

The Structure of the Intermetallic Phase $\gamma(\text{Mo-Al})\text{-Mo}_3\text{Al}_8$

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The molybdenum-aluminium phase diagram has been investigated in the region 12–40 wt.% aluminium. The phase Mo_3Al_8 has been isolated and a complete structure determination carried out. The structure is monoclinic with $a=9.208$, $b=3.6378$, $c=10.065$ Å and $\beta=100^\circ 47'$. The phase appears to exist over a composition range, the sample analysed having molybdenum replacing aluminium atoms to the extent of about 5%. The interatomic distances in Mo_3Al_8 are compared with those in other molybdenum-aluminium phases.

1. Introduction

The molybdenum-aluminium system has been investigated by a number of workers. Sperner (1959)

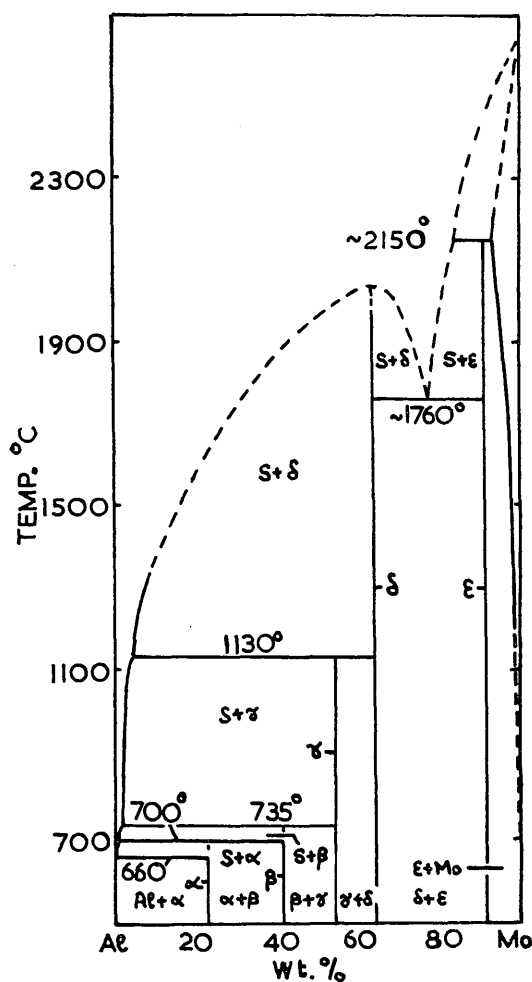


Fig. 1. The molybdenum-aluminium phase diagram (Sperner, 1959).

determined the phase diagram shown in Fig. 1, which contains the phases αMoAl_{12} , βMoAl_5 , γMoAl_3 , δMoAl_2 and $\epsilon\text{Mo}_3\text{Al}$. The structures of three of these phases had already been determined (MoAl_{12} , Adam & Rich (1954), MoAl_5 , Adam & Rich (1955), Mo_3Al , Wood *et al.* (1958)). Sperner considered that the γ phase corresponded to the composition MoAl_3 (45.75 wt.% Al) and had a tetragonal cell with $a=6.297$ Å and $c/a=1.588$.

Recently, Clare (1961) has investigated the aluminium-rich end of the phase diagram and has found that the phases richest in aluminium are MoAl_{12} and MoAl_7 . The latter phase was shown to be monoclinic with

$$a=5.12, b=13.0, c=13.5 \text{ \AA}; \beta=95^\circ;$$

no structure determination was undertaken.

The present work establishes the existence of a phase Mo_3Al_8 (43 wt.% Al). The structure of this phase has been determined and it is suggested that, although it is monoclinic, it corresponds to that of the γ phase described by Sperner.

