THE CONSTITUTION AND AGE-HARDENING CHARACTERISTICS OF CERTAIN DURALUMIN-TYPE ALLOYS

THESIS

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by

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S Y N O P S I S

The thesis is divided into three sections.

SECTION I.

Isothermal sections at 500°c. have been studied in the ternary system aluminium-copper-manganese and in the quaternary system aluminium-copper-magnesium manganese to enable a correlation to be made of the constitution with the ageing characteristics of certain Duralumin-type alloys. The compositional ranges covered were approximately 0-6% copper, 0-5% magnesium and 0-2% manganese. In the quaternary isothermals, sections have been taken at constant manganese contents of 0.6, 1.2 and 1.8% and at constant copper contents of 3 and 4.5% respectively. No quaternary compound was detected. The quaternary isothermals have been discussed with reference to the perspective views of various phase regions.

SECTION II.

The effect of manganese additions up to 2% on the ageing characteristics of aluminium-copper alloys containing 3 and 4.5% copper was investigated by tensile measurements. It was found that (i) the shape of the ageing curves for 0.1% proof stress and tensile strength was similar to that of hardness/ageing curves, (ii) manganese additions of 0.5% or more refined the grain size and gave greater tensile strength and elongation in the fully-aged condition.

The relationships between the properties and the constitution and the significance of grain size and modes of precipitation have been discussed.

SECTION III.

The effect of manganese additions on the age-hardening characteristics of the aluminium-copper-magnesium alloys has been studied by hardness measurements. It was found that (i) the manganese in the solid-solution increases the as-quenched and peak-hardness, (ii) the concentration of manganese beyond the solid solubility limit increases the as-quenched and peak-hardness but decreases the age-hardening capacity due to the formation of the T-phase, (iii) the T-phase has an accelerating effect on the ageing process.

The various effects have been analysed with reference to the constitution and the precipitation process of the alloys.

An appendix has been added which summarises the results of an investigation of fractional nucleation in an aluminium - 4.25% copper alloy.

Previous work relevant to all the three sections and the appendix has been reviewed.

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SECTION III

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INTRODUCTION

Duralumin has played an important role in the engineering construction of the modern era, since its discovery by ALFRED WILM in 1911. The alloy system containing copper, magnesium, manganese, iron and silicon has been the subject of extensive investigation, made in order to understand the mechanism of its property of age-hardening, and to develop better and stronger alloys.

The early workers were concerned mainly with the compilation of data on the mechanical properties of these alloys. A small amount of work was done on the structural ageing characteristics by using X-ray techniques, but due to the comparatively inadequate techniques then available the interpretation proved to be controversial. Moreover, early workers were handicapped by not having a high-purity grade of aluminium and, for this reason, accurate data could not be obtained on the basic systems to furnish the information about the role played by individual elements. Thus these limitations made the understanding of the ageing process difficult.

In recent years more comprehensive information has been obtained on the structural ageing characteristics by the use of advanced X-ray and electron microscope

techniques and high-purity materials. Knowledge about the role played by each element is also being compiled by the use of high-purity materials.

The most important binary system, forming the basis of Duralumin is that of aluminium-copper. Systematic work has been carried out on binary aluminium-copper alloys by GAYLER and PRESTON (1929, 1932), GAYLER (1940, 1946), GUINIER (1938, 1939) and HARDY and co-workers (1951, 1954). The main features of the ageing process in the aluminium-copper system have been well established by the work of the above mentioned and many other investigators.

Aluminium-copper-magnesium is the basic ternary system in the Duralumin alloys. HARDY (1954-55) has carried out an extensive study of alloys of this system. The structural ageing characteristics have been studied by NISHIMURA and MURAKAMI (1951), BAGARYATSKI (1948, 1950) and LAMBOT (1950) and an explanation has been proposed. The age-hardening characteristics of the aluminium-copper-manganese, aluminium-copper-iron, aluminium-copper-silicon, and aluminium-copper-magnesium alloys have been studied by CHITTY (1958).

For the understanding of the mechanism of ageing of Duralumin it is necessary to study first the ageing characteristics of all the constituent systems, because

of the complex nature of the senary system involved in Duralumin. It was, therefore, decided to study the ageing characteristics of the quaternary alloys as a function of the effects of adding a fourth element to the basic aluminium-copper-magnesium system. The present investigation is mainly concerned with aluminium-copper-magnesium-manganese alloys.

It will be appreciated that the knowledge of the constitutional picture at the solution-treatment temperature is necessary in order to analyse and understand the effects of alloying additions. There was no information available on the constitution of the quaternary aluminium-copper-magnesium-manganese system and it was therefore decided to study isothermal sections at 500°C, over the range of compositions 0 - 6% copper, 0 - 5% magnesium and 0 - 2% manganese. The information on the aluminium-copper-manganese isothermal at 500°C was rather conflicting, which necessitated the extension of the constitutional study to the ternary system over the range 0 - 5% copper and 0 - 2% manganese. Microscopical examination of annealed samples was the method used in the constitutional work.

The picture of the role played by each element in Duralumin, drawn from the hardness measurements only, was

thought to be inadequate and an attempt was made to substantiate this picture and to bridge certain gaps by studying the effects of ageing on the tensile properties of certain aluminium-copper and aluminium-copper-manganese alloys.

Thus the whole project is divided into three sections; the first dealing with the constitution of the alloys, the second dealing with the effects of ageing on the tensile properties of certain aluminium-copper and aluminium-copper-manganese alloys, and the third dealing with the effects of manganese additions on the age-hardening characteristics of aluminium-copper-magnesium alloys.

An appendix is added to these three sections which summarises a small amount of work done on the application of the SCHEIL'S (1935) "Fractional Nucleation Theory" to the ageing process of an aluminium-copper alloy.

SECTION I

"THE EQUILIBRIUM RELATIONS AT 500°C, IN SOME ALUMINIUM-COPPER-MANGANESE AND ALUMINIUM-COPPER-MAGNESIUM-MANGANESE ALLOYS".

CHAPTER 1

PREVIOUS WORK ON CONSTITUTION

GENERAL CONSIDERATIONS

One of the main aims of the present investigation was to study the effects of manganese additions on the age-hardening characteristics of ternary aluminium-copper-magnesium alloys. The complex alloys of the system aluminium-copper-magnesium-manganese are solution-treated at a temperature just below the lowest melting eutectic in the system, to dissolve the maximum amounts of the alloying elements. The solution-treated alloys are quenched and the precipitation of the constituents is thereby suppressed. The quenched alloys age-harden at room temperature or at elevated temperatures. Age-hardening is affected by the different modes of precipitation of the dissolved elements, depending upon the time and temperature of the ageing.

It is necessary therefore, to look into the constitutional picture of these alloys at the solution-treatment temperature before the effects of the different alloying elements on the ageing characteristics can be assessed. Moreover, a satisfactory choice of the

alloys for age-hardening studies is only possible if the constitution of the alloys at the solution-treatment temperature, over the range under investigation, is thoroughly known.

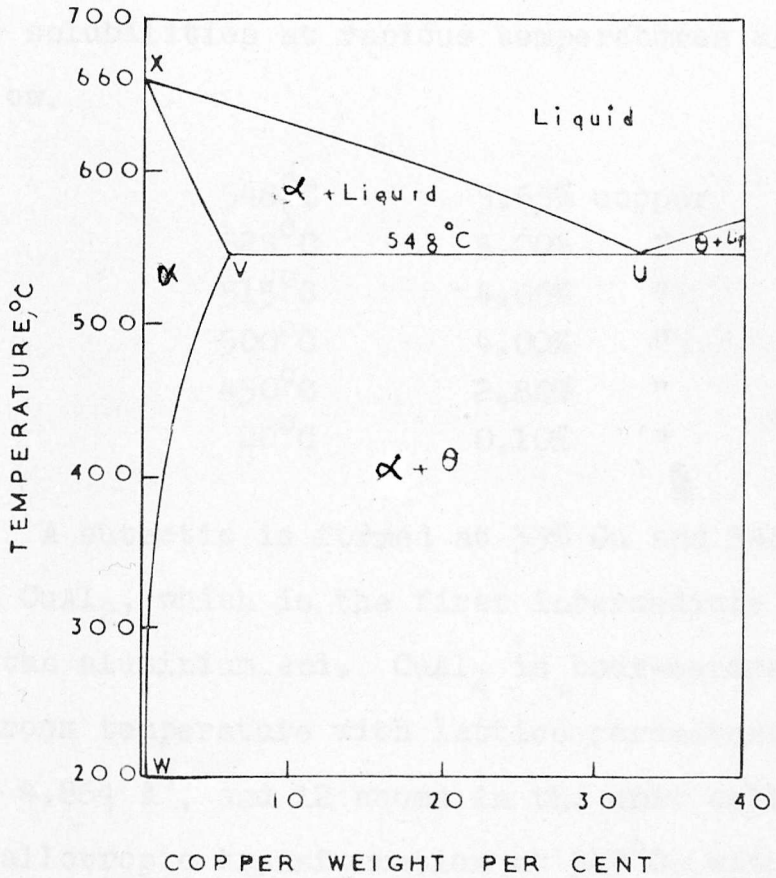
These prime considerations led the present author to study the equilibrium relations in the aluminium-copper-magnesium-manganese system at the solution-treatment temperature.

The understanding of the equilibrium relations in quaternary systems is complicated and a knowledge of the relevant portions of the equilibrium diagrams for the binary and ternary systems is necessary. The information available on the relevant systems is summarised in the following pages.

The System Aluminium-Copper

The equilibrium diagram for the aluminium-copper system is well established and the aluminium-rich end of the diagram is shown in fig.(1 - 1), as reported by RAYNOR (1950) and based on the work of several investigators (HISATSUNE, 1934; TASAKI, 1925; STOCKDALE, 1922, 1924, 1933; DIX and RICHARDSON, 1926; STENZEL and WEERTS, 1933; PHILLIPS and BRICK, 1933; BRADLEY and JONES, 1933).

ALUMINIUM - COPPER



The Aluminium end of the Equilibrium Diagram of the system Aluminium-Copper (G.V. Raynor)

		Per Cent Copper
Liquidus	UX	33.0-0.00
Solidus	VX	5.70-0.00
Solid Solubility	VW	5.70-0.20
Phase	α	Al Solid Solution
"	θ	$CuAl_2$

(Fig 1-1)

Copper is soluble in aluminium to a certain extent and its solubility decreases with decreasing temperature. The solubilities at various temperatures are reported below.

548°C	5.65% copper
525°C	5.00% "
515°C	4.65% "
500°C	4.00% "
450°C	2.80% "
20°C	0.10% "

A eutectic is formed at 33% Cu and 548°C between Al and $CuAl_2$, which is the first intermediate phase appearing at the aluminium end. $CuAl_2$ is body-centred tetragonal at room temperature with lattice parameters, a = 6.054 A°, c = 4.864 A°, and 12 atoms in the unit cell. It undergoes an allotropic transformation at 547°C with a change in volume. Its composition at high temperatures does not correspond to the formula $CuAl_2$; it contains 52.5% Cu at 548°C, to 53.5% Cu at 519°C instead of the required 54.1% Cu. Another form of $CuAl_2$ is known: it is tetragonal with lattice parameters a = 8.20 A°, c = 11.6 A° or a = 5.8 A°, c = 5.71 A°; depending upon the plane

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Footnote:- All the percentages used in the present work are by weight unless otherwise stated.

considered as the basis. Though this phase is designated as $CuAl_2$ by usage, an alloy of composition corresponding to the formula lies just outside the region of homogeneity of the phase.

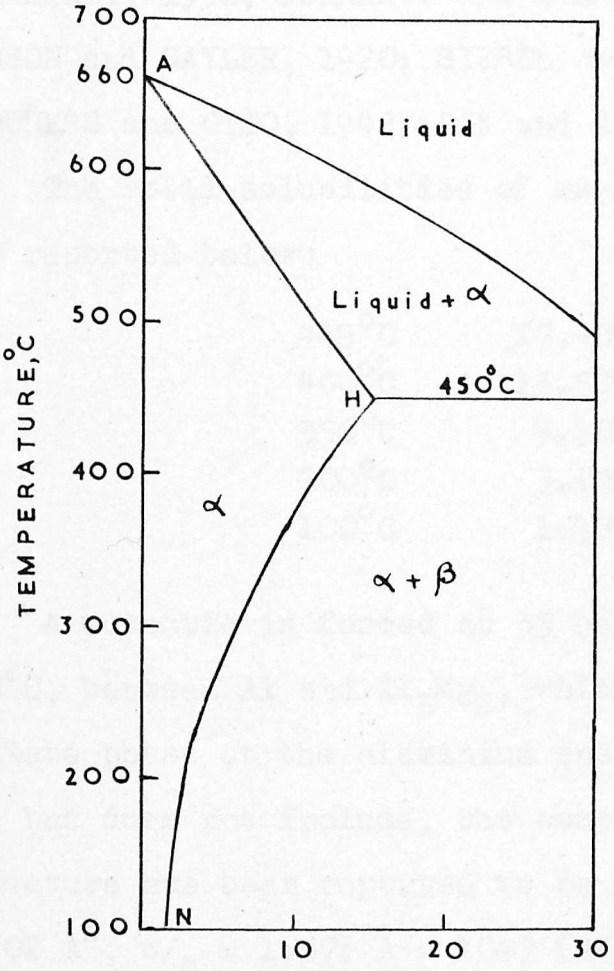
It was shown that the compound $CuAl_2$ does not dissolve appreciable quantities of magnesium (LAVES and WITTE, 1936) and this has been confirmed by other investigators (LITTLE et al., 1944), who have reported that, even with as little as 0.10% Mg, a second phase is clearly present in alloys annealed at 460°C.

While studying the effects of manganese additions on the phase $CuAl_2$, it has been found that, although $CuAl_2$ has a homogeneity range along the binary aluminium-copper axis, additions of as little as 0.10% manganese cause the appearance of a ternary phase (RAYNOR, 1944). The solubility of manganese in $CuAl_2$ must thus be smaller than 0.10 per cent and for the present investigation may be considered negligible.

The System Aluminium-Magnesium

The binary aluminium-magnesium equilibrium diagram has been thoroughly investigated and fig.(1 - 2) shows the aluminium end of the diagram reported in the "annoted at

ALUMINIUM–MAGNESIUM



		Per Cent Magnesium
Solidus	AH	0·00 – 15.35
Solid Solubility	NH	1.9 – 15.35

The Aluminium end of the Equilibrium Diagram of the system Aluminium–Magnesium (G.V. Raynor)

(Fig 1–2)

equilibrium diagram for "Aluminium-Magnesium" No.5, (RAYNOR) which is based on the work of various authors (KAWAKAMI, 1936; KURNAKOV and MIKHEEVA, 1938, 1940; HANSON and GAYLER, 1920; SIEBEL and VOSSKUHLER, 1939; BROCHERS and OTTO, 1942; DIX and KELLER, 1929).

The solid solubilities of magnesium in aluminium are reported below:

449°C	17.40% magnesium
400°C	13.50% "
350°C	9.90% "
200°C	3.10% "
100°C	1.90% "

A eutectic is formed at 35 per cent magnesium and 450°C, between Al and Al_3Mg_2, which is the first intermediate phase at the aluminium end. This phase extends up to, but does not include, the composition Al_3Mg_2. The structure has been reported to be hexagonal (a = 11.38 $\pm$0.02 A°, $c/_a$ = 1.57; A = 104) (REIDERER, 1936) and as cubic, of face-centred type (a = 28.13 A°; A = 1172) (PERLITZ, 1944). Hanemann et al. chose to put this phase in the cubic system (HANEMANN and SCHRADR , 1952). The phase is assigned a formula $Al_8Mg_5(\beta)$ by some authors (TOLLNER, 1941). The weight percentage of magnesium differs slightly in these two formulae: wt. per cent Mg

in Al_3Mg_2 = 37.54 and in $Al_8Mg_5(\beta)$ = 36.04.

The System Aluminium-Manganese

The aluminium end of the equilibrium diagram of the system Al-Mn is shown in fig.(1 - 3) from the annoted at equilibrium diagram (PHILLIPS), which is based on the findings of several workers (DIX et al., 1933; BUTCHERS et al., 1943; and HOFMANN, 1938).

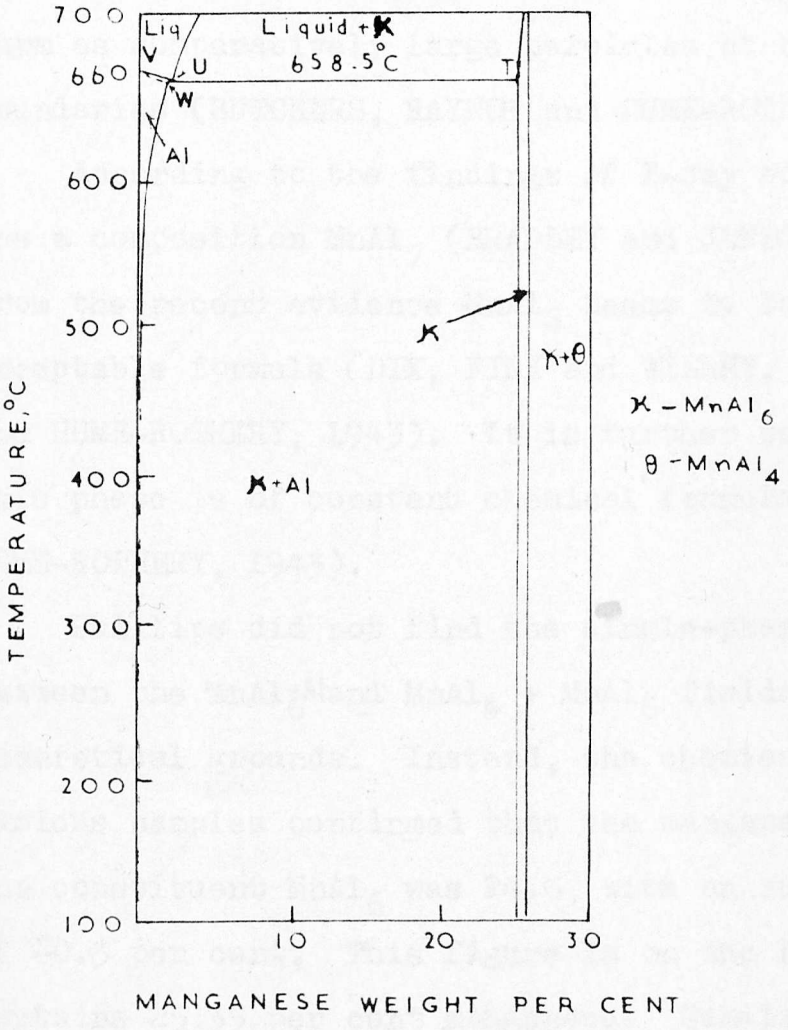
The solid solubility of manganese in aluminium is reported below:

658°C	1.82% manganese
600°C	0.95% "
550°C	0.60% "
500°C	0.36% "
400°C	0.09% "
300°C	0.02% "

A eutectic is formed between Al and Al_6Mn at 658°C: values for the eutectic composition of between 2.00 and 1.82 per cent manganese have been reported by various workers.

Al_6Mn is the first stable intermediate phase to appear at the aluminium end of the diagram. The separation of Al_6Mn in hyper-eutectic alloys is often accompanied by marked supercooling. The Al-Al_6Mn eutectic

ALUMINIUM – MANGANESE



The Aluminium end of the Equilibrium Diagram of the system

Aluminium - Manganese (H.W.L. Phillips)

		Per Cent, Manganese
Liquidus	UV	2.00 – 0.00
Solidus	WV	1.82 - 0.00
Solid Solubility		1.82 at 658.5 to 0.02 at 300°C
Point	T	25.1

(Fig 1–3)

does not show any characteristic eutectic structure. It has been found that in slowly cooled hypo-eutectic alloys with primary α, the eutectic Al-Al_6Mn tends to form as comparatively large particles at the grain boundaries (BUTCHERS, RAYNOR and HUME-ROTHERY, 1943).

According to the findings of X-ray work, the phase has a composition $MnAl_7$ (BRADLEY and JONES, 1931), but from the recent evidence $MnAl_6$ seems to be a more acceptable formula (DIX, FINK and WILLEY, 1933; RAYNOR and HUME-ROTHERY, 1943). It is further suggested that this phase is of constant chemical formula (RAYNOR and HUME-ROTHERY, 1943).

Phillips did not find the single-phase field lying between the $MnAl_6$ + Al and $MnAl_4$ + $MnAl_6$ fields as expected on theoretical grounds. Instead, the chemical analyses of various samples confirmed that the manganese content of the constituent $MnAl_6$ was 24.6, with an analytical tolerance of $\pm$0.3 per cent. This figure is on the low side: $MnAl_6$ contains 25.35 per cent manganese. Similar discrepancies were found by other authors (DIX et al., 1933) who reported 25.8 per cent for the manganese content of this phase. It was therefore suggested that the constituent may not correspond to any exact chemical formula (PHILLIPS, 1943).

The crystals of $MnAl_6$ were isolated and the

crystallographic constants were determined. The structure was reported to be orthorhombic with a = 6.51, b = 7.57 and c = 8.87 ^{o}A; and four formula units per cell (HOFMANN, 1938).

$MnAl_6$ crystals were extracted from the annealed specimens of a ternary aluminium-copper-manganese alloy. Chemical analysis revealed the presence of only 0.19% copper, while the X-ray diffraction pattern showed that the lattice spacings were within the limits of experimental error the same as for pure Al_6Mn. Further investigations showed that $MnAl_6$ cannot take up copper into solid solution either in the presence or in the absence of magnesium and zinc (RAYNOR, 1944). However, according to a recent paper (PHRAGMEN, 1950) the solubility of copper in Al_6Mn is appreciable, and it has been suggested that a formula $(Al, Cu)_6Mn$ should be assigned to this constituent in the presence of copper. However, the percentage of copper dissolved is small enough to write Al_6Mn as the formula even in the presence of copper, to avoid confusion.

The solubility of iron in $MnAl_6$ is quite appreciable. Raynor's work showed that iron can replace manganese up to 50 per cent in the constituent $MnAl_6$ and its formula may then be written as $Mn_{1/2}Fe_{1/2}Al_6$ (RAYNOR, 1944).

