

INTERMETALLIC PHASES IN THE ALUMINIUM-MANGANESE BINARY SYSTEM*

M. A. TAYLOR†

The region of the aluminium-manganese phase diagram from 33 to 45 wt.% manganese has been investigated by means of X-ray analysis, density measurements, and microsections. Two previously unknown intermetallic compounds have been isolated, and a third known phase shown to be stable only at high temperatures. Crystallographic and chemical studies of the various phases are described, and corrections to the published phase diagram are suggested.

PHASES INTERMETALLIQUES DANS LE SYSTEME BINAIRE ALUMINIUM-MANGANESE

Le diagramme de phase aluminium-manganèse a été étudié dans la région de 33 à 45% (en poids) de manganèse par une analyse aux rayons X, par des mesures de densité et par l'observation de microsections. Deux composés intermétalliques inconnus ont été isolés. L'auteur a observé également qu'une troisième phase déjà identifiée n'est stable qu'aux températures élevées.

L'étude cristallographique et chimique des diverses phases est décrite et des corrections sont suggérées à propos des diagrammes de phase antérieurement publiés.

INTERMETALLISCHE VERBINDUNGEN IM SYSTEM ALUMINIUM-MANGAN

Im Phasendiagramm Aluminium-Mangan wurde das Gebiet von 33 bis 45 Gewichts-Prozent Mangan röntgenographisch, densitometrisch und metallographisch untersucht. Zwei bisher unbekannte intermetallische Verbindungen wurden isoliert, von einer dritten wurde gezeigt, daß sie nur bei hohen Temperaturen stabil ist. Es werden kristallographische und chemische Untersuchungen der verschiedenen Phasen beschrieben und Korrekturen an den veröffentlichten Phasendiagrammen vorgeschlagen.

INTRODUCTION

Attempts to produce the 'MnAl₃' phase referred to by Hofmann⁽¹⁾ revealed several errors in the published Al-Mn phase diagram (Hansen⁽²⁾). A melt at 34.6 per cent Mn‡ quenched from 850°C contained hexagonal crystals with unit cell dimensions:

$$a = 19.95 \pm 0.01 \text{ \AA}$$
$$c = 24.52 \pm 0.01 \text{ \AA}$$

This phase is hereafter referred to as $\mu(\text{AlMn})$. A second melt at 40.0 per cent Mn, also quenched from 850°C, contained hexagonal crystals with unit cell dimensions:

$$a = 7.54 \pm 0.01 \text{ \AA}$$
$$c = 7.90 \pm 0.01 \text{ \AA}$$

This phase is referred to as $\phi(\text{AlMn})$. Each of these ingots contained more than one phase. Neither of the two hexagonal phases had previously been found in the Al-Mn binary system, and furthermore the 'MnAl₃' phase could not be found in either ingot.

These observations led to an investigation of the aluminium-rich region of the phase diagram, and suggestions for its correction have been made. It must be stressed here that the prime purpose of the investigation was not the exact determination of the

form of the phase diagram (and hence no thermal analysis has been done), but rather to establish the chemical compositions and crystallographic characteristics of the various intermetallic compounds found in the system, and to examine their stability at a limited number of temperatures.

A survey of the literature showed that knowledge of the region from 35–45 per cent Mn is very uncertain, but that the region 0–35 per cent Mn appears to be reasonably well established. Eleven melts were therefore made up at 1 per cent composition intervals in the range 35–45 per cent Mn and annealed at 780°C; these were examined by X-ray powder photographs, density measurements and microsections. Selected single crystals were examined by X-ray oscillation photographs. Subsequently sixteen further melts, in a wider composition range, were made up, annealed at various temperatures, and examined by the above methods.

PREVIOUS WORK

Many investigations of the Al-Mn system have been reported, and the reader is referred to Hansen⁽²⁾ (from which Fig. 1 has been adapted) for a detailed discussion and relevant references. Only points of particular interest in relation to the present work are mentioned here.

The nature of the phases X and 'MnAl₃' is still uncertain. The exact composition and homogeneity range of the phase 'MnAl₃' is not satisfactorily

* Received March 16, 1959.

† Crystallographic Laboratory, Cavendish Laboratory, Cambridge. Now at Metallurgy Division, A.E.R.E., Harwell.