2. Material

Alloy specimens were prepared by heating pressed compacts of the two metal powders. The starting materials were 150–300 mesh powders containing less than 0.1% by weight of metallic impurities. Two-gram compacts were prepared at each of the compositions

Table 1. X-ray powder photographic examination of (Mo-Al) alloys

| Alloy numbers | Composition before heat treatment | Phases indicated by X-ray powder photographs |
|---------------|-----------------------------------|-------------------------------------------------------|
| 1 | 12.3 wt.% Al | Mo_3Al |
| 2 | 17 | $\text{Mo}_3\text{Al} + \text{Mo}_3\text{Al}_8$ |
| 3 | 22 | $\text{Mo}_3\text{Al} + \text{Mo}_3\text{Al}_8$ |
| 4 | 30 | $\text{Mo}_3\text{Al} + \text{Mo}_3\text{Al}_8$ |
| 5 | 35 | $\text{Mo}_3\text{Al}_8 + \text{trace Mo}_3\text{Al}$ |
| 6 | 40* | Mo_3Al_8 |
| 7 | 43 | Mo_3Al_8 |

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* This ingot was analyzed by Messrs. Johnson Matthey & Co. Ltd., and contained 38.2 wt.% Al after heat treatment.

listed in Table 1; the compacts were melted in alumina boats under 10^{-5} mm. Hg pressure using an induction heater. Each ingot was allowed to cool slowly to room temperature during a period of about 5 min. Powder specimens were examined with $\text{Co } K\alpha$ radiation and the results are summarized in Table 1. No evidence was obtained for the existence of the δ phase (MoAl_2) in these melts. Fragments from the crushed alloys 6 and 7 gave good single-crystal X-ray photographs and a specimen of approximately cubic shape and side 0.05 mm., selected from ingot 6, was used in the structure determination.

3. Unit cell and space group

Laue, oscillation and Weissenberg photographs confirmed that the unit cell is monoclinic and provided approximate values of the lattice parameters. The lattice parameters a , c and β were determined by the θ -method described by Weisz, Cochran & Cole (1948), but with a Geiger counter and linear ratemeter replacing the photographic film used by them. The b parameter was found by the method of Farquhar & Lipson (1946); the values obtained were:

$$\begin{aligned} a &= 9.208 \pm 0.003, & b &= 3.6378 \pm 0.0003, \\ c &= 10.065 \pm 0.003 \text{ \AA}, & \beta &= 100^\circ 47' \pm 3'. \end{aligned}$$

The volume of the unit cell is therefore 331.2 \AA^3 . The density of the crystals, determined by the displacement method, was $5.28 \pm 0.05 \text{ g.cm.}^{-3}$, so that the mass content of the unit cell is $1052 \pm 11 \text{ A.M.U.}$ Chemical analysis gave an aluminium content of 38.2 wt. %.

The formula Mo_3Al_8 corresponds to 43 wt. % Al and two formula units per unit cell results in a mass content of 1008 A.M.U. with a calculated density of 5.04 g.cm.^{-3} . The differences between these calculations and the observed values are satisfactorily accounted for in the refinement of the structure (see section 6, below).

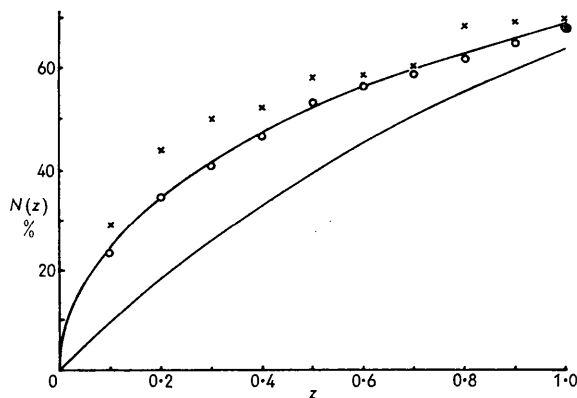


Fig. 2. Tests for centrosymmetry:

○ [010] zone
× [100] zone.

Laue & Weissenberg photographs indicate that the structure is C -face centred and that the Laue symmetry is $2/m$. The possible space groups are therefore $C2$, Cm and $C2/m$. These can be distinguished by the presence or absence of a centre of symmetry in the [010] and [100] projections. Wilson statistical tests were therefore applied to intensities from Weissenberg photographs for the [010] and [100] zones, and the results are shown in Fig. 2. Both observed distributions are consistent with a centrosymmetric structure and the space group $C2/m$ was therefore chosen.

