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The Preparation and Crystal Structure of Some Ternary Silicides Containing Uranium and Transition Metals

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The crystal structure of some new ternary silicides of the general composition $U_4M_5Si_3$ ($M = Cr, Mn, Fe$) has been determined by means of the x-ray powder diffraction method. The structure which belongs to the C14 ($MgZn_2$) type is characterized by a statistical distribution of both kinds of smaller atoms. The chemical composition of the monophase specimens is probably temperature dependent. At lower temperatures it may approach the formula U_2M_3Si . In some of these systems ternary compounds UM_2Si_2 were also identified. They were found to be isostructural with the previously reported ThM_2Si_2 compounds. A novel method for the preparation of uranium alloys with the use of the electron beam melting is described.

INTRODUCTION

During the investigation of the ternary systems U-M-Si ($M =$ transition metal) we noticed that two prominent structure types, C14($MgZn_2$) and $D1_3(BaAl_4)$ appear most frequently. While the homogeneity region of the $D1_3$ type compounds seems to be very narrow, the composition of the Laves phases (C14 type) is probably temperature dependent, and the ratio M versus Si changes continuously from 1.67 to 3 (or perhaps even more). Therefore, as far as we know at present, the composition can vary up to $U_4M_5Si_3$, probably in relation to the nature of the transition metal. If the structure of Laves phases is in any sense controlled by the electron to atom ratio, a regularity in the sequence of different transition metals should be found. This could be done in future by an exact determination of the point where the C15 type (UMn_2, UFe_2, UCo_2) changes to C14 type as well as a determination of the upper limit of the silicon content. In this article the crystal structure of the new ternary Laves phases $U_4M_5Si_3$ ($M = Cr, (Mn), Fe$) is being reported.

EXPERIMENTAL

Materials

The turnings of the vacuum-melted reactorgrade uranium were mixed up with the corresponding metals and silicon, both in powder form. The following materials were used: chromium (purity not quoted) — The Coleman & Bell Co., manganese 99.9% — L. Light and Co., and iron p. a. — Chinoin, Budapest. Silicon powder — 200 mesh — Merck, Darmstadt, was purified by treating with hydrochloric and hydrofluoric acid and rinsed with deionized water. Such powder had a specific resistivity of approximately 0.1 ohm · cm.

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Sample Preparation

The uranium turnings mixed with the powder of the corresponding metal and silicon was transferred into the specially designed apparatus for hydrogenation. Hydrogen was purified catalytically by means of the DEOXO purifier and dried over phosphorus pentoxide. The whole apparatus was evacuated several times to approximately 10^{-3} torrs and washed with hydrogen. Hydrogenation was then carried out under a slight overpressure of hydrogen at 220–260°C¹. The extremely fine powder of UH_3 enabled very intimate mixing of the components on shaking the tube. The lower end of the tube was allowed to cool by withdrawing the heater. Approximately 15–20 ml of toluene dried over sodium, was poured in from the tap funnel. The powder was suspended by vigorous shaking and quickly transferred into the porcelain dish. The paste-like precipitate was put into the special demountable mold and pressed by a hydraulic press into the form of a prism $5 \times 5 \times 25$ mm. A thin molybdenum wire pressed onto one end of the specimen and served later as a suspension. After removing the die, the compact was wetted with toluene and quickly mounted into the specially designed electron beam furnace². The chamber of the furnace was evacuated by means of a rotary pump and uranium hydride decomposed to metallic uranium by heating the cathode of the electron beam source. When the evolution of hydrogen ceased, the whole system was coupled to the oil diffusion pump, trapped with liquid air end evacuated to a vacuum better than 5×10^{-5} torrs as measured by a Penning type ionisation gauge. This started the exothermic reaction between silicon and the metallic components with subsequent melting. One drop of each sample was allowed to fall into a heavy, cold copper container. The evaporation of the more volatile components (Si, Cr, Mn and Fe) was not an obstacle to this method because experiments have shown that the overall weight loss does not exceed 2 per cent, certain amount of material being lost through spitting.

X-Ray Procedure

Samples for the x-ray studies were generally taken from the center of the molten specimens. They were crushed in an agate mortar under toluene in order to avoid oxidation. All x-ray diffraction patterns were obtained by means of a recording Philips diffractometer provided with a Geiger counter tube, filtered CuK radiation being used throughout the work. The use of the copper radiation in this particular case resulted in relatively high background.