‡ Weight percentages are used throughout this paper.

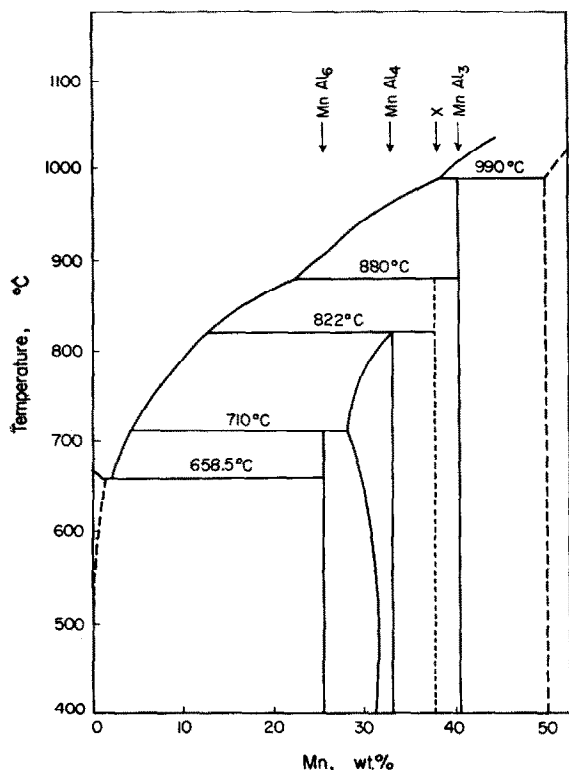


FIG. 1. Aluminium-rich region of published aluminium-manganese phase diagram Hansen⁽²⁾. Adapted by permission from *Constitution of Binary Alloys* by M. Hansen. Copyright McGraw-Hill Book Co. (1958).

established, although Hofmann⁽¹⁾ isolated crystals of the phase, measured its unit cell dimensions, and gave its chemical composition (from chemical analyses of the single crystals) as 41 per cent Mn. Phillips⁽³⁾ established the phase X as having a composition between 33.7 and 41.4 per cent Mn and suggested it may be the phase found with monoclinic or triclinic habit in ingots of 20–40 per cent Mn. Hofmann⁽¹⁾ and Bland⁽⁴⁾ determined the unit cell dimensions of this triclinic crystal—i.e. $\delta(\text{AlMn})$ —and the latter gave its composition, from crystallographic considerations, as 42.5 per cent Mn (i.e. $\text{Mn}_4\text{Al}_{11}$), in agreement with the previous statement of Hanemann & Schrader⁽⁵⁾ that it is richer in manganese content than MnAl_3 . It seems possible, in view of the disagreement of the various compositions assigned, that the phase described by Phillips is not $\delta(\text{AlMn})$ but a different phase, probably $\mu(\text{AlMn})$ or $\phi(\text{AlMn})$.

In addition to the peritectic temperatures associated with the formation of MnAl_6 and MnAl_4 , thermal arrests have also been observed at 880°C,^(3,6) at 920°C⁽⁶⁾ and at 990°C.^(7–9) The effect at 920°C was not observed by Phillips, and has therefore not been given in the published phase diagram; furthermore,

correlation between the formation of the phases X and ' MnAl_3 ' and the thermal arrests has not been satisfactorily established.

It must be added here that Phillips, on whose work the phase diagram in the region 30–45 per cent Mn is to a large extent based, was unable to anneal his specimens to equilibrium in the range 34–37 per cent Mn.

To summarise, one can say that knowledge of the composition and homogeneity ranges of the phases with composition between 35–45 per cent Mn appears reasonably well established.

IDENTIFICATION OF INTERMETALLIC PHASES

Possible methods of identification include recognition of crystal habit, chemical analysis, etching characteristics and X-ray analysis. In the present work it was decided that identification could best be carried out in terms of crystallographic characteristics, but that supporting evidence from as many other sources as possible is also necessary. The chemical composition is, of course, essential in the description of any phase.

PREPARATION OF SPECIMENS

The methods used to produce pure homogeneous ingots are now described. The manganese and aluminium were each of 99.99 per cent purity. The alloys were melted in recrystallized alumina crucibles, under a protective atmosphere of argon.

