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The intermetallic compound phases of the system aluminium-manganese-zinc

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[Plates 3 and 4]

The system aluminium-manganese-zinc has been examined in the range 0 to 95 % of zinc, and 0 to 3 % of manganese. Attention was directed only to the constitution of the alloys above the solidus. Using micrographic and X-ray methods, and the chemical analysis of crystals separated from slowly cooled alloys, it has been shown that, according to composition, the phases MnAl_6 , T_1 , MnAl_4 , T_2 , T_3 and MnAl_3 may crystallize as primary constituents. Both MnAl_6 and MnAl_4 dissolve small quantities of zinc; the phases T_1 , T_2 and T_3 are ternary compounds. The phase T_1 is characterized by a ratio of four aluminium atoms to one of combined solutes, and an electron:atom ratio of 1.85, calculated on the basis of the Pauling theory of transitional metals. According to this theory, transitional metal atoms have vacancies for electrons in their atomic orbitals, and the present experiments in conjunction with earlier work suggest that these may be filled up as a consequence of alloy formation. The phases T_2 and T_3 may be represented respectively by the formulae Mn_2ZnAl_9 and $(\text{Mn} \cdot \text{Zn})_5\text{Al}_{11}$. MnAl_3 , which can dissolve small quantities of zinc, enters into equilibrium at a ternary eutectic (Zn 95 %, Mn 0.05 %, 378° C) with the primary solid solutions in zinc and aluminium respectively.

1. INTRODUCTION

In the course of work on the equilibrium relations in the systems aluminium-manganese-nickel and aluminium-manganese-copper (Raynor 1944*a, b*), it was shown that the ternary compounds which were formed, and which entered into equilibrium with the primary aluminium-rich solid solution, could be regarded as based upon a common plan. In the latter system, the ternary compound extends from copper 7.8, manganese 12.1, aluminium 80.1 atomic % to copper 6.9, manganese 15.0, aluminium 78.1 atomic %, and appears to be based upon the arrangement $(\text{Cu} \cdot \text{Mn})\text{Al}_4$. The composition which is in equilibrium with both CuAl_2 and the primary aluminium-rich solid solution corresponds almost exactly with the arrangement $\text{Cu}_2\text{Mn}_3\text{Al}_{20}$. In the aluminium-manganese-nickel system the corresponding ternary compound is also based upon the arrangement $(\text{Ni} \cdot \text{Mn})\text{Al}_4$, and experiment suggests that it is almost of the fixed composition $\text{Ni}_4\text{Mn}_{11}\text{Al}_{60}$.

The variations in the compositions characterizing these two ternary compounds have been interpreted (Raynor 1944*b*) in terms of the Pauling theory of the transitional metals (Pauling 1938). According to this theory, 5.78 electrons of the 3*d* and 4*s* quantum groups of the atoms of the transitional metals of the first long period may be regarded as responsible for cohesion, while the remainder occupy 'atomic orbitals', of which 2.44 are available. For the transitional metals of the first long

period, therefore, vacancies for electrons exist in the atomic orbitals. If it is assumed that these vacancies may be filled by electrons absorbed from the structure as a whole when the transitional metal forms a minor constituent of a binary or ternary alloy, the electron:atom ratios for the ternary compounds in the aluminium-manganese-copper and aluminium-manganese-nickel systems respectively may be evaluated as 1.86 and 1.84.* Further evidence in favour of this absorption of electrons by transitional metals has been obtained by a consideration of the lattice spacings of the primary solid solutions of chromium and manganese in aluminium (Raynor 1945).

It appears possible, therefore, that in this type of aluminium-rich ternary alloy the ternary compound which exists in equilibrium with the primary solid solution tends to be based upon an electron:atom ratio of approximately 1.85, and at the same time to satisfy the condition that there should be four atoms of aluminium to one atom of combined solutes. The latter condition must clearly depend upon size relationships between the atoms composing the structure.

In order to gain further information with regard to this possibility, the system aluminium-manganese-zinc has been investigated. In this case the substitution of zinc for nickel or copper leaves the atomic size relationships relatively unaffected; the valency factor, however, increases by unity on passing from copper to zinc. The system would be expected, therefore, to contain a ternary compound based upon the ratio of four aluminium atoms to one of combined solutes, but with the composition so adjusted as to preserve the electron:atom ratio at approximately 1.85. Assuming that aluminium and zinc respectively contribute to the structure, 3 and 2 electrons per atom, and that manganese, in accordance with Pauling's theory, has vacancies for 3.66 electrons per atom, the predicted composition of the expected ternary compound is:

Manganese 28.01, Zinc 6.40, Aluminium 65.59 weight %.

2. PREVIOUS WORK

(a) *The binary systems*

The equilibrium diagrams of the binary systems aluminium-zinc and aluminium-manganese are satisfactorily established. Figure 1 shows the diagram for the aluminium-zinc alloys (Raynor 1943) according to the results of the most reliable work. The liquidus curves fall smoothly from the freezing points of the pure metals to a eutectic at 95% of zinc and a temperature of 382° C. The solid solubility of aluminium in zinc is limited, but that of zinc in aluminium is extensive. Between the composition limits 31.6 and 78% of zinc, and the temperature limits 365° and 275° C, this solution splits up into a mixture of two face-centred cubic phases.

Figure 2 shows the equilibrium diagram of the aluminium-manganese system, based upon the results of Dix, Fink & Willey (1933), Phillips (1943), Butchers &

* The aluminium-manganese-copper ternary phase has a range of homogeneity. The electron:atom ratio is calculated for the composition which is in equilibrium with $MnAl_6$ and the aluminium-rich solid solution.