4. Collection of Intensities

Normal-beam, zero-layer Weissenberg photographs were taken with [010] and [100] as oscillation axes. $\text{Mo } K\alpha$ radiation and packs of five films were used. The diffraction spots were of similar shape in the two zones and an intensity scale was prepared using the $(10\bar{5})$ reflection. Reflections out to $\sin \theta/\lambda = 1.2 \text{ \AA}^{-1}$ in the [010] zone and $\sin \theta/\lambda = 1.4 \text{ \AA}^{-1}$ in the [100] zone were measured by visual comparison with this scale. The intensities were corrected for Lorentz and polarization factors and allowance was made for the resolution of the $\alpha_1\alpha_2$ doublet by scaling F_o to F_c in the regions of $\sin \theta/\lambda$. For the size of the crystal used (approximately 0.05 mm. cube) the scaling also corrects for changing absorption in the specimen to within the accuracy of the measurements.

5. The approximate structure

The [010] Patterson function for $\frac{1}{4}$ of the unit cell is shown in Fig. 3. One peak (A) in the asymmetric unit is just over twice the weight of the other peaks, which

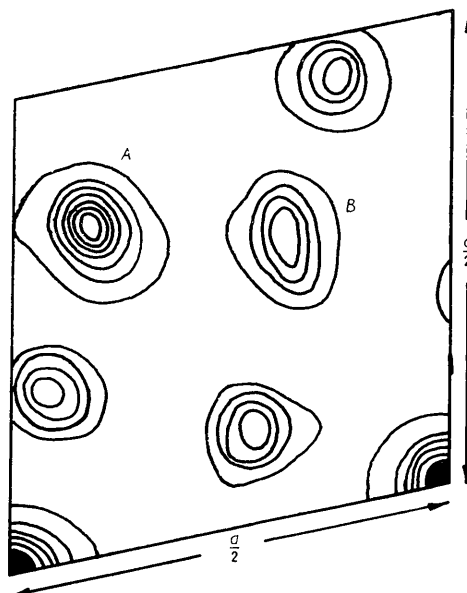


Fig. 3. [010] Patterson function for Mo_3Al_4 .

are all of approximately the same weight. The peak B is at twice the vector distance from the origin of the peak A . It was concluded that the three molybdenum atoms which lie within the projected cell of $a/2 \times c$ might lie on a centre of symmetry at the origin, at A and at its centrosymmetrically related position. The z parameter of A was approximately $1/3$, which results

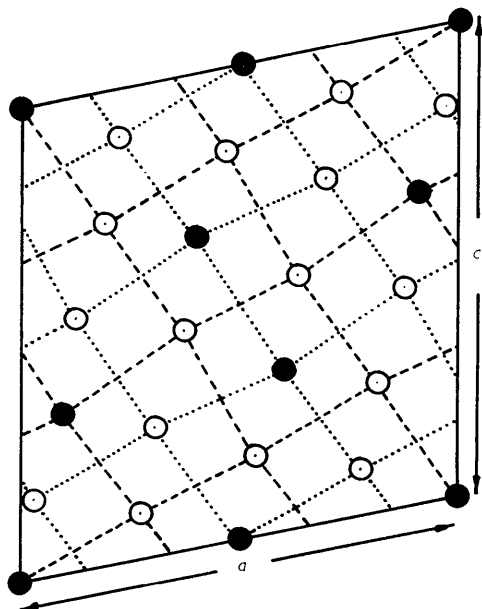


Fig. 4. The b -axis projection of the Mo_3Al_8 structure. The full circles represent molybdenum atoms and the open circles aluminium atoms. Dashed lines link atoms at height $y=0$ and dotted lines link those at $y=1/3$.

in the molybdenum atoms being distributed at every $c/3$ in a line projection along $[001]$. This prediction was in agreement with the observed $00l$ intensities, which were strong for $l=3, 6, 9, 11$ and 12 and weak for the intermediate values of l .

Structure factors were calculated out to $\sin \theta/\lambda = 0.6 \text{ \AA}^{-1}$ for the $h0l$ reflections and a structure containing only three molybdenum atoms: the signs of 40 large structure factors were considered to be uniquely determined. All but two of these structure factors had positive signs and a synthesis of the corresponding F_o 's, resembled the Patterson function in the position of all its peaks. It was then realized that the structure illustrated in Fig. 4 gave reasonable interatomic distances, twelve-fold coordination and a good agreement with the Patterson function. This trial structure gave an R factor of 0.30 for $h0l$ reflections out to $\sin \theta/\lambda = 0.6 \text{ \AA}^{-1}$ and this was reduced appreciably by successive $F_o - F_c$ syntheses.