For a given specimen the aluminium and the manganese were melted together in an induction furnace. The resulting ingot was then cracked up and remelted in the induction furnace, this being done to ensure that all the manganese melted and to attempt to homogenise the ingot. The specimen was then annealed in a resistance furnace and finally quenched. The average weight of a specimen was twelve grams.

Previous work indicated that long anneals are necessary even at high temperatures in order to attain equilibrium conditions in these alloys. Some evaporation from the ingots, however, occurs during this prolonged annealing. To determine its extent, and also to check the long-range homogeneity in an ingot, a specimen of initial composition 35 per cent Mn was made and a piece of it analysed. The analysis yielded 34.7 per cent Mn, thus verifying that the evaporation was small and the long-range homogeneity satisfactory.

Details of the various annealing treatments are given below:

Melts A were made at 1 per cent composition intervals in the range 35–45 per cent Mn and

annealed for 10 days at 780°C. It was found that the 'MnAl₃' phase (taking Hofmann's crystallographic data as a means of identification) was not stable in this region, and that melts at 35 and 36 per cent Mn had not reached equilibrium. Melts *B* were quenched from 950°C, after being annealed at this temperature for half an hour. This was done to test for the existence of 'MnAl₃' at temperatures above 780°C.

Melts *C* were annealed at 850°C for 14 days. This was done in a successful attempt to produce equilibrium in alloys of the same compositions as those that had not reached equilibrium in Melts *A*. Melts *C* showed the existence of a phase with composition apparently between MnAl₄ (i.e. 33.5 per cent Mn) and 35 per cent Mn.

Melts *D* were therefore made at 33–35 per cent Mn and annealed for 2 weeks at 810°C. Equilibrium was attained in these ingots.

METHODS OF EXAMINATION OF INGOTS

(a) Density measurements

The density of the ingot was measured by the displacement method, using distilled water. The ingots were cracked open and several solid pieces from each were used. Measurements made on three different specimens from each ingot gave a mean value of the density reproducible to within ± 1 per cent.

The specimens were slightly porous, and therefore slightly less dense than crystallographically ideal crystals. The degree of porosity should, however, be similar in ingots that have undergone identical heat treatments, and it may be assumed that the actual density is in some approximately fixed ratio to the ideally perfect density. The validity of this approximation is shown by the results below.

In a plot of density versus composition for ingots after similar heat treatments, peaks of maximum density may be expected at the stoichiometric compositions of the various intermetallic phases, and minima in the intermediate two-phase regions.

(b) Metallography

Microsections of samples from each ingot were prepared. Etching by total immersion for about 30 sec in $\frac{1}{2}$ per cent HF was found to outline the various phases satisfactorily.

(c) X-ray examination

Powder photographs of representative samples from each ingot were taken using FeK α * radiation.

* FeK α , although not the most suitable for use with these alloys, was the only available radiation.

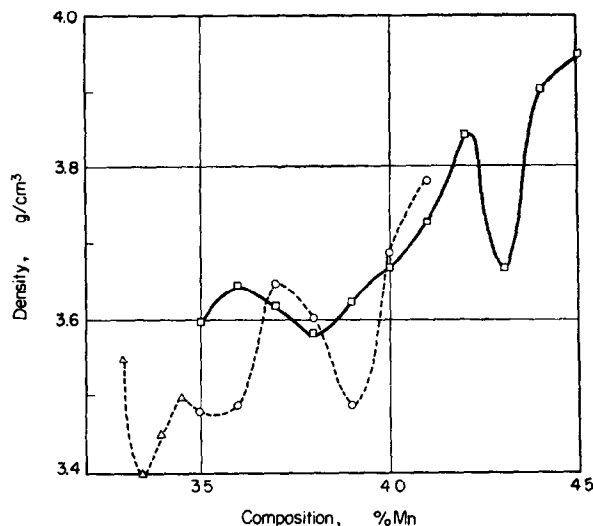


FIG. 2. Density measurements of aluminium-manganese alloys.
 □ Specimens annealed at 780°C for 10 days (*A*)
 ○ Specimens annealed at 850°C for 14 days (*C*)
 △ Specimens annealed at 810°C for 14 days (*D*).