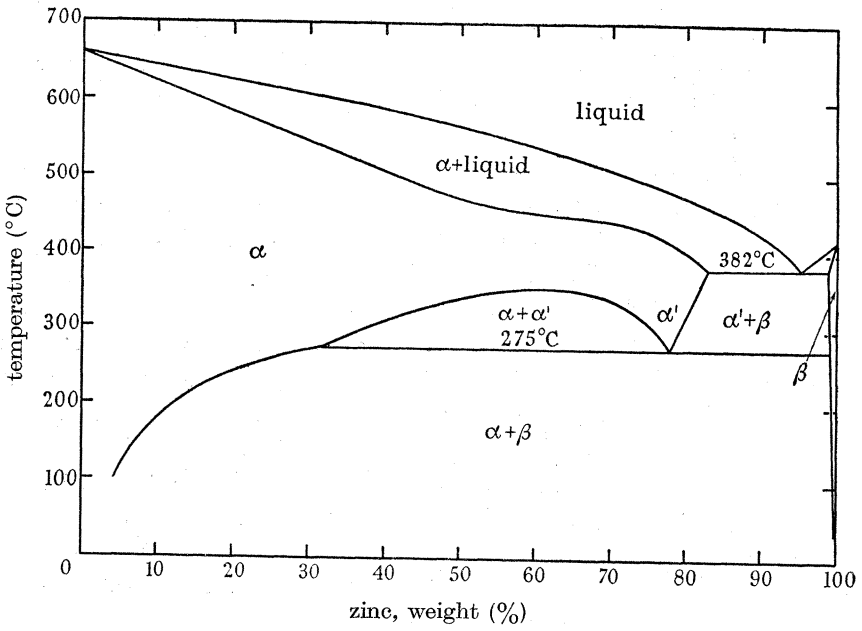


FIGURE 1

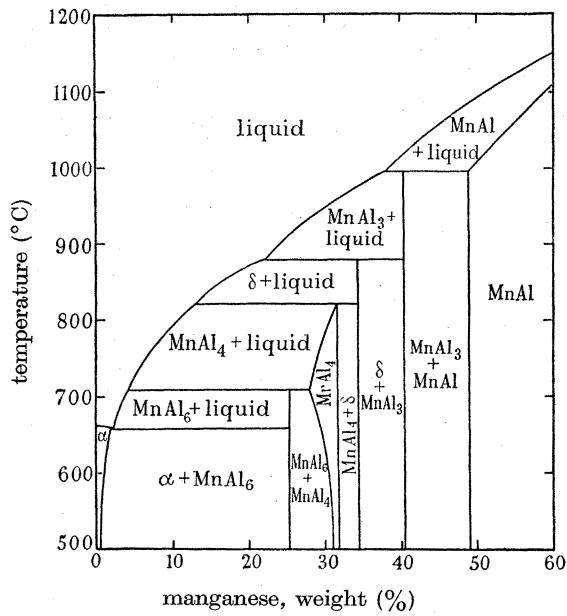


FIGURE 2

Hume-Rothery (1945) and Köster & Bechthold (1938). A eutectic point, at which $\text{liquid} \rightleftharpoons \alpha + \text{MnAl}_6$, occurs at 1.95% of manganese and a temperature of 658.5°C; the solid solubility of manganese in aluminium is limited, particularly at low temperatures. MnAl_6 is formed by a peritectic reaction at 710°C from MnAl_4 , which in turn is formed peritectically from a δ -phase containing approximately 34% of manganese. Further peritectic reactions involve the formation of δ from MnAl_3 , and of MnAl_3 from MnAl , which is a phase with a wide range of homogeneity extending from 49 to 67% of manganese. Each of the four peritectic reactions tends to remain incomplete on cooling, so that structures which are not in equilibrium are readily obtained.

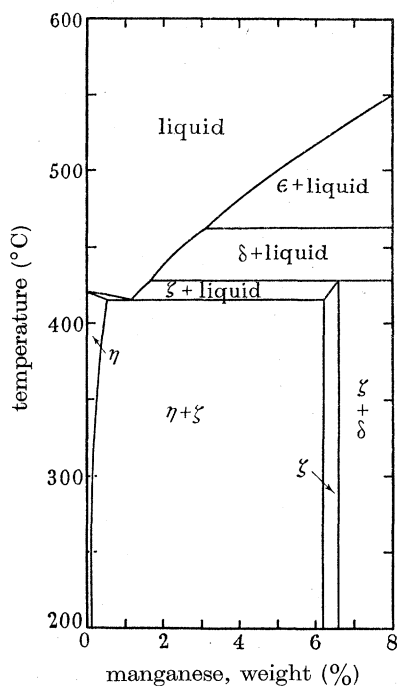


FIGURE 3

The zinc-rich portion of the zinc-manganese system as given by Schramm (1940) is shown in figure 3. A eutectic is formed at 416°C between the zinc-rich solid solution, which can hold 0.5% of manganese in solid solution at this temperature, and a monoclinic ζ -phase containing 6.2% of manganese. Further peritectic reactions, involving the ϵ - and δ -phases of this system, occur at 462° and 428° C, but these are of little importance for the present work.

(b) *The ternary system*

No previous work on the aluminium-rich alloys of the system aluminium-manganese-zinc appears to have been published. Experiments on the equilibrium relations in the zinc-rich corner of the phase diagram have, however, been reported by

Gebhardt (1942), and are summarized in figures 4 and 5, which show respectively the projection of the surfaces of primary separation, and the equilibrium relations in the solid state at 350° C. At U_T (zinc 99.15, aluminium 0.55, manganese 0.3%; 412.5° C) the liquid and the binary zinc-manganese ζ -phase react together to form the zinc-rich solid solution and a phase denoted V . A ternary eutectic involving the aluminium-rich and zinc-rich solid solutions and the compound V is formed at E_T (378° C). The composition of the eutectic point is given as 95% of zinc and 0.04% of manganese. This point is therefore almost coincident with the binary aluminium-zinc eutectic. Figure 5 shows that at temperatures close to that of the eutectic the zinc-rich solid solution can take up approximately 0.5% of manganese and 1.0% of aluminium, while the face-centred cubic solid solution based on aluminium can take up approximately 83.0% of zinc. The composition of this latter phase which enters into equilibrium with the zinc-rich solid solution and the V -phase, however, corresponds with only 0.05% of manganese. The composition of the V -phase was not accurately established; it had the characteristics of an intermetallic compound, and extrapolation of the sides of the three-phase triangle inside which it is in equilibrium with the aluminium-rich and zinc-rich solid solutions suggested that it contained little zinc, and approximately 30% of manganese.

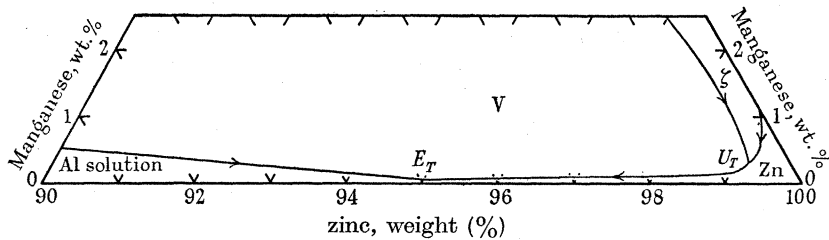


FIGURE 4

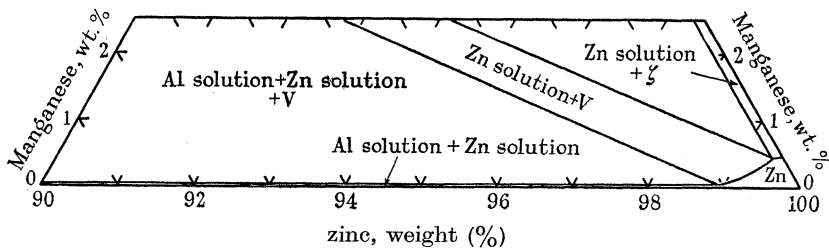


FIGURE 5

From a comparison of figures 1, 2 and 4, it is clear that the ternary aluminium-manganese-zinc equilibrium diagram must contain a very long eutectic valley, stretching from the binary aluminium-manganese eutectic to the ternary eutectic point at 95% of zinc. In this respect the system differs from those previously examined; this is of importance with respect to the number of phases which may enter into equilibrium with the aluminium-rich solid solution.

3. EXPERIMENTAL METHODS

Preliminary experiments, involving the annealing of chill-cast alloys having compositions within the range 0 to 5 % of manganese and 0 to 60 % of zinc, showed that equilibrium was very difficult to attain within a reasonable time of annealing. Many alloys, after annealing periods of more than 3 weeks, showed four phases, in the form of hard particles of three different types, in considerable relief, set in a matrix of aluminium-rich solid solution. Experiments indicated that these phases were all present in the chill castings, and that the elimination of the unstable phase or phases by subsequent annealing was very slow. In order, therefore, to obtain information with regard to the phases which might be present, it was decided to investigate the system by the method of slow cooling from the melt, with subsequent micrographical examination. Difficulties encountered made it essential to extract and examine the primary crystals deposited in the alloys.

(a) *Materials used*

The materials used in the preparation of the alloys were as follows:

(i) Pure zinc. The only elements detected spectrographically, and their approximate amounts, were: lead 0.0001 %, cadmium 0.00005 % and calcium 0.0001 %. For certain preliminary alloys, zinc of 'Crown Special' grade was used. It contained: lead 0.0007 %, cadmium 0.0010 %, iron 0.0010 % and copper 0.0002 %. These materials were presented by the Imperial Smelting Corporation, Ltd., of Avonmouth, to whom the authors express their sincere gratitude.

