.13 and 0.18, respectively, and those assigned to u and v are 0.61 and 0.03, respectively. The space group is D^{16}_{2h} – Pbnm. The calculated density is 9.03 g. cm.$^{-3}$.

The Th_3Si_2 Phase.—Preparations with Si:Th atomic ratios of about 0.82 yield, in addition to ThSi, a diffraction pattern very similar to that for U_3Si_2. Calculated $\sin^2\theta$ values were fitted readily to a unit cell with tetragonal symmetry. The space group of U_3Si_2 is D^5_{4h} – P4/mbm with two metal atoms in $(0, 0, 0), (1/2, 1/2, 0)$, four metal atoms in $\pm (u, u + 1/2, 1/2), (1/2 - u, u, 1/2)$, and four silicon atoms in $\pm (v, v + 1/2, 0), (1/2 - v, v, 0)$. Intensities calculated for the thorium silicide using Zachariasen's values[6] of u and v (u = 0.18, v = 0.39) for U_3Si_2 gave satisfactory agreement with observed intensities. The silicide, therefore, is Th_3Si_2, isostructural with U_3Si_2. The cell is primitive tetragonal with a_0 = 7.835 ± 0.003 Å. and c_0 = 4.154 ± 0.005 Å. and has a calculated density of 9.80 g. cm.$^{-3}$. Table III gives data for the first 18 crystallographic spacings of this phase.

TABLE II

CRYSTALLOGRAPHIC DATA FOR ThSi

hkl	$\sin^2\theta$ Obsd.	$\sin^2\theta$ Calcd.	I[a] Obsd.	I[a] Calcd.[b]
110	0.0267	0.0267	w	38
020	.0383	.0382	m$^-$	84
101	.0517	.0516	m	167
120	.0554	.0554	m	112
111	.0611	.0611	s	265
200	Absent	.0684	..	0
021	0.0727	.0727	s	174
210	.0779	.0780	s	214
121	.0898	.0898	m	111
130	.1032	.1032	m	102
220	Absent	.1067	..	0
211	0.1123	.1124	m	82
131	.1380	.1376	m	11
002		.1378		63
221	Absent	.1411	..	0
040	Absent	.1530	..	0
230	Absent	.1545	..	4
310	Absent	.1636	..	5
112	0.1652	.1645	w$^-$	8
140	.1699	.1701	w	44
022	.1765	.1760	w	21
041	.1882	.1874	m$^+$	59
231		.1889		107

[a] w, weak; m, medium; s, strong. [b] These are Zachariasen's values for the intensities of USi[6] and are within the error of visual observation since the scattering factor of thorium differs little from that of uranium.

TABLE III

CRYSTALLOGRAPHIC DATA FOR Th_3Si_2

hkl	$\sin^2\theta$ Obsd.	$\sin^2\theta$ Calcd.	I[a] Obsd.	I[a] Calcd.
100	Absent	0.0097	..	0.0
110	0.0194	.0194	w	27.2
001	.0343	.0344	w$^-$	16.3
200	Absent	.0387	..	3.0
101	Absent	.0441	..	0.0
210	0.0485	.0484	m$^+$	117.8
111	.0537	.0538	m	55.9
201	.0730	.0732	s$^+$	259.2
220	.0774	.0774	w$^+$	74.9
211	.0829	.0828	s	190.3
300	Absent	.0871	..	0.0
310	0.0968	.0968	m$^+$	117.1
221	Absent	.1119	..	0.8
301	Absent	.1216	..	0.0
320	0.1259	.1258	w^{--}	8.5
311	Absent	.1312	..	3.4
002	0.1371	.1378	m$^-$	51.5
102	Absent	.1474	..	0.0

[a] w, weak; m, medium; s, strong; vs, very strong.

Discussion

Since phases identified as USi_3 and U_3Si have been found in the uranium–silicon system, corresponding phases were intensively sought in the thorium–silicon system. Preparations of higher initial silicon content than $ThSi_{3.0}$ gave diffraction patterns of α-$ThSi_2$ and silicon, and those of lower silicon content than $ThSi_{0.5}$ gave patterns of Th_3Si_2 and thorium as well as considerable amounts of ThO_2. Thorium silicides of formulas $ThSi_3$ and Th_3Si either do not exist or are of limited stability. Apparently plutonium also does not form an MSi_3 phase.[8]

Chemical Properties.—Finely powdered samples of the thorium silicides were tested with twelve common chemical reagents. Samples were allowed to stand for at least 12 hours in each reagent.

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(8) O. J. C. Runnalls and R. R. Boucher, *Acta Cryst.*, **8**, 592 (1955).

(9) H. Schachner, H. Nowotny and H. Kudielka, *Monatsh. Chem.*, **85**, 1140 (1954).

Solutions and samples were then heated to the boiling point of the solutions for several minutes. In no instance was a reaction observed on heating if none had occurred with cold solutions.