LITTLE, RAYNOR and HUME-ROTHERY (1947) reported an alloy with 1 to 3 per cent manganese as possibly containing three phases: α-aluminium, $MnAl_6$ and a phase termed G. It was suggested that the G phase may be a metastable one. They also reported that the constituent G disappeared when the cast alloys were annealed for prolonged periods of 8 days or more at 600°C; but on annealing at 550°C, the proportion of G diminished very slowly and even after 40 days the alloy still contained a considerable amount of this phase. The chemical composition of this phase was not determined as it was always accompanied by the constituent $MnAl_6$. An X-ray diffraction photograph showed that the G phase has a crystal structure identical with that of the ternary 'G' phase in the system aluminium-chromium-manganese. The 'G' phase in the ternary system indicated a composition of $CrMn_4Al_{65}$ or $(Cr, Mn)Al_{13}$. If it is assumed that one atom of chromium is equivalent to one atom of manganese the formula of 'G' will be $MnAl_{13}$. If it is assumed that the electron concentration in the sense used by RAYNOR and LITTLE (1945) remains constant, the composition of G will be $MnAl_{12.6}$, whereas if 3 atoms of manganese are equivalent to 2 atoms of chromium as in the case of the ternary solid solution in $CrAl_7$ the formula

of G would be $MnAl_{11.8}$, which may be compared with the compound WAl_{12} in the system aluminium-tungsten (CLARK, 1940).

According to another paper (LITTLE and HUME-ROTHERY, 1948) the constituent 'G' crystallises in a cubic lattice with a = 13.25 kX. It was not possible to measure the density of the 'G' phase, but if the composition is assumed to be $MnAl_{12}$, the known densities of aluminium and manganese suggested that the density of 'G' phase will be approximately 3.0; and it seemed probable that the unit cell of the G phase was associated with 12 molecules of $MnAl_{12}$. LITTLE and HUME-ROTHERY have also reported the effects of different additions on the stability of the 'G' phase. With the exception of chromium all the other additions studied had a suppressing effect on the 'G' phase. The additions of small amounts of copper reduced the proportion of 'G' slightly, while larger amounts of copper produced a greater reduction. The addition of cobalt suppressed 'G' considerably and the relative amount of G to $MnAl_6$ decreased steadily as the percentage of cobalt was increased. Similarly the addition of magnesium also caused a decrease in the stability of G, the effect being about the same as that of a corresponding weight percent of cobalt. Additions of approximately 0.2 percent iron

or silicon completely suppressed the formation of G in alloys annealed at 550°C. In the case of iron, the effect was very marked and small percentages of iron were thought to neutralize the effect of chromium. It is also noted (AXON and HUME-ROTHERY, 1948) that the G phase is not observed in a wide range of ternary, quaternary and quinary alloys of the system Al-Mg-Zn-Mn-Si, containing 1 per cent silicon, annealed to equilibrium at 460°C.

Two interesting papers were published in 1948 (DUDEK, MAHL and SEEMANN, 1948; SEEMANN and DUDEK, 1948) in which it was reported that when alloys containing manganese were annealed at 500°C, alternate bands or zones of particles and homogeneous matrix were visible when examined under the electron microscope. The particles were thought to be a very finely dispersed manganese-containing phase, and were reported as U-phase. Even after 8 hours annealing at 500°C the fine phase was clearly detected when etched with hot nitric acid, instead of 0.2% HF. As the temperature of solution treatment was increased the U-phase showed a finer and finer form while in the ternary alloys containing copper, the phase $CuAl_2$ slowly vanished. It was also observed that the $CuAl_2$ particles definitely showed a marked orientation. The

U-phase was not observed in cast samples, but annealing treatment at 350° to 500°C dissolved the precipitate at grain-boundaries and gave rise to the U-phase instead, at the grain-boundaries: which on further prolonged annealing covered the whole grain.

The U-phase was found to take up large amounts of iron, which behaviour is comparable to the ability of Al_6Mn in taking up iron replacing manganese up to 50 per cent. It was also shown by the same authors that manganese has some effect on the recrystallisation of aluminium alloys, but no details were given.

The U-phase was always present in the slowly-cooled binary Al-Mn alloys and it formed through a peritectic reaction analagous to Al_6Mn. Rapid cooling suppressed the U-phase but it precipitated when the alloys were annealed at 500°C. The etching characteristics of the U-phase were different with and without the presence of iron. At high temperatures, U-phase went to the grain-boundaries and reacted with the eutectic. In continuous casting methods, the formation of the U-phase is completely suppressed by rapid cooling.

It was suggested (AXON and BAGCHI, 1954-55) that this finely dispersed precipitate described above should preferably be termed as U-constituent rather than the U-phase.

The System Aluminium-Copper-Magnesium

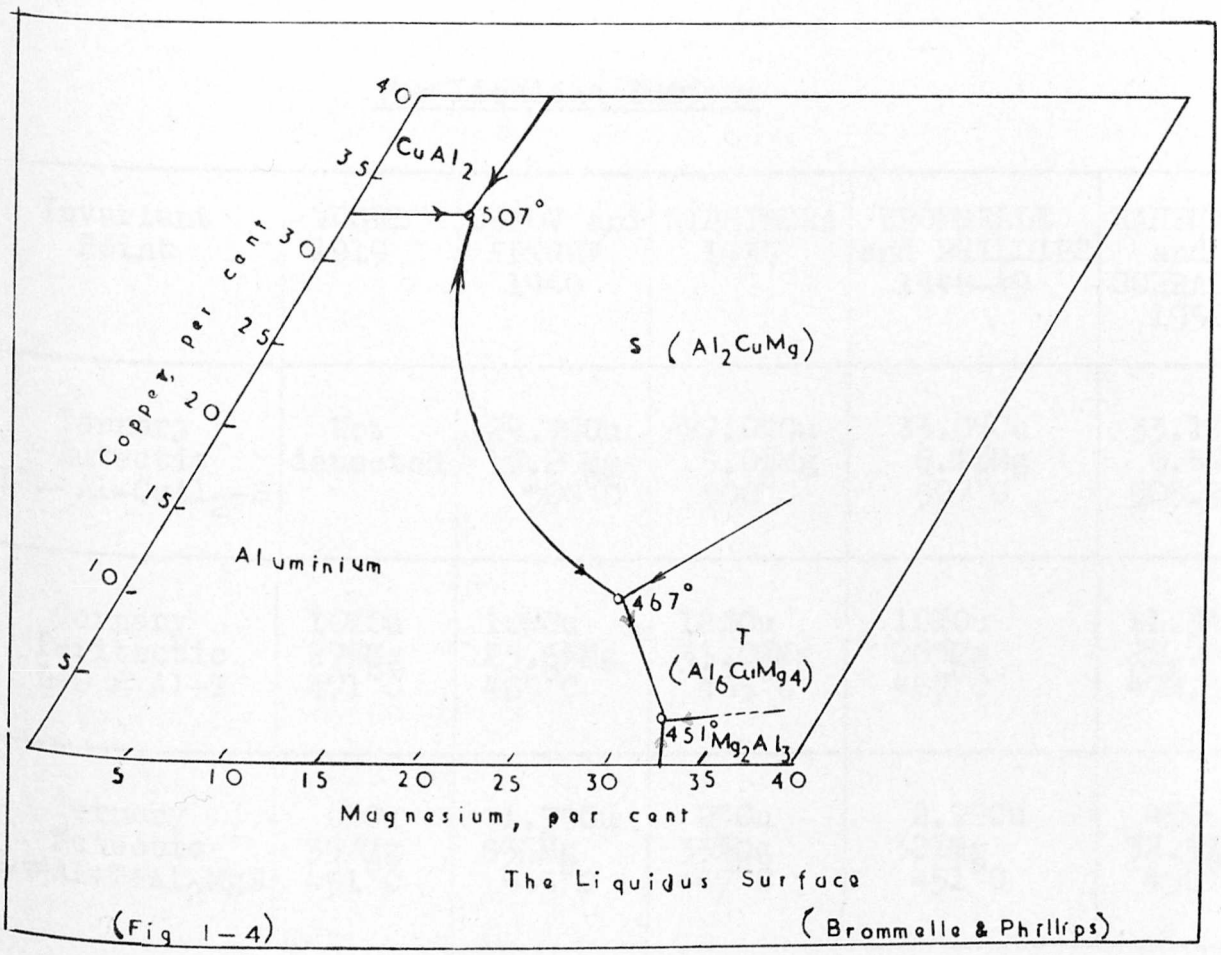
It is now generally agreed that, in the aluminium-rich corner of the aluminium-copper-magnesium system, two binary phases, $CuAl_2$ (θ) and Mg_2Al_3 (β) and two ternary phases Al_2CuMg(S) and Al_6CuMg_4(T) are present: Fig,(1 - 4). The section Al-S is a quasibinary and divides the aluminium corner of the ternary system into two parts in which the phases present are, (i) Al-$CuAl_2$-S, and (ii) Al-S-T-Mg_2Al_3 respectively. The dividing line between the two partial systems is thus that along which the ratio of Cu:Mg is equiatomic, or 2.6 : 1 in percentage by weight.

The liquidus surface is shown in fig.(1 - 4). (BROMMELLE and PHILLIPS, 1948-49)

In colour, crystal habit, hardness and etching behaviour, $CuAl_2$ and S are not very different and perhaps that is why earlier workers did not detect S and believed that $CuAl_2$ was capable of dissolving considerable quantities of magnesium (VOGEL, 1919). A ternary phase, T, was discovered and a formula Al_6CuMg_4 was assigned to it. The findings of various workers on the liquidus invariant points are tabulated below.

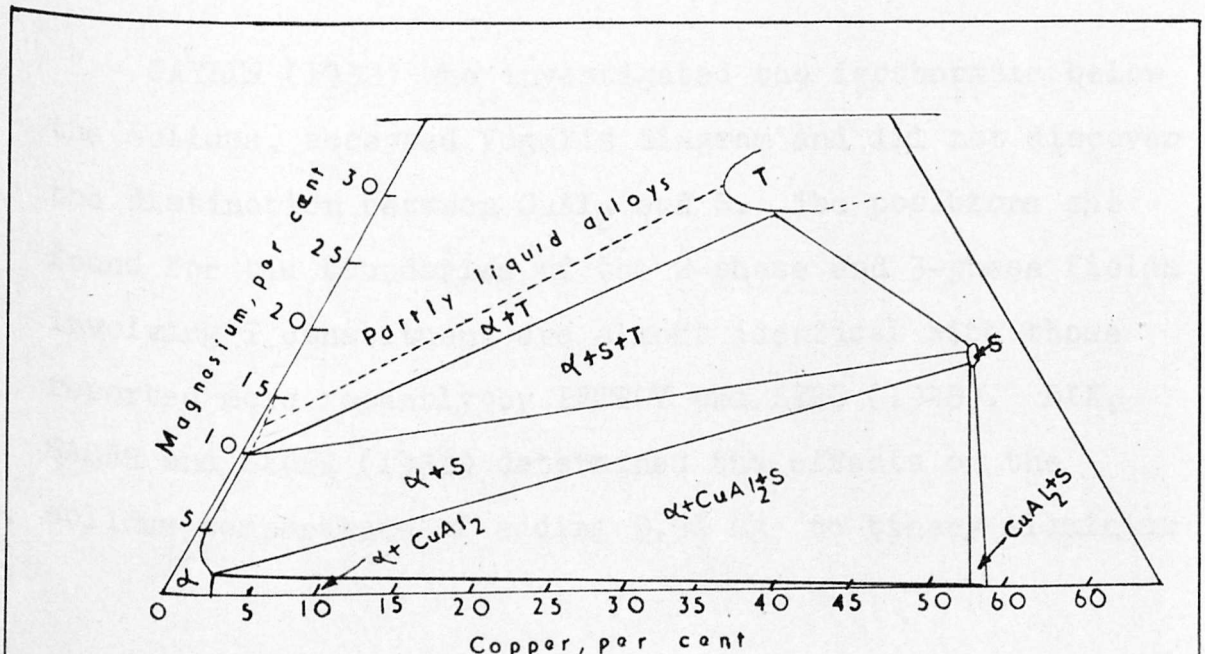
The System

ALUMINIUM–COPPER–MAGNESIUM



The Liquidus Surface

(Fig 1–4) (Brommelle & Phillips)



(Fig 1–5) The 460°C Isotherm (Little, Hume-Rothery & Raynor)

The Liquidus Surface

Invariant Point	VOGEL 1919	URZOV and PETROV 1946	NISHIMURA 1937	BROMMELLE and PHILLIPS 1948-49	HANEMANN and SCHRADER 1952
Ternary Eutectic $L \rightleftharpoons Al-CuAl_2-S$	Not detected	29.7%Cu 7.2%Mg 500°C	27.0%Cu 5.0%Mg 500°C	33.0%Cu 6.1%Mg 507°C	33.1%Cu 6.8%Mg 506.5°C
Ternary Peritectic $L+S \rightleftharpoons Al+T$	10%Cu 27%Mg 471°C	10%Cu 25.6%Mg 465°C	12%Cu 33.0%Mg 465°C	10%Cu 26%Mg 467°C	11.3%Cu 25.7%Mg 472.3°C
Ternary Eutectic $L \rightleftharpoons Al+T+Al_2MgS$	0%Cu 35%Mg 451°C	1.5%Cu 83%Mg 445°C	2%Cu 33%Mg 447°C	2.7%Cu 32%Mg 451°C	4%Cu 32.3%Mg 450°C

GAYLER (1932) who investigated the isothermals below the solidus, accepted Vogel's diagram and did not discover the distinction between $CuAl_2$ and S. The positions she found for the boundaries of the 2-phase and 3-phase fields involving T constituent are almost identical with those reported more recently by PETROV and BERG (1946). DIX, SAGER and SAGER (1932) determined the effects on the solidus temperature of adding 0.5% Mg, to binary aluminium

copper alloys. They also found that magnesium did not dissolve to any appreciable extent in $CuAl_2$. Their findings are consistent with more recent work (LITTLE, HUME-ROTHERY and RAYNOR, 1944).

'T' is formed peritectically from 'S' and liquid over a wide range of compositions, the invariant point at which Al, S and T are in equilibrium with liquid lying at approximately 26% Mg, 10% Cu, 467°C. In alloys rich in copper and magnesium S and T do not separate directly from the liquid, but are formed as the result of a peritectic reaction between a constituent termed U and the liquid. A chemical formula $Al_2Cu_3Mg_2$ was assigned to this phase (PORTEVIN and BASTEIN, 1932).

The existence of Al_6CuMg_4(T) was confirmed and it was reported to be cubic and isomorphous with $Al_2Mg_3Zn_3$ (LAVES et al., 1935). Laves and Witte found that $CuAl_2$ does not dissolve magnesium appreciably and that a ternary phase existed to which they gave a formula $Al_5Cu_2Mg_2$. This phase is now known as S. They also discovered another ternary compound to which a formula, $Al_{10}Cu_7Mg_8$, was assigned and confirmed the existence of AlCuMg (LAVES and WITTE, 1936). The existence of the phase now known as 'S' was also confirmed by SCHÜTZ (1937), who used the methods of

thermal analysis. He suggested that an approximate formula would be $Al_{11}Cu_4Mg_4$ and not $Al_5Cu_2Mg_2$.

The system was studied over a wide range of compositions and chemical formulae were assigned to S and T phases by Nishimura: S($Al_{13}Cu_7Mg_8$), T(Al_5CuMg_4) (NISHIMURA, 1937). The quasibinary nature of the system Al-S was confirmed by Petrov, who reported that $CuAl_2$-S was also a quasibinary (PETROV, 1938). Obinata and Mutuzaki published results of an X-ray investigation of the crystal structure of the phase S. They gave its composition as $Al_5Cu_2Mg_2$, and stated that it crystallised in the tetragonal system (OBINATA and MUTUZAKI, 1941). However, these findings were not confirmed by other workers, (PERLITZ and WESTGREN, 1943) who reported the nearest formula as Al_2CuMg for the S-phase.

The following table summarises the findings of various workers, on the phases found in the aluminium-rich corner of the system Al-Cu-Mg.

Reference	S-(formula)	T-(formula)	N-(formula)
VOGEL, 1919	-	Al_6CuMg_4	-
PORTEVIN et al., 1932	-	-	Al_2CuMg
LAVES et al., 1935, 1936	$Al_5Cu_2Mg_2$	Al_6CuMg_4	-
SHUTZ, 1937	$Al_{11}Cu_4Mg_4$	-	-
NISHIMURA, 1937	$Al_{13}Cu_7Mg_8$	Al_5CuMg_4	-
OBINATA et al. 1941	$Al_5Cu_2Mg_2$	-	-
PERLITZ et al. 1943	Al_2CuMg	-	-
GUERTLER et al. 1943	$Al_5Cu_2Mg_2$	Al_6CuMg_4	-
PETROV, 1938	Al_2CuMg	Al_6CuMg_4	$Al_2Cu_4Mg_3$
HUME-ROTHERY, 1948	Al_2CuMg	Al_6CuMg_4	$Al_7Cu_3Mg_6$
Best authenticated	Al_2CuMg	Al_6CuMg_4	$Al_7Cu_3Mg_6$

The constituent S crystallises in orthorhombic symmetry, a = 4.00, b = 9.23, c = 7.14 Kx, with 16 atoms in the unit cell (PERLITZ and WESTGREN, 1943) and the T-phase has a cubic lattice, a = 14.25 Kx (LAVES et al., 1935).

The isothermal section at 460°C Fig.(1 - 5) was studied over a wide range of compositions by LITTLE,

HUME-ROTHERY and RAYNOR, (1944), and some determinations were made over a limited range at 375°C. These workers confirmed that $CuAl_2$ has a limited capacity to dissolve magnesium and placed the limit below 0.1 per cent. They also showed that the aluminium apex of the three-phase triangle Al-$CuAl_2$-S follows the equiatomic line very closely with falling temperature. They further determined the homogeneity ranges of the constituents S and T, which they showed could be represented fairly closely by the formulae Al_2CuMg and Al_6CuMg_4. They found that the Al-S solid solubility curve obeyed the mass action law,

$$[Cu \times Mg] = K$$

where square brackets denote concentrations in atomic percentages and K is a constant; and they further showed that the change of the solubility product with temperature could be represented by the equation

$$\mathrm{Log}_{10}K = A - \frac{B}{\theta}$$

where A and B are constants and θ is the absolute temperature.

Vrazov and Petrov redetermined the liquidus over a wide range of compositions and their diagram is in close agreement with that of Nishimura (VRAZOV and PETROV, 1946). The chief difference lies in the chemical formulae assigned

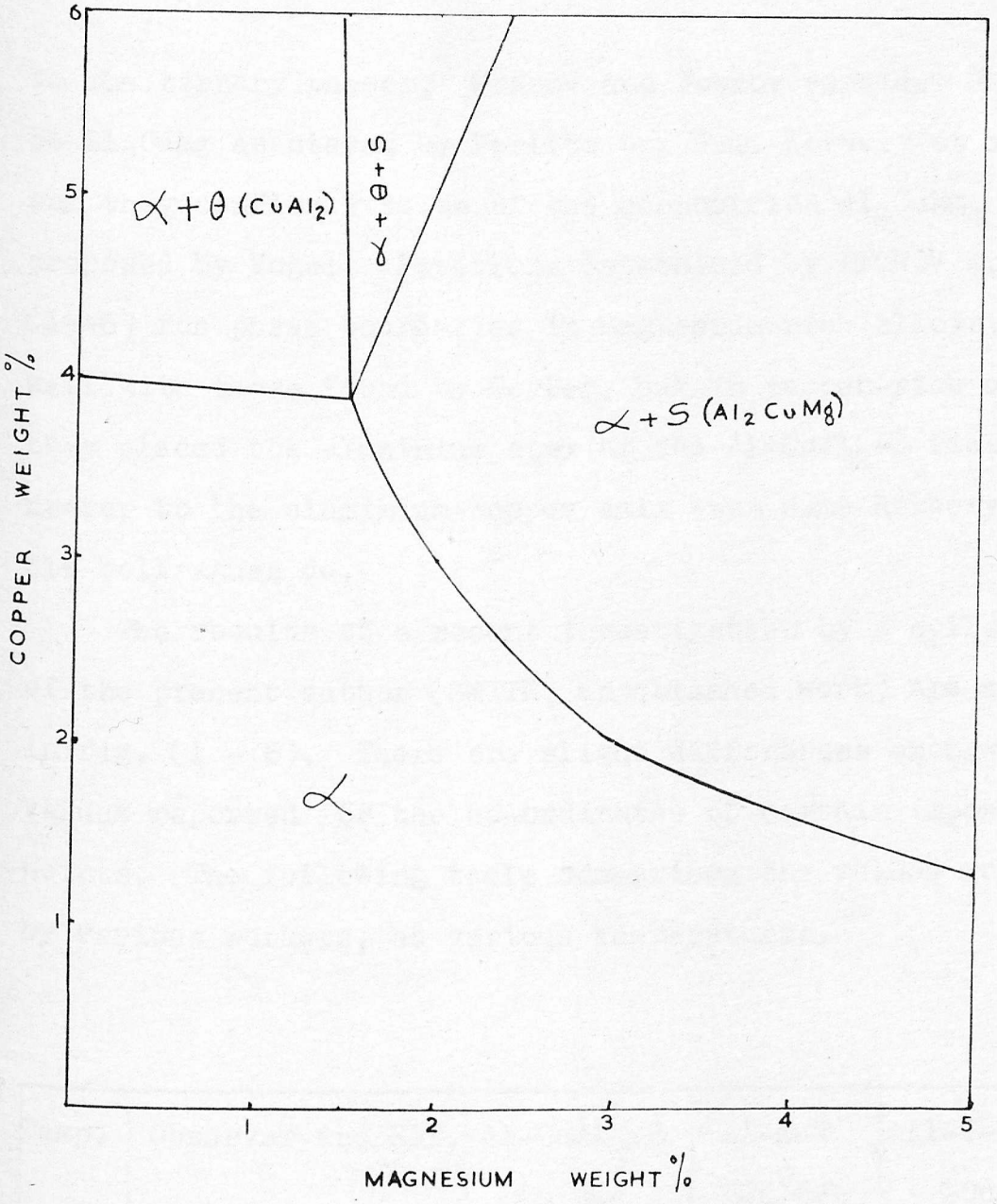


Fig- (1–6) – 500° C. ISOTHERMAL OF THE SYSTEM

ALUMINIUM– COPPER– MAGNESIUM

(Smith)

to the ternary phases. Vrazov and Petrov consider S to be Al_2CuMg as stated by Perlitz and Hume-Rothery et al. and they confirm T to be of the composition Al_6CuMg_4 as proposed by Vogel. Positions determined by PETROV and BERG (1946) for phase boundaries in magnesium-rich alloys, agree well with those found by Gayler, but in copper-rich alloys they placed the aluminium apex of the Al-$CuAl_2$-S field much nearer to the aluminium-copper axis than Hume-Rothery and his colleagues do.