(ii) Super-purity aluminium, kindly presented by the British Aluminium Company, Ltd.

(iii) Aluminium-manganese master alloys, of which one, containing 9.52 % of manganese, was presented by the Mond Nickel Company, and the other, containing 5.25 % of manganese, was presented by the British Aluminium Company, Ltd. These master alloys were prepared from pure materials, and the authors' thanks are due to the laboratories in which they were produced.

(b) *Preparation of alloys*

Alloys containing less than 60 % of zinc were prepared in quantities of 50 to 100 g. Those containing 60 to 95 % of zinc were made up in quantities of 100 g. In all cases weighed-out quantities of aluminium and the aluminium-manganese master alloy were melted together in a crucible lined with an alumina-fluorspar mixture, using a small electric crucible furnace. After thorough stirring with a sintered alumina stirring rod, the requisite quantity of pure zinc was added and quickly stirred into the melt, which was then allowed to cool slowly in the furnace. The rates of cooling varied somewhat at different stages of the research, but were in general of the order of 1 to 2° C/min.

When cold, the cylindrical ingots were sectioned longitudinally, and one section ground, polished and examined metallographically. The results of the micrographic

examination were difficult to interpret; no etching reagent was found which would satisfactorily differentiate between different intermetallic compound crystals, and the constitution could only be judged qualitatively from the general appearance of the microsections.

(c) *Extraction of primary crystals*

Primary, and secondary, crystals present in the alloys were extracted by an electrolytic method. Each ingot was made the anode of an electrolytic cell (figure 6), of which the cathode was a nickel strip and the electrolyte a mixture of dilute hydrochloric and nitric acids. Under these conditions, using a current density of approximately 0.1 amp./sq.in., and a potential difference of 8 V, the solid solution matrix was slowly dissolved away. The intermetallic compound crystals present fell away to the bottom of the cell. When sufficient residue for examination had collected, the electrolysis was stopped, and the residue well washed with 50 % nitric acid, followed by several washings with distilled water. After rinsing with alcohol, the residue was dried by gentle heating.

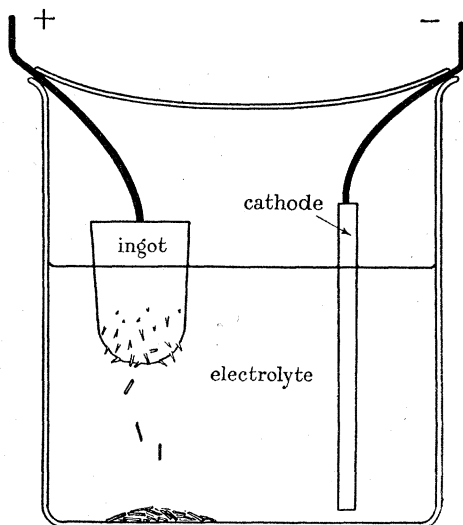


FIGURE 6

All residues were first examined under a binocular microscope. Details of these experiments are given below. In all cases the extracted crystals were clean and apparently unattacked by the reagents used for extraction. Crystal faces were often well developed and of very high reflectivity.

In no case, under any conditions of cooling which were attempted, were homogeneous residues obtained. Examination under the microscope showed that the extracted residues were mixtures of two, or sometimes three, different intermetallic compounds, with clearly differentiated habits. In order to identify these, crystals of each crystallographic type were hand-picked, using forceps, from the mixture,

and submitted to chemical analysis. In critical cases X-ray examination was also used. Analysis confirmed the differentiation of the various phases on the basis of their observed habits.

(d) *Analytical method*

Since the hand sorting of extracted residues was somewhat laborious, analytical methods capable of giving accurate results with small quantities of material were explored. In general, 0.2 to 0.3 g. of residue could be collected from the mixtures by picking out good crystals about whose crystallographic habit there could be no reasonable doubt.

The analytical method finally adopted, after repeated tests on synthetic solutions containing aluminium, manganese, and zinc in approximately the same concentration as that to be expected during the assay of extracted crystals, was as follows:

The crystals were dissolved in the minimum quantity of 50% sulphuric acid, and the clear solution made alkaline with caustic soda until the hydroxides of zinc and aluminium had redissolved. Hydrogen peroxide was added, and the mixture boiled to decompose excess of this reagent. The supernatant liquid was filtered from the precipitate of hydrated manganese dioxide using a sintered glass crucible. To determine the manganese, the precipitated dioxide was dissolved in nitric acid containing a little sulphurous acid, and the solution diluted and boiled. The solution was oxidized with sodium bismuthate, filtered, and the manganese in the filtrate estimated in the usual way by the addition of an excess of ferrous ammonium sulphate and back-titration with potassium permanganate solution. The zinc was estimated in the acidified filtrate from the manganese precipitate by direct titration with standard potassium ferrocyanide solution (containing a little potassium ferricyanide), using diphenylamine as an internal indicator. All solutions employed were regularly standardized, and reproducible results were obtained throughout the research.

(e) *X-ray examination*

Certain specimens of extracted crystals were submitted to X-ray examination. For this purpose they were crushed to powder in an agate mortar, and mounted

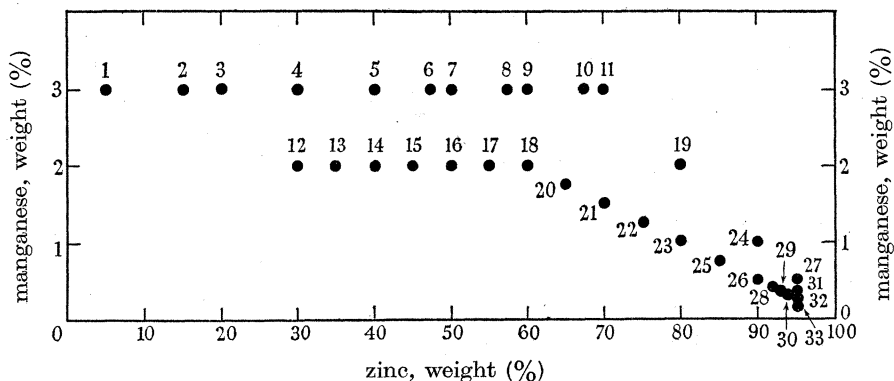


FIGURE 7

on hairs in the usual manner with canada balsam dissolved in xylol. Specimens were exposed, in a cylindrical Debye-Scherrer camera, to iron $K\alpha$ radiation from a Metropolitan-Vickers demountable X-ray machine.

In the course of the work, thirty-three alloys were examined. Their compositions are shown diagrammatically in figure 7. In order to facilitate description of individual alloys, compositions will be referred to in terms of the weight percentages of manganese and zinc in the alloy. Thus, the term 'alloy 2.0/80' refers to an alloy containing 2.0% of manganese and 80% of zinc.

4. THE MICROSTRUCTURES OF THE ALLOYS

As noted above, all alloys were carefully examined micrographically before residue extraction. In general, these examinations were not informative, owing to the fact that it was extremely difficult to distinguish between the intermetallic compound phases with any certainty in either the unetched or etched conditions. The hard crystals, being set in a much softer matrix, were always seen in considerable relief, which was difficult to avoid. In addition, the large difference in electrochemical characteristics of the particles and the matrix led to all etching reagents giving vigorous attack on the matrix, leaving the hard particles relatively unaffected. No marked differences in relief between various types of hard particles were observed. Distinctions in the shapes of particles in the microsections were noted, but subsequent examination of the extracted residues showed that such distinctions could be quite misleading. No detailed description of the microstructures observed will therefore be given, except in so far as they assist the interpretation of the results and the construction of the diagram showing the surfaces of primary separation.