Large single crystals of each phase were identified by means of rotation photographs, and powdered so as to produce "standard" powder photographs of each phase. From comparison of the former photographs with the "standards", the phases present in a given alloy could be identified. The unit cell of a phase can, in principle, be determined from its powder photograph, but unambiguous results cannot be guaranteed, and single-crystal rotation photographs were used to determine the unit cells of the various phases.

EXPERIMENTAL RESULTS

(a) Density measurements

The results of the density determinations are given in Figs. 2 and 3.

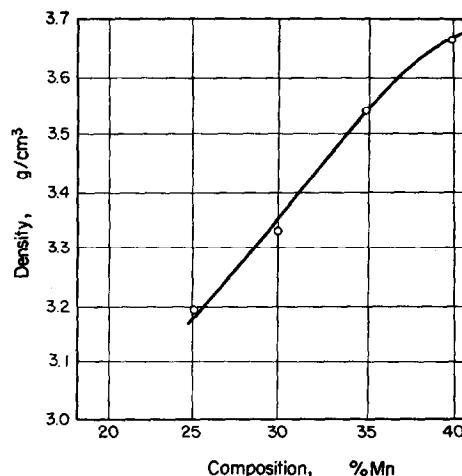


FIG. 3. Density measurements of aluminium-manganese alloys. Specimens quenched from 950°C (*B*).

TABLE 1. Aluminium-manganese intermetallic phases identified by X-ray powder photographs

Melts A: annealed for 10 days at 750°C											
Composition (%Mn)	35	36	37	38	39	40	41	42	43	44	45
Phases observed	$\phi\mu\delta$	$\phi\delta\mu$	$\phi\delta$	$\phi\delta$	$\delta\phi$	$\delta\phi$	$\delta\phi$	$A\delta$	$A\delta$	$A\delta$	$A\delta$
Melts C: annealed for 14 days at 850°C											
Composition (%Mn)	35	36	37	38	39	40	41				
Phases observed	$\phi\mu$	$\phi\delta$	$\phi\delta$	$\phi\delta$	$\delta\phi$	$\delta\phi$	$\delta\phi$				
Melts D: annealed for 14 days at 810°C											
Composition (%Mn)	33		33½		34		34½				
Phases observed	MnAl ₄		MnAl _{4,μ}		μ,MnAl ₄		μ				
Melts B: quenched from 950°C											
Composition (%Mn)	25		30		35		40				
Phases observed	'MnAl ₃ ', ϕ,μ ,MnAl ₄		'MnAl ₃ ', ϕ,μ		'MnAl ₃ ', ϕ,μ		A, 'MnAl ₃ '				

The phase present in the greater amount is listed first in each case.

The plots of density against composition in Fig. 2 suggest that intermetallic phases may occur in the alloys *A* at compositions close to 36 and 42 per cent Mn, in alloys *C* close to 37 per cent Mn and in alloys *D* close to 34½ per cent Mn; intermetallic compounds were in fact found very close to these compositions. Fig. 3 shows the variation of density with composition for a series of alloys quenched from 950°C. It is not, of course, claimed that this is an infallible method of determining the existence of intermetallic compounds; it is, however, expected to give indications which, in this case, proved very useful.

(b) X-ray examination

The results obtained from the X-ray powder photographs are given in Table 1. Phase *A* is the intermetallic compound richer in manganese than $\delta(\text{AlMn})$: it was not studied here, as it was not of immediate interest. The unit cells of the various phases are given in Table 2. The phases $\phi(\text{AlMn})$ and

$\mu(\text{AlMn})$ were previously unknown in the binary Al-Mn system: the unit cell dimensions obtained for MnAl₆, MnAl₄, 'MnAl₃' and $\delta(\text{AlMn})$ agreed with those given in the listed references.

(c) Microsections

The X-ray examination had shown certain of the melts *A* to contain three phases: this implies that the material had not reached an equilibrium state, and microsections of these specimens were therefore particularly valuable. Microsections of other specimens were taken, with the intention both of confirming the results of the X-ray work and of identifying the etching characteristics of the various phases prior to an examination of the ingots containing three phases.

Photographs of certain microsections are reproduced:

Fig. 4 shows a specimen of 39 per cent Mn after annealing for 10 days at 780°C. The two phases δ and ϕ are indicated. δ and ϕ were distinguished as follows: an ingot of 41 per cent Mn was known (from the X-ray data) to contain only a small amount of ϕ and hence the etching colour of each phase was deduced. This procedure was also applied to determine the etching characteristics of other phases.