The results of a recent investigation by a colleague of the present author (SMITH, unpublished work) are shown in fig. (1 - 6). There are slight differences amongst the values reported for the co-ordinates of certain important points. The following table summarises the values reported by various workers, at various temperatures.

Temp.	Observer and Ref.	Al-$CuAl_2$-S		Al-S-T		Al-T-Mg_2Al_3	
		%Cu	%Mg	%Cu	%Mg	%Cu	%Mg
500°c	NISHIMURA, 1937	3.50	0.50	-	-	-	-
	HUME-ROTHERY et al., 1948	3.90	1.50	-	-	-	-
	PETROV and BERG, 1946	3.60	0.80	-	-	-	-

(Contd.)

Temp.	Observer and Ref.	Al-$CuAl_2$-S		Al-S-T		Al-T-Mg_2Al_3	
		%Cu	%Mg	%Cu	%Mg	%Cu	%Mg
500°C	SMITH (Unpublished)	3.90	1.50	-	-	-	-
445°C	NISHIMURA, 1937	3.0	0.3	0.20	6.00	0.20	8.50
	KUZNESTOV and GUSEVA, 1940	2.80	0.70	0.60	7.50	0.60	14.30
	HUME-ROTHERY et al., 1944, 1948	2.50	1.10	0.20	9.00	-	-
	PETROV and BERG, 1946	2.00	0.60	0.30	8.50	0.30	10.50
400°C	GAYLER, 1923	-	-	0.40	8.00	0.40	8.50
	NISHIMURA, 1937	-	-	0.20	5.00	0.20	7.00
	KUZNESTOV and GUSEVA, 1940	1.70	0.40	0.60	6.20	0.60	10.30
	HUME-ROTHERY et al., 1944, 1948	1.70	0.80	-	-	-	-
	PETROV and Berg, 1946	1.40	0.40	0.30	7.40	0.20	9.50
300°C	GAYLER, 1923	-	-	0.40	6.50	0.40	7.30
	NISHIMURA, 1937	2.5	0.20	0.20	4.00	0.20	5.00
	KUZNESTOV and GUSEVA, 1940	0.80	0.30	0.60	4.30	0.60	5.00

(Contd.)

Temp.	Observer and Ref.	Al-$CuAl_2$-S		Al-S-T		Al-T-Mg_2Al_3	
		%Cu	%Mg	%Cu	%Mg	%Cu	%Mg
300°C	HUME-ROTHERY et al., 1944, 1948	0.50	0.30	-	-	-	-
	PETROV and BERG, 1946	0.60	0.20	0.10	5.00	0.10	5.60

The results of Hume-Rothery et al. and those of Smith are in close agreement. The apex point has been bracketted rather more closely by Smith, and for this reason, his values are taken for the present work. Smith's diagram, fig.(1 - 6), also shows that the Al-S solid solubility curve obeys the law of mass action represented by the equation

$$[Cu][Mg] = K,$$

but the change of the solubility product with temperature represented by the equation

$$\log_{10} K = A - \frac{B}{\theta}$$

cannot be completely applied.

The System Aluminium-Copper-Manganese

The aluminium-rich corner of this system was first studied by Rosenhain and Lantsberry, who identified an aluminium-rich compound, $MnAl_3$, but gave no details of the ternary structure (ROSENHAIN and LANTSBERRY, 1910). KRINGS and OSTMANN (1927) used thermal and microscopical methods to investigate the constitution of the system; they identified no ternary compound and concluded that the phases $MnAl_4$, $CuAl_2$ and aluminium formed a ternary eutectic of composition Cu - 29.6% and Mn - 3%, freezing at 536°C.

SAWAMOTO (1933) investigated the system over the range 0 - 40% Cu and 0 - 30% Mn. He reported the occurrence of a peritectic reaction

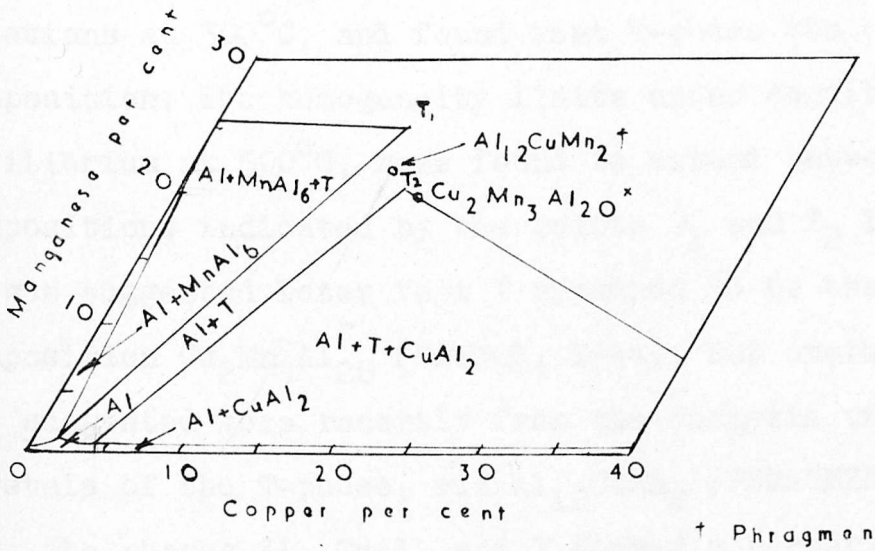
$$Liq + Al_5Mn \rightleftharpoons Al_3Mn + (Al) \quad \text{at } 630^{\circ}C$$

at a composition of 8.3 percent copper and 1.75 percent manganese. The ternary eutectic of 30.5 percent copper and 0.65 percent manganese solidified at 544°C; and contained the phases $MnAl_3$, $CuAl_2$ and aluminium.

PETRI (1938) used thermal and microscopical methods to study the alloys over the range 0 - 45% copper and 0 - 17% manganese. He reported the phases: aluminium solid solution (Al), $MnAl_6$, $MnAl_4$, $MnAl_4$, $MnAl_3$ and

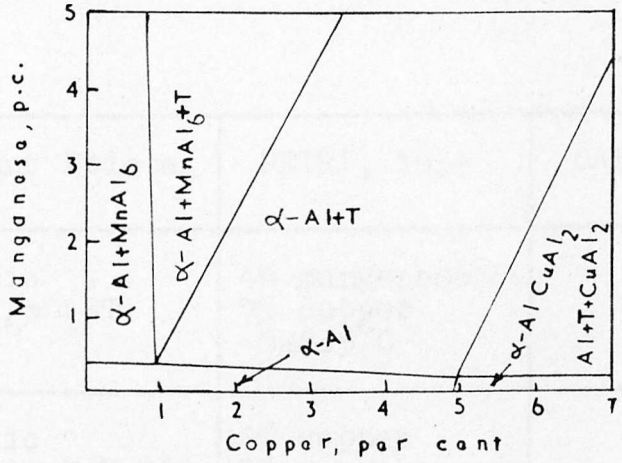
The System

ALUMINIUM - COPPER - MANGANESE



The 500° Isotherm (Petri)

(Fig 1-7)



The 525°C, Isotherm (Hofmann)

(Fig 1-8)

ternary phases T and Y. Petri investigated the equilibrium relations at 500°C, and found that T-phase was of variable composition; its homogeneity limits under conditions of equilibrium at 500°C, were found to extend between two compositions indicated by the points T_1 and T_2 in fig.(1-7). It was suggested later that T appeared to be based on the composition $Cu_2Mn_3Al_{20}$ (RAYNOR, 1944), but another formula was suggested more recently from the analysis of the crystals of the T-phase, viz. $Al_{12}CuMn_2$ (PHRAGMEN, 1950).

The phases Al, $CuAl_2$ and T formed a ternary eutectic containing 31.5% copper and 0.8% manganese, freezing at 547.3°C. Petri also reported the occurrence of several peritectic invariant reactions. These invariant points, together with those reported by other investigators, are tabulated below.

Invariant Points	PETRI, 1938	DAY and PHILLIPS, 1948
Peritectic $Liq+MnAl_6 \rightleftharpoons \alpha+T$	4% manganese 7% copper 628.5°C	14.85% copper 0.90% manganese 616°C
Peritectic $Liq+MnAl_4 \rightleftharpoons T+MnAl_6$	8% copper 8% manganese 700°C	15.75% copper 2.20% manganese 625°C

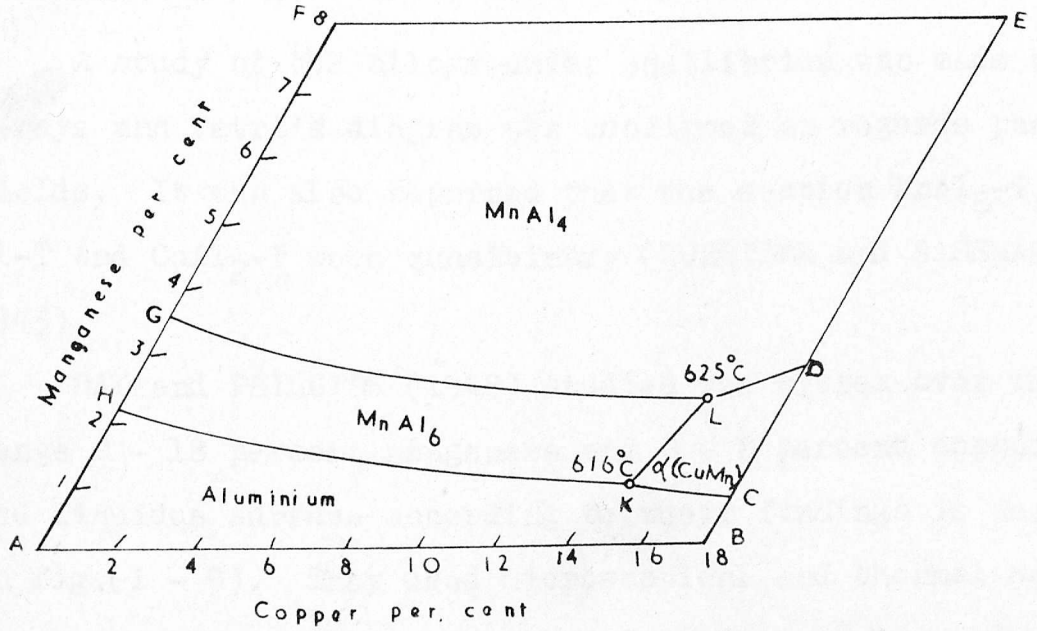
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Invariant Points	PETRI, 1938	DAY and PHILLIPS, 1948
Peritectic $Liq+MnAl_3 \rightleftarrows T+MnAl_4$	12% copper 14% manganese -	- - -
Eutectic $Liq \rightleftarrows \alpha+T+CuAl_2$	31.5% copper 0.8% manganese 547.3°C	32.5% copper 0.60% manganese 547.5°C

The constituent T, extracted from an alloy in which it occurred as primary crystals was examined by Petri, using X-rays. He found that it crystallised in the orthorhombic system: a = 7.69, b = 24.06, c = 12.48 Å. The particular crystal examined had a composition 19 percent copper and 24 percent manganese. Another ternary phase designated 'Y' was found to occur in alloys rich in copper and manganese and was found to be orthorhombic: a = 14.79, b = 12.60, c = 12.43 Å.

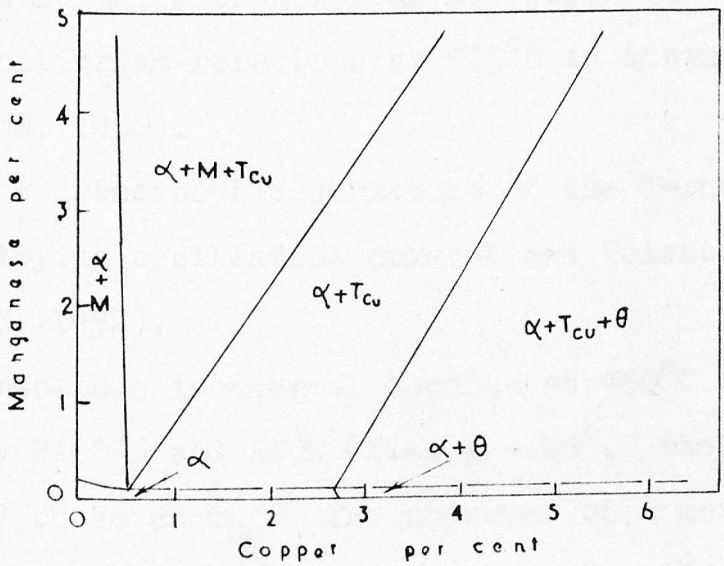
MONDOLFO (1943) studied the system and proposed a liquidus surface showing a region in which primary $(Cu,Mn)Al_4$ separates, extending from $MnAl_4$ on the manganese axis to the eutectic. He did not find any ternary compound.

Aluminium - Copper - Manganese



THE LIQUIDUS SURFACE (Day & Phillips)

(Fig 1-9)



The 460°C Isotherm (Bagchi & Axon)

(Fig 1-10)

A study of the alloys under equilibrium was made by X-rays and Petri's diagram was confirmed as regards phase fields. It was also reported that the section $MnAl_6$-T, Al-T and $CuAl_2$-T were quasibinary (GUERTLER and RASSMANN, 1943).

DAY and PHILLIPS (1948) studied the system over the range 0 - 18 percent manganese and 0 - 8 percent copper and the liquidus surface according to their findings is shown in fig.(1 - 9). They used microscopical and thermal methods for the study of alloys prepared from high purity materials.

Isothermal diagrams at 600, 525 and 400°C were published as a result of the study of equilibrium relations at these temperatures made by employing electrical resistance and microscopical methods. The diagram showing the equilibrium relations at 525°C is shown in fig.(1 - 8) (HOFMANN, 1950).

The orthorhombic structure of the T-phase was confirmed by employing oscillating crystal and Weissenberg techniques (ROBSON, 1952).

Ansolidus isothermal section at 460°C was published in 1954 by BAGCHI and AXON (Fig. 1 - 10). They designated the ternary phase as T_{Cu}. The presence of a metastable phase, G, was reported in alloys annealed at 460°C and the view

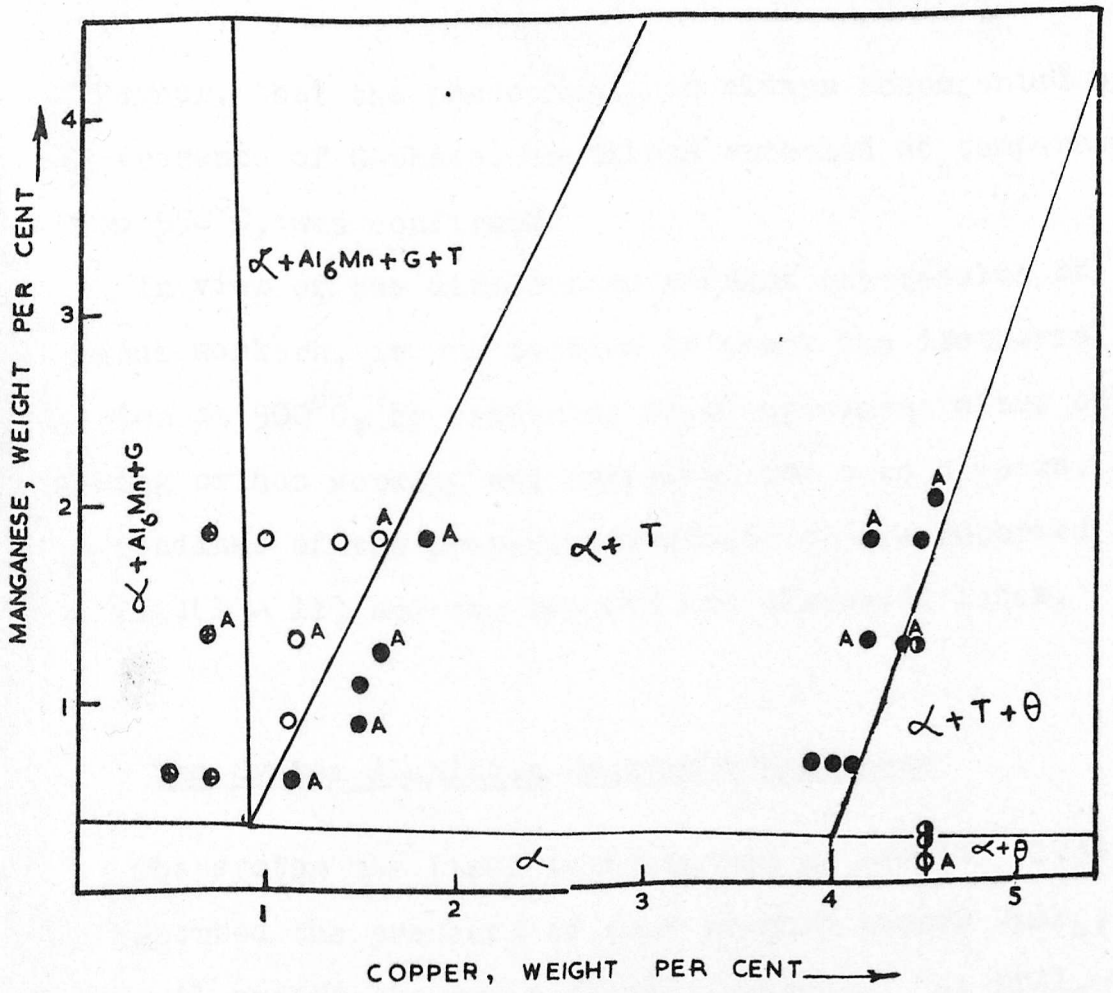


Fig. (1-11) — The Equilibrium Relations in Aluminium Alloys Containing 0 — 5% Copper and 0 — 2% Manganese at 500°C

KEY TO SYMBOLS IN THE PRESENT WORK

- α - (Solid Solution)
- α + Al6Mn + G
- α + T
- α + θ
- α + T + θ
- α + Al6Mn + G + T
- α + T + S
- α + T + θ + S
- α + θ + S

of Raynor, that the phase $MnAl_6$ is always accompanied by the presence of G-phase, in alloys annealed at temperatures below 550°C, was confirmed.

In view of the differences amongst the results of various workers, it was decided to check the isothermal section at 500°C, by examining alloy specimens after cold-working or hot working and annealing for 4 to 5 weeks. The findings of the present investigation are reported in the fig.(1 - 11) and the results are discussed later.

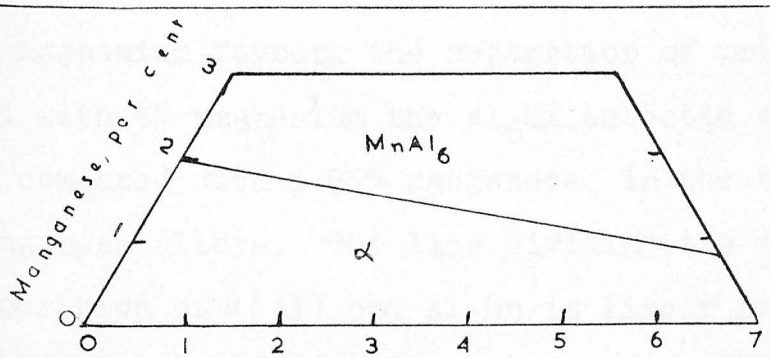
The System Aluminium-Magnesium-Manganese

The system was first investigated by LEEMANN (1938), who reported the presence of four primary phases $MnAl_4$, $MnAl_6$, Al and Mg_5Al_8 and a ternary eutectic: Al-$MnAl_4$-Mg_5Al_8; 26.4 percent Mg, 2.35 percent Mn, 437°C. It was further shown that magnesium additions reduce the field of primary separation of $MnAl_6$, until at about 22% magnesium it completely disappears (fig.1 - 15) (MONDOLFO, 1943).