The first point to be noted is that the crystals in the microsections of alloys 3.0/20, 3.0/30 and 3.0/40 were mostly homogeneous but occasionally included small spines of a slightly darker material (figure 8, plate 3). Since these crystals were subsequently shown to be $MnAl_6$, it was concluded that these compositions were just on the edge of the field in which the phase $MnAl_4$ deposits as primary crystals, but that these small first-deposited crystals were quickly surrounded, by peritectic reaction, by thick sheaths of $MnAl_6$, which then continued to separate as the primary constituent until the temperature was reached at which $MnAl_6$ and the primary solid solution separate together.

No further evidence of peritectic sheaths round cores of a different material was obtained in alloys containing less than 90% of zinc, with the exception of alloys 3.0/70 and 2.0/80. Alloy 3.0/70 showed primary needles, some of which had spines of darker material, and secondary plates, some of which, in cross-section, had the appearance of needles. A portion of the microstructure is shown in figure 9, plate 3. Alloy 2.0/80 showed primary crystals of a dendritic type (figure 10, plate 3), together with plate-like material. A few of the dendritic crystals, however, possessed small spines of darker material. In both these cases, therefore, the alloys lie on the edge of a region in which some unidentified phase deposits, which is subsequently trans-

formed by peritectic reaction into the phase which predominates in the actual microstructure.

The alloys containing 90 and 95 % of zinc will be discussed below with regard to the nature of the ternary eutectic.

Figures 8 to 13, plate 3 show a representative series of microstructures in which the phases have been identified as a result of the experiments described in the following sections.

5. GENERAL DESCRIPTION OF EXTRACTED RESIDUES

It was not possible, from the micrographic examination, to decide how many phases existed in equilibrium with the primary solid solution, or to assess the limits of their occurrence. In the examination of extracted residues by means of the binocular microscope, however, seven distinct forms of intermetallic compound crystal were observed.

The extracts from alloys 3·0/5 and 3·0/15 consisted entirely of long needle-shaped crystals in the form of rectangular prisms (figure 14, plate 4). These crystals were exactly of the form associated in earlier work (Raynor 1944*b*; Raynor & Hume-Rothery 1943) with the compound MnAl_6 .

The extract from alloy 3·0/20 was also predominantly of this type, but contained in addition a small amount of a different type. The latter crystals were small, regular in shape, and approximately equi-axed as shown in figure 15, plate 4. Extracts from alloys 3·0/30 and 2·0/30 showed an increasing amount of this constituent in addition to the suspected MnAl_6 crystals, while those from alloys 2·0/35 and 3·0/40 consisted almost entirely of the regular-shaped crystals, with a small amount of the suspected MnAl_6 phase. In addition, the extracts from 2·0/35 and 3·0/40 contained a few very fine long needles, which were clearly of a different type from those which were suspected to be MnAl_6 . The thin needles are shown in figure 16, plate 4.

This behaviour was interpreted as indicating that in these alloys MnAl_6 was the primary constituent, but that a secondary separation of the equi-axed crystals took place. This view was confirmed by the fact that, in the extracts from all alloys between this range of compositions and 65 % of zinc, no suspected MnAl_6 crystals were observed. The residues consisted largely of the equi-axed crystals, which were somewhat increased in size, together with the fine needles, which increased in amount as the zinc content of the parent alloy increased. In this range of compositions, therefore, the equi-axed crystals form the primary constituent, and are followed by a separation of fine needles.

At zinc contents greater than 65 %, none of the regular equi-axed crystals were observed. The extract from 3·0/67·4 consisted almost entirely of the thin needles, while those from alloys 3·0/70 and 1·5/70 contained large amounts of these needles. It was concluded that in this range the thin needles were the primary phase. It was observed that the needles were approximately hexagonal in cross-section, and

microstructures of these alloys before residue extraction showed areas which were very similar in appearance to those containing hexagonal MnAl_4 crystals published by Phillips (1943).

In addition to primary needles, the extracts from alloys 3.0/70 and 1.5/70 contained plates, which were very thin, of high reflectivity, and sometimes considerable area. These plates tended to be rectangular in shape, as illustrated in figure 17, plate 4. The amount of the thin plate-like crystals increased considerably in the extract from alloy 1.25/75, but the primary crystals were still of the needle type. This evidence suggests that primary crystallization of the needles is followed by a secondary deposition of the thin plates. With the alloys employed, the region in which the plates separate as primary crystals was not observed.

The extracts from alloys 2.0/80, 1.0/80, 0.75/85 and 0.5/90 all showed primary crystals of a completely different type from any observed in alloys less rich in zinc. The crystals were of a peculiar dendritic form, as indicated in figure 18, plate 4, with the surfaces parallel to the directions of the dendritic arms almost parallel to each other. Secondary crystals were also present in these extracts and took the form of thin shiny plates of a different type from those previously observed. These thin plates (figure 19, plate 4) had a high reflectivity and were seen under the microscope to possess characteristic hexagonal markings on their surfaces. They were very fragile and easily broke into pieces during the sorting operations. In the unsorted residue, however, many complete plates were seen to be approximately hexagonal in shape.

The residue from alloy 1.0/90 was, however, of a different type; this contained no dendritic crystals, but was composed of a mixture of two types of flat plates, of which one was easily recognizable as the same material as the shiny plates met with in the 0.5/90 alloy. The other crystals appeared to be of a new type, and the constitution of this alloy is discussed more fully below in connexion with the nature of the ternary eutectic.

In this work, therefore, the existence of several types of primary crystals, according to the composition of the ternary alloy, was recognized. The persistence with which two or more types of crystal are deposited from the melt is explained by the very long eutectic valley extending from the aluminium-manganese axis almost to the aluminium-zinc axis at 95% of zinc. Reference to figure 20, which shows schematically the forms of primary surfaces in a hypothetical equilibrium diagram containing a long eutectic valley, indicates that, whatever primary phase separates, deposition of one or more other phases will follow. An alloy of composition X , on cooling to the liquidus surface, will deposit the primary A phase, and the composition of the remaining liquid will, on further cooling, move towards the eutectic valley pq . When the composition of the liquid reaches this line, simultaneous deposition of α and A occurs, and the composition of the liquid moves along the line pq towards q . When the point r has been passed, α and B separate together; after passing the point s , α and C separate, and so on. The process continues as long as there is any liquid left; if cooling were sufficiently rapid for solidification to end

at the ternary eutectic q , the alloy X would contain, in addition to primary A , crystals of the B , C and D phases. Under the conditions used in the experiments, the rate of cooling was sufficiently slow to limit the number of intermetallic compound phases present to two or sometimes three.

