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Electron diffraction data on new compounds in the system platinum-aluminum.

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Takahashi & Mihama (1957) prepared evaporated films of Au–Al and showed that one can form intermetallic compounds in the system by heating the films in the electron microscope. Using selected area diffraction they were able to obtain electron diffraction patterns which showed the crystallographic relationships between several compounds in the system gold–aluminum.

Weaver & Brown (1962) prepared films of gold–aluminum by evaporating gold on to a glass slide and then evaporating aluminum on to the gold. They determined diffusion coefficients by measuring the change in reflectivity with time while annealing at low temperatures. They also showed by electron diffraction that the intermetallic compounds Au_2Al and $AuAl_2$ formed at the interface of the two metals during the annealing.

In the present study films of platinum and aluminum were examined by electron microscopy and electron diffraction while they were heated in the electron microscope. Three phases not reported in the literature, as well as several known phases, were observed. It was not possible to observe orientation relationships between the phases.

Experimental

The films were prepared in the following manner. A weighed amount of platinum foil was evaporated at normal incidence on to the surface of freshly cleaved mica at room temperature. Enough aluminum to make a 50/50% or 78/22% by weight combination of platinum–aluminum was then evaporated on to the surface of the platinum. By controlling the weights of the metals evaporated the total thickness of the combined films was kept at about 500 Å. The pressure in the vacuum chamber during evaporation varied between 10^{-4} and 10^{-5} mmHg. The films were separated from the mica by lowering it into distilled water. Sections of the films were mounted on stainless steel specimen grids and were observed while heating from room temperature to 600 °C in the heating stage of a Hitachi HU-11 electron microscope. Films were not heated above 600 °C because of the formation of $\gamma\, Al_2O_3$. Electron micrographs and electron diffraction patterns by the selected area method were obtained from areas of the films showing new phases. Further examinations by electron microscopy and high resolution electron diffraction were made after cooling the specimens to room temperature.

During the examination of the films the compounds PtAl, $PtAl_2$, Pt_3Al and Pt_5Al_3 were observed. Unlike the compounds reported in this paper they did not appear with any regularity within the temperature range studied.

Results

On raising the temperature of 50/50% Pt–Al films by approximately 8°/min a phase was formed at 410 °C consisting of single crystals up to 25 μ in size. Although this compound was observed at temperatures as high as 510 °C it was usually found to be unstable above 450 °C. On cooling from 410 °C further growth of the compound occurred. When films of 78/22% Pt–Al were heated at the same rate the compound was formed at 360 °C. Selected area diffraction patterns of crystals in three orientations were obtained. From these patterns it was deduced that the crystal was face-centered cubic with orientations on the (101), (112) and (100) planes. Specimens cooled from 450 °C to room temperature were placed in position for high resolution electron diffraction and Debye–Scherrer patterns were obtained along with reflections from platinum. The unit cell was found to be $a = 4{\cdot}10 \pm 0{\cdot}01$ Å. Interplanar spacings and estimated intensities are given in Table 1.

Table 1. *Observed interplanar spacings for compound formed at* 410 °C *on heating* 50/50% *by weight* Pt–Al *films in the electron microscope*

hkl	*d*	Intensity
111	2·36 Å	Very strong
200	2·05	Strong
220	1·45	Strong
311	1·235	Medium strong
222	1·180	Weak
400	1·025	Very weak
331	0·941	Medium
420	0·917	Medium
422	0·837	Weak
511	0·788	Weak
440	0·723	Very weak
531	0·694	Weak
600	0·683	Weak

Cell dimension: $a = 4{\cdot}10 \pm 0{\cdot}01$ Å
Face-centered cubic lattice

As the temperature was increased to 480 °C circular patches up to 2–3 μ in diameter appeared on the films. Within these patches were crystallites of a new compound less than 0·5 μ in size which persisted up to about 570°. When 78/22% Pt–Al films were examined in the same way this compound formed at 450 °C. Because of the small size of the crystals and the heavy population within these areas it was impossible to obtain single-crystal diffraction patterns. Debye–Scherrer patterns from these small circular areas were obtained by selected area diffraction. Upon cooling the specimen, high resolution patterns were obtained from larger areas which included many of these patches as well as the areas between them. The selected area diffraction patterns contained only the reflections from the new phase plus those of platinum. By comparing this pattern with the high resolution patterns it was possible to sort out any other phases which might have been included in the latter. Actually, the high resolution patterns did contain reflections from the cubic phase formed at 410 °C plus those of platinum. All other reflections in the pattern were accounted for by indexing the compound as hexagonal with

$$a = 4{\cdot}22 \pm 0{\cdot}01,\ c = 5{\cdot}17 \pm 0{\cdot}01\ \text{Å} \quad \text{and} \quad c/a = 1{\cdot}225\,.$$

The compound appears to be isostructural with Pt_2Ga_3 which has the space group $P\bar{3}m1$ (D_{3d}^3) of the Ni_2Al_3 type. Interplanar spacings and estimated intensities are given in Table 2.