BUTCHERS et al. (1943) redetermined a number of points in the range 0 - 5% magnesium and 0 - 2% manganese. Fig.(1 - 12) shows the surface of separation and the ~~liquidus isothermal~~. They also showed that the additions

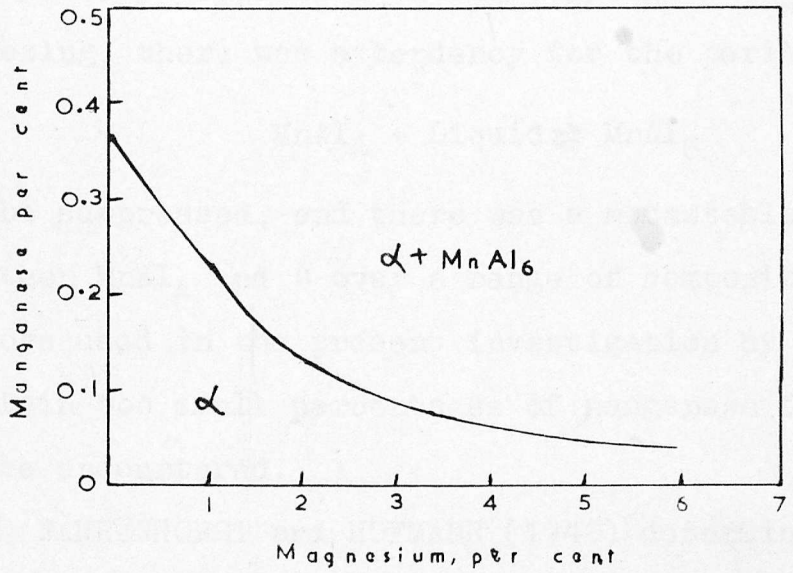
The System

ALUMINIUM–MAGNESIUM–MANGANESE



The Surface of Primary Separation

(Fig 1–12) (Butchars, Raynor, & Hume-Rothery)



The 500°C Isotherm

(Little, Raynor, & Hume-Rothery)

(Fig 1–13)

of magnesium favour the separation of primary Al_6Mn, and with 5% magnesium the Al_6Mn eutectic occurs at 1.04% Mn as compared with 1.97% manganese, in the binary aluminium-manganese alloys. The line dividing the field of primary separation of α(Al) and Al_6Mn is linear and within the experimental accuracy its equation is given by

$$0.186(Mg) + (Mn) = 1.97$$

where (Mg) and (Mn) are the weight percentages respectively

According to Leemann's work, fig.(1 - 15), the phases met with in stable equilibrium are α and compound $MnAl_6$. He stated that, in alloys containing sufficient manganese for primary separation of the compound $MnAl_4$ to occur on freezing, there was a tendency for the peritectic reaction

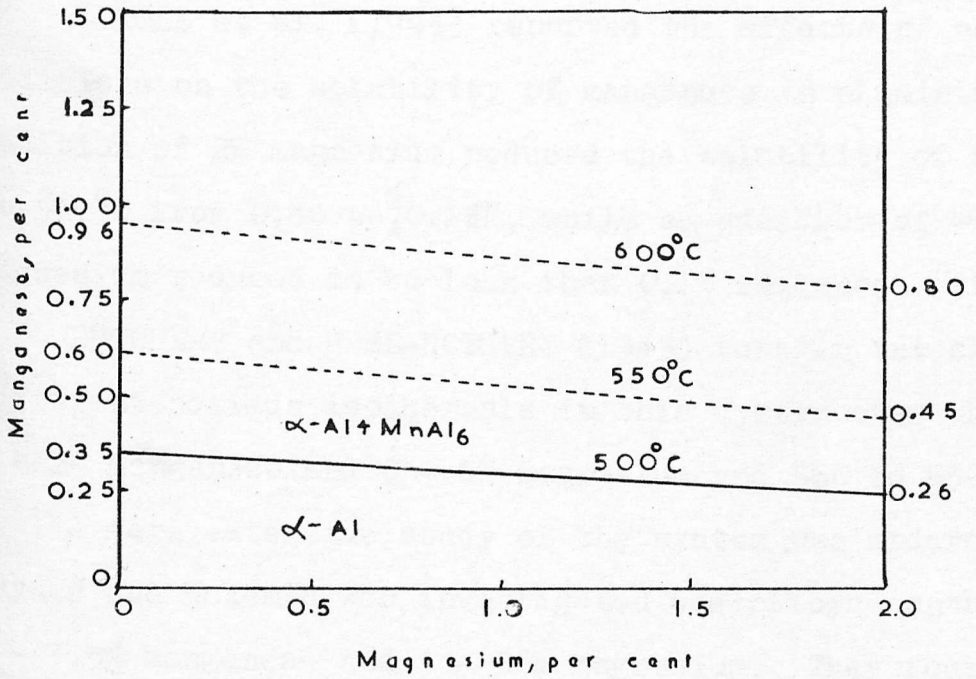
$$MnAl_4 + \text{Liquid} \rightleftharpoons MnAl_6$$

to be suppressed, and there was a metastable equilibrium between $MnAl_4$ and α over a range of composition. The alloys used in the present investigation by the author, contain too small percentages of manganese for this effect to be encountered.

FAHRENHORST and HOFMANN (1940) determined the equilibrium at 500, 550 and 600°C, in alloys containing 0 - 2% manganese and 0 - 2% magnesium. The solubilities

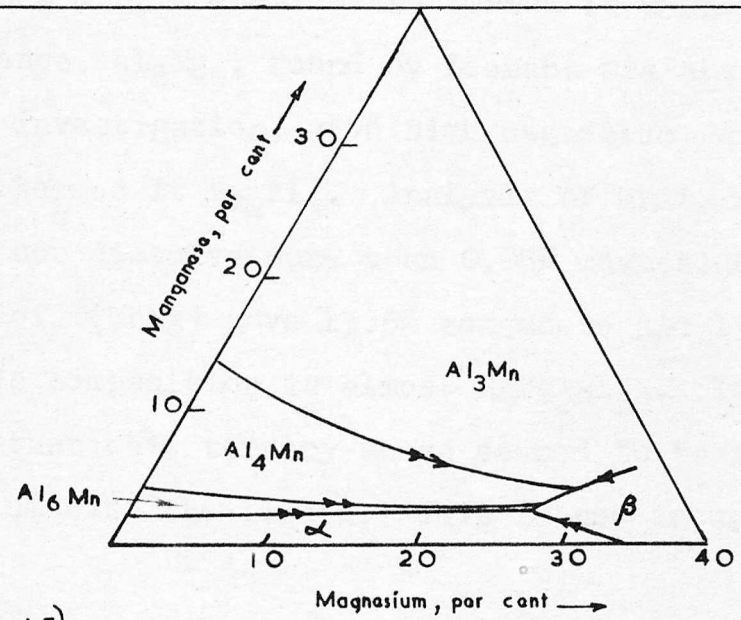
The System

ALUMINIUM–MAGNESIUM–MANGANESE



The 500, 550, & 600°C Isotherms (Fahrenhorst & Hofmann)

(Fig 1–14)



(Fig. 1–15)

Primary Crystallisation in Stable System Al–Mg-Mn

(Leeman)

were determined by electrical resistance methods. Their findings are shown in fig.(1 - 14).

LITTLE et al. (1943) reported the effects of magnesium additions on the solubility of manganese in aluminium. An addition of 2% magnesium reduced the solubility of manganese at 500°C from 0.36 to $<$0.2%, while an addition of 4% magnesium reduced it to less than 0.1% manganese (fig.1 - 13).

BUTCHERS and HUME-ROTHERY (1945) further investigated different solidus isothermals in this system over the range 0 - 2% manganese and 0 - 6% magnesium and 560 to 650°C.

A more extensive study of the system was undertaken by Raynor and Wakeman who investigated the alloys containing 0 - 3.5% manganese and 5 - 36% magnesium. They found a ternary compound in alloys containing higher percentages of manganese and of magnesium and termed it T(MnMg). The binary phase, Al_8Mg_5, found by Leemann was also encountered in their investigation, with high magnesium percentages, but they termed it Mg_2Al_3. Analysis of $MnAl_6$ showed that it could not dissolve more than 0.08% magnesium and the analysis of T(MnMg) gave 13.5% manganese and 13.7% magnesium. The atomic composition is almost $MnMg_2Al_{10}$. It was reported that this ternary phase seemed to be in equilibrium with the liquid. This is not in agreement

with the findings of Leemann, who has reported the constitution in the solid state at the end of solidification (WAKEMAN and RAYNOR, 1948-49).

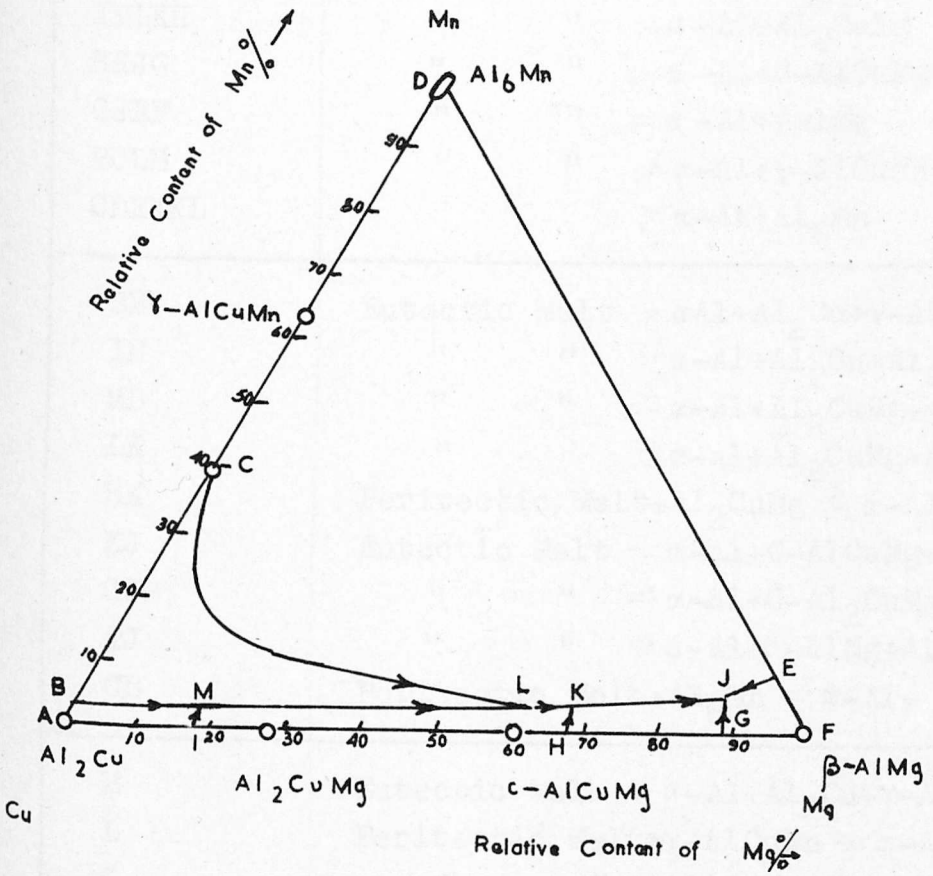
The System Aluminium-Copper-Magnesium-Manganese

Very few investigations of quaternary systems are reported in the literature. The aluminium-copper-magnesium-manganese system has been studied by PHRAGMEN (1950).

In addition to the phases present in the subsidiary ternary systems, PHRAGMEN found one unstable quaternary phase in this system. This is designated Z-AlCuMgMn; it is light grey in colour and does not show birefringence. Z-AlCuMgMn is decomposed by heating an alloy for 80 hours at 490°C. The results of his investigation are summarised in fig.(1 - 16), which consists of six different regions. Within each of these regions, solid aluminium and one other phase separates eutectically from the melt. The following table shows the reactions involved in the regions (melt + two solids), along the boundary lines (melt + three solids) and at the points (melt + four solids).

The System

ALUMINIUM – COPPER – MAGNESIUM – MANGANESE



(Fig 1–16) — The Projection of the Liquidus Surface of the System Al-Cu-Mg-Mn on the Plane Through the Concentration Tetrahedron, Cutting at the Points Shown.

(Phragmen)

Region, line or point	Equilibrium Reaction
ABMI	Eutectic Melt $\rightleftharpoons \alpha$ -Al+Al_2Cu
IMLKH	" " $\rightleftharpoons \alpha$ -Al+Al_2CuMg
HKJG	" " $\rightleftharpoons \alpha$ -Al+C-AlCuMg
GJEF	" " $\rightleftharpoons \alpha$ -Al+βAlMg
BCLM	" " $\rightleftharpoons \alpha$-Al+$\gamma$-AlCuMn
CDEJKL	" " $\rightleftharpoons \alpha$-Al+$Al_6Mn$
BM	Eutectic Melt $\rightleftharpoons \alpha$Al+$Al_2Cu$+$\gamma$-AlCuMn
IM	" " $\rightleftharpoons \alpha$-Al+$Al_2Cu$+$Al_2CuMg$
ML	" " $\rightleftharpoons \alpha$-Al+$Al_2CuMg$+$\gamma$-AlCuMn
LK	" " $\rightleftharpoons \alpha$-Al+$Al_2CuMg$+$Al_6Mn$
HK	Peritectic Melt+$Al_2CuMg \rightleftharpoons \alpha$-Al+C-AlCuMg
KJ	Eutectic Melt $\rightleftharpoons \alpha$-Al+C-AlCuMg+$Al_6Mn$
GJ	" " $\rightleftharpoons \alpha$-Al+C-$Al_2CuMg$+$\beta$AlMg
EJ	" " $\rightleftharpoons \alpha$-Al+$\beta$-AlMg+$Al_6Mn$
CL	Peritectic Melt+$Al_6Mn \rightleftharpoons \alpha$-Al+ AlCuMn
M	Eutectic Melt $\rightleftharpoons \alpha$-Al+$Al_2Cu$+$\gamma$-AlCuMn+$Al_2CuMg$
L	Peritectic Melt+γ-AlCuMn $\rightleftharpoons \alpha$-Al+$Al_2CuMg$+$Al_6Mn$
K	" " +$Al_2CuMg \rightleftharpoons \alpha$-Al+C-AlCuMg+$Al_6Mn$
J	Eutectic Melt $\rightleftharpoons \alpha$-Al+C-AlCuMg+$\beta$AlMg+$Al_6Mn$

CHAPTER II

EXPERIMENTAL PROCEDURE

MATERIALS USED

The materials used in the present investigation were all of high purity since small amounts of other elements might have introduced unwanted phases. The British Aluminium Co. Ltd. supplied the super-purity aluminium. Manganese and copper were added in the form of master alloys, while magnesium was added to the melt in the elemental form. The manganese master alloys were supplied by the British Aluminium Co. Ltd., while copper-hardener was prepared in the foundry by melting electrolytically-refined copper and super-purity aluminium in an alumina-lined crucible. The analyses of the materials used are given below.

	Si	Fe	Cu	Mn	Al
Super Purity Al	0.0010	0.0010	0.0015	-	99.997 (by difference)
Mn-Master Alloy	0.0040	0.0315	0.0015	9.48	Remainder
	0.0065	0.0599	0.0025	9.30	"
Cu-Master Alloy	N.A	N.A	56.10	N.A	"
Super-purity Mg	-	-	-	-	-

CRUCIBLES

It was very important to use crucibles which would not contaminate the melt, in particular to avoid contamination by silicon. Salamander crucibles, lined with pure alumina and 7% fluorspar were used and chemical analyses of typical alloys showed an absence of contamination.

METHODS OF LINING

Pure alumina with 7% added fluorspar was mixed with a thick solution of gum in water. The interior walls of the crucibles were coated with the paste and dried at 110°C; the crucibles were then slowly heated up to 700°C, after which the temperature was raised much more rapidly to 1350°C. Linings made in this way proved capable of withstanding a considerable number of melts, ranging up to twenty, although linings were rather friable and inclined to powder. No difficulties were encountered in removing the shell after each melt.

MELTING FURNACE

Melting of the charges was carried out in a small furnace of the electric resistance type. This method was preferred to gas-melting because of the avoidance of

contamination from combustion products. The maximum temperature could be varied by adjusting the current and thus overheating of the charges, which could lead to severe losses by oxidation, was kept to a minimum.

PRODUCTION OF INGOTS

It was necessary to produce ingots which could be worked and then easily sealed in lengths of glass tubing to undergo prolonged annealing treatments. This put a limit to the ingot diameter. Ingots of quarter-inch diameter were found to be suitable for the purpose. These could be given a light hot or cold working by pressing to form approximately a square cross-section, and then could be sealed in tubing without much difficulty.

The alloys containing higher percentages of manganese tended to crack when cold pressed and were therefore hot worked at about 450°C. The loads used to press the ingots were of the order of 10 tons p.s.i., and it was not necessary to vary them appreciably over the range of alloys made.

QUALITY OF INGOTS

Purity of the ingots and close agreement of the actual composition with the nominal composition was of

vital importance for the constitutional work. The surface qualities could be slightly neglected, but precautions to avoid the entrapment of non-metallic inclusions, which might lead to erroneous results, had to be exercised.

The lining of the crucible served to protect the melt from the impurities which might have been introduced by the crucible material, whilst the temperature control minimised the oxidation and hence oxide inclusions. The oxide skin on the surface of the molten aluminium was disturbed as little as possible and thus loss by oxidation and introduction of oxides into the ingots were further reduced.

MELTING PROCEDURE

Weighed amounts of super purity aluminium were added to a hot crucible and then allowed to melt in the furnace. Use of a hot crucible minimised the time of heating of the charge, thus reducing oxidation. When the aluminium was in the molten state, copper hardener was introduced under the surface of the molten metal by means of a carbon rod: manganese hardener was then added. The use of an alumina rod instead of a carbon rod was preferred for stirring after the addition of manganese hardener, in order to avoid any possibility of the formation of manganese . . .

carbide. Magnesium was added last, in pieces as large as possible, to avoid burning, and then the molten charge was stirred with the graphite rod. In spite of all the precautions, some oxide skin was formed and had to be skimmed off before pouring.

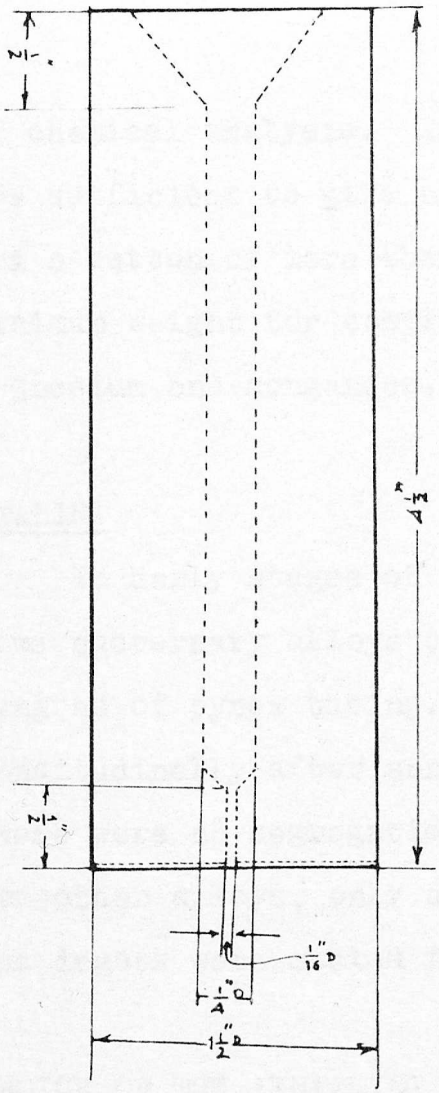
MOULD

Graphite moulds of dimensions shown in fig.(1 - 17) were used.

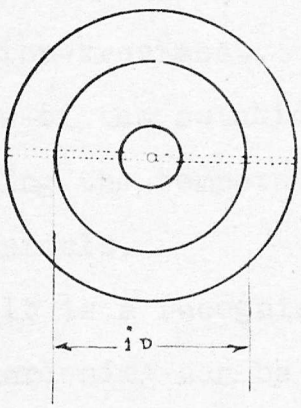
A small hole was drilled in the bottom of the mould for the escape of gases and compressed air. Very fine grooves made on the bottom of the mould served for the escape of the gases from the hole to the atmosphere.

Inverting the mould, and breaking the small wire formed on the bottom due to the flow of the metal through the hole into the groove, removed the ingot from the mould. The ingots were then numbered. No difficulty was encountered in removing the ingots in this way, as long as the inner surface of the mould was not spoiled.

The mould design shows a small head at the top for feeding the metal. This head held a considerable amount of the melt which solidified as a button on the top of the ingot. This button was cut from the ingot and numbered and preserved to take drillings for the purpose



ELEVATION



PLAN

FIG. (1 - 17) — THE MOULD

of chemical analysis. The calculated charge of 25 grammes was sufficient to give an ingot for the microscopical work and a button of more than 12 grammes, the latter being the minimum weight for complete chemical analysis for copper, magnesium and manganese.

SEALING

In early stages of the work, the complete ingots of some quaternary alloys containing 0.6% Mn, were sealed in lengths of pyrex tubing. These alloys were examined longitudinally after annealing and it was confirmed that there were no segregation effects. Subsequently therefore, for other alloys, only small portions from the middle of the ingots were sealed for annealing.

CHOICE OF THE ANNEALING TREATMENT TEMPERATURE

The purpose of this treatment was to obtain equilibrium amongst the phases at the temperature of solution-treatment. It was therefore necessary to make a choice of the solution-treatment temperature before deciding the temperature of the determination of the isothermals.

It is a recognised fact that the best results in age-hardening can be expected when the maximum possible

amounts of alloying elements are dissolved in the solid solution. This means that the solution-treatment should be carried out at a temperature as high as possible. The upper limit to this temperature is fixed by the lowest melting eutectic in a particular system.

The present investigation extends over the range 0 - 6% Cu, 0 - 5% Mg, and 0 - 2% Mn, as these are the maximum percentages of these alloying elements generally met with in Duralumin-type alloys. Within this compositional range, according to NISHIMURA (1937) and URAZOV and PETROV (1946) a eutectic exists in the ternary Al-Cu-Mg system, which melts at 500°C. The more recent work of BROMMELLE and PHILLIPS (1948 - 49) shows that it melts at 507°C, and this is confirmed by the work of HANEMANN and SCHRADER (1952), who quote the eutectic temperature as 506.5°C. Because of the differences amongst the results of the above workers, a determination of the ternary eutectic temperature was thought necessary.

It was also decided to determine the temperature of the quaternary eutectic reported by PHRAGMEN (1950).

Two alloys were made for the determination: the ternary alloy containing nominally 30% Cu and 6% Mg, and the quaternary alloy, 12% Cu, 4% Mg and 2% Mn.

The charges of 100 grammes were made from the weighed

materials and melted in alumina-lined crucibles in a furnace of the electric resistance type. A graphite rod was used to stir the melt and a chromel-alumel thermocouple calibrated against super-purity aluminium (99.997%) was used in conjunction with a Tinsley vernier-potentiometer and a mirror galvanometer to note the rate of change of temperature. The thermocouple was inserted in an alumina sheath and the sheath in turn was in direct contact with the melt.

The ternary Al-Cu-Mg alloy gave an inverse cooling curve with the lowest arrest at 504.0°C, whilst the same alloy showed the lowest arrest at 506.5°C on the inverse heating curve. The cooling curve for the quaternary alloy indicated that the eutectic solidified at 502.5°C, whilst the heating curve confirmed the melting point of the eutectic to be 506.5°C. Thus, there was an appreciable supercooling during solidification in both alloys.

A second consideration of the choice of the solution-treatment temperature was the fact that a large volume of data on the ageing characteristics of Al-Cu-Mg alloys has been compiled by HARDY (1954-55) and CHITTY (1958). These workers solution-treated their alloys at 500°C, which is one of the temperatures generally used in industrial practice. This seems to be a commercially-controllable

temperature without undue danger of partially melting the alloys. It was therefore decided that the quaternary alloys should also be solution-treated at the same temperature so as to obtain comparable results.