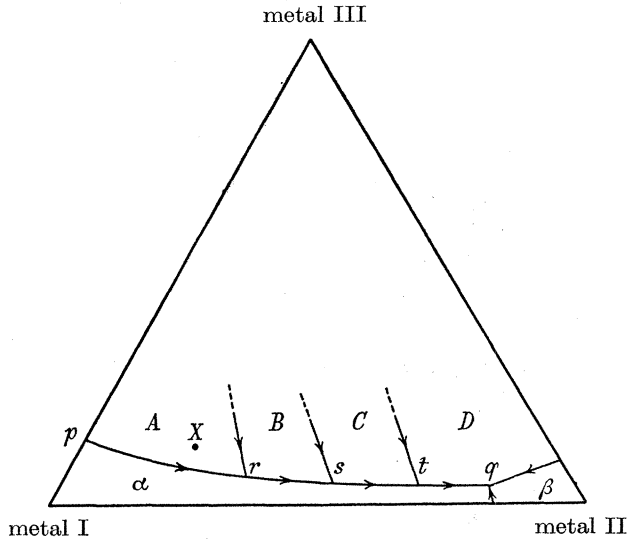


FIGURE 20

6. ANALYTICAL RESULTS

The results of the chemical analysis of thirty-five pure specimens, hand-sorted as previously described, are given in table 1, which is self-explanatory, and are plotted in figure 21. In some cases, where the composition of a phase had been

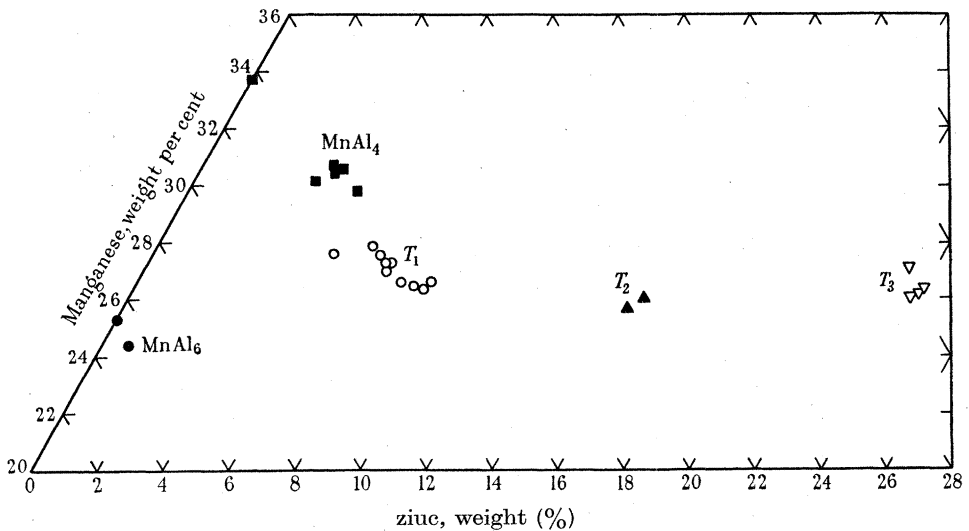


FIGURE 21

established by the determination of both manganese and zinc, the manganese alone was estimated in order to confirm the identification of the crystals in other extracts.

Reference to figure 21 shows that the compositions of the crystals extracted from alloys containing less than 95 % of zinc fall into five distinct groups. The analyses

TABLE 1

alloy	type of extracted crystal	Mn %	zinc %
3·0/5	prismatic needles	—	0·36
3·0/30	prismatic needles	23·88	—
2·0/30	prismatic needles	24·41	0·78
2·0/35	regular equi-axed	27·90	6·51
3·0/40	prismatic needles	23·95	—
	regular equi-axed	27·3	—
2·0/40	regular equi-axed	27·6	5·5
	thin needles	27·55	6·92
2·0/45	regular equi-axed	30·2	—
	thin needles	27·29	7·4
3·0/47·4	regular equi-axed	30·2	3·66
3·0/50	regular equi-axed	27·97	6·48
	regular equi-axed	27·18	—
2·0/50	thin needles	27·3	7·18
	regular equi-axed	30·6	4·3
2·0/55	regular equi-axed	26·98	7·4
	thin needles	30·1	—
3·0/60	regular equi-axed	26·65	8·01
	thin needles	26·37	8·8
2·0/60	regular equi-axed	30·2	—
	thin needles	26·49	8·45
1·75/65	regular equi-axed	30·68	4·01
	thin needles	26·65	8·92
3·0/67·4	regular equi-axed	30·53	4·07
	thin needles	30·3	—
3·0/70	thin needles	30·75	—
1·5/70	thin plates	25·70	15·37
1·25/75	thin needles	29·75	5·15
	thin plates	26·06	15·70
2·0/80	dendritic crystals	26·01	23·81
1·0/80	dendritic crystals	27·14	23·15
0·75/85	dendritic crystals	26·35	24·03
0·5/90	dendritic crystals	26·13	23·92
0·25/95	plates with hexagonal markings	38·88	0·5*
0·35/95	rectangular plates	50·23	none detected*

* See § 8.

confirm that the prismatic needles are MnAl_6 , which can take up small amounts of zinc into solid solution. The regular equi-axed crystals, the thin plates, and the dendritic crystals clearly correspond with three different ternary compounds, which have been denoted T_1 , T_2 and T_3 respectively. The analysed compositions of the thin needles suggest that they correspond with MnAl_4 , which has zinc in solid solution. Further reference is made to this point in §§ 7 and 10.

7. X-RAY RESULTS

In order to confirm the indications of the analytical and micrographic experiments, a series of X-ray diffraction patterns was obtained. Comparison of the pattern given by the rectangular prism crystals from alloy 2.0/30 with that obtained from a sample of pure MnAl_6 extracted from a binary aluminium-manganese alloy showed without doubt that these crystals were correctly identified as MnAl_6 .

Diffraction patterns given by pure MnAl_4 crystals were similarly compared with that given by a typical specimen of the thin needles, separated from alloy 2.0/35. The patterns obtained were very closely similar in the general arrangement of the lines. The diffraction lines in the films obtained from the needle-shaped crystals showed some very slight differences in position when compared with the corresponding MnAl_4 lines; this may easily be accounted for by the presence of zinc in the extracted crystals. The general agreement of the patterns suggests clearly that the needle-shaped crystals correspond with a solid solution of zinc in the binary aluminium-manganese compound MnAl_4 .

Photographs were also taken of T_1 crystals from alloy 3.0/47.4, T_2 crystals from alloy 1.25/75, and T_3 crystals from alloy 2.0/80. These showed patterns which, as expected, were characteristically different from each other, and from those of the phases of the binary aluminium-manganese system. These photographs, owing to relatively high general background scattering, were not suitable for reproduction. It is hoped, however, to present a more detailed X-ray study of these phases later.

8. EQUILIBRIUM IN THE REGION OF THE EUTECTIC

As explained in §2 the ternary eutectic, according to the work of Gebhardt, involves equilibrium between the aluminium solid solution, the zinc solid solution, and a compound V containing little zinc and approximately 30% of manganese. In an effort to characterize the phase V more closely, slowly cooled alloys with compositions in the neighbourhood of the eutectic were examined. As already indicated, alloy 1.0/90 gave a residue composed of two types of flat plates, one roughly rectangular in shape, and the other of irregular shape and high reflectivity, similar to those observed in other specimens. The microstructure of this alloy showed that many of the crystals were cored, thus rendering the extract unsuitable for accurate analysis. Alloy 0.5/90 was free from these defects, and the extract consisted of the dendritic T_3 phase (see table 1) together with the irregular shiny plates. These results suggest that, although the primary crystals in alloys 1.0/90 and 0.5/90 were different, both were followed by the crystallization of the thin shiny plates, in the former case by a peritectic reaction, and in the latter case by secondary deposition as explained in §5. Alloy 0.5/95 showed a microstructure similar to that of alloy 1.0/90, and a similar extract was obtained, which was, because of the coring observed, unsuitable for analysis. An alloy of composition 0.25/95, however, showed a microstructure in which the crystals were almost entirely free from any peritectic inclu-

sions; the extracted residue contained a few of the rectangular type of plate, and a quantity of the thin shiny material. An alloy containing slightly more manganese (0.35%) contained the same two types of crystal, but with the amounts reversed. It appeared clear, therefore, that in both cases the rectangular type of crystal separated first, followed by the shiny plates. The ternary eutectic therefore involves equilibrium between the latter and the two solid solutions. Confirmation of this view was given by the extract from alloy 0.15/95, which, though very small in amount, consisted entirely of the thin shiny plates.