Fig. 5 shows the specimen of 35 per cent Mn after annealing for 10 days at 780°C. The three phases δ , ϕ and μ are indicated. The μ phase etches in a rather similar colour to δ , but since X-ray analysis has shown that three phases are present, a distinction can be made. The appearance of the μ phase as a relatively fine deposit suggests that it may possibly grow at the expense of the δ phase after a sufficiently long anneal. These considerations showed the need for Melts *C* and *D*. X-ray examination showed these further melts each to consist of two phases: this was confirmed by microsection examination, which also showed the μ phase to occur as a coarser deposit (as anticipated) than in the three-phase ingot.

Fig. 6 shows a specimen of 35 per cent Mn annealed for 14 days at 850°C, phases μ and ϕ being indicated.

Fig. 7 shows a specimen of 34 per cent Mn annealed

TABLE 2. Unit cell dimensions of aluminium-manganese intermetallic compounds

Phase	Crystal system	Unit cell dimensions	Previous measurements
MnAl ₃	Orthorhombic	$a = 6.50 \text{ \AA}$ $b = 7.55 \text{ \AA}$ $c = 8.87 \text{ \AA}$	Hofmann ⁽¹⁾ Nicol ⁽¹¹⁾
MnAl ₄	Hexagonal	$a = 28.4 \text{ \AA}$ $c = 12.4 \text{ \AA}$	Hofmann ⁽¹⁾ Bland ⁽¹²⁾
$\mu(\text{AlMn})$	Hexagonal	$a = 19.95 \text{ \AA}$ $c = 24.52 \text{ \AA}$	—
$\phi(\text{AlMn})$	Hexagonal	$a = 7.54 \text{ \AA}$ $c = 7.90 \text{ \AA}$	—
'MnAl ₃ '	Orthorhombic	$a = 12.59 \text{ \AA}$ $b = 14.80 \text{ \AA}$ $c = 12.42 \text{ \AA}$	Hofmann ⁽¹⁾
$\delta(\text{AlMn})$	Triclinic	$\{ a = 5.1 \text{ \AA}$ $b = 17.1 \text{ \AA}$ $c = 5.0 \text{ \AA}$ $\alpha = 93^\circ$ $\beta = 100^\circ$ $\gamma = 89^\circ$ $\}$	Bland ⁽¹²⁾ Hofmann ⁽¹⁾

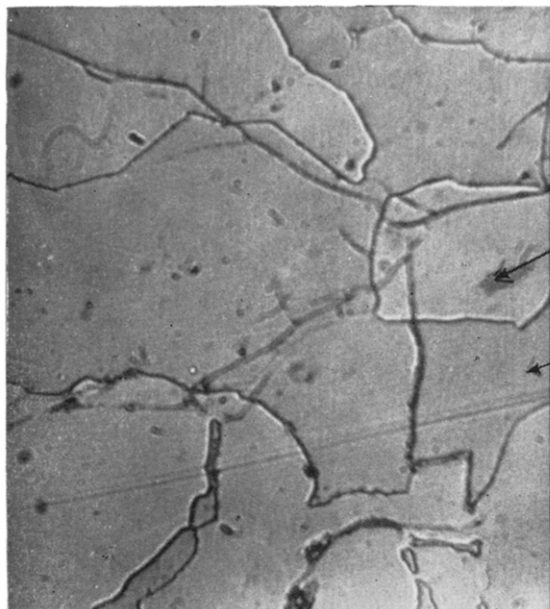


FIG. 4. Microsection of Al-39 per cent Mn annealed for 10 days at 780°C. $\times 400$