ANNEALING TREATMENT

The specimens, sealed in glass tubes, were loaded into an aluminium box which was then covered with an aluminium lid. The box was placed in a large air-circulating furnace of the resistance type, a constant temperature of 500 $\pm 2^{\circ}C$ being maintained by a controller-recorder instrument. The exact temperature was measured by means of a platinum-rhodium thermocouple whose hot-junction was inserted inside the aluminium box.

TIME OF SOLUTION TREATMENT

The diffusion of manganese is sluggish and hence long times of annealing are required for equilibrium. PETRI (1938), used times up to 14 days in determining his isothermal sections in the ternary aluminium-copper-manganese system. AXON (1952-53) who determined sections of the Al-Cu-Mg-Si diagram at $460^{\circ}C$, employed annealing times of up to 3 to 4 weeks: even with these times, it is possible that equilibrium was not reached (COLLINS, 1955).

It was decided, therefore, in the present work to anneal the alloys for an initial time of at least four weeks after mechanical working. The microsections were then examined and, in some cases, alloys were resealed, annealed for a further period of 4 weeks and re-examined. No change in the constitution was detected.

The phase boundaries of the various sections were found to be consistent with one another. Thus, although it cannot be claimed with certainty that equilibrium had been attained, it appears that the conditions approximated to equilibrium.

QUENCHING

The specimens were quenched by rapidly transferring them from the furnace into a large tank containing water. The water was stirred by a rod in order to improve the efficiency of quenching.

Generally, the tubes were found to have been coated by a very thin layer of magnesium during annealing, giving rise to a bluish-purple shining surface. This is a general phenomenon found in the case of alloys containing magnesium which evaporates from the surface at the annealing temperature to condense on the inner surface of the tubes.

PREPARATION OF MICROSECTIONS

Quenched alloys were cut and polished on both top and bottom surfaces on an emery belt. The surfaces were numbered and five, six or more specimens were mounted, as was convenient, in a diakon mounting.

POLISHING

Wet silicon carbide papers of different grades were used for rough polishing. A constant stream of water was passed over the paper while polishing; this served as a lubricant and also removed the grit particles or silicon carbide particles which could otherwise scratch the specimen-surface unevenly.

The sequence of polishing operations was as follows:

i) First polishing on the lathe by taking a very fine cut on the surface of the mounting.

ii) Rubbing on a 300 grade paper in one direction only.

iii) Polishing on a 400 grade silicon carbide paper at a direction perpendicular to that in the second step.

iv) Polishing in a direction 90^{o} to that in the third step on an alumina-wax pad, the pad being frequently cleaned by benzene so that it would not permanently retain undesired particles which could scratch the specimen surface.

v) Cleaning the mounting thoroughly in benzene and polishing on a rotating wheel covered with a selvyt cloth, smeared with diamond paste of 0 - 2 micron grade. 3 in 1 cinnamon oil was used as a lubricant. This polishing was found quite satisfactory and the diamond dust once used would generally last for continuous work of about a week, giving a fairly economic method. (Sometimes auto-polishing was used).

vi) Whenever it was desired to take a photomicrograph, a hand finish was necessary on a selvyt cloth covered with magnesia (Silvo polishing was sometimes used, but it tended to etch some constituents and to produce corrosion of certain phases, in particular the ternary constituent S). Heavy magnesia was ground in a mortar and then allowed to stand in a long measuring cylinder for at least 2 to 3 hours. Heavier particles settled down while a solution containing very fine particles was siphoned from the top 3 or 4 inches. This was preserved in a stoppered bottle and used for the final polishing of the specimens.

Sometimes it was found convenient to polish the specimens on a diamantine wheel before polishing on a diamond wheel. This intermediate step reduced the time of polishing and the results were quite consistent.

CLEANING

After polishing by hand on a cloth, specimens were cleaned under a stream of water, but in cases where polishing on a diamond wheel was the final step, they were cleaned in benzene or acetone and dried with methyl alcohol. Acetone cleaning was preferred as benzene tended to give a greasy surface. The specimens were dried with a hot-air blast and were then ready for microscopical examination.

MICROSCOPICAL EXAMINATION

The transverse sections of the central portions of the ingots were examined under the microscope at different magnifications in the etched and unetched conditions, the etchant being used as found convenient.

MICROSCOPE AND LIGHT SOURCE

A binocular microscope was used in collaboration with high intensity light. Generally, the light was filtered through a "Wratten filter" or a ground glass. This source of light was found to be very useful in differentiating between the phases.

SCOPE OF THE INVESTIGATION AND MICROGRAPHY OF ALLOYS

It was decided to carry out the study over the range

0 - 6% Cu, 0 - 5% Mg and 0 - 2% Mn. Within the range of compositions studied, six phases were identified. They may be listed as follows.

1) α -(Aluminium solid solution)-Fig.1 - 18.

This formed the continuous phase in all the alloys investigated. It contains some copper and manganese in the ternary alloys and also some magnesium in the quaternary alloys. Variations in the copper or magnesium contents did not show any detectable variations in the appearance in the unetched condition. It is unattacked by all the etchants used in the present work.

2) ($MnAl_6$) - Fig.1 - 18

This constituent retains, in the ternary and quaternary alloys, the characteristic crystal habit which it exhibits in the binary alloys of the aluminium-manganese system. The crystals are irregular in outline, purplish-pink in colour and are slightly attacked by dilute sodium hydroxide, 0.5% hydrofluoric acid or Keller's reagent.

3) G($MnAl_{12}$) Fig.1 - 18

This metastable phase was always present with Al_6Mn. It is lighter in colour as compared to Al_6Mn and is outlined by 0.5% HF. Both the phases are similar in crystal habit.

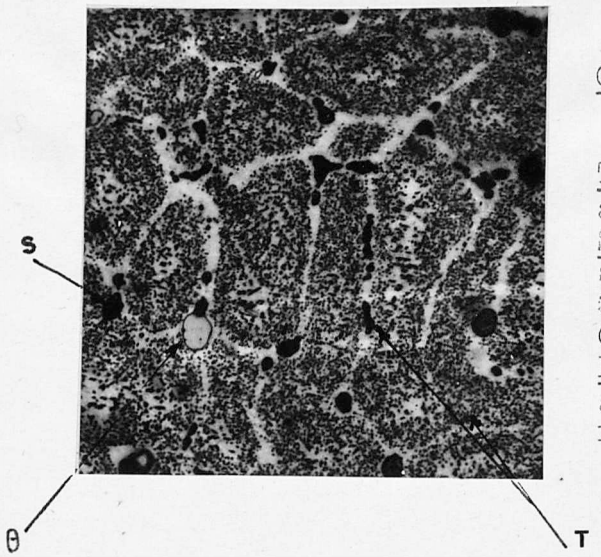


Fig (1-20)
COMPOSITION: 6.02% Cu
2.35% Mg
and 1.20% Mn
TREATMENT: Annealed at 500°C for 5 weeks.
STRUCTURE: α(solid solution), s(Al_2CuMg) θ(Al_2Cu) and T($Al_{12}CuMn_2$)
ETCHANT: 10.0% NaOH at 50°C for 2 min.
x 600.

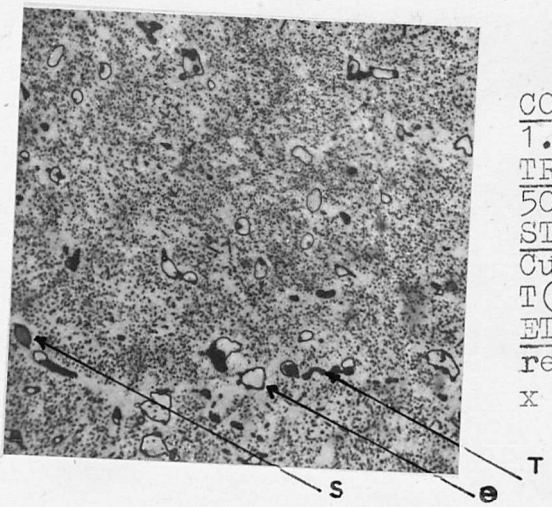


Fig.(1-19)
COMPOSITION: 6.0% Cu, 1.8% Mg and 1.8% Mn.
TREATMENT: Annealed at 500°C for 5 weeks.
STRUCTURE: α, S(Al_2CuMg), θ(Al_2Cu) and T($Al_{12}CuMn_2$)
ETCHANT: Keller's reagent for 25 secs.
x 600.

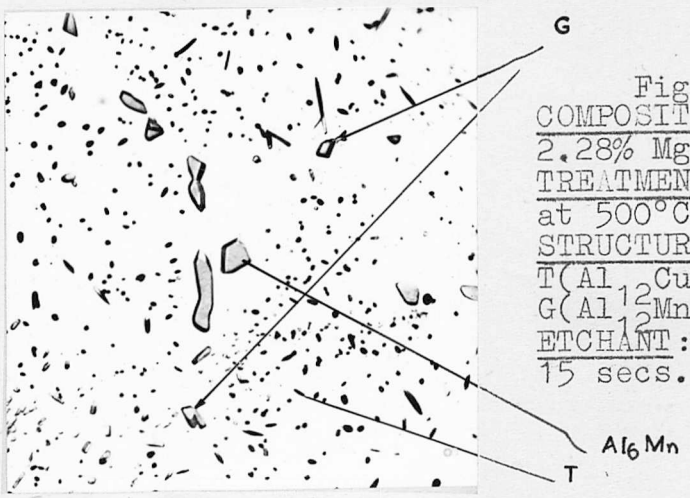


Fig.(1-18)
COMPOSITION: 1.0%Cu, 2.28% Mg, 1.2% Mn
TREATMENT: Annealed at 500°C for 5 weeks.
STRUCTURE: Al_6Mn, T($Al_{12}CuMn_2$) and G($Al_{12}Mn$)
ETCHANT: 0.5% HF. 15 secs. x 1250.

4) θ($CuAl_2$) Fig.1 - 19

In the unetched condition, it is pale pink in colour and forms round-shaped globules on long annealing. It is not attacked by HF or acid mixture, but can be readily confirmed by the ferric nitrate etch, which darkens it.

5) T($Al_{20}Cu_2Mn_3$ or $Al_{12}CuMn_2$) Fig.1 - 19

It is more rounded in outline than $MnAl_6$ and is rather darker in colour in the unetched condition. It is darkened by hydrofluoric acid or the mixed-acid etch.

6) S(Al_2CuMg) Fig.L - 20

It is very similar in habit, colour and etching behaviour to $CuAl_2$. With experience S and θ can be distinguished from one another in the unetched specimens as the former is slightly darker and often more in relief.

The following table summarises the etching behaviour of the above mentioned constituents.

Constituent	$Fe(NO_3)_3$ 25%; 30sec. by Swabbing	HF 0.5% 15 secs. Swabbing	HNO_3, 25% 160°F; 40 secs. immersion	Acid Mixture 0.5% HF 1.5% HCl 2.5% HNO_3 15 secs. immersion	NaOH, 10% 160°F. 5 secs. immersion	H_3PO_4, 10% 2 mins. immersion
$\theta(CuAl_2)$	Dark brown to Black	Un-attacked	Black	Un-attacked	Light to dark Brown	Un-attacked
$S(CuMgAl_2)$	Black	Slightly Brown	Black	Slightly dark Brown	Black	Brown
$MnAl_6$	Un-attacked	Slightly darkened	Un-attacked	Un-attacked	Brown to Blue	Un-attacked
$G(Al_{12}Mn)$	Un-attacked	Outlined	Un-attacked	Un-attacked	Un-attacked	Un-attacked
$T(Al_{20}Cu_2Mn_3)$	Un-attacked	Brown to dark	Un-attacked	Dark Brown	Dark Brown	Un-attacked

Five quaternary isothermal sections at a constant percentage of one of the elements were determined: of these, three were at constant manganese and two at constant copper contents. One ternary section, aluminium-copper-manganese, was also studied. All the isothermal sections were investigated at 500°C.

The ranges of composition were as follows:

1) 0 - 6% Cu, 0 - 5% Mg and 0.6% Mn - quaternary
2) 0 - 6% Cu, 0 - 5% Mg and 1.2% Mn - "
3) 0 - 6% Cu, 0 - 5% Mg and 1.8% Mn - "
4) 0 - 2% Mg, 0 - 2% Mn and 3.0% Cu - "
5) 0 - 2% Mg, 0 - 2% Mn and 4.5% Cu - "
6) 0 - 5% Cu, 0 - 2% Mn - - ternary

The three sections at constant manganese contents were taken at 0.6, 1.2 and 1.8% as representative of the equilibrium relations over the range 0 - 6% Cu, 0 - 5% Mg and 0 - 2% Mn. The alloys for age-hardening were then chosen with constant content of copper at 3 and 4.5% and therefore, two more quaternary sections at 3 and 4.5% copper contents were investigated to assist the analysis and understanding of the age-hardening characteristics.

Altogether about 200 alloys were made to determine the equilibrium in various sections and the summary of their study is given in the diagrams in the next chapter.

The nominal compositions of the alloys are tabulated in the appendix II. The alloys, which were chemically analysed by the British Aluminium Co. Ltd., have been marked by the letter A, whilst those marked by the letters 'N.A' were not analysed.

It was found that nominal compositions were in reasonable agreement with the values reported by the chemical analysis and therefore only critical alloys, deciding the positions of the boundary lines were sent for analysis.

The degree of accuracy of the nominal compositions may be taken as $\pm 0.1\%$.

CHAPTER III

RESULTS, DISCUSSION AND CONCLUSIONS

THE TERNARY SYSTEM ALUMINIUM-COPPER-MANGANESE

In the alloys over the range of composition 0 - 5% Cu, 0 - 2% Mn. The phases derived from the binary systems aluminium-copper and aluminium-manganese and also the ternary phase T, first reported by PETRI (1938), were found. Thus, altogether five phases were identified: α-aluminium solid solution, ($CuAl_2$) from the aluminium-copper system, (fig.1 - 1), Al_6Mn from the aluminium-manganese system (fig.1 - 3), G($Al_{12}Mn$) the binary phase reported as metastable, and the ternary phase T ($Al_{20}Cu_2Mn_3$) or ($Al_{12}CuMn_2$) from the aluminium-copper-manganese system (fig.1 - 7).

The microscopical examination of the alloys annealed at 500°C, showed the phase fields occurring in this isothermal section to be α-solid solution, (α+Al_6Mn+G), (α+Al_6Mn+G+T), (α+T), (α+T+θ) and (α+θ). The general form of the diagram is in accordance with the isothermal sections at 400 and 525°C, investigated by HOFMANN (1950) and with the isothermal at 460°C reported by BAGCHI and AXON (1954). HOFMANN did not find the G phase which, however, was reported by the latter workers to accompany

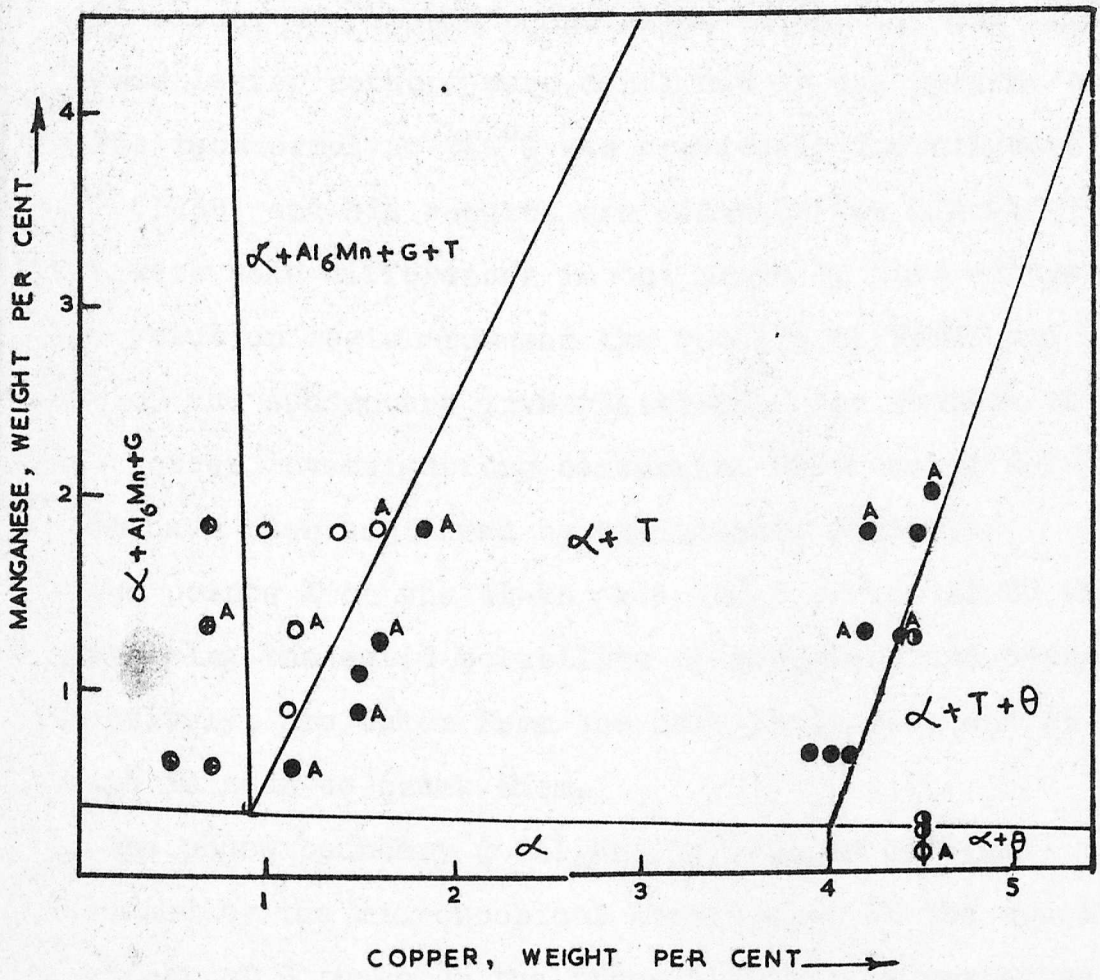


Fig. (1–1) — The Equilibrium Relations in Aluminium Alloys Containing O — 5% Copper and O — 2% Manganese at 500°C

KEY TO SYMBOLS IN THE PRESENT WORK

- α - (Solid Solution)
- α + Al6Mn + G
- α + T
- α + θ
- α + T + θ
- α + Al6Mn + G + T
- α + T + S
- α + T + θ + S
- α + θ + S

in all cases, the stable phase Al_6Mn at 460°C. The findings of these latter authors were confirmed in the present work.

The isothermal at 500°C was previously investigated by PETRI (1938) and his results are shown in the fig.(1 - 7). There were some differences in the shape of the α-aluminium solid solution region between the results of PETRI and those of the subsequent investigations. The results of these latter investigations concerning the α-solid solution region have been confirmed by the present author.

1. The points X on the Al-Mn axis and Y on the Al-Cu axis representing the solid solubility of manganese and copper respectively, are taken from the data available, and no attempt is made to check them.

2. The phase boundary $(\alpha + Al_6Mn + G)/(\alpha + Al_6Mn + G + T)$ is bracketted by the microscopical examination of the specimens. The effect of G phase on the phase boundary is neglected, and the latter is drawn in the direction of the point Al_6Mn on the Al-Mn axis, assuming that Al_6Mn has a negligible homogeneity range.

3. It was extremely difficult to identify Al_6Mn and G or T, whenever the percentage of manganese was just in excess of the solid solubility limit because of the U constituent formed by these phases. Pin-holes and U constituent may easily be mistaken for one another in

alloys annealed at 500°C. It was therefore decided to draw the phase boundary limiting the α-solid solution region by interpolation or extrapolation from the results of the previous workers. The phase boundaries $\alpha/(\alpha+Al_6Mn+C)$, $\alpha/(\alpha+T)$ and $\alpha/(\alpha+\theta)$ are, therefore, not closely bracketted. The solubility of manganese seems to be less than 0.2% in the alloys containing more than 3% Cu.

4. The phase boundary $(\alpha+\theta)/(\alpha+T+\theta)$ is drawn in the direction of the point $CuAl_2$ on the Al-Cu axis, neglecting the homogeneity range of θ.

5. The composition of the ternary phase T is found to vary. However, the actual positions of the two points representing $Al_{20}Cu_2Mn_3$ and $Al_{12}CuMn_2$ are not widely separated (fig.1 - 7).

The present work on the quaternary system tended to show that the formula for the T-phase may be $Al_{12}CuMn_2$. The phase boundaries $(\alpha+Al_6Mn+T)/(\alpha+T)$ and $(\alpha+T)/(\alpha+T+\theta)$, beyond the portions determined by bracketting were, therefore, drawn in the direction of the point $Al_{12}CuMn_2$.

The results of the microscopical examination are summarised in the fig.(1 - 11). The phase boundaries are reasonably bracketted by those alloys, of which critical ones were chemically analysed.

THE QUATERNARY ISOTHERMALS

Representation of the System

A four-component system has four subsidiary ternary and six subsidiary binary systems. Alloy compositions in each of these systems may be plotted on triangular diagrams, and the quaternary system may in turn be represented by a regular tetrahedron, the faces of which are the triangular diagrams of the four ternary systems. This method of describing the compositions of a quaternary system was first suggested by ROOZEBOOM (1894) and has been the main method used to represent the isothermal equilibria in the quaternary alloys.

If the content of one of the components is constant, the contents of the remaining three components may then be represented by an equilateral triangle, which forms a section through the complete concentration tetrahedron. The temperature axis may then be erected at right-angles to the triangle mentioned (HANEMANN and SCHRADER, 1943).

The isothermals for quaternary alloys have generally been represented by keeping the content of one of the components constant. This method gives a picture of the equilibrium relations amongst the various phases of the quaternary system, represented on a two-dimensional

diagram. In the present investigation, isothermal equilibrium relations were studied in two ways; by keeping the manganese content constant and varying the percentages of copper and magnesium, and, (2) by keeping the copper content constant and varying the manganese and magnesium contents. Thus, the sections at constant manganese content lie in the planes parallel to the aluminium-copper-magnesium triangle of the tetrahedron, the corners of which represent 100 percent of aluminium, copper, magnesium and manganese respectively; the constant copper sections lie in the planes parallel to the aluminium-magnesium-manganese triangle of the above tetrahedron. The intercepts made by these planes on the Al-Mn and Al-Cu axes represent the respective constant manganese or constant copper contents of the isothermals.