As shown in table 1, analysis of the thin irregular plates proved them to contain 38.88% of manganese, and 0.5% of zinc, while the rectangular plates contained 50.23% of manganese. Reference to figure 2 makes it very probable that the former are to be identified with the phase MnAl_3 , which occurs at 40% of manganese in the binary diagram, and the latter with the phase MnAl , the aluminium-rich boundary of which occurs at approximately 50% of manganese.

It is therefore confirmed that the intermetallic compound phase which enters into the ternary eutectic contains very little zinc, and the experiments suggest that it is the phase MnAl_3 . Equilibrium relations in this region are, however, complex, and with a small increase in manganese content above that of the ternary eutectic, MnAl may separate as primary crystals. The diagram given by Gebhardt (figure 4) has therefore to be modified, and his V -phase identified with MnAl_3 . The form of the surfaces of primary separation above 90% of zinc, as suggested by the present work combined with that of Gebhardt, is given in figure 22.

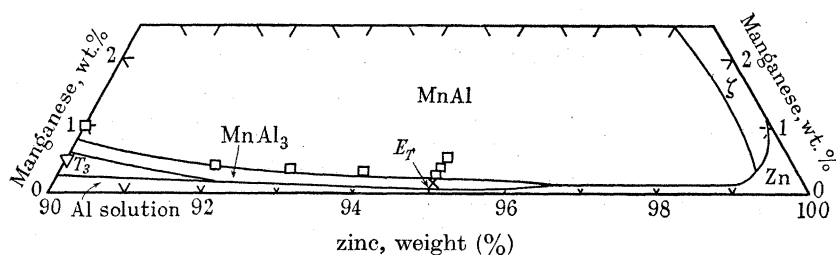


FIGURE 22

9. THE SURFACES OF PRIMARY SEPARATION

From the results described in the preceding sections, a diagram showing the form of the surfaces of primary separation may be constructed. This is shown in figure 23, which is self-explanatory. The boundaries of these regions of primary separation are only to be considered as approximate at the higher manganese contents, but the intersections of the boundaries with the eutectic valley are accurately established by the points plotted on the diagram.

Several features of interest are presented in figure 23. In the first place, the extension of the primary MnAl_3 and primary MnAl fields from the aluminium-manganese axis almost to the manganese-zinc axis, as suggested by these experi-

ments, is remarkable. It results in the crystallization, in the neighbourhood of 95 % of zinc and at temperatures of the order of 380° C, of compounds which separate only at temperatures above 900° C in the binary system aluminium-manganese.

Again, the extension of the primary MnAl₄ field to the eutectic valley is of interest, and is easily understood as a consequence of the existence of this long valley, running nearly parallel to the aluminium-zinc axis of the ternary diagram.

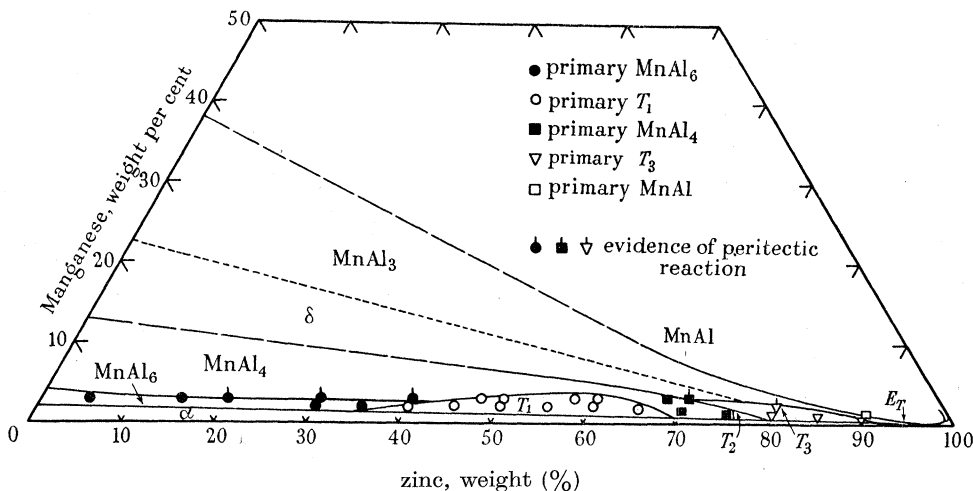
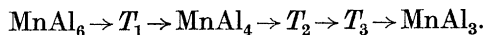


FIGURE 23

The present experiments provide no evidence that the field corresponding with the primary crystallization of the δ -phase of the binary aluminium-manganese system extends to the eutectic valley. The succession of phases deposited on passing along the eutectic valley towards the ternary eutectic is



The boundary between the primary MnAl₃ and primary δ field can therefore not extend to the eutectic valley, and has been tentatively inserted as a dotted line in figure 23.

According to the experiments described, alloy 1.25/75 deposits primary MnAl₄, while alloy 1.0/80 deposits primary T₃ crystals. Between these two compositions, however, separation of the T₂ phase occurs, so that the region in which this phase crystallizes as the primary constituent must be confined to a narrow range of compositions between 75 and 80 % zinc, as shown.

10. DISCUSSION

The results described in the preceding sections indicate that the equilibrium relations above the solidus in the system aluminium-manganese-zinc, with small amounts of manganese, are complex in nature. No fewer than six different regions

of primary separation extend to the eutectic valley which joins the binary aluminium-manganese eutectic to the zinc-rich ternary eutectic. All six of the phases which crystallize in these primary fields may therefore be expected to exist, in the solid alloys, in equilibrium with the primary solid solution based on aluminium. This somewhat unusual state of affairs is due essentially to the wide solid solubility of zinc in aluminium.

(a) *The compound MnAl₆*

Up to a zinc content of approximately 35 % at 2 % of manganese, or 43 % at 3 % of manganese, the primary phase is MnAl₆, which can take up small quantities of zinc. The composition of the MnAl₆ crystals which separated from alloy 2.0/30 shows that at least 0.78 % of zinc may be held in solid solution. Since MnAl₆ will separate from alloys richer in zinc, it is improbable that this amount of zinc corresponds with the maximum solid solubility of zinc in MnAl₆. The maximum solubility is not likely, however, greatly to exceed this value. The analysed composition of the crystals from alloy 2.0/30 corresponds with the formula Zn_{0.03}Mn_{0.96}Al₆, thus providing some evidence that zinc replaces manganese in the compound atom for atom.

(b) *The ternary compound T₁*

In a region from 35 to approximately 69 % of zinc, for manganese contents between 1 and 3 %, the ternary compound T₁ crystallizes as the primary constituent. The composition of this compound is of particular interest, from the point of view of the theory referred to in § 1. As stated above the compound may be expected to possess a composition based upon a ratio of four aluminium atoms to one of combined solutes, and an electron : atom ratio of 1.85.