RESULTS

X-ray diffraction records of strictly monophase specimens were indexed on the basis of a hexagonal unit cell. Correlation of the unit cell dimensions with the previously reported isomorphous phase $\text{U}_4\text{Mo}_5\text{Si}_3$ ³ is given in Table I. In all cases a unit cell contains one formula unit. The systematically absent reflections were 001 and hhl for l odd, so that the space group is $\text{P6}_3/\text{mmc}$

TABLE I
Unit Cell Dimensions of $\text{U}_4\text{M}_5\text{Si}_3$

	a (Å)	c (Å)	c/a
$\text{U}_4\text{Mo}_5\text{Si}_3^*$	5.370 ± 0.002	8.582 ± 0.005	1.59 ₈
$\text{U}_4\text{Cr}_5\text{Si}_3$	5.199 ± 0.002	8.098 ± 0.005	1.55 ₇
$\gg \text{U}_4\text{Mn}_5\text{Si}_3 \ll^{**}$ (U_3Mn) $\text{Mn}_{6.2}\text{Si}_{1.8}$	5.158 ± 0.002	7.972 ± 0.005	1.54 ₅
$\text{U}_4\text{Fe}_5\text{Si}_3$	5.142 ± 0.002	7.759 ± 0.005	1.50 ₉

* Reported earlier³

** See text

TABLE II
Atomic Coordinates

4U,(U ₃ Mn)	in	4(f)	$\pm \left(\frac{1}{3}, \frac{2}{3}, z \right)$
			$\pm \left(\frac{1}{3}, \frac{2}{3}, \frac{1}{2} - z \right)$
5Cr(Mn,Fe) and 3Si	in	2(a)	(0, 0, 0)
			$\left(0, 0, \frac{1}{2} \right)$
	and	6(h)	$\pm \left(x, 2x, \frac{1}{4} \right)$
			$\pm \left(2\bar{x}, \bar{x}, \frac{1}{4} \right)$
			$\pm \left(x, \bar{x}, \frac{1}{4} \right)$
	x		$= -\frac{1}{6}$
	^z U ₄ Cr ₅ Si ₃		= 0.067
	^z »U ₄ Mn ₅ Si ₃ «		= 0.062
	^z U ₄ Fe ₅ Si ₃		= 0.062

TABLE III
Diffractometer Data for U₄Cr₅Si₃

h k. l	sin ² θ _o	sin ² θ _c	I _o	I _c
1 0. 0	0.0293	0.0293	60.2	55.9
0 0. 2	0.0363	0.0362	28.4	26.1
1 0. 1	0.0384	0.0384	56.7	48.2
1 0. 2	0.0654	0.0656	32.7	27.7
1 1. 0	0.0879	0.0879	106.6	113.4
1 0. 3	0.1106	0.1108	154.7	136.4
2 0. 0	0.1170	0.1172	22.3	22.4
1 1. 2	0.1240	0.1242	94.6	100.9
2 0. 1	0.1263	0.1263	51.6	46.7
0 0. 4	—	0.1450	—	1.2
2 0. 2	—	0.1535	—	0.9
1 0. 4	0.1737	0.1740	5.1	3.1
2 0. 3	0.1984	0.1985	24.1	24.0
2 1. 0	0.2049	0.2049	6.8	4.4
2 1. 1	0.2142	0.2139	8.6	9.5
1 1. 4	—	0.2327	—	0.7
2 1. 2	0.2413	0.2410	6.8	8.2
1 0. 5	0.2554	0.2555	13.7	21.4
2 0. 4	—	0.2618	—	0
3 0. 0	0.2634	0.2634	13.7	21.6
3 0. 1	—	0.2725	—	0
2 1. 3	0.2866	0.2863	56.7	61.8
3 0. 2	0.2998	0.2996	20.6	24.6
0 0. 6	0.3257	0.3257	5.1	5.1
2 0. 5	0.3432	0.3432	21.5	26.7

TABLE IV
 Diffractometer Data for »U₄Mn₅Si₃« — (U₃Mn)Mn_{6.2}Si_{1.8}

h k l	sin ² θ _o	sin ² θ _c	I _o
1 0 0	0.0299	0.0298	45
0 0 2	0.0376	0.0374	62
1 0 1	0.0392	0.0391	50
1 0 2	0.0672	0.0672	40
1 1 0	0.0893	0.0894	98
1 0 3	0.1140	0.1139	190
2 0 0	0.1192	0.1191	18
1 1 2	0.1267	0.1268	165
2 0 1		0.1285	
0 0 4	—	0.1496	—
2 0 2	—	0.1565	—
1 0 4	0.1793	0.1794	18
2 0 3	0.2033	0.2033	26
2 1 0	—	0.2085	—
2 1 1	0.2181	0.2178	26
1 1 4	0.2388	0.2389	15
2 1 2	0.2458	0.2459	10
1 0 5	0.2637	0.2635	36
3 0 0	0.2676	0.2680	10
2 0 4		0.2687	
3 0 1	—	0.2774	—
2 1 3	0.2924	0.2926	75
3 0 2	0.3044	0.3054	14
0 0 6	0.3367	0.3366	24
3 0 3	0.3531	0.3522	44
2 0 5		0.3529	
2 2 0	0.3575	0.3574	10
2 1 4		0.3581	