Although the section formed by such planes through the complete tetrahedron is represented by an equilateral triangle, the results of microscopical examination of the quaternary alloys are generally represented on rectangular co-ordinates, in cases where the percentages of the three components are very small, as compared with that of the main component of the system.

500°C ISOTHERMAL SECTIONS AT CONSTANT MANGANESE CONTENTS

Results

In all, three sections were studied, keeping the manganese content constant at 0.6, 1.2 and 1.8% respectively, over the range 0 - 6% copper and 0 - 5% magnesium.

The Phases Identified

Only the phases derived from the subsidiary binary and ternary systems were found in these alloys. Thus the six phases present were: α-aluminium solid solution, $\theta(CuAl_2)$, Al_6Mn, $G(Al_{12}Mn)$, $T(Al_{20}Cu_2Mn_3)$ or $(Al_{12}CuMn_2)$ and $S(Al_2CuMg)$.

The general forms of all the three sections are very similar. Microscopical examination of the alloys showed that adding various amounts of manganese to the ternary Al-Cu-Mg system introduces the phases Al_6Mn, $G(Al_{12}Mn)$ and T.

The results of the microscopical examination are summarised in the figs(1 - 21), (1 - 22) and (1 - 23) for the 0.6, 1.2 and 1.8% constant manganese sections respectively.

It may be seen that no single phase field, as present

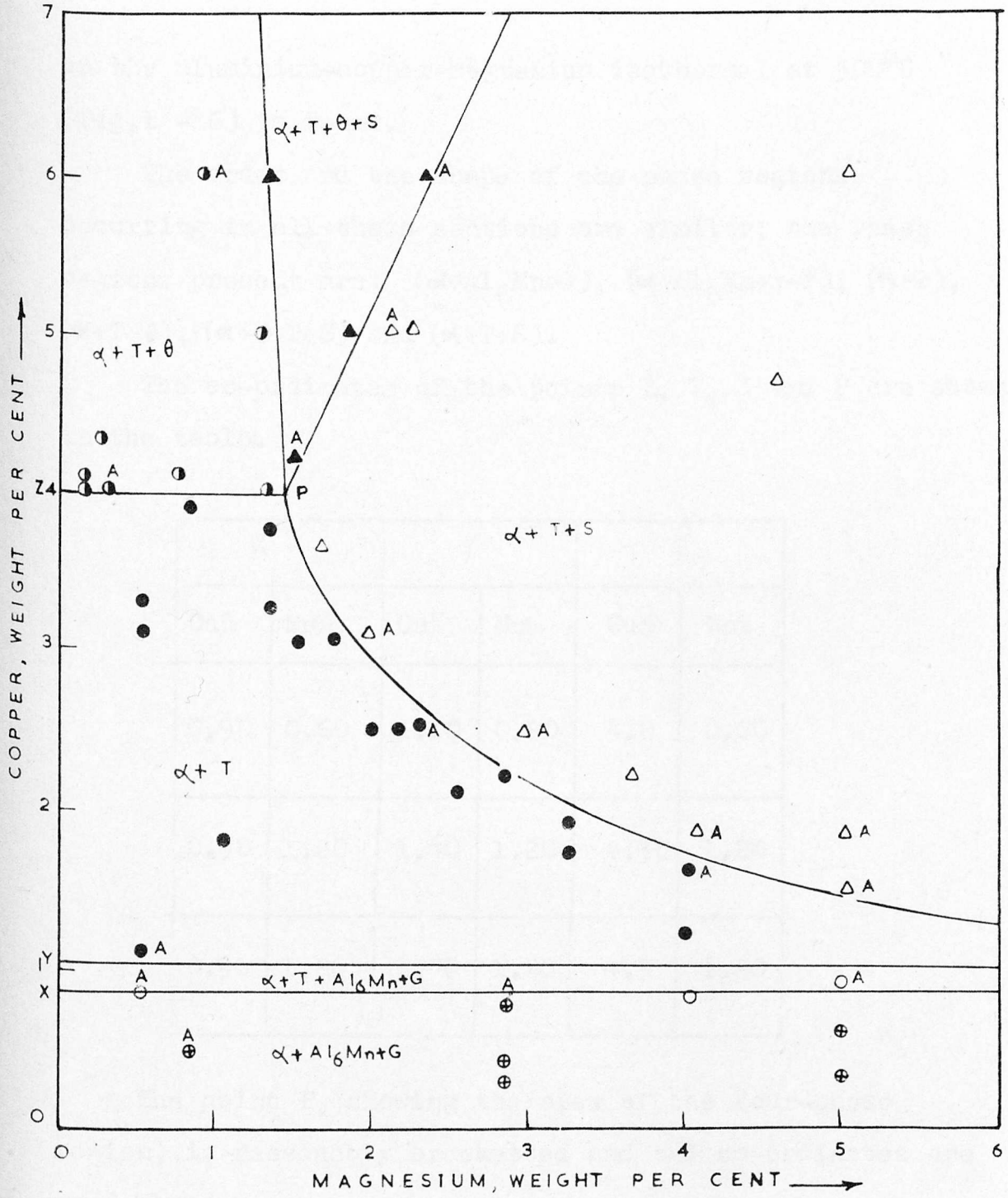


Fig. (1–21)— The Equilibrium Relations in Aluminium Alloys Containing 0–6 p.c. Copper 0–5 p.c. Magnesium & 0.6 p.c. Manganese at 500° C

in the aluminium-copper-magnesium isothermal at 500°C (fig.1 - 6) is found.

The order and the shape of the phase regions occurring in all these sections are similar; the phase regions present are: (α+Al_6Mn+G), (α+Al_6Mn+G+T), (α+T), (α+T+θ), (α+θ+T+S) and (α+T+S).

The co-ordinates of the points X, Y, Z and P are shown in the tables.

X		Y		Z	
Cu%	Mn%	Cu%	Mn%	Cu%	Mn%
0.90	0.60	1.10	0.60	4.0	0.60
0.90	1.20	1.40	1.20	4.30	1.20
0.90	1.80	1.70	1.80	4.5	1.80

The point P, showing the apex of the four-phase region, is reasonably bracketted and the co-ordinates are as follows:

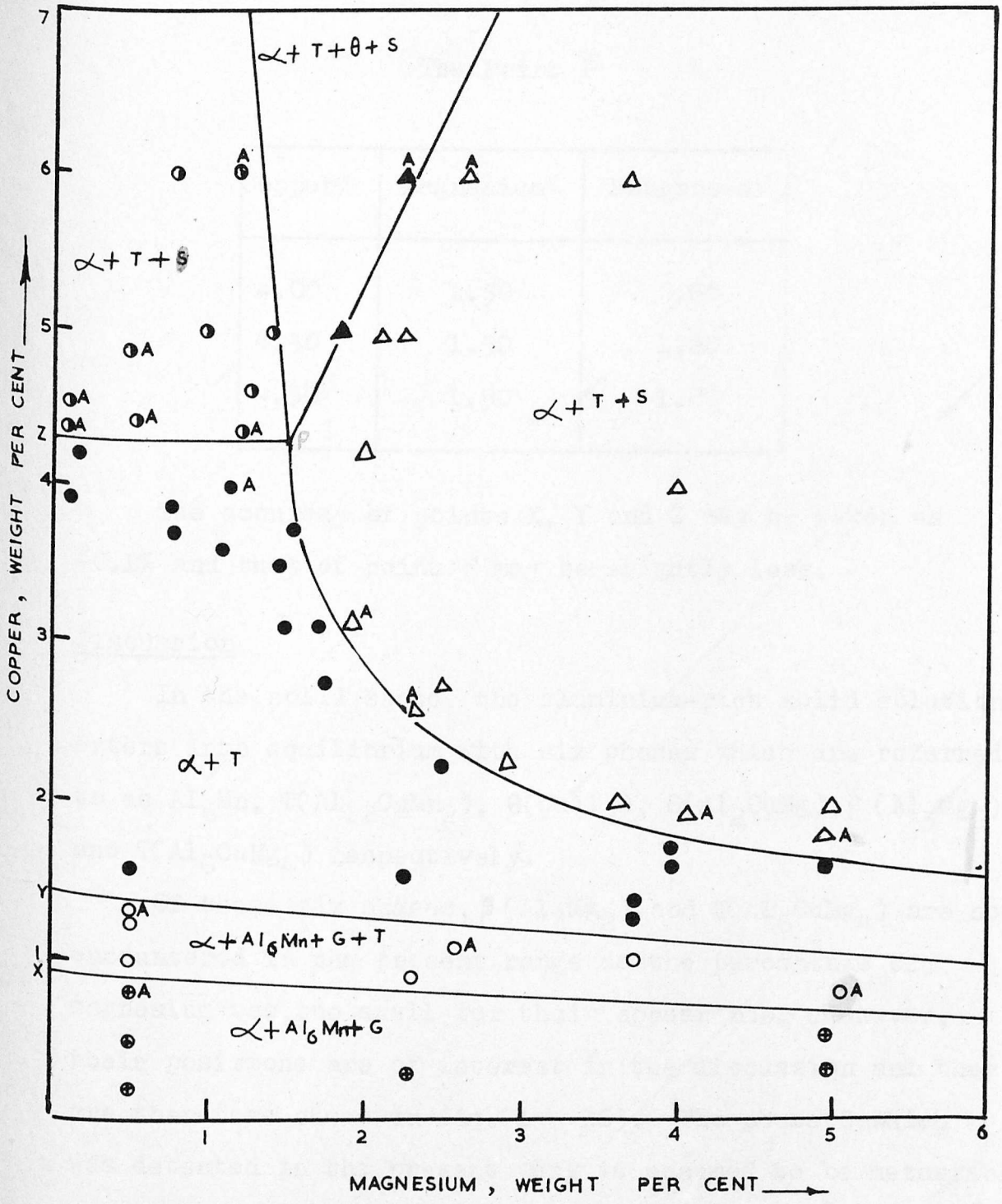


Fig. (1—22) —— The Equilibrium Relations in Aluminium Alloys Containing 0—6% Copper, 0—5% Magnesium and 1.20% Manganese at 500°C

The Point P

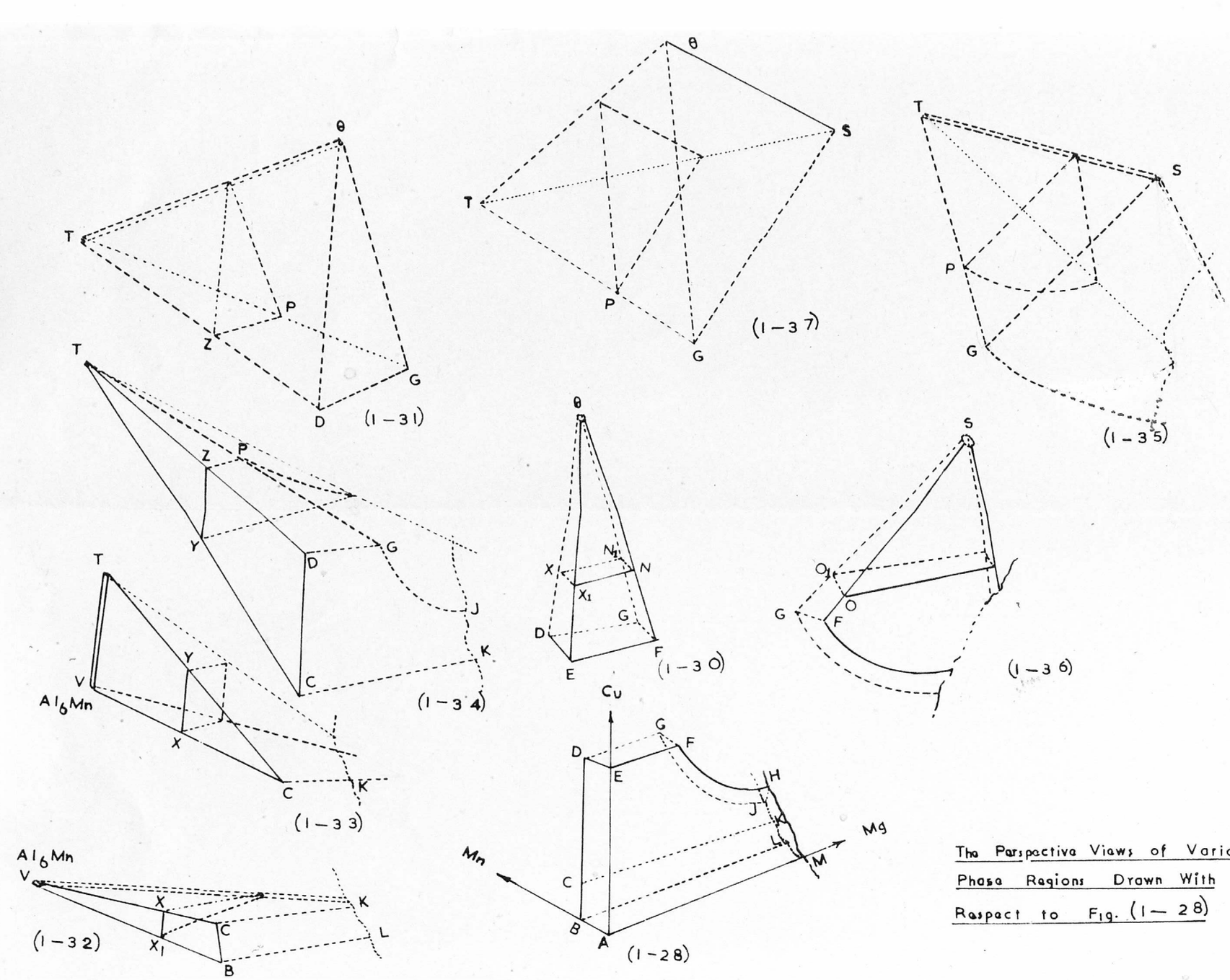
Copper%	Magnesium%	Manganese%
4.00	1.50	0.60
4.30	1.50	1.20
4.50	1.50	1.80

The accuracy of points X, Y and Z may be taken as $\pm$0.1% and that of point P may be slightly less.

Discussion

In the solid state, the aluminium-rich solid solution enters into equilibrium with six phases which are referred to as Al_6Mn, $T(Al_{12}CuMn_2)$, $\theta(CuAl_2)$, $S(Al_2CuMg)$, $\beta(Al_3Mg_2)$ and $T(Al_6CuMg_4)$ respectively.

Of these six phases, $\beta(Al_3Mg_2)$ and $T(Al_6CuMg_4)$ are not encountered in the present range as the percentage of magnesium was too small for their appearance. However, their positions are of interest in the discussion and they are therefore shown in fig.(1 - 26). The phase G which was detected in the present work is assumed to be metastable throughout the discussion and though it is referred to in describing the phase regions and the phase boundaries, its



The Perspective Views of Various Phase Regions Drawn With Respect to Fig. (1—28)

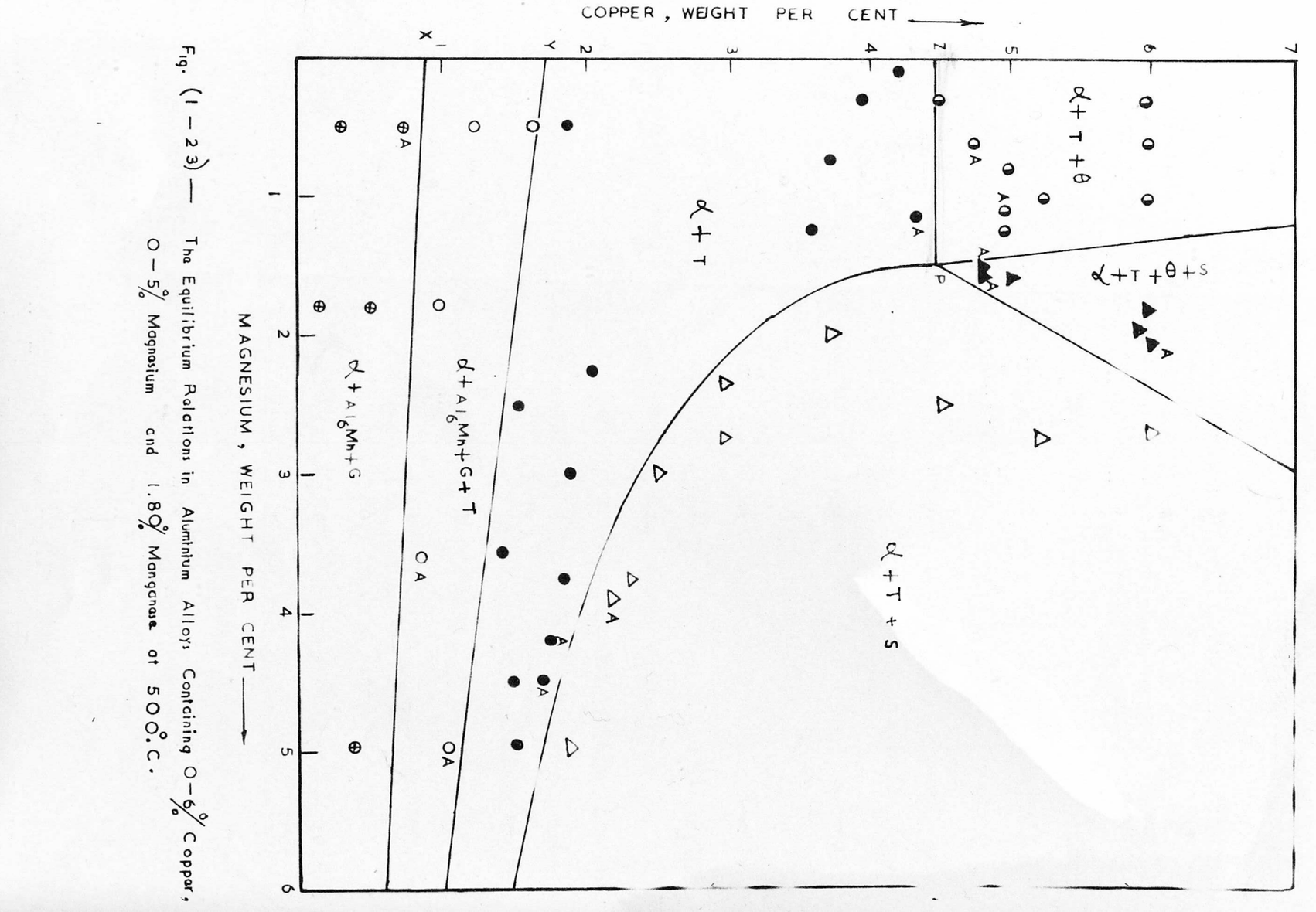


Fig. (1—23) — The Equilibrium Relations in Aluminium Alloys Containing 0—6% Copper, 0—5% Magnesium and 1.8% Manganese at 500°C.

effect on them was not studied.

Fig.(1 - 26) shows the general equilibrium relations of these phases. Two-phase regions are represented by rods joining the phases in question, three-phase regions by laminae enclosed by such rods, and the four-phase regions by the tetrahedra formed by the tie-lines joining the phases. The compositions of the phases are taken from the data available. In the case of the T phase, where the data are rather conflicting, the composition given by the formula $Al_{12}CuMn_2$ is taken for the present work.

Fig.(1 - 27) shows the 500°C isothermals in the three ternary systems drawn on the faces of the tetrahedron in the aluminium-rich corner. The four corners of the tetrahedron represent 100 per cent of each element, respectively. The α-solid solution region as seen from the aluminium corner with aluminium-copper-magnesium as the basal triangle is shown in the perspective view of this space model.

For practical purposes, over the small compositional range of the three components of the system the sections through such a tetrahedron are generally shown on rectangular co-ordinates. The usual system is, therefore, followed in the presentation of the present work.

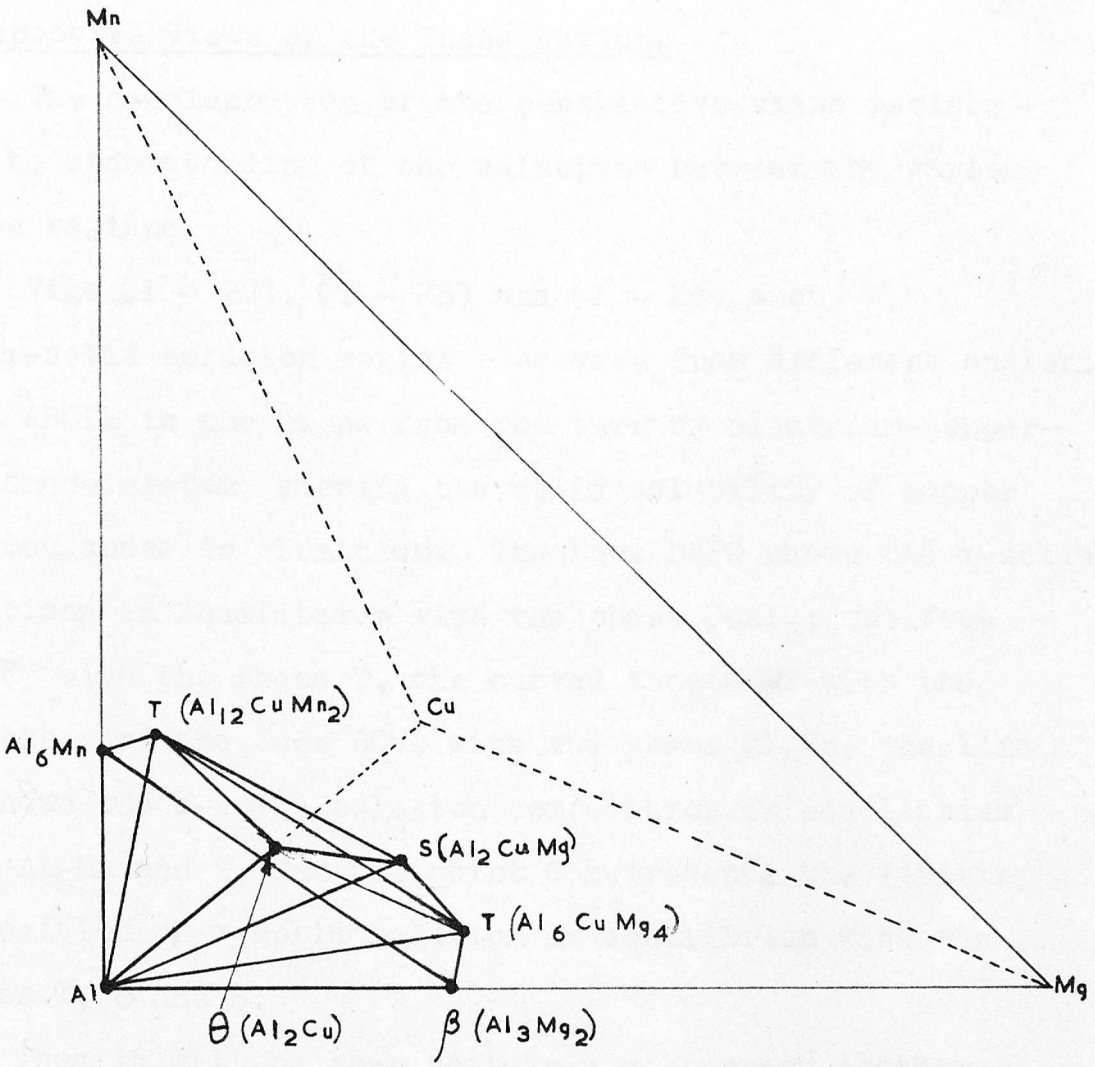


FIG. (1 – 26) — ALUMINIUM CORNER OF THE SYSTEM AIUMINIUM–COPPER – MAGNESIUM – MANGANESE SHOWING VARIOUS PHASE REGIONS IN THE SOLID STATE

Perspective Views of the Phase Regions

The consideration of the perspective views assists in the understanding of the relations between the various phase regions.