6. Refinement of the structure

The refinement of the $[010]$ projection was continued using $F_o - F_c$ syntheses. The atomic scattering factors were generated from the analytical constants for Mo and Al₀ tabulated by Forsyth & Wells (1959). The molybdenum curve was corrected for the contribution $-\Delta f' = 1.7$, as calculated by Dauben & Templeton (1955). The imaginary component, $\Delta f'' = 0.9$, makes no significant difference to the amplitude or phase of any of the calculated structure factors and it was not included in the final calculations.

When the R factor had been reduced to 0.14 for all the 400 $h0l$ reflections out to $\sin \theta/\lambda = 1.2 \text{ \AA}^{-1}$, the

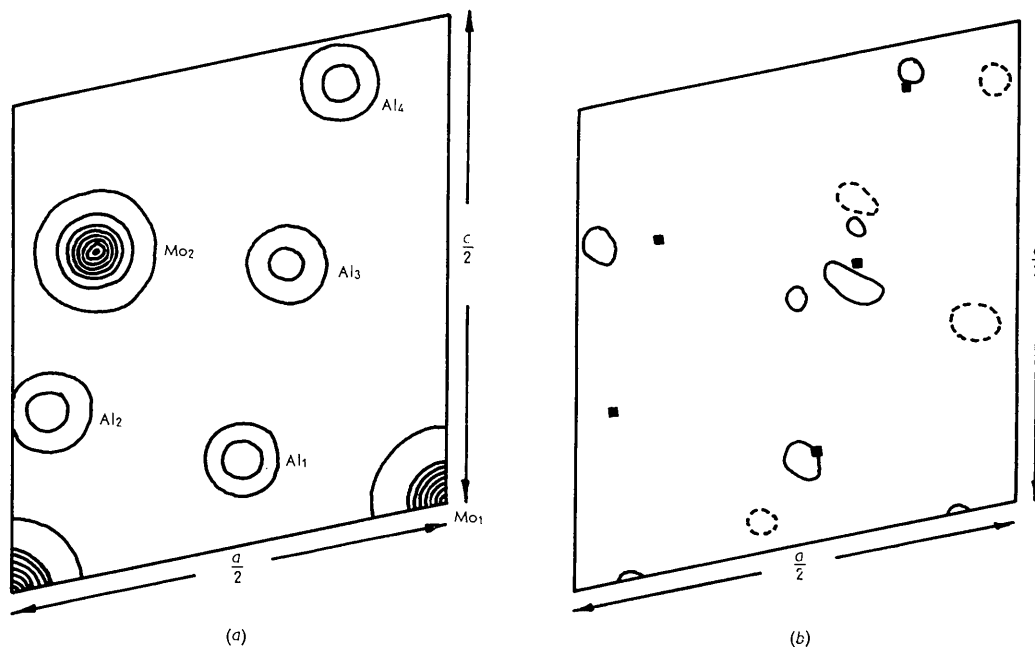


Fig. 5. Final F_o and $(F_o - F_c)$ $[010]$ Fourier projections. (a) F_o . The contours are at equal arbitrary intervals. (b) $(F_o - F_c)$. The contour intervals are one-eighth those of the F_o ; negative contours are shown as broken lines. Squares mark the atomic sites.

only significant features remaining in the F_o-F_c synthesis were positive regions centred on all the aluminium positions. These positive regions were produced entirely by low-angle differences (i.e. those associated with reflections having $\sin \theta/\lambda < 0.5 \text{ \AA}^{-1}$) and therefore did not result from an incorrect choice of temperature factors for the atoms. The observed composition and mass content of the unit cell (see section 3 above) show an excess of molybdenum over that corresponding to the formula Mo_3Al_8 . The R factor for the [010] projection was lowered to 0.09 by introducing 5% molybdenum into the aluminium positions. The resulting F_o-F_c synthesis showed no significant features and is illustrated, together with the corresponding F_o synthesis, in Fig. 5. Much better agreement is obtained between the observed and calculated mass contents, densities and compositions corresponding to the structure with Mo replacing 5% of the Al atoms than with those relating to the 'ideal' formula Mo_3Al_8 . The values are summarized in Table 2: the observed composition corresponds to a replacement of Al to the extent of 5.75%.