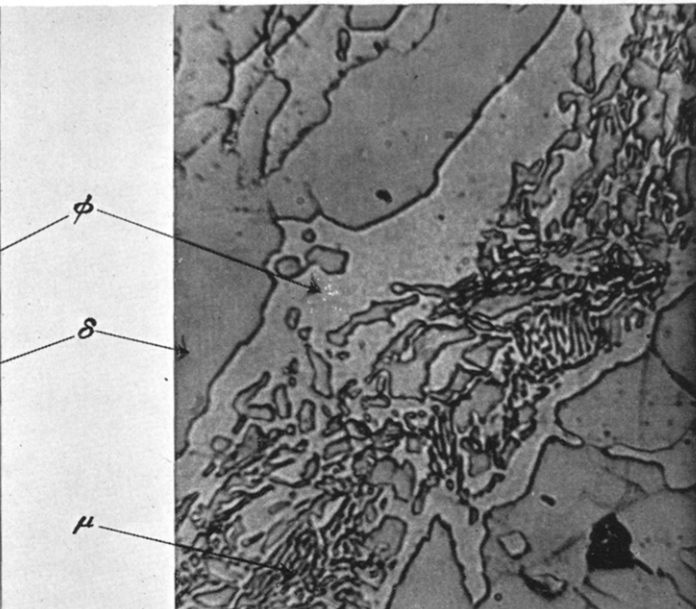


FIG. 5. Microsection of Al-35 per cent Mn annealed for 10 days at 780°C. $\times 400$

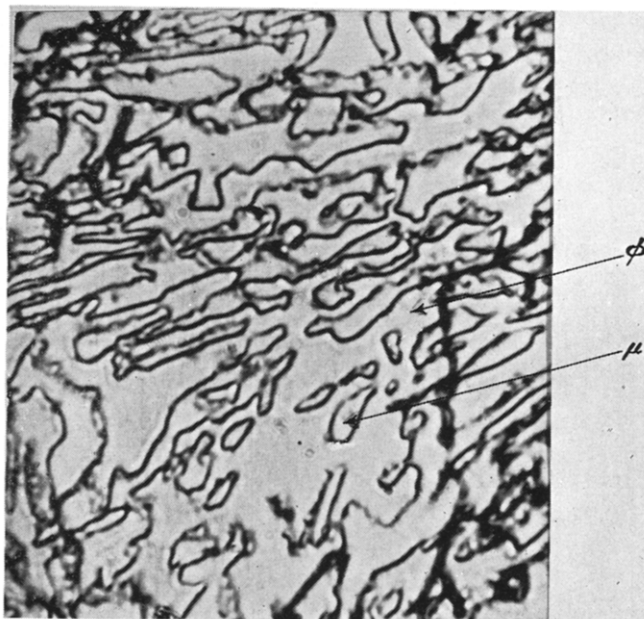


FIG. 6. Microsection of Al-35 per cent Mn annealed for 2 weeks at 850°C. $\times 800$

for two weeks at 810°C; the crystals of MnAl_4 in a background of $\mu(\text{AlMn})$ are clearly visible.

Micrographic examination of the ingots *B* (quenched from 950°C) showed them to contain several phases (as many as four in some cases) distributed in a cored fashion. The quench had not been very rapid, and the constituents present could not all be identified with absolute certainty; the investigation was not continued. The two points of interest were (i) that the ingots at 25, 30 and 35 per cent Mn contained a

primary deposit (' MnAl_3 ') different from that in the 40 per cent Mn ingot (presumably *A*) and (ii) that no crystals of the δ phase were observed in these ingots.

Fig. 8 shows a specimen of 35 per cent Mn quenched from 950°C.

DISCUSSION

A complete description of a series of intermetallic compounds requires not only unit cell measurements,



FIG. 7. Microsection of Al-34 per cent Mn annealed for 2 weeks at 810°C. $\times 400$

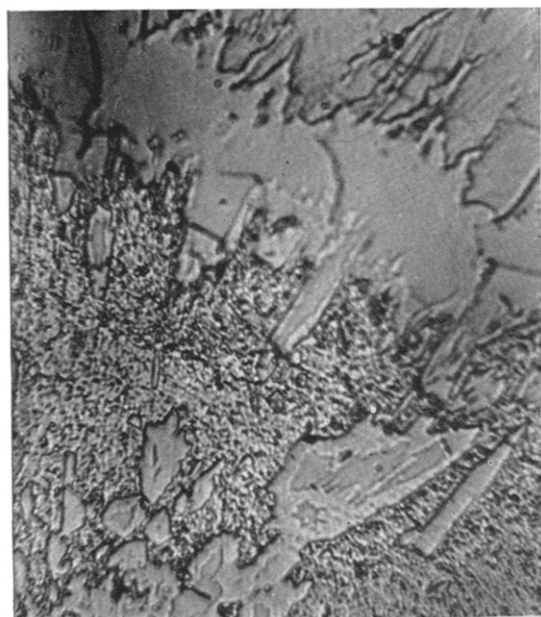


FIG. 8. Microsection of Al-35 per cent Mn quenched from 950°C.