Figs.(1 - 27), (1 - 28) and (1 - 29) show the α-solid solution region as seen from different angles.

ABCDE is the plane from the ternary aluminium-copper-manganese system, showing the solid solubility of copper and manganese in aluminium. The face DEFG shows the α-solid solution in equilibrium with the phase $CuAl_2$; the face CDGJK, with the phase T, the curved face GJHF with the S-phase, and the face BCKL with the phase Al_6Mn; the line CK shows the α-solid solution composition in equilibrium with Al_6Mn and T, and the point G represents the limiting composition of α-solid solution in equilibrium with the phases T, θ and S.

Thus it will be seen that, in a quaternary isothermal, α-solid solution in equilibrium with a single phase is represented by a plane, with two phases by a line and with three phases by a point.

The limiting α-solid solution is of great importance in the present investigation, as it will be used to analyse the age-hardening results.

Considering the phase rule as applied to metallic

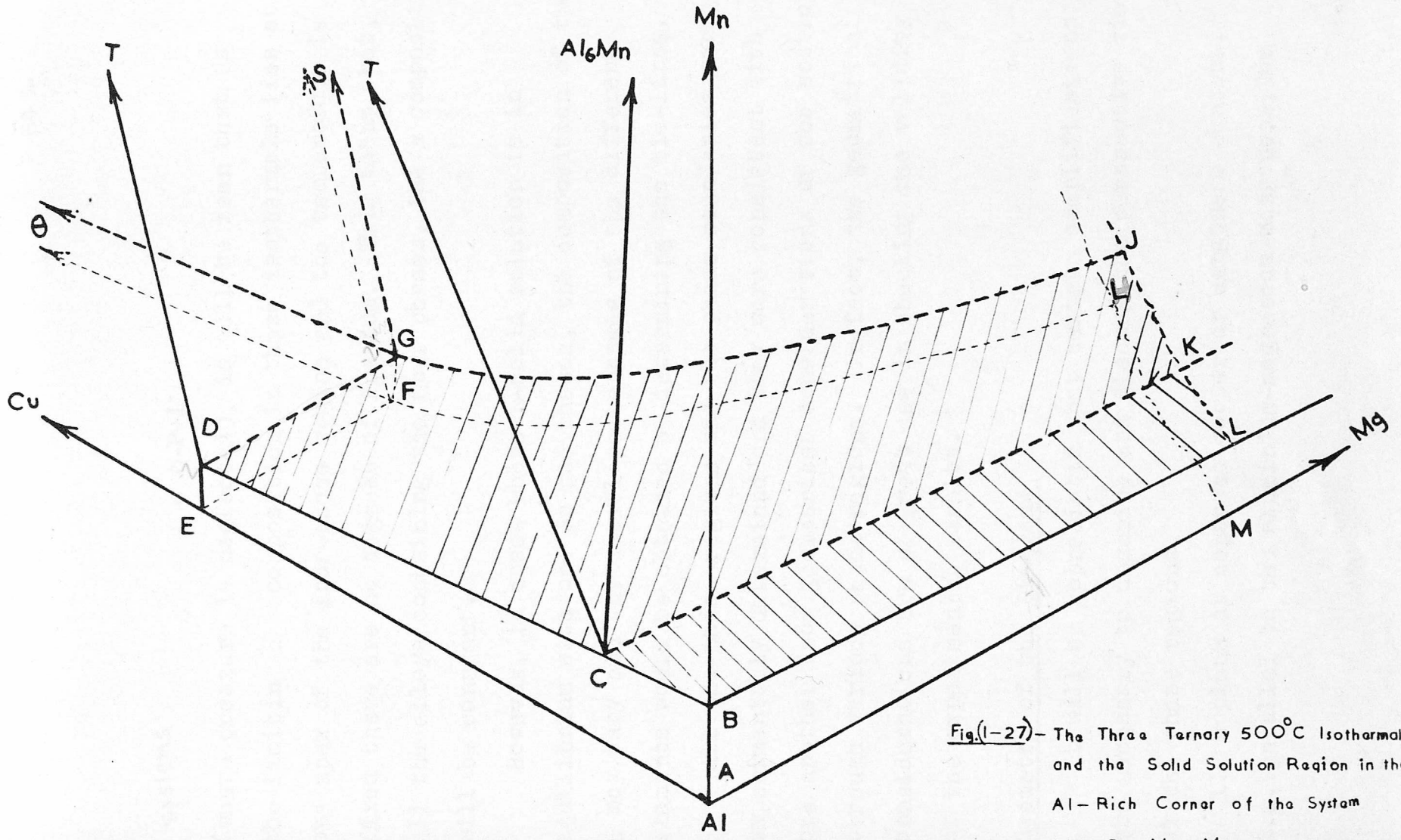


Fig.(1-27)- The Three Ternary 500°C Isothermals and the Solid Solution Region in the Al-Rich Corner of the System Al-Cu-Mg-Mn.

systems

$$f = C-P+1$$

(where pressure is neglected), it will be seen that as the limiting α composition in these isothermals lies at one apex of the four-phase region and the temperature is fixed there are no degrees of freedom. This means that, in all the alloys containing the four phases, the α composition will be constant.

However, in cases where α-solid solution is in equilibrium with one or two phases, the composition of the α may vary and the actual percentages of the different elements would be obtained by determining the tie-lines.

All the phase regions and the phase boundaries were experimentally determined and they were consistent with one another from geometrical considerations of the sections through various phase regions. In fact, the geometrical considerations are of great use in checking the validity of the experimental results.

Geometry of the Diagrams

It will be appreciated that certain simplifications are necessary to describe and discuss the perspective views of the phase regions.

1. A plane at constant copper or manganese content, i.e. parallel to the aluminium-magnesium-manganese, or

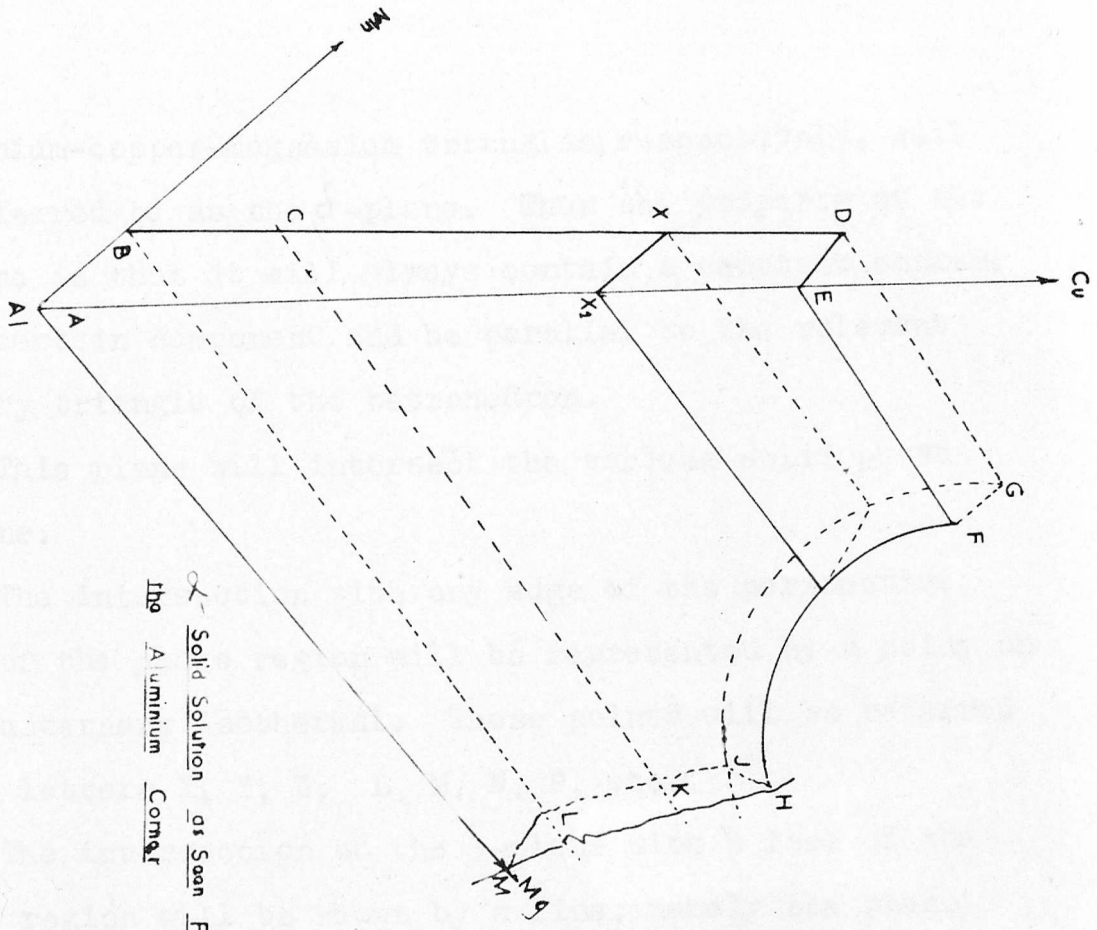


Fig (1 – 28)

α – Solid Solution as Seen From the Aluminium Corner

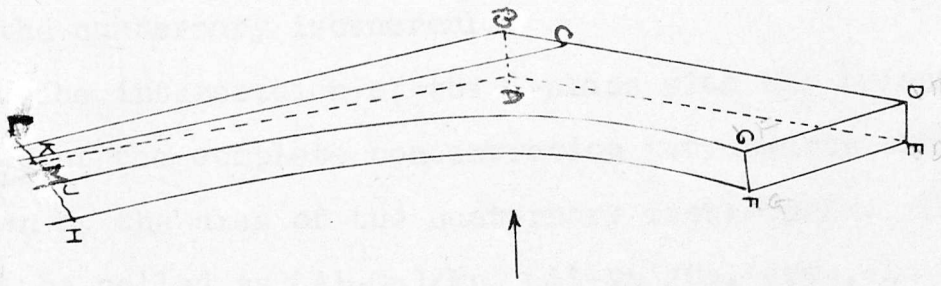


Fig (1 – 29)

α – Solid Solution, as Seen From Within the Tetrahedron Looking Towards the Aluminium Corner.

aluminium-copper-magnesium triangles, respectively, will be referred to as the δ-plane. Thus the property of the δ-plane is that it will always contain a constant content of a certain component and be parallel to the relevant ternary triangle of the tetrahedron.

This plane will intersect the various solid phase regions.

2. The intersection with any edge of the perspective view of the phase region will be represented by a point on the quaternary isothermal. These points will be referred to by letters X, Y, Z; L, M, N, P, etc.

3. The intersection of the δ-plane with a face of the phase region will be shown by a line, namely the phase boundary, on the quaternary isothermal.

4. The sections through the perspective views of different phase regions will be shown by the phase fields on the quaternary isothermals.

5. The intersection of the δ-plane with the triangular faces of the complete concentration tetrahedron will be shown by the axes of the quaternary isothermals. The axes will be called as (Al-Cu)/Mn, (Al-Mn)/Cu, etc., in which the component having the constant content in that section will be written after the stroke.

The Points X and Y

Fig.(1 - 32) is a part of the perspective view of the (α+Al_6Mn) phase region. It stands on the face BCKL of the fig.(1 - 28). The δ-plane at constant manganese content is shown to intersect the face BCV at X_1 and X. Of these, point X_1 lies on the Al-Mn axis and is represented by the constant manganese content of a particular section. The point X lies on the (Al-Cu)/Mn axis and shows the extent of the (α+Al_6Mn) phase region on the quaternary isothermal.

Fig.(1 - 33) is a part of the (α+Al_6Mn+T) phase region standing on the line CK of fig.(1 - 28). CV of the fig.(1 - 32) forms one edge of this region, showing that these two phase regions are adjacent to each other.

The δ-plane intersects the edges CV and CT at X and Y; Y will lie on the (Al-Cu)/Mn axis of the quaternary isothermal and will show the extent of the (α+Al_6Mn+T) phase region.

It will be seen from these two perspective views that as the manganese content of the alloys increases, the point X shifts towards Al_6Mn and the point Y towards T; thus the phase field (α+Al_6Mn) will reduce until it is completely eliminated at about 25% manganese, and the (α+Al_6Mn+T) phase field will widen with increasing manganese.

The Points Z and P

Fig.(1 - 34) stands on the face CDGJK of the α-solid solutions region. It shows the part of (α+T) phase region. The δ-plane intersects the edges CT and DT at Y and Z.

Z lies on the (Al-Cu)/Mn axis and represents the extent of the phase region (α+T) on the quaternary isothermal. It can be seen that, as the manganese content increases, the point Z shifts towards T; thus the extent of the phase region (α+T) also increases along the (Al-Cu)/Mn axis.

The point P represents the intersection of the δ-plane with the edge GT of the phase region (α+T). This is actually one apex of the four phase region. As the manganese content increases, this point moves towards T, and thus the other co-ordinates also change: copper increases from 3.9 to 12.6% and magnesium decreases from 1.5 to 0.0% at T.

Fig.(1 - 31) shows the perspective view of the (α+θ+T) region, standing on the faces DG and TDG of the figs.(1 - 30) and (1 - 34). The δ-plane give a wedge-shaped section through the phase region and thus the (α+θ+T) phase field will be of this shape and will go on diminishing as the manganese content is increased.

The four phase regions (α+θ+T+S) in all the quaternary

isothermals at constant manganese contents are obtained by the δ-plane cutting through the phase region ($\alpha+\theta+T+S$) shown in the fig.(1 - 37). This phase region will be triangular and will also diminish as the manganese content is increased. The point P was determined by the microscopical examination and checked by using the property of the tetrahedron, that the compositions of the phases at corners of the tetrahedron are fixed.

It was found that if the formula for T was taken to be $Al_{20}Cu_2Mn_3$ the results of the microscopical examination were rather inconsistent with those of the mathematical deductions. The formula for T was therefore taken to be $Al_{12}CuMn_2$ and, on the same basis, this formula is used throughout the present investigation.

The limiting solubility of copper in the ternary system is taken to be 3.9% and, of magnesium, to be 1.5%.

The formula $Al_{12}CuMn_2$ gives the percentages of copper and manganese as 12.6 and 22.1% respectively for the T-phase. At the point G (fig.1 - 37) the percentages of the alloying contents are: 3.9% Cu, 1.5% Mg and 0.2% Mn. (It is assumed that the maximum solubility of manganese at the point G will be about 0.2%).

The co-ordinates of the point P may now be calculated. For instance, in the 0.6% manganese section, the manganese

content changes by 0.4% from the point G towards the point T. Now the copper content changes from 3.9 to 12.6% and magnesium from 1.5 to 0%, from G to T; therefore, for an increase of 0.4% in the manganese content, the increase in copper content will be $= (\frac{0.4}{21.9} \times 8.7) \simeq 0.15\%$ and the decrease in magnesium content would be $= (\frac{0.4}{21.9} \times 1.5) \simeq 0.03\%$.

The decrease in magnesium content is neglected over the range under the present work.

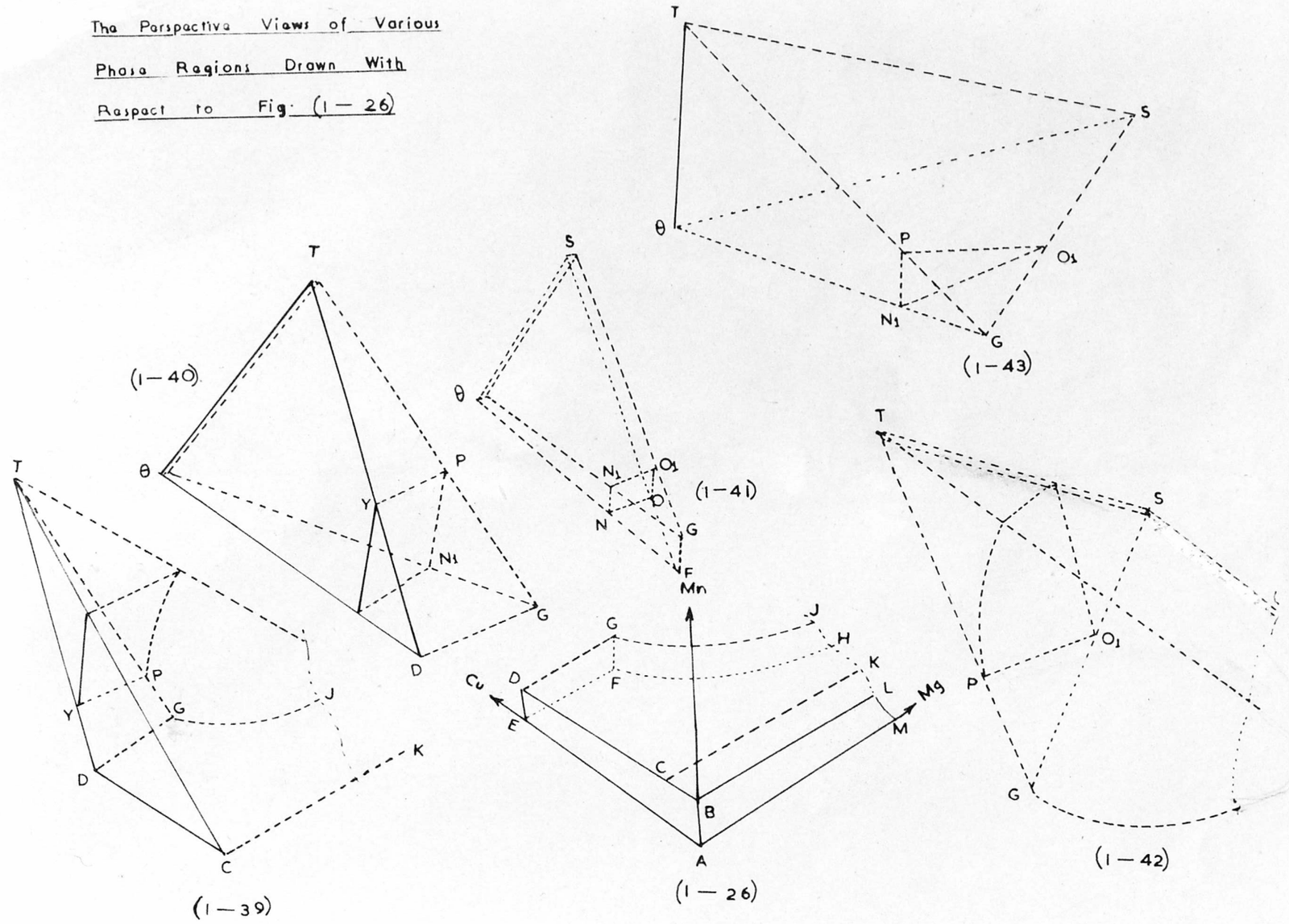
Fig.(1 - 35) shows the δ-plane through a part of the perspective view of the phase region (α+T+S). It can be seen that on the quaternary isothermal the phase field (α+T+S) would thus be bounded by a curved phase boundary (α+T)/(α+T+S) and the straight phase boundary (α+T+θ+S)/ (α+T+S).

500°C ISOTHERMALS AT CONSTANT COPPER CONTENTS

Results

Two sections were studied at constant copper contents of 3 and 4.5%, respectively, over the range 0 - 2% magnesium and 0 - 2% manganese.