Table 2. Cell contents

| | 'Ideal' Mo_3Al_8 | 5% Mo in Al positions | Observed |
|-----------------------------|-------------------------------------|--------------------------|-----------------|
| Mass content A.M.U. | 1008 | 1062 | 1052 ± 11 |
| Composition wt. % Al | 43 | 38.6 | 38.2 |
| Density g.cm. ⁻³ | 5.04 | 5.34 | 5.28 ± 0.05 |

The [100] projection was refined so that any departure from centrosymmetry in the structure might be detected. If the space group is $C2/m$, the short y axis constrains all atoms to lie on the mirror planes at $y=0$ and $\frac{1}{2}$, but the space group $C2$ would allow the y parameters to vary about these values. No indication of non-centrosymmetry was obtained and the final R factor was 0.09 for all $0kl$ reflections out to $\sin \theta/\lambda = 1.4 \text{ \AA}^{-1}$. Molybdenum was again substituted for 5% of the aluminium atoms and no significant differences remained in the final F_o-F_c synthesis.

Table 3 lists the final atomic coordinates with their standard deviations, which have been calculated from the final F_o and F_o-F_c syntheses by the method

Table 3. Final atomic parameters together with their standard deviations

| Atom | Position (0, 0, 0; $\frac{1}{2}, \frac{1}{2}, 0$) + | x | $\sigma(x)$ | z | $\sigma(z)$ |
|---------------|------------------------------------------------------|--------|-------------|--------|-------------|
| Mo_1 | 2(a) 0, 0, 0 | | | | |
| Mo_2 | 4(i) $x, 0, z; \bar{x}, 0, \bar{z}$ | 0.0938 | 0.0002 | 0.6597 | 0.0002 |
| Al_1 | 4(i) $x, 0, z; \bar{x}, 0, \bar{z}$ | 0.2720 | 0.0010 | 0.9060 | 0.0010 |
| Al_2 | 4(i) $x, 0, z; \bar{x}, 0, \bar{z}$ | 0.4600 | 0.0010 | 0.1780 | 0.0010 |
| Al_3 | 4(i) $x, 0, z; \bar{x}, 0, \bar{z}$ | 0.1872 | 0.0010 | 0.2785 | 0.0010 |
| Al_4 | 4(i) $x, 0, z; \bar{x}, 0, \bar{z}$ | 0.3670 | 0.0010 | 0.5420 | 0.0010 |

Table 4. Interatomic distance in Mo_3Al_8 , together with their standard deviations

| Atom | Neighbour | Distance | Standard deviation | Other neighbours |
|---------------|-----------------|----------|--------------------|-----------------------------------------------------------------------------------------|
| Mo_1 | 4 Al_1 | 2.805 Å | 0.007 Å | |
| | 2 Al_1 | 2.838 | 0.010 | |
| | 4 Al_2 | 2.627 | 0.007 | |
| | 2 Al_3 | 3.003 | 0.010 | |
| Mo_2 | 1 Mo_2 | 3.353 | 0.004 | |
| | 1 Al_1 | 2.705 | 0.010 | |
| | 2 Al_2 | 2.554 | 0.007 | |
| | 2 Al_3 | 2.700 | 0.007 | |
| | 1 Al_3 | 2.772 | 0.010 | |
| | 1 Al_4 | 2.974 | 0.010 | |
| | 2 Al_4 | 2.799 | 0.007 | |
| | 2 Al_4 | 2.854 | 0.007 | |
| Al_1 | 2 Al_1 | 2.709 | 0.010 | |
| | 2 Al_2 | 2.813 | 0.010 | |
| | 1 Al_2 | 2.754 | 0.014 | |
| | 1 Al_2 | 2.953 | 0.014 | |
| | 2 Al_3 | 2.675 | 0.010 | 1 Mo_2 , 2 Mo_1 , 1 Mo_1 |
| Al_2 | 2 Al_3 | 2.813 | 0.010 | |
| | 1 Al_3 | 2.878 | 0.014 | |
| | 1 Al_4 | 2.966 | 0.014 | 2 Mo_1 , 2 Mo_2 , 2 Al_1 , 1 Al_1 , 1 Al_1 |
| Al_3 | 2 Al_4 | 2.675 | 0.010 | 1 Mo , 2 Mo_2 , 1 Mo_2 , 2 Al_1 , |
| | 1 Al_4 | 2.852 | 0.014 | 2 Al_2 , 1 Al_2 |
| Al_4 | 2 Al_4 | 2.825 | 0.010 | 2 Mo_2 , 2 Mo_2 , 1 Mo_2 , 1 Al_2 , 1 Al_3 |
| | 1 Al_4 | 2.736 | 0.014 | 2 Al_3 |

