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The Crystal Structures of Os_2Al_3 and $OsAl_2$

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The crystal structures of Os_2Al_3 and $OsAl_2$ have been determined from single-crystal X-ray data. Os_2Al_3 is tetragonal and the cell dimensions are $a = 3.106$ and $c = 14.18$ Å. $OsAl_2$ is of the $MoSi_2$-type and tetragonal with $a = 3.16$ and $c = 8.30$ Å. These structures are related to OsAl of the CsCl-type.

X-Ray studies on osmium-aluminium alloys quenched from temperatures above 1300°C have revealed the existence of the phases OsAl, Os_2Al_3, $OsAl_2$, and Os_4Al_{13}. The structure of OsAl has been reported earlier by Esslinger and Schubert as being of the CsCl-type.[1] The structure of Os_4Al_{13} is described in a previous paper by the present author [2] and the structures of Os_2Al_3 and $OsAl_2$ are given here.

EXPERIMENTAL

The preparation of the osmium-aluminium alloys by arc-melting was described in a previous paper.[2] The alloys have been further treated by heating in a high-vacuum induction furnace at temperatures above 1300°C. An alumina crucible was used. The cooling time from these temperatures down to 100°C is about 5 sec. For the compositional region so far studied, $OsAl_{1.0-3.2}$, the phase analysis showed the same phases to exist in the arc-melted and in the annealed samples, *viz.* the four mentioned above.

Crystals were obtained from the crushed melts. Single-crystal data were registered in a Weissenberg camera using CuK radiation and the intensities of the reflections were estimated visually. The unit-cell dimensions were obtained from powder patterns obtained in a Guinier camera using Cu$K\alpha_1$ radiation and with KCl as an internal standard.

THE STRUCTURES

OsAl. The Guinier powder pattern given by an arc-melted sample of OsAl stoichiometry was found to correspond to a cubic structure of CsCl-type with the cell constant

$$a = 3.001 \pm 0.001 \text{ Å}$$

and in good agreement with the earlier reported $a = 3.00_5$ Å.[1] The colour of this phase is remarkable, being "copper-gold-yellow" in the temperature

Table 1. The Guinier powder pattern of Os_2Al_3 ($CuK\alpha_1$).

hkl	$\sin^2\Theta_{obs}$	$\sin^2\Theta_{calc}$	I_{obs}	I_{calc}
002	0.01179	0.01179	w	1.6
004	0.04718	0.04718	m	16.2
101	0.06440	0.06444	vs+	23.8
103	0.08806	0.08803	m−	5.9
006	0.10612	0.10616	vw	1.1
110	0.12303	0.12298	st	18.8
112	—	0.13478	—	0.6
105	0.13516	0.13521	vst	39.5
114	0.17015	0.17017	m	11.4
008	0.189	0.18874	vvw	1.3
107	—	0.20599	—	0.1
116	0.22920	0.22915	w	1.7
200	0.24595	0.24596	m	8.2
202	—	0.25776	—	0.3
204	0.29312	0.29315	m−	6.3
0010	0.295	0.29490	w	2.5
109	0.301	0.30036	m	8.2
211	0.31040	0.31040	m−	7.2

Table 2. Interatomic distances in Os_2Al_3 (Å).

Os −	4 Al_1	2.48	Al_1 −	4 Os	2.48	Al_2 −	8 Os	2.68
	4 Al_2	2.68		1 Os	2.72		2 Al	2.68
	1 Al_2	2.87		1 Al_2	2.68		4 Al	3.11
	1 Os	3.08		4 Al_1	2.80			
	4 Os	3.11		4 Al_1	3.11			

Table 3. Interatomic distances in $OsAl_2$ (Å).

Os −	8 Al	2.59	Al −	4 Al	2.71
	2 Al	2.84		4 Os	2.59
	4 Os	3.16		2 Os	2.84
				4 Al	3.16

Table 4. The Guinier powder pattern of $OsAl_2$ ($CuK\alpha_1$)

hkl	$\sin^2\Theta_{obs}$	$\sin^2\Theta_{calc}$	I_{obs}	I_{calc}
002	0.03439	0.03443	m	6.4
101	0.06794	0.06795	st	9.1
110	0.11877	0.11869	m	5.8
103	0.13677	0.13682	m +	9.4
004		0.13773	vvw	0.8
112	0.15325	0.15312	w +	3.7
200	0.23737	0.23738	w	2.4
114	0.25642	0.25642	w −	1.6
202	0.27182	0.27181	w −	1.9
105	0.27455	0.27454	w −	2.1
211	0.30533	0.30533	w +	2.8
006	0.30995	0.30988	vvw	1.0
213	0.37430	0.37419	st	7.6
204		0.37510	w −	1.4
116	0.42829	0.42858	w	4.1

region investigated while all other phases so far known in this system are greyish. Similarly coloured phases have been found, however, in the platinum and palladium-aluminium systems.

