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An X-Ray Investigation of Ruthenium-Aluminium Alloys

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Phase analysis studies on ruthenium-aluminium alloys performed on the basis of X-ray powder patterns have shown this system to be rather complicated. The existence of the phases RuAl, Ru_2Al_3, $RuAl_2$, $RuAl_{\sim 2.5}$, and Ru_4Al_{13} has been demonstrated. RuAl, prepared by arc-melting, is of the CsCl-type of structure with $a = 2.95$ Å. The powder pattern of Ru_2Al_3 demonstrates clearly that this phase is isomorphous with Os_2Al_3 and its tetragonal cell dimensions are $a = 3.079$ and $c = 14.33$ Å. The crystal structure of $RuAl_2$ has been determined and refined by least-squares techniques on the basis of X-ray single-crystal data. The lattice parameters for the orthorhombic cell are $a = 8.012$, $b = 4.717$, and $c = 8.785$ Å. $RuAl_2$ is of the $TiSi_2$-type of structure. A comparison is made between the ruthenium-aluminium and osmium-aluminium systems.

The crystal structure of Ru_4Al_{13} has recently been reported.[1] Further studies on the ruthenium-aluminium system have revealed the existence of several new phases, described below, *viz.* RuAl, Ru_2Al_3, $RuAl_2$, and $RuAl_{\sim 2.5}$.

EXPERIMENTAL

The ruthenium-aluminium alloys were prepared from weighed amounts of ruthenium powder (L. Light & Co., about 99.99 %) and aluminium ribbon (E. Merck A. G., at least 99.99 %) by melting in an electric arc furnace under an atmosphere of argon. The melts were about 0.1 cm^3 in volume and were rapidly cooled by the water-cooled copper base of the furnace. The alloys, thus prepared, were also lump-annealed at 950°C for one week and then quenched in water. The heat treatment was carried out in sealed, evacuated silica tubes. Tantalum foils protected the alloys from reacting with the silica.

PHASE ANALYSIS

X-Ray powder photographs were taken in a Guinier focusing camera with $CuK\alpha_1$ radiation. The patterns given by the arc-melted samples revealed the existence of four intermediary compounds at the compositions RuAl, $RuAl_2$, $RuAl_{\sim 2.5}$, and Ru_4Al_{13}. The stoichiometry of Ru_4Al_{13} has been inferred from the structure investigation reported earlier.[1] In samples heat-treated at

950°C the phases $RuAl_2$ and Ru_4Al_{13} were found to remain unchanged. The $RuAl_{\sim 2.5}$ phase did not exist in samples quenched from 950°C which, however, were found to contain a new phase, $RuAl_{1.5}$, not observed in the arc-melted samples. The results of the phase analysis are given in Table 1. Annealed

Table 1. Phases in the ruthenium-aluminium system as indicated by X-ray powder photographs.

$RuAl_x$	arc-melted samples	lump-annealed at 950°C
$x = 0.50$	Ru + RuAl	—
0.75	Ru + RuAl	—
1.00	RuAl	—
1.25	RuAl + $RuAl_2$	RuAl(?) + Ru_2Al_3 + $RuAl_2$
1.50	RuAl + $RuAl_2$	Ru_2Al_3 + $RuAl_2$ + RuAl(?)
1.75	$RuAl_2$ + RuAl	$RuAl_2$ + Ru_2Al_3
2.00	$RuAl_2$ + trace $RuAl_{\sim 2.5}$ + trace Ru_4Al_{13}	$RuAl_2$
2.25	$RuAl_{\sim 2.5}$ + Ru_4Al_{13} + trace $RuAl_2$	$RuAl_2$
2.50	$RuAl_{\sim 2.5}$ + Ru_4Al_{13}	$RuAl_2$ + trace Ru_4Al_{13}
2.70	$RuAl_{\sim 2.5}$ + Ru_4Al_{13}	$RuAl_2$ + Ru_4Al_{13}
3.0	Ru_4Al_{13}	Ru_4Al_{13}
4.0	Ru_4Al_{13} + Al	—
6.0	Ru_4Al_{13} + Al	—

samples in the ranges 0—50 and 75—100 atom % aluminium have not been investigated.