suggested by Lipson & Cochran (1953). Tabulated values of F_o and F_c are available. The interatomic distances are given in Table 4.

7. Discussion

The structure is related to body-centred cubic and is formed by the superposition of distorted-square, planar nets. These planes of atoms are perpendicular to the y axis and the plane at $y=0$ is related to that at $y=\frac{1}{2}$ by the C -face centring.

The mean interatomic distances in the four known molybdenum-aluminium phases are given in Table 5; they suggest that the interatomic interactions are comparable in all four compounds and they are not inconsistent with Goldschmidt's atomic diameter of 2.8 Å for both elements. In Mo_3Al_8 , the transition-metal atoms avoid contact with each other, the shortest Mo-Mo distance being 3.35 Å. The mean Mo-Al and Al-Al distances are nearly equal (2.76 and 2.79 Å respectively) though the shortest interatomic distances of 2.63 and 2.55 Å are between molybdenum and aluminium atoms. This suggests that the strongest interaction is between aluminium and the transition-metal atoms, but the shortening of the bonds is less marked than that arising in alloys between aluminium and the first group of transition metals, Ti-Ni (see, for example, Taylor, 1954).

Table 5. Mean interatomic distances in Å for the (Mo-Al) phases

| Mean interatomic distance | MoAl_{12} | MoAl_5 | Mo_3Al_8 | Mo_3Al |
|---------------------------|--------------------|-----------------|--------------------------|------------------------|
| Mo-Al | 2.72* | 2.79* | 2.76 | 2.77 |
| Al-Al | 2.84* | 2.79* | 2.79 | — |
| Mo-Mo | — | — | 3.35 | 2.92 |

* These distances are obtained by assuming that MoAl_5 is exactly isostructural with WAl_5 and MoAl_{12} with WAl_{12} .

It appears certain that the phase can extend in composition to the Mo-rich side of Mo_3Al_8 and reach the approximate formula $\text{Mo}_{3.4}\text{Al}_{7.6}$ (38.2 wt.% Al). Woolf (1961) has analyzed two melts which, from X-ray powder photographs, appear to contain only Mo_3Al_8 . He found the compositions to be 45.8 and 45.3 wt.% Al, indicating that the phase can also extend to the Al-rich side of the ideal composition at 43 wt.% Al.

There is a close similarity in the behaviour of molybdenum and tungsten in respect of their alloys. The phases Co_7Mo_6 , Fe_7Mo_6 , MoAl_{12} , MoAl_5 , etc., are isostructural with the phases containing tungsten in place of molybdenum. The (W-Al) phase diagram proposed by Clark (1940) shows, in the range 25–31 at.% W, two phases (WAl_3 and W_3Al_7) which are stable only at temperatures above 1300 °C. Clark regarded the exact compositions of these phases as uncertain and further work is being undertaken to determine whether either phase is isostructural with Mo_3Al_8 .

Further investigation of the Mo-Al phases will include single-crystal studies of the alloys MoAl_{12} and MoAl_7 . The research forms part of a project supported by the Air Force Office of Scientific Research of the Air Research and Development Command, United States Air Force, through its European Office, under Contract No. AF 61 (052)–50. Some of the equipment used was purchased with the help of a generous award from the Government Grants Committee of the Royal Society.

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