Os_2Al_3. Single crystals of Os_2Al_3 were taken from an arc-melted sample of this stoichiometry that had been heated for 20 h at 1400°C in the induction furnace. The cell dimensions were obtained from a Guinier powder photograph giving a tetragonal unit cell with

$$a = 3.106 \pm 0.001, \quad c = 14.184 \pm 0.002 \text{ Å}.$$

Single-crystal data were registered with rotation around the [110] direction. The crystals formed by Os_2Al_3 are graphite-like and give diffuse reflections. The structure was derived from these data and the atomic parameters were refined from successive ϱ_o and ϱ_c projections. The following structure was found:

Unit-cell content	:	2 Os_2Al_3
Space group	:	*I4/mmm* (139)
4 Os in 4 (*e*)	:	0, 0, 0.391_2
4 Al_1 in 4 (*e*)	:	0, 0, 0.18_9
2 Al_2 in 2 (*a*)	:	0, 0, 0

The powder pattern is given in Table 1 which also includes the intensities calculated for the structure derived. The interatomic distances are given in Table 2.

$OsAl_2$. An arc-melted sample of $OsAl_2$ was investigated. The powder pattern gave the following tetragonal dimensions:

$$a = 3.162 \pm 0.003, \quad c = 8.302 \pm 0.005 \text{ Å}.$$

Single-crystal data were registered by rotation around the *a* axis. The symmetry and cell dimensions suggested the structure to be of the $MoSi_2$-type. The

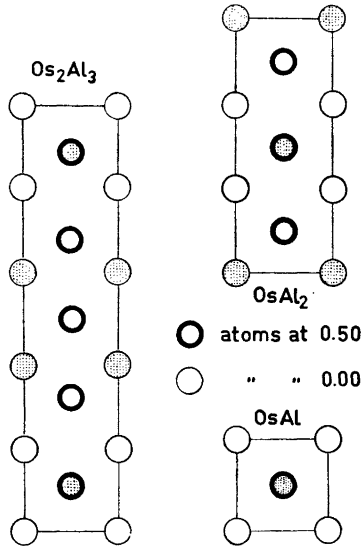

Fig. 1. The unit-cells of OsAl, Os_2Al_3, and $OsAl_2$. The osmium atoms are dotted.

atomic parameter was refined from successive ϱ_o and ϱ_c projections. The following structure was derived:

Unit-cell content	:	2 $OsAl_2$
Space group	:	*I4/mmm* (139)
2 Os in 2 (*a*)	:	0, 0, 0
4 Al in 4 (*e*)	:	0, 0, 0.34_2

The powder data are given in Table 4 which also gives a comparison between the observed and calculated intensities. The interatomic distances are given in Table 3.

DISCUSSION

The structures of Os_2Al_3 and $OsAl_2$ are illustrated in Fig. 1. The structural relationship between the three phases is obvious. Thus Os_2Al_3 and $OsAl_2$ may be described as being built up by CsCl-type units to a height of five and three times that of OsAl, respectively. The *c* axes of the tetragonal unit cells are reduced while the *a* axes are expanded in comparison with the cell parameter of OsAl.

The structure of Os_2Al_3 described above shows a pronounced similarity in its general architecture with the Au_2Nb_3 structure.[3] The distribution of the various kinds of atoms in the latter structure is different, namely:

4 Nb in 4 (*e*):	0,	0,	0.40
4 Au in 4 (*e*):	0,	0,	0.20
2 Nb in 2 (*a*):	0,	0,	0

The 8 + 6 coordination found in OsAl, with the interatomic distances 2.60 Å and 3.00 Å, respectively, is deformed in Os_2Al_3 and $OsAl_2$ to approximate 10 + 4 coordinations, except for Os in Os_2Al_3 which is approximately 9 + 5 coordinated. The Os-Al distances are within the range 2.46-2.86 Å previously found in Os_4Al_{13}.[2]

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