but also the specification of their homogeneity ranges. From the X-ray and microsection work it is possible to fix the compositions, given in Table 3, at which each phase is stable. This method of assigning a composition to a phase is more satisfactory than chemical analysis of the single crystals, as these may be deficient in one element and thus not yield the exact composition. Only two of the intermetallic compounds reported above—i.e. MnAl_4 and $\mu(\text{AlMn})$ —have been grown as single-phase ingots, probably because many have very narrow composition ranges.

In Table 3 the 'crystallographic' compositions of the phases for which they are known are also listed. (The 'crystallographic' composition is that of a crystal in which every atomic site is filled by the atom of the correct type.) It is, of course, quite possible that a

phase is not stable at its true 'crystallographic' composition.⁽¹⁰⁾ The agreement between the observed compositions and the 'crystallographic' compositions is good.

The published phase diagram (Fig. 1) has been shown to be incorrect, and though this work was not primarily designed to correct it, some tentative suggestions for improvement may be made.

It seems possible that the thermal arrest at 920°C observed by Dix *et al.*⁽⁶⁾ does represent a peritectic reaction associated with the formation of some intermetallic phase. The present work has shown ' MnAl_3 ' to be stable at 950°C but not below 850°C; also $\delta(\text{AlMn})$ was not observed as a constituent of any melts quenched from 950°C. These facts and the other results reported above are all explained by the proposed phase diagram given in Fig. 9. The existence of the horizontal dotted line is not established, but is suggested in an attempt to produce a phase diagram in accordance with the facts; the temperature of the dotted line lies above 850°C. The intermetallic compounds richer in manganese than MnAl_4 are shown as line compounds, as their composition ranges, being small, have not been established.

TABLE 3. Chemical compositions of aluminium-manganese intermetallic phases

Phase	Composition from present work (%Mn)	'Crystallographic' composition (%Mn)	Composition suggested by density measurements (%Mn)
MnAl_4	33*	unknown	—
$\mu(\text{AlMn})$	34.5	unknown	34.5-35
$\phi(\text{AlMn})$	36-37	38 (Taylor ⁽¹³⁾)	36-38
' MnAl_3 '	—	unknown	—
$\delta(\text{AlMn})$	41.5	42.5 (Bland ⁽⁴⁾)	42

* MnAl_4 is generally assumed to exist over a finite composition range; the composition 33 per cent Mn represents the manganese-rich limit of such a range.

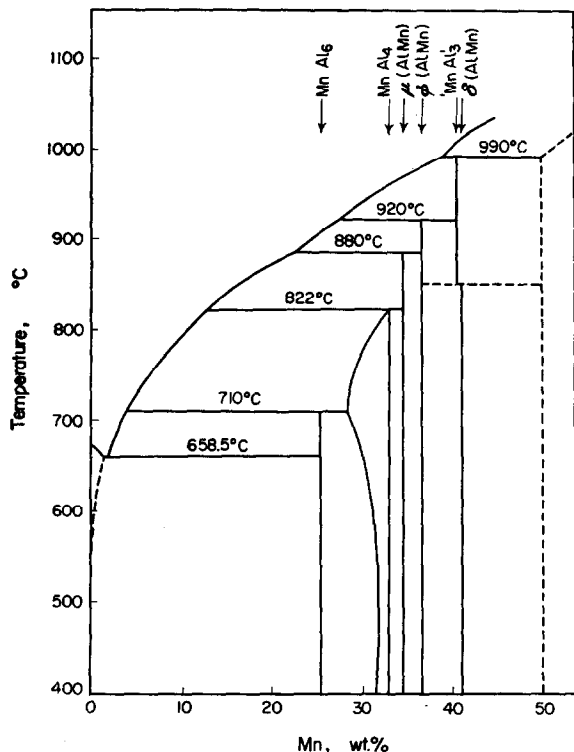


FIG. 9. Aluminium-rich region of suggested aluminium-manganese phase diagram.

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