For calculation of electron : atom ratios for structures containing transitional metals, it is assumed that each transitional metal atom absorbs from the structure as a whole sufficient electrons to fill up its 'atomic orbitals' to the maximum permissible extent. According to the theory developed by Pauling (1938), the transitional metals of the first long period have the following vacancies per atom in their atomic orbitals:

Cr	Mn	Fe	Co	Ni
4.66	3.66	2.66	1.71	0.61

In the system aluminium-manganese-zinc, therefore, each aluminium atom contributes three electrons to the structure and each zinc atom contributes two; each manganese atom, however, absorbs 3.66 electrons from the structure as a whole.

In figure 24, the line *ab* represents a constant ratio of four aluminium atoms to one of combined solutes, while the line *cd* represents a constant ratio of 1.85 valency electrons per atom of the structure, calculated as indicated above. When the compositions of the compound T₁ as determined by analysis are also plotted, it is seen that, except for the residue from alloy 3.0/40 which may have been contaminated with a small amount of MnAl₆, the points representing extracts from alloys containing less than 55 to 60 % of zinc lie accurately on the of line constant atomic

ratio. The point representing the sample with the least zinc in it corresponds almost exactly with the intersection of the constant atomic ratio line and the constant electron : atom ratio line, and is therefore in excellent agreement with the predicted composition (§ 1). It is clear, therefore, that the formation of this compound depends upon the simultaneous satisfaction of two factors—an electron : atom ratio of 1.85 and a ratio of four aluminium atoms to one atom of combined solute. The compound is analogous to the ternary compounds observed in the aluminium-manganese-nickel and aluminium-manganese-copper systems.

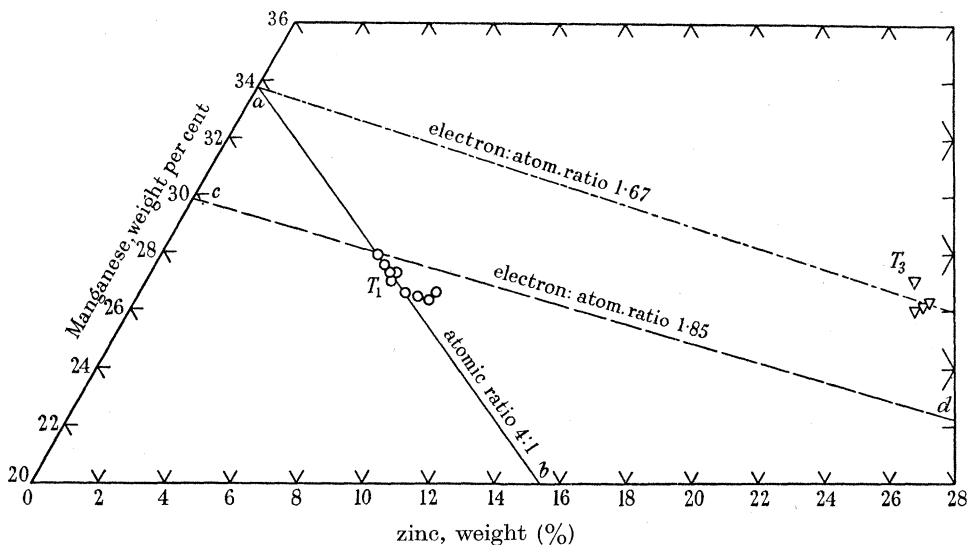


FIGURE 24

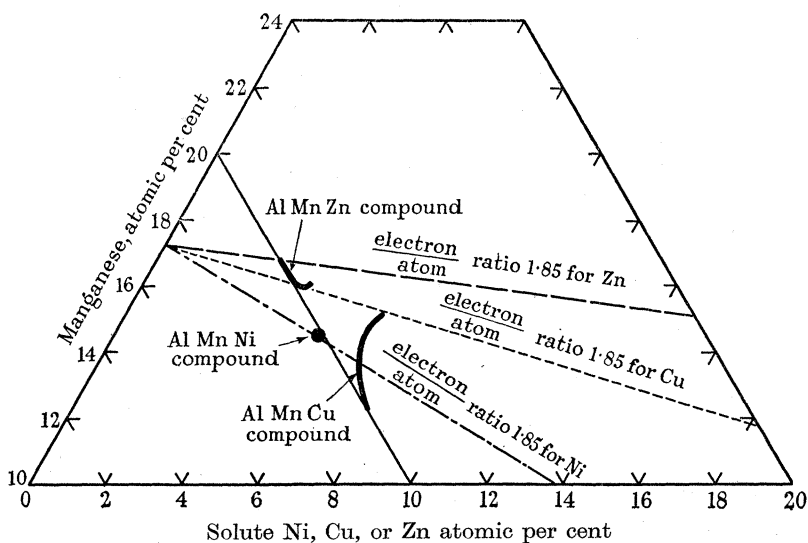


FIGURE 25

To facilitate comparison, in figure 25 the compositions of the corresponding ternary compounds in the alloys of aluminium and manganese with copper, nickel, and zinc are plotted in atomic percentages, and the constant atomic ratio and electron:atom ratio lines are also shown.

Reference to figure 24 shows that, as the zinc percentage of the alloy from which the crystals were extracted increases, the composition of the primary T_1 crystals moves initially along the line ab , but for alloy zinc contents of more than 55% of zinc, begins to deviate from this line. In this connexion, it should be remembered that the temperature at which the primary separation occurs decreases as the zinc content of the alloy increases. The points plotted therefore correspond with the compositions of the T_1 phase at different temperatures.

(c) *The compound MnAl₄*

According to the results given in figure 23, the primary MnAl₄ field extends, at low manganese contents, only from approximately 69 to 76% of zinc. All the specimens analysed for both manganese and zinc, except that from alloy 1.25/75, therefore correspond with secondary crystals. Since the phase is clearly of variable composition, the compositions of secondary crystals represent an average only. It is this factor which accounts for the close agreement of the analysis from all samples except that from alloy 1.25/75. This extract, since it was obtained from an alloy at the extreme zinc-rich end of the region in which MnAl₄ crystallizes as the primary constituent, probably represents roughly the limiting solubility of zinc in MnAl₄. Zinc therefore dissolves in the compound MnAl₄ up to a limit of approximately 5.2%, the substitution of zinc for manganese being approximately atom for atom.

(d) *The ternary compound T₂*

The composition of the ternary compound T_2 is also of interest, since it corresponds accurately with the formula Mn₂ZnAl₉. The electron:atom ratio of this compound, according to the scheme outlined above, is 1.81. If, however, the contribution to the structure of two atoms of manganese together with one of zinc is considered, it is seen that there remain 5.32 vacancies to be filled by electrons from the structure as a whole. This is very similar to the contribution (5.13 vacancies) of three cobalt atoms, and it is possible that the compound is analogous to CoAl₃, which has an electron:atom ratio of 1.82.

(e) *The ternary compound T₃*

The ternary compound T_3 cannot be represented by as simple a formula as the compound T_2 . It appears to conform most closely with the arrangement (MnZn)₅Al₁₁, or Mn_{2.8}Zn_{2.2}Al₁₁. It may be significant that the electron:atom ratio of this compound is close to that of MnAl₄, as shown in figure 24.

From the results of these experiments, therefore, it is clear that both size and electronic factors may operate together in intermetallic systems of the type examined.