All thorium silicides reacted with concentrated hydriodic acid, concentrated hydrochloric acid, concentrated hydrofluoric acid and aqua regia. None of the silicides reacted with 20% sodium hydroxide, 30% hydrogen peroxide, 0.1 *N* potassium permanganate or 5% nitric acid. Only Th_3Si_2 reacted appreciably with 36 *N* H_2SO_4 although both Th_3Si_2 and ThSi reacted with 6 *N* H_2SO_4. Only ThSi was even slightly attacked by concentrated nitric acid. All compounds except Th_3Si_2 were attacked by 5% hydrochloric acid.

All the thorium silicides were unstable on prolonged standing in air. They disintegrated slowly to form a fine black powder which was amorphous to X-rays. Samples of ThSi sometimes reacted with air rather rapidly. Melting points were not determined, but α-$ThSi_2$ and "β-$ThSi_2$" samples showed no sign of melting when heated to 1670° while samples of Th_3Si_2 were melted at 1700°. Samples of ThSi were never obtained free of "β-$ThSi_2$" or Th_3Si_2 and may be stable over only a limited temperature range.

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The Formation of Unipositive Nickel by Electrolysis in Concentrated Salt Solutions[1,2]

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The reduction of Ni(II) at the dropping mercury electrode leads to the formation of Ni(I) where the concentration of various salts, such as $NaClO_4$, $LiClO_4$, $Ca(ClO_4)_2$, NaCl and KCl, is made sufficiently high. In general, the formation of Ni(I) becomes clearly evident at salt concentrations of about one molar and becomes the principal process where the salt concentration is made two to three molar. Evidence for the formation of Ni(I) lies in a comparison of the observed diffusion currents with directly measured diffusion coefficients, the existence of an intermediate state of nickel that reacts with bromate, and the fact that the amount of metallic nickel produced per Faraday of electricity in the concentrated solutions is much less than that obtained in dilute salt solutions. Various experiments to characterize the plus one state of nickel are described and some possible explanations of the phenomenon are presented.

In the course of a study of the mechanism of reduction of the first transition group metals at the dropping mercury electrode, it has been found that nickel shows a marked difference in behavior from the other members of this group in concentrated salt solutions. This paper is concerned with a study of the reduction of Ni(II) in concentrated salt solutions and the evidence that Ni(I) is obtained as the primary product under certain conditions.

Experimental

A Sargent Model XII Polarograph was used to record the current–voltage curves. The electrolysis cell was of the H-type, with a sintered glass disk and an agar plug separating the two arms. Oxygen was swept out of the solutions with purified nitrogen. All measurements were made at 25 ± 0.03°.

All reagents were reagent grade chemicals except $LiClO_4$ and $Ca(ClO_4)_2$, which were crystallized out of solution prepared by the action of perchloric acid on the corresponding carbonates.

Results

Current–Voltage Curves of Nickel in Concentrated Solutions of Various Salts.—Current–voltage curves of Ni(II) in NaCl solutions from 0.1 to 3.0 *M* containing 10^{-3} *M* HCl are shown in Fig. 1. Curve 1 in Fig. 1 shows a single continuous c.v. curve corresponding to the reduction of Ni(II) to the metal. Curve 2 obtained in 1 *M* NaCl shows a distinct change in slope which suggests either a stepwise reduction of Ni(II) or possibly the reduction of two Ni(II) species, that have different activation energies of reduction, which are not maintained in equilibrium. Curves 3 and 4 show the effect of increasing the NaCl concentration to 2 and 3 *M*, respectively. The change in slope becomes more marked as the salt concentration is increased and the height of the first section of the c.v curve decreases. The limiting current of the first section will be referred to as i_1. It is measured approximately by the intersection of the extrapolated slopes of the initial and second "linear" sections of the c.v. curves. Values of i_1 so obtained are quite uncertain where a curve such as 2 is analyzed and become reasonably precise for curves such as 3 and 4.

In the light of data presented subsequently in this paper the curves in Fig. 1 are to be interpreted as follows. The reduction of Ni(II) is a two-step process. In 0.1 *M* NaCl the Ni(I) initially produced disproportionates rapidly or is immediately further reduced to metal at the electrode and the total diffusion current corresponds to complete reduction to the metal. In 1 *M* NaCl, curve 2, the activation energy for electrode reduction of Ni(I) has increased so that the stepwise nature of the reduction becomes observable. Where the NaCl is made 3 *M* this kinetic "stabilization" of Ni(I) has become almost complete and the limiting current i_1 is due almost entirely to reduction to Ni(I) with only a very small contribution by further reduction to the metal. It should be noted that the Ni(I), which is about 10^{-3} *M*, need only have a half-life greater than a few milliseconds to account for curves 3 and 4.

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[2] Presented before the Physical and Inorganic Division of the 128th National ACS Meeting, Minneapolis, Minn., September, 1955.