Table 2. *Observed interplanar spacings for compound formed at* 460 °C *on heating* 50/50% Pt–Al *films in the electron microscope*

hkl	*d*	Intensity
001	5·16 Å	Medium strong
100	3·64	Strong
101	2·98	Strong
102, 110	2·11	Very strong
111	1·95	Medium
200	1·83	Weak
003, 201	1·727	Medium
112	1·635	Very weak
103	1·564	Weak
202	1·492	Medium strong
210	1·382	Weak
113, 211	1·332	Medium strong
203	1·255	Very weak
212, 300, 104	1·218	Medium strong
301	1·187	Very weak
302, 114	1·105	Weak
213	1·078	Weak
204, 220	1·055	Weak

Cell dimensions: $a = 4{\cdot}22 \pm 0{\cdot}01$ Å
$c = 5{\cdot}17 \pm 0{\cdot}01$
$c/a = 1{\cdot}225$
Probable space group: $P\bar{3}m1$ (D_{3d}^3)

With more rapid heating of a 50/50% Pt–Al film (about 10°/min) a compound was formed at 410 °C with a crystallite size not exceeding 2 μ. Also present were small crystallites of $PtAl_2$. From single-crystal patterns of crystals in three different orientations it was determined that the compound was orthorhombic with

$$a = 9{\cdot}79 \pm 0{\cdot}04, \quad b = 11{\cdot}28 \pm 0{\cdot}05 \quad \text{and} \quad c = 6{\cdot}58 \pm 0{\cdot}03 \text{ Å}.$$

The crystal orientations were (001), (010) and (101). This compound was also formed when 78/22% Pt–Al films were heated to 510 °C and then cooled.

Discussion

Because of the small size and quantity of the compounds observed, no elementary analysis was obtained. It is of interest to note that Klemm, Dorn & Huch (1958) reported evidence of a compound existing between 65 and 70 at.% platinum. If one plots a curve of unit cell dimensions *versus* atomic percentage of platinum for the cubic compounds Pt_3Al, PtAl and $PtAl_2$ the point for the cubic phase ($a = 4{\cdot}10$ Å) found in this investigation falls on the curve at a composition of approximately 66·7% platinum, suggesting the compound Pt_2Al.

Table 3. *Comparison of structures of compounds in the systems* Pt–Al *and* Pt–Ga

Compound	Structural type	Cell dimensions	Reference
PtGa	*B*20	$a = 4{\cdot}90$ Å	Esslinger & Schubert (1957)
PtAl	*B*20	$a = 4{\cdot}865$ Å	
$PtGa_2$	*C*1	$a = 5{\cdot}923$ Å	Zintl, Harder & Haucke (1937)
$PtAl_2$	*C*1	$a = 5{\cdot}922$ Å	
Pt_2Ga_3	$D5_{13}$	$a = 4{\cdot}23$ Å $c = 5{\cdot}18$ Å $c/a = 1{\cdot}223$	Hellner & Laves (1947)
Pt_2Al_3 (?)		$a = 4{\cdot}22$ Å $c = 5{\cdot}17$ Å $c/a = 1{\cdot}225$	This work

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An application of Taylor's method for determining the relative positions of molecules.

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A systematic method of solving the position problem in crystal structure determination, devised by Taylor (1954, 1957) is based upon the principle of the structure-factor graph (Bragg & Lipson, 1936) and has been successfully used on a number of structures.

In the paper describing the basic principle and the theory of the method, Taylor & Morley (1959) pointed out that the method can be applied in a completely objective way to structures for which both the shape and the orientation of the molecule are exactly known; they felt, however, that it could probably be more useful at an earlier stage of the structure determination, when there is still considerable doubt about the precise shape and orientation of the molecule. It will be shown in the present paper that when applied to the determination of the structure of 4,4′-dihydroxythiobenzophenone monohydrate, Taylor's method proved capable of deter-

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