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The crystal structure of Zr_2Al.

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The crystal structure of the intermetallic compound Zr_2Al has been determined from powder photographs using a sample of alloy prepared at A.E.R.E., Harwell, by arc melting in argon, annealing in vacuo for three weeks at 900 °C., and then quenching.

The specimen had a nominal composition of 8·7% Al by weight and had been tentatively assigned the formula Zr_3Al in accordance with the equilibrium diagram published by McPherson & Hansen (1954). The alloy specimen was extremely hard and great difficulty was experienced in producing a fine powder by filing.

The initial Debye–Scherrer photographs, which were taken using filtered Cu $K\alpha$ radiation with a 19 cm. precision camera designed by Adam (1954) were extremely complex and suffered from a heavy background especially at high θ. After a prolongued annealing of the powder in vacuo (14 days at 600 °C.) the X-ray pattern obtained was considerably simpler. The heavy background which was associated with the Zr fluorescence excited by the continuous spectrum from the copper target was reduced to a minimum by taking a long exposure at low voltage (4 days at 18 kV.). In final photographs obtained, all except the weakest lines up to $\sin^2\theta = 0{\cdot}9800$ could be measured accurately with the illuminated-fibre measuring device used.

From the data given by Keeler & Mallery (1955) for the structure of Zr_3Al, the lines on the powder film associated with this structure were identified. Several diffuse lines belonging to α-zirconium were also recognized and the remaining lines were indexed on a hexagonal unit cell with:

$$a = 4{\cdot}8939 \pm 0{\cdot}0005,\ c = 5{\cdot}9283 \pm 0{\cdot}0005\ \text{Å};$$
$$c/a = 1{\cdot}211 \pm 0{\cdot}001\ .$$

The equilibrium diagram suggests the possibility that the two phases Zr_3Al and Zr_2Al exist in equilibrium with some α-zirconium with the heat treatment given to the specimen. It was assumed, therefore, that the new phase indexed above was Zr_2Al and the crystallographic analysis was pursued on this basis.

The atomic volumes of elementary Zr and Al suggest that the number of 'molecules' of Zr_2Al in the unit cell is two, giving the calculated density as 5·67 g.cm.$^{-3}$. The density of a specimen of the alloy measured by means of a density bottle was 5·78 g.cm.$^{-3}$. Since the specimen contained an appreciable fraction of Zr_3Al, whose theoretical density is 5·98 g.cm.$^{-3}$, it is reasonable to suppose that the observed phase is Zr_2Al and that the unit cell contains two formula units.

Systematic absences gave $P6_3/mmc$ as a possible space group, and the size of cell and axial ratio correspond to the requirements of the $B8_2$ structure as exemplified by Ni_2In. Line intensities have been calculated on this basis with the atoms in the following positions:

2Zr(I): $0, 0, 0$
2Zr(II): $\frac{1}{3}, \frac{2}{3}, \frac{3}{4}$
2Al: $\frac{1}{3}, \frac{2}{3}, \frac{1}{4}$.

An absorption factor based on the measured density of the powder specimen has been included in the calculated intensities given in Table 1. The agreement between the calculated intensities and those estimated visually from the films is quite good.

The final values for a and c were obtained by using a Nelson–Riley extrapolation of the measured values of $\sin^2\theta$ given in Table 1. Using these values for the unit cell the interatomic distances are as follows:

2ZrI –ZrI $= c/2 = 2{\cdot}9641 \pm 0{\cdot}0003$ Å
6ZrI –ZrII $= (a^2/3 + c^2/16)^{\frac{1}{2}} = 3{\cdot}1906 \pm 0{\cdot}0003$ Å
6ZrII–Al $= (a^2/3 + c^2/16)^{\frac{1}{2}} = 3{\cdot}1906 \pm 0{\cdot}0003$ Å
3ZrII–Al $= \sqrt{(3)}\,.\,a/3 = 2{\cdot}8254 \pm 0{\cdot}0002$ Å
2ZrII–Al $= c/2 = 2{\cdot}9641 \pm 0{\cdot}0003$ Å

Table 1. *X-ray data*

	$\sin^2\theta\ (\times 10^4)$		Relative intensities	
hkil	Observed	Calculated	Observed	Calculated
1000	335	338	*vvw*	2·0
$10\bar{1}1$	506	508	*mw*	8·6
0002	—	682	—	0·26
$11\bar{2}0$	999	1004	*vs*	31
$10\bar{1}2$	1016	1016	*vs*	31
$20\bar{2}0$	—	1335	—	0·57
$20\bar{2}1$	1502	1506	*vvw*	2·9
$11\bar{2}2$	—	1678	—	0·6
$10\bar{1}3$	1858	1860	*vw*	8·0
$20\bar{2}2$	2005	2010	*ms*	16
$21\bar{3}0$	—	2328	—	0·6
$21\bar{3}1$	2493	2496	*mw*	3·5*
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0004	2711	2711	*vvw*	3·7
$20\bar{2}3$	—	2853	—	1·5
$30\bar{3}0$	2996	2988	*s*	10
$21\bar{3}2$		3002		21
$10\bar{1}4$	—	3045	—	0·46
$30\bar{3}2$	—	3663	—	0·28
$11\bar{2}4$	3705	3703	*mw*	17
$21\bar{3}3$	—	3845	—	2·2
$22\bar{4}0$	3978	3979	*w*	7·6
$20\bar{2}4$	—	4034	—	0·38
$31\bar{4}0$	—	4309	—	0·35
$31\bar{4}1$	4480	4477	*vvw*	2·0
$10\bar{1}5$	—	4560	—	1·04
$22\bar{4}2$	—	4652	—	0·21
$31\bar{4}2$	4983	4982	*mw*	14
$21\bar{3}4$	—	5024	—	0·7
$40\bar{4}0$	—	5298	—	0·18
$40\bar{4}1$	—	5461	—	0·94
$20\bar{2}5$	—	5550	—	0·96
$30\bar{3}4$	5684	5684	*mw*	13
$31\bar{4}3$	5825	5824	*vvw*	2·0
$40\bar{4}2$	5973	5972	*vw*	7·0
0006	—	6084	—	0·05
$32\bar{5}0$	—	6287	—	0·37
$10\bar{1}6$	6415	6414	*vw*	7·2
$32\bar{5}1$	—	6455	—	2·1
$21\bar{3}5$	—	6539	—	2·2
$22\bar{4}4$	6674	6673	*w*	14