The phase relationships around the composition RuAl appear to be very complicated and further studies of this compositional region at temperatures around 1000°C seem desirable. The powder pattern of the arc-melted sample RuAl showed the structure of this phase to be of the CsCl-type with $a = 2.95$ Å. However, powder photographs of samples annealed between 1200°—800°C indicate the existence of one or more additional CsCl-like phases around the composition RuAl.

Heat-treatments of several preparations at different temperatures, undertaken in order to get single phase samples of $RuAl_{1.5}$ and $RuAl_{\sim 2.5}$ were unsuccessful. This may depend on slow reactions and (or) the quality of the lumps annealed. Metallographic examination of pellets formed by arc-melting small amounts of the samples showed that these were very often heterogeneous.

The phase Ru_2Al_3

As mentioned above, no single phase preparation of $RuAl_{1.5}$ could be obtained by lump-annealing at temperatures between 800—1200°C. The powder pattern of the alloy $RuAl_{1.5}$ quenched from 1100°C is given in Table 2. From a comparison of this pattern and the corresponding one in the osmium-aluminium system it was deemed very likely that there exists a compound Ru_2Al_3 isomorphous with the Os_2Al_3 phase earlier reported.[2] The reflections

Table 2. The Guinier powder pattern of the alloy $RuAl_{1.50}$ annealed at 1100°C ($CuK\alpha_1$).

		Ru_2Al_3			$RuAl_2$		
I_{obs}	$\sin^2\theta_{obs}$	h k l	$\sin^2\theta_{calc}$	h k l	$\sin^2\theta_{calc}$	
w	0.01160	0 0 2	0.01156			
m	0.04360			1 1 1	0.04359	
m	0.04630	0 0 4	0.04624			
st	0.06547	1 0 1	0.06548			
vw diffuse	0.06596					RuAl-type phase
w	0.06775			2 0 2	0.06772	
m	0.08856	1 0 3	0.08860			
w	0.10510			1 1 3	0.10509	
w	0.11757			3 1 1	0.11753	
vw	0.12285			0 0 4	0.12299	
st	0.12517	1 1 0	0.12518			
m	0.13258					RuAl-type phase
vst	0.13483	1 0 5	0.13484			
vw	0.13733			0 2 2	0.13740	
vw	0.14364			2 2 0	0.14362	
vw	0.14787			4 0 0	0.14787	
m	0.17140	1 1 4	0.17142			

of Ru_2Al_3 were thus indexed by assuming a tetragonal cell with the following unit cell dimensions:

$$a = 3.079 \pm 0.002 \text{ Å}$$
$$c = 14.33 \pm 0.01 \text{ Å}$$

The intensities observed in the powder photograph are in a good agreement with those calculated for an Os_2Al_3-type of structure.

A comparison of the cell dimensions of Os_2Al_3 and Ru_2Al_3 shows that c/a is different for the two compounds, *viz.* 4.54 and 4.65, respectively. However, the cell volumes are about the same, *viz.* 137 Å^3 and 135 Å^3. The atomic volume of Os is about 0.3 Å^3 larger than that of Ru in the pure elements.

The phase $RuAl_2$

Single crystals of $RuAl_2$ could be obtained from an arc-melted sample of this stoichiometry. Single-crystal data were collected with a Weissenberg camera using MoK radiation. The reflections were registered with multiple film techniques, iron foils being inserted between the film sheets in order to obtain an appropriate degree of absorption. The Laue symmetry was found to be *mmm*. The cell dimensions obtained from the Guinier powder photographs were:

$$a = 8.012 \pm 0.002 \text{ Å}$$
$$b = 4.717 \pm 0.001 \text{ Å}$$
$$c = 8.785 \pm 0.002 \text{ Å}$$

The symmetry and cell dimensions suggested the structure to be of the $TiSi_2$-type. The three-dimensional Weissenberg data, registered with the crystal rotated around the [011] axis, were used in a refinement of the structure

by the least-squares method. 60 independent reflections from two layer-lines were used in the calculation and the final R value was 6.7 %. The structure derived and the final parameters are:

Unit cell content: 8 $RuAl_2$
Space group: *Fddd* (No. 70)

8 Ru in 8(*a*)	0,0,0	$B = (0.30 \pm 0.03)$ Å^2
16 Al in 16(*e*)	0.3296 ± 0.0016, 0,0	$B = (0.51 \pm 0.10)$ Å^2

The powder data are listed in Table 3 which also gives a comparison

Table 3. The Guinier powder pattern of $RuAl_2$ ($CuK\alpha_1$).

h k l	$\sin^2\theta_{obs}$	$\sin^2\theta_{calc}$	I_{obs}	I_{calc}
1 1 1	0.04358	0.04359	st	10.9
2 0 2	0.06772	0.06772	m+	2.3
1 1 3	0.10508	0.10509	m	2.8
3 1 1	0.11751	0.11753	st	11.3
0 0 4	0.12289	0.12299	m+	10.2
0 2 2	0.13737	0.13740	st	9.3
2 2 0	0.14350	0.14362	m	3.4
4 0 0	0.14783	0.14787	w	2.2
8 1 3	0.17900	0.17902	m	6.7
1 1 5	0.22806	0.22808	vw	1.0
1 3 1	0.25686	0.25689	vw	0.9
5 1 1	0.26544	0.26540	vw	0.8
2 2 4	0.26660	0.26661	m	3.3
4 0 4	0.27082	0.27086	w	1.9
4 2 2	0.28529	0.28527	m	3.6
3 1 5	0.30199	0.30202	m	3.6
2 0 6	0.31366	0.31370	vw	1.5
1 3 3	0.31838	0.31838	vw	0.8
5 1 3	0.32698	0.32690	vw	0.6
3 3 1	0.33078	0.33082	m	3.3

between the observed and calculated intensities. The interatomic distances are given in Table 4. These distances are within the range of distances found in Ru_4Al_{13}.[2]

Table 4. The interatomic distances in $RuAl_2$ (Å).

Ru—4 Al	2.57	Al—2 Al	2.60
2 Al	2.64	2 Al	2.68
4 Al	2.73	1 Al	2.73
4 Ru	3.20	2 Ru	2.57
		1 Ru	2.64
		2 Ru	2.73
		4 Al	3.20

The phase $RuAl_{\sim 2.5}$

This phase was found in the arc-melted samples around the composition Ru_2Al_5. No single crystal has been found and the powder pattern has not

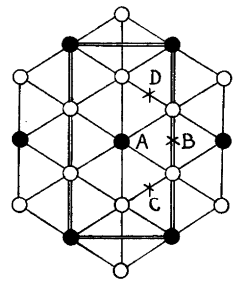

Fig. 1. Network of atoms of the (001) plane of $RuAl_2$ ($TiSi_2$-type) and the (110) plane of $OsAl_2$ ($MoSi_2$-type). ● Transition metal atom. ○ Aluminium or silicon atom.

been interpreted. The following reflections given by this phase may be used for identification:

I_{obs}	$\sin^2\theta_{obs}$ (Cu$K\alpha_1$)
m	0.0237
m	0.0390
w	0.0557
st	0.0564
m	0.0570

DISCUSSION

There are great similarities between the ruthenium-aluminium and the osmium-aluminium systems. In both systems the structures of phases of the stoichiometries *Me*Al, Me_2Al_3, *Me*Al_2, and Me_4Al_{13} are now known. *Me*Al and Me_2Al_3 each has the same structure in the two systems. The structural relationships between Os_4Al_{13} and Ru_4Al_{13} have recently been demonstrated.[1]

$OsAl_2$ is of the $MoSi_2$-type while $RuAl_2$ is of the $TiSi_2$-type. The relationship between the two structural types is well known.[3] The atomic arrangement in the (110) plane of $OsAl_2$ (or $MoSi_2$) is shown in Fig. 1. $MoSi_2$ is built up by the sequence AB whereas $TiSi_2$ and $RuAl_2$ show the stacking ABCD. A third member of this group of structures is $CrSi_2$ with the sequence ABC.

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