(D_{6h}⁴)⁴. The examination of the relative intensities led us to the conclusion that the atomic position should follow the same pattern as in U₄Mo₅Si₃ *i. e.* be of MgZn₂ type. Satisfactory agreement between the observed and calculated intensity values was obtained assuming the atomic co-ordinates given in Table II. Complete calculations were performed only for U₄Cr₅Si₃. The comparison of the observed and the calculated sin² θ values and relative intensities are given in Tables III, IV and V. The values of the intensity of reflections I_c were calculated using the formula

$$I_c \sim F^2 \cdot M \cdot \frac{1 + \cos^2 2\theta}{\sin^2 2\theta \cos \theta}$$

where M stands for a multiplicity factor. Interatomic distances are listed in Table VI.

DISCUSSION

Two different possibilities of partially disordered structure, giving very close agreement between the calculated and observed intensities, were discussed in connection with the crystal structure of U₄Mo₅Si₃³. This type of statistical distribution of smaller atoms in the ternary Laves phases seems to be of general importance. This can be illustrated by the results reported by E. I.

TABLE V
 Diffractometer Data for $U_4Fe_5Si_3$

h k.l	$\sin^2\theta_o$	$\sin^2\theta_c$	I_o
1 0.0	0.0300	0.0299	55
0 0.2	0.0399	0.0394	76
1 0.1		0.0398	
1 0.2	0.0696	0.0693	38
1 1.0	0.0897	0.0897	125
1 0.3	0.1188	0.1186	215
2 0.0		0.1197	
1 1.2	0.1294	0.1292	192
2 0.1		0.1295	
2 0.2	—	0.1571	—
0 0.4	—	0.1577	—
1 0.4	—	0.1876	—
2 0.3	0.2087	0.2084	35
2 1.0		0.2094	
2 1.1	0.2193	0.2193	26
1 1.4	—	0.2474	—
2 1.2	—	0.2488	—
3 0.0	0.2691	0.2693	20
1 0.5	0.2763	0.2763	25
2 0.4	—	0.2773	—
3 0.1	—	0.2791	—
2 1.3	0.2979	0.2981	74
3 0.2	0.3086	0.3087	32
0 0.6	0.3546	0.3548	20
3 0.3	—	0.3579	—
2 2.0	0.3585	0.3590	40
2 0.5	0.3664	0.3660	34
2 1.4		0.3671	

TABLE VI
 Interatomic Distances in $U_4M_5Si_3$

Atom	Nearest atom	Number of atoms	Distance (Å)			
			Mo	Cr	Mn	Fe
U 4(f)	U 4(f)	1	3.23	2.96	2.99	2.92
	U 4(f)	3	3.28	3.08	2.99	2.98
	(M,Si) 2(a)	3	3.15	2.99	2.98	2.96
	(M,Si) 6(h)	9	3.13	3.05	3.02	3.00
(M,Si) 2(a)	(M,Si) 6(h)	6	2.64	2.52	2.45	2.44
(M,Si) 6(h)	(M,Si) 6(h)	4	2.68	2.60	2.58	2.57

Gladischevsky and coworkers for the compounds found in the systems Mn-Ni(Co)-Si, V-Co(Ni)Si, W-Co(Ni)Si, Mo-Co(Ni)Si^{5,6,7} and some others. It is interesting to notice that in the systems containing manganese, it takes up the role of the biggest atom i. e. the atom occupying the position 4(f). In these structures the radius of the manganese atom at the position 4(f) is 1.48 Å which is very close to the radius of the uranium atom (1.52 Å). Therefore, at least partial mutual replacement could be expected. This was actually confirmed by a large number of our experiments. While the alloys of the composition

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IZVOD

Preparacija i kristalna struktura nekih ternarnih silicida koji sadrže uran i prelazne metale

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Opisana je nova metoda preparacije višekomponentnih legura s uranom. Hidriranjem urana dobiva se fini prah UH_3 koji miješanjem s drugim komponentama daje vrlo homogenu smjesu. Otpresci takvih smjesa tale se bez kontakta s posudom pomoću elektronskog snopa u uređaju originalne konstrukcije.

Određena je kristalna struktura dobivenih spojeva s općom formulom $U_4M_5Si_3$. Pokazano je da se radi o Lavesovim fazama tipa C 14 sa statističkim rasporedom malih atoma.

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ZAGREB

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