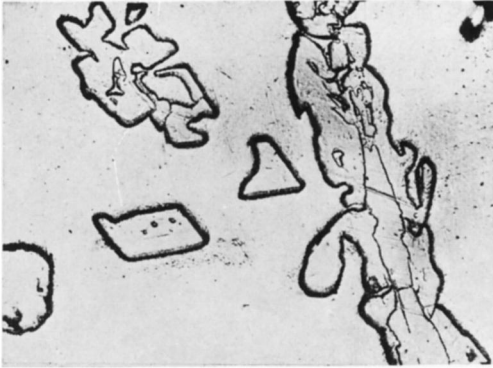


FIGURE 8

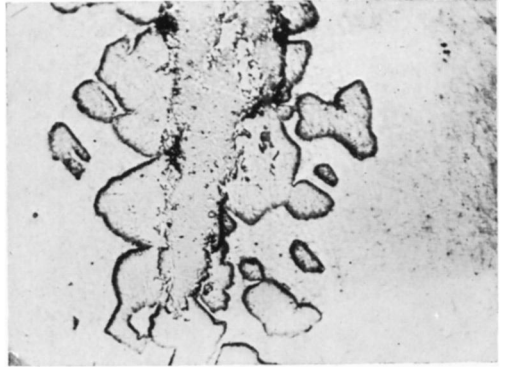


FIGURE 9

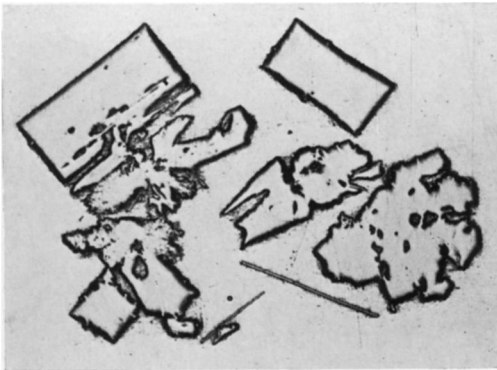


FIGURE 10

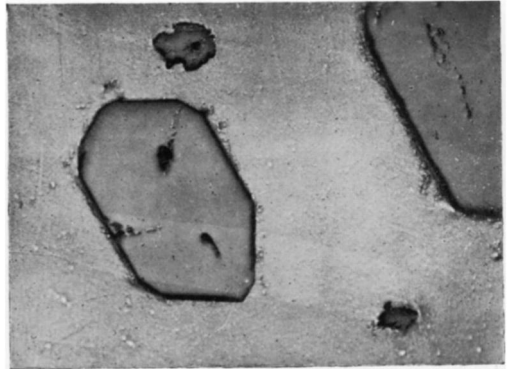


FIGURE 11

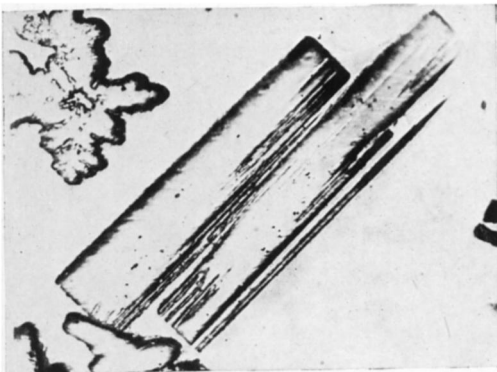


FIGURE 12

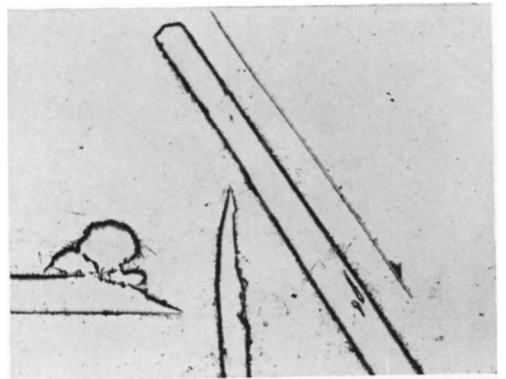


FIGURE 13

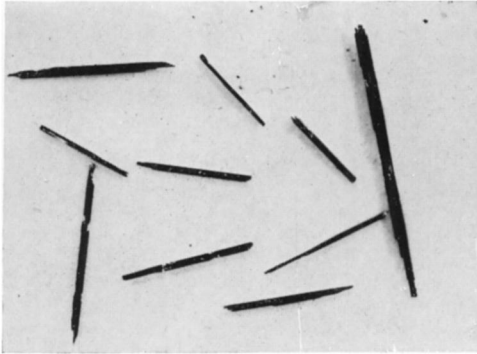


FIGURE 14



FIGURE 15

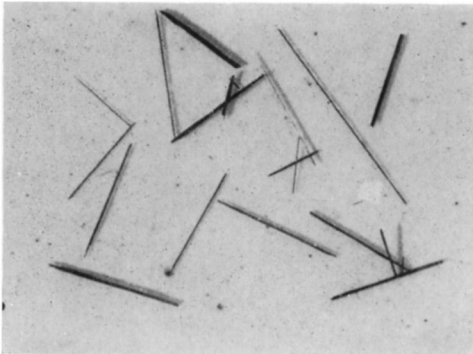


FIGURE 16

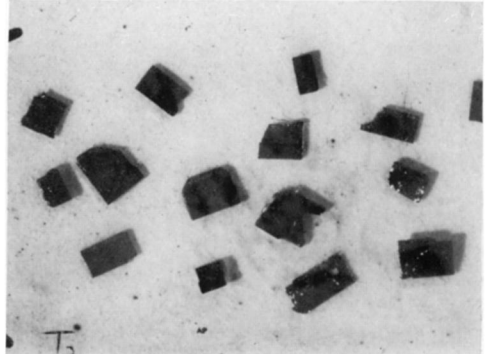


FIGURE 17

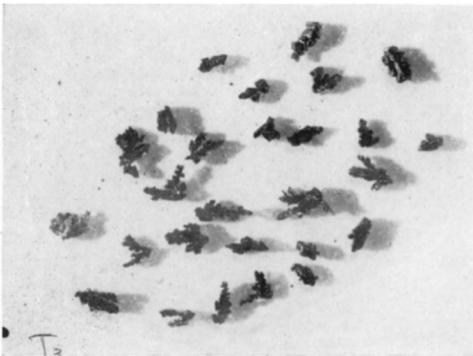


FIGURE 18



FIGURE 19

In particular, it is very probable that, when present as a minor constituent in alloys based upon a solvent of relatively high valency, transitional metals absorb electrons from the structure as a whole by filling up the vacancies in the atomic orbitals postulated by the Pauling theory.

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DESCRIPTION OF PLATES 3 AND 4

PLATE 3

- FIGURE 8. Crystals of $MnAl_6$ with spines of $MnAl_4$, alloy 3.0/30. $\times 125$.
 FIGURE 9. Cored crystal in alloy 3.0/70. $\times 125$.
 FIGURE 10. Dendritic T_3 crystals and plates of $MnAl_3$, alloy 2.0/80. $\times 125$.
 FIGURE 11. Polygonal T_1 crystal in alloy 2.0/55. $\times 125$.
 FIGURE 12. Needles of $MnAl_4$ in alloy 1.25/75. $\times 125$.
 FIGURE 13. Cross-sections of plates of T_2 in alloy 1.25/75. $\times 125$.

PLATE 4

- FIGURE 14. Extracted crystals of $MnAl_6$. $\times 2.5$.
 FIGURE 15. Extracted crystals of ternary compound T_1 . $\times 5$.
 FIGURE 16. Extracted crystals of $MnAl_4$. $\times 5$.
 FIGURE 17. Extracted crystals of ternary compound T_2 . $\times 5$.
 FIGURE 18. Extracted crystals of ternary compound T_3 . $\times 5$.
 FIGURE 19. Extracted crystals of $MnAl_3$. $\times 5$.