Table 1 (*cont.*)

	$\sin^2 \theta$ ($\times 10^4$)			Relative intensities	
hkil	Observed	Calculated		Observed	Calculated
$40\bar{4}3$	—	6812		—	1·1
$41\bar{5}0$	6957	6945	diffuse	*ms*	15
$32\bar{5}2$		6959			16
$31\bar{4}4$	—	7002		—	0·81
$11\bar{2}6$	—	7073		—	0·23
$20\bar{2}6$	7404	7403		*vw*	8·7
$41\bar{5}2$	—	7618		—	0·5
$40\bar{4}4$	—	7792		—	0·53
$32\bar{5}3$	—	7801		—	0·31
$50\bar{5}0$	—	8263		—	0·27
$21\bar{3}6$	8393	8393		*ms*	24
$50\bar{5}1$	—	8431		—	1·9
$31\bar{4}5$	—	8518		—	3·9
$10\bar{1}7$	—	8604		—	2·1
$33\bar{6}0$	8936	8922		*ms*	15
5052		8937			16
$32\bar{5}4$	—	8980		—	1·7
$30\bar{3}6$	—	9053		—	0·45
$42\bar{6}0$	—	9252		—	1·1
$42\bar{6}1$	—	9420		—	0·79
$40\bar{4}5$	—	9507		—	4·1
$20\bar{2}7$	—	9594		—	4·6
$33\bar{6}2$	—	9596		—	0·65
$41\bar{5}4$	9646	9639		*vs*	111

* Line overlap with Zr_3Al. All values below dotted line refer to α_1, components.

vvw = very very weak; *vw* = very weak; *w* = weak; *m* = medium weak; *ms* = medium strong; *s* = strong; *vs* = very strong.

Discussion

The $B8_2$ structure proposed for Zr_2Al is the 'filled-up' version of the NiAs ($B8_1$) structure which is common among binary alloys of a transition metal such as Ni, Fe, Mn, etc., and a metalloid such as Se, Sb, Te, etc. The $B8_1$ structure is very versatile and often considered as a hexagonal close-packed arrangement of metalloid atoms with the metal atoms filling the octahedral holes. Variations in composition, within the same alloy system, are possible as the trigonal voids become filled-up with metal atoms, the completely filled-up version ($B8_2$) having the composition Me_2X. In the process of filling up, the c/a ratio decreases and approaches a limiting valve of $(3/2)^{\frac{1}{2}}$ for Ni_2In (Raynor, 1959). If it be supposed that aluminium behaves like a metalloid in Zr_2Al then it is not surprising to find the $B8_2$ structure appearing in the Zr–Al system, having a c/a value of 1·21. This unusual behaviour of aluminium has been observed before in Zr_5Al_3 (Wilson, Sams & Renouf, 1959) and in Th_3Al_2 (Braun & Vucht, 1955).

The $D8_8$ structure of the Nowotny phases Me_5X_3 may be regarded as a modification of the $B8_2$ structure and since this also occurs in the Zr–Al system as Zr_5Al_3, it is interesting to speculate on the reasons for the appearance of both phases. The striking feature of both structures is the major skeleton formed of rows of compressed Zr atoms along the vertical six-fold axes. The same feature occurs in the Zr_4Al_3 structure (Wilson, Spooner & Thomas, 1960) and in the σ phase of the transition elements. The latter are fully triangulated shell structures in which the atoms in the vertical rows have oblate coordination polyhedra with coordination number $Z14$ (Frank & Kasper, 1959). Although the Zr_5Al_3 and Zr_2Al structures are not fully triangulated according to the rules of Frank & Kasper, the Zr atoms along the vertical rows have the same coordination number $Z14$ and are compressed to give oblate coordination polyhedra. Thus, it seems that the packing of the Zr and Al atoms, considered as unequal spheres, is a major factor in stabilising the two phases in the Zr–Al system. It might be supposed that the failure to find a σ phase in this system is due to the large disparity between the radii of the Zr and Al atoms.

Apart from Ti_5Sn_3 and Ti_2Sn, Zr_5Al_3 and Zr_2Al are the only compounds from the same binary system crystallizing in the $D8_8$ and $B8_2$ structures. The reasons for this are not clear. In the titanium–tin system, $r_{Ti} < r_{Sn}$ whilst in the zirconium–aluminium system $r_{Zr} > r_{Al}$. On the other hand Ti and Zr have a certain chemical affinity and belong to the same sub-group of the periodic table whilst Al and Sn have no chemical affinity but each is characterized by having no incomplete d shell. On this basis, the two phases cannot be regarded as electron compounds but it may be supposed that in addition to packing there is a small electron-concentration factor which contributes to the stability of each phase.

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