Tha Parspactiva Viaws of Various Phasa Ragions Drawn With Raspact to Fig. (1 — 26)



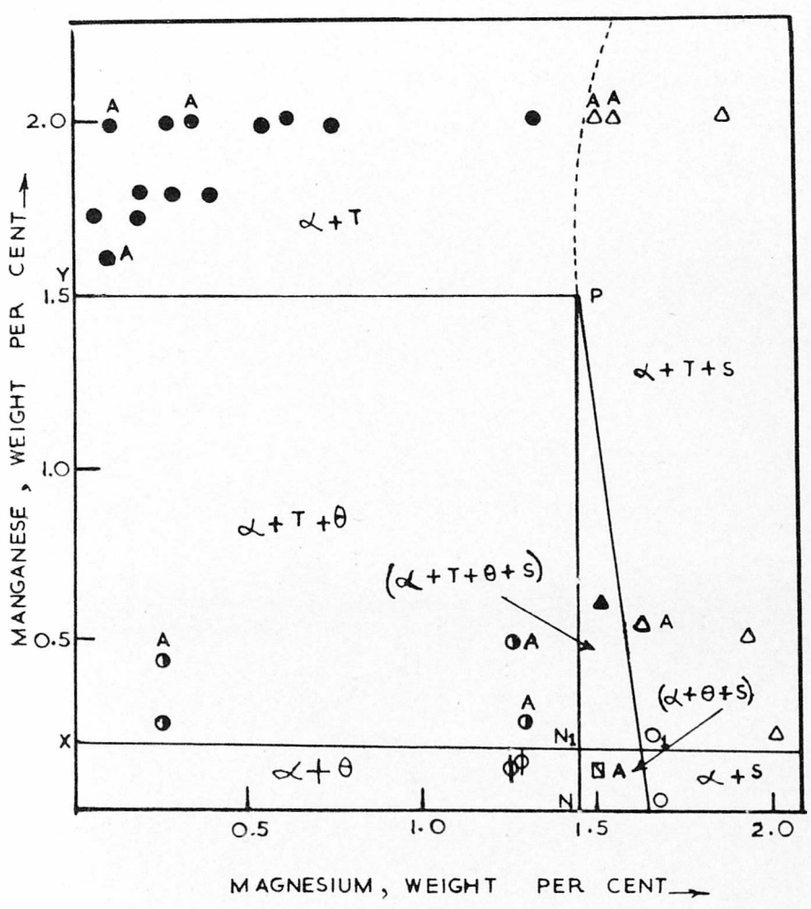


Fig. (1—25) — Tha Equilibrium Ralations in Aluminium Alloys Containing 0—2% Magnasium, 0—2% Manganasa and 4.5% Coppar at 500°C

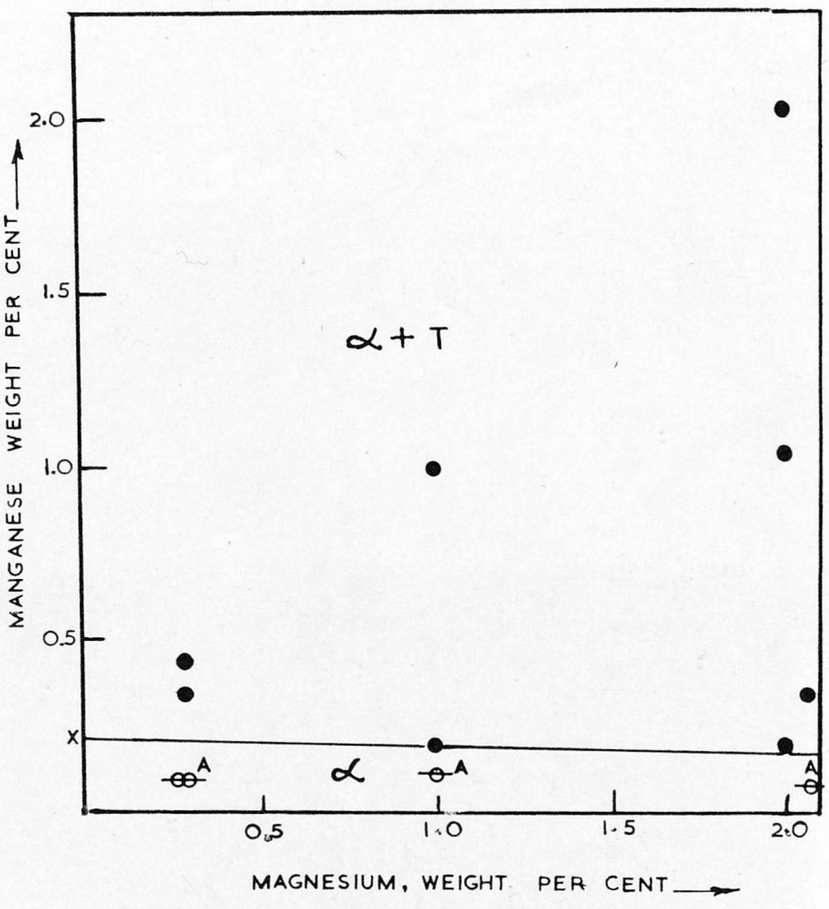


Fig. (1—24) — Tha Equilibrium Ralations in Aluminium Alloys Containing 0—2% Magnasium, 0—2% Manganasa and 3.0% Coppar at 500°C

The Phases Identified

In all, six phases were found, they were: α-(aluminium solid solution), $\theta(CuAl_2)$, Al_6Mn, $G(Al_{12}Mn)$, $T(Al_{12}CuMn_2)$ and $S(Al_2CuMg)$.

3% Copper Isothermal

Only two phase regions were found in this section over the range studied.

1) α-(aluminium solid solution):

The phase region extends approximately up to 0.20% manganese on the (Al-Mn)/Cu axis of the quaternary isothermal. The point X shows the termination of this phase field. Considering the fig.(1 - 28), it will be seen that the point X_1 obtained by the intersection of the δ-plane with the Al-Cu axis of the perspective view, showing the α-solid solution, is represented by the constant copper content of these alloys, whilst the point of intersection of the δ-plane with the edge BCD of the diagram, shown by X, gives the solid solubility limit of manganese at that copper content, in the isothermal at 500°C.

2) The second phase region is formed by (α+T) and extends from 0.20 to 2.1% manganese on the (Al-Mn)/Cu axis.

4.5% Copper Isothermal

The phase regions found in this section over the range studied, are: (α+θ), (α+θ+T), (α+T), (α+θ+S), (α+θ+T+S), (α+S+T) and (α+S).

Discussion

The Points X and Y (fig.1 - 30)

Following the same principle of intersecting the edges of the perspective views by the δ-planes, it will be seen from the fig.(1 - 30) that the phase region (α+θ) is intersected by the δ-plane at 4 points; of these, X_1 represents the constant copper content of the alloys.

X occurs at about 0.2% manganese and shows the extent of (α+θ) phase field along the (Al-Mn)/Cu axis of the quaternary isothermal. Further increase in the copper content would very slightly alter the position of the point X.

Consider figs.(1 - 39) and (1 - 40). The δ-plane intersects the edge DT of these two perspective views at Y. Fig.(1 - 39) shows a part of the (α+T) region standing on the DGJKC face of the fig.(1 - 26) and also it shows that the face TGD is in common with the region (α+θ+T) shown in the fig.(1 - 40). It is evident that as the copper content increases, the extent of (α+θ+T) region would also

increase.

The Points N, N_1, O and O_1 (fig.1 - 30, 41)

Point N shows the extent of ($\alpha+\theta$) region along the (Al-Mg)/Cu axis. Fig.(1 - 41) shows the ($\alpha+\theta+S$) and fig.(1 - 30) shows the ($\alpha+\theta$) region. The δ-plane intersects the edges G and F of these two diagrams at N_1 and N, while the edges GS and FS of the fig.(1 - 41) are intersected at O_1 and O respectively.

Thus the points N, N_1, O, O_1 actually represent a section through ($\alpha+\theta+S$) phase region and therefore this region would be very small on the quaternary isothermal. However, the extent of this phase field would increase along the (Al-Mg)/Cu axis and decrease along the (Al-Mn)/Cu axis, with increasing copper content.

The Point P (fig.1 - 43)

The point P shows the intersection of the δ-plane with the edge T of the tetrahedron.

Fig.(1 - 43) is a tetrahedron showing the equilibrium relations amongst α, θ, T and S. The section (PN_1O_1) by the δ-plane at constant copper content is seen to be triangular. (See also fig.1 - 25).

Fig.(1 - 42) shows a part of the ($\alpha+T+S$) solid solution region. The section through this phase region

forms the (α+T+S) region on the quaternary isothermal.

The phase field (α+S) on the quaternary isothermal extending from the point O on the (Al-Mg)/Cu axis is obtained by the δ-plane through the fig.(1 - 36).

The following table gives the co-ordinates of these points in the section containing a constant content of copper at 4.5%.

Points	Manganese	Magnesium
X	0.20	-
Y	1.50	-
N	-	1.45
O	-	1.65
P	1.50	1.45

The co-ordinates of points N, O and P have been determined mainly from the geometrical considerations. The accuracy of the points X, Y, N and O may be taken as $\pm$0.1% and that of point P is probably slightly less.

Conclusion

The results of the microscopical examination for the constant copper and constant manganese sections are shown in figs.(1 - 21 to 1 - 25). The phase boundaries have

been reasonably bracketted in these isothermal sections, and it is found that the phase fields and phase boundaries are consistent with those arrived at from the considerations of the perspective views of various regions.

SECTION II

THE EFFECT OF AGEING ON THE TENSILE PROPERTIES OF CERTAIN DURALUMIN-TYPE ALLOYS

CHAPTER I

HISTORICAL SURVEY

The effects of ageing on various properties in general, and on tensile properties in particular, of the Duralumin-type alloys, have been briefly summarised in the following pages, with a view to assisting in the understanding of the nature and the analysis of ageing curves obtained in the present work. Some references are made to the effects of ageing on the properties of other alloys also, in cases where they seem to throw more light on the subject.

The review is extended to a few more aspects, not related to the effects of ageing, but with the tensile properties, as the discussion of some of the present results is based on them.

Extensive work on the changes in the tensile properties during ageing was carried out by MERICA et al. (1921), who reported an increase in tensile strength and a decrease in the percentage elongation of the Duralumin-type alloys on quenching from high temperature followed by ageing at various temperatures.

GAYLER and PRESTON (1929) studied the changes in

hardness, tensile strength, density, electrical resistance and lattice parameter of five typical aluminium alloys of the systems Al-Cu, Al-Mg-Si and Al-Cu-Mg-Si. Changes in lattice parameter and density suggested that precipitation was occurring during ageing. X-ray analysis also showed that the crystals were in a disturbed state which was gradually relieved on ageing at higher temperatures. The increase in the electrical resistance during the early stages of ageing was considered to be caused by the presence of minute precipitate particles, causing the lattice distortion. The rates of increase in the hardness and the tensile strength were found to correspond closely, i.e. the maximum tensile strength was reached at approximately the same time as the maximum hardness. However, the alloy containing 4.5% copper gave a comparatively greater value for tensile strength when it was quenched from 500°C, and then aged at 150°C. The ageing treatments were continued only for 7 days.

In 1932, while reviewing the whole field and considering the theoretical aspects in the light of more recent information, MERICA found it necessary to modify his original precipitation theory. He postulated the "Knot" theory, to explain the effects of ageing on various properties. It was observed in the case of alloys

containing $CuAl_2$, that the properties changed on ageing, before any precipitation could be detected. This was thought to be the chief anomaly which could not be explained by the precipitation theory of ageing.

This "Knot" theory was supported by JENKINS and BUCKNALL (1935), who found a logarithmic relationship between the time to reach the maximum on the hardness/ageing curve at constant temperature and the temperature itself. Thus, for a given alloy, plotting the logarithm of the time to reach maximum hardness against the reciprocal of the absolute ageing temperature gave a straight line. A similar relationship was found for the logarithm of the time required to reach the maximum electrical resistance and maximum tensile strength, when plotted against the reciprocal of absolute temperature. The relationship could be expressed in the form

$$t = C^{m/T}$$

where t is the time of ageing in hours (to maximum hardness, or resistance or tensile strength), T is the absolute temperature of ageing, m and C are constants. This relationship was shown to hold for a range of ageing systems.

It was pointed out that the formation of knots in the ageing alloys would be, in essence, a diffusion process as

postulated by MERICA. The effect of temperature upon the rate of intermetallic diffusion was known to be logarithmic in nature, the rate increasing markedly with temperature. If the "Knot" theory were correct, the rate of formation of knots would control the whole of ageing process, so that it would not be surprising to find a logarithmic relationship between the time taken to reach a definite stage in the ageing process (in this particular case, the point of maximum tensile strength or hardness) and the reciprocal of the absolute temperature. The observed relationship thus supported the theory.

ROSENHAIN (1931), found that the mechanical properties of some copper-based ageing alloys were not changed in a parallel manner. When aged, a copper alloy with 0.7% Fe showed a hardness increase from 35.8 V.D.H. to 52.5 V.D.H., while the tensile strength was changed only from 13 tons p.s.i. to 15 tons p.s.i. Another alloy of copper, with 0.95% P, increased in hardness from 43 to 52 V.D.H. on ageing, while no appreciable change took place in the tensile strength. Alloys of the Cu-Be system showed a change in hardness and tensile properties on similar lines. ROSENHAIN suggested that the ageing treatment has a different effect upon the strength of the grain boundaries and the interior of the grains. Moreover, the type of

deformation imposed in the tensile test was not the same as in the hardness test. It was therefore natural to expect that the hardness and tensile strength may not reach the maximum in the same time.

BOHNER (1920) aged an aluminium alloy containing 4% Cu and 2% Si at various temperatures subsequent to quenching from the solution treatment temperature and investigated the effect of ageing on the tensile strength. The tensile strength and hardness of the alloys reached a maximum after a short time of ageing treatment at higher temperatures, while the peak value was reached after longer times as the heat-treatment temperature was lowered; the maximum hardness was found to increase at lower temperatures of ageing although the maximum occurred after longer times.

FINK and SMITH (1936) and FINK, SMITH and WILLEY (1940) investigated the effects of ageing on various properties and made a microscopical study of the precipitation during ageing. It was suggested that the most reliable criteria of the extent of ageing are yield strength and elongation. Binary Al-Mg and Al-Cu alloys showed a precipitation before any substantial change occurred in the yield strength, on ageing at or above 100°C. Alloy samples of the systems Al-Cu, Al-Cu-Mg, Al-Cu-Fe, Al-Cu-Si and Al-Cu-Mn showed an increase in yield strength and a decrease in elongation

during ageing at room temperature.

DIX (1945) concerned his work with the effects of ageing, at different temperatures, on the tensile and compressive properties of some highly complex alloys of the quinary system Al-Cu-Mg-Mn-Si. The results are summarised as follows:

1) The alloys aged even at $0^{\circ}C$, and, at this temperature, tended to reach the same maximum values for tensile strength and yield strength as those of the alloys aged at room temperature. However, in the former case, there was an incubation period of 1 day, while alloys aged at room temperature showed an absence of incubation period.

2) The ageing effect was found to be completely suppressed at $0^{\circ}F$ ($-18^{\circ}C$ approx.).

3) The compressive strength was found to be increased by ageing at higher temperatures, viz. around $165^{\circ}C$ ($340^{\circ}F$) and gave a value equivalent to the tensile yield strength.

4) The yield strength was found to rise appreciably after ageing at higher temperatures if the alloys were subjected to a 5% cold work, subsequent to quenching.

5) The percentage elongation was found to be decreased.

6) The ratio of yield strength to tensile strength

was observed to be increased from 0.6 for the alloys in the quenched condition to 0.9 for fully aged alloys.

GEISLER (1949) considered the whole of ageing as a combined effect of coherent precipitation, depletion of solid solution, matrix-recovery or recrystallisation, dispersion hardening and coalescence. He developed some ideal curves with arbitrary scales to explain the changes in ductility, proof stress, tensile strength, hardness, etc. during ageing in the light of the variables mentioned above. He concluded that the ageing curve is complicated and numerous relatively commonplace reactions may contribute to its shape and that little significance can be attached to any one of the contributing reactions. GEISLER, commenting on the tendency to intergranular fractures and decrease in ductility on ageing at elevated temperatures, attributed these effects to the localised over-ageing at grain-boundaries. This has little or no influence on yield strength but conceals some of the increase in tensile strength or the fracture strength.

It will be interesting, at this stage, to see the effect of different modes of precipitation on the modes of fracture, and of some alloying elements, particularly copper and manganese on the mode of precipitation.

The effects of iron, manganese and chromium on the

alloys of the system Al-Mg-Si were studied by CHADWICK et al. (1953-54), and it was shown that increasing amounts of manganese and chromium reduced the ductility of the as-quenched alloys, while 0.1% proof stress and tensile strength were increased. When these alloys, with or without the addition of iron, were aged, they showed a corresponding increase in 0.1% proof stress and tensile strength with increasing manganese and chromium. Elongation values, however, did not exhibit the usual inverse relationship to tensile strength and proof stress. In fact, the basis alloy was quite brittle, but ductility, as measured by elongation or bending properties, was increased by additions of iron and still further improved by manganese or chromium; maximum elongation was obtained with 0.2% or more of either manganese or chromium. It was suggested that the properties of alloys in different conditions of heat-treatment are influenced in a very considerable measure by actual precipitation process. Precipitation at grain boundaries during final low-temperature ageing was thought to be specially undesirable, since it resulted in a brittle condition in which intercrystalline fracture during bending or tension occurred.

CHADWICK et al. reported three different types of precipitation in these alloys, and in each one the

particles were sufficiently large to be easily resolved under the optical microscope. The first type was found in manganese- and chromium-bearing alloys which had been cast and then heated at 500°C before hot rolling; the precipitates which, when first formed were presumably (Fe, Mn)Al_6 or (Fe, Cr)Al_7, remained throughout the operations and gave a banded structure. The second type of precipitate was of large particle size, and was thrown down in the alloys during hot-rolling and cold-working operations, presumably by nucleation on slip planes. This precipitate was taken into solid solution again on solution treatment: it appeared to be Mg_2Si. The third type occurred on final artificial ageing at 160°C and was probably also Mg_2Si. In the absence of chromium or manganese, it occurred at grain boundaries, causing pronounced mechanical weakness. As manganese and chromium were increased, the amount of precipitate at the grain boundaries, and the associated intercrystalline weakness diminished. No grain boundary precipitation was detected in the dark-banded areas associated with the first type of precipitation referred to above, and it seemed possible that this precipitation provided alternative sites for the nucleation of Mg_2Si.

In another paper, also by CHADWICK et al. (1957), the views about the effect of manganese and chromium

additions were confirmed, during the study of stress corrosion of the alloys of the system Al-Mg-Zn. They also found that the grains were elongated in the direction of rolling even after prolonged annealing, in the case of alloys containing both manganese and chromium or chromium alone, and attributed the higher stress-corrosion-resisting properties of such alloys to the grain refinement and elongated grain shape.

In the course of discussion on the findings of CHADWICK et al., it was suggested by DAY (1957) that the preferential submicroscopic precipitation, during ageing, is accompanied by the formation of denuded grain-boundary zones and this was, in all probability, associated with the increased susceptibility to stress corrosion. An alloy in which preferential grain-boundary precipitation predominates would exhibit these characteristics, and thus it would appear that the more general mode of precipitation in chromium and copper-bearing quinary alloys accounts for its superiority as much as does its elongated grain structure.

In 1950, GILBERT and HADDEN, and PERRYMAN and HADDEN published two papers to explain the behaviour of an aluminium - 7% magnesium alloy, when aged and subsequently stressed. It was shown that there was a close relationship

between grain-boundary β-precipitate and the stress corrosion susceptibility; maximum susceptibility occurred when the precipitate was continuous at the grain boundaries. These alloys showed a tendency to rapid intercrystalline failures when aged at elevated temperatures and stressed.

PERRYMAN and BLADE (1950) reported the hardening of aluminium-zinc alloys on ageing. When the alloys were aged at 100°C, they hardened with the formation at the grain-boundaries of zinc-rich particles and a 'light phase', which was considered to be the aluminium solid solution stable at that temperature of ageing. At ageing temperatures above 100°C, no light phase was found. It was considered therefore that at 100°C the precipitation process was discontinuous. They found that the tensile tests on aged specimens gave intercrystalline fractures and attributed this effect to the ductile phase formed at the grain boundaries. This view was supported by similar experiments on an aluminium-4% copper alloy, which was heat-treated in such a way as to obtain the ductile phase at the grain boundaries by higher localised rates of precipitation.

CROWAN'S (1946) experiment on the fracture of tin-welded blocks of iron showed that the fracture took place at the tin/iron interface and not in the tin itself.

Orowan explained this by showing that the tin was in a state of hydrostatic pressure, because when the two iron blocks were stressed, the tin-weld had to undergo plastic deformation to relieve the axial stresses. However, since it was welded to the upper and lower portions, the tin-weld could not deform plastically and instead set up transverse stresses. The specimens were found to withstand stresses up to 5½ times the tensile strength of tin, but this state of hydrostatic pressure ultimately produced failures at the tin/iron interface, which corresponds to an intercrystalline failure.

Following Orowan's work, it was suggested that there were three main boundaries in heat-treated alloys which had to be considered:

i) Boundaries lying parallel to the applied stress with neither shear stresses in the plane nor transverse tensile stresses on them.

ii) Boundaries lying perpendicular to the applied stress, which were in hydrostatic tension as explained above.

iii) Boundaries lying at some angle to the applied stress, which will be subjected to some component of shear.

The resolved shear stress along a number of the boundaries of type (iii) will, if the applied stress is more than a certain value, be sufficient to cause creep

in the ductile phase (new solid solution). There will thus be stress relaxation along these boundaries, and a large stress will be built up on the boundaries of type (ii). Plastic deformation is prevented at this type of boundary because of the constraint exerted by the grain on the new solid solution, and so brittle fracture would occur.

The study of the plastic deformation of certain aluminium alloys made by THOMAS and NUTTING (1957), with the aid of electron microscope led them to the following suggestion concerning intercrystalline failures in the aged alloys. In cases where the precipitated particles at the boundaries form a continuous network, the transfer of slip across the grain boundary is prevented. At higher ageing temperatures, the spacing of the precipitates is greater, and the slip lines can then pass from one grain to another, and thus the susceptibility to intercrystalline failures is reduced.

HARRIS and VARLEY (1953-54) showed that the brittleness of fully heat-treated alloys of the aluminium magnesium-silicon series was dependent upon composition. When the alloys were solution treated at 540°C and subsequently heat-treated at 175°C for 8 hours, excess silicon was found to be necessary for brittleness, but the amounts of

excess silicon to give a certain degree of brittleness varied with the percentages of magnesium silicide and iron present. Microscopical examination indicated that the maximum brittleness as denoted by Izod-tests was probably associated with the preferential precipitation at the grain-boundaries of either free silicon or magnesium silicide, or both, forming a continuous network. Additions of manganese in the approximate range of 0.4 to 0.7% to brittle aluminium-magnesium-silicon alloys had the important effect of inhibiting the precipitation at the grain boundaries: it was explained by a possible nucleation effect of $(Mn, Fe)Al_6$ for the precipitation of Mg_2Si and silicon, which might thus largely prevent their preferential precipitation at the grain boundaries. Recently, COLLINS (1958) published a paper on the aluminium-magnesium-silicon-copper system, and has shown the effects of constitutional factors on the tensile properties of annealed and aged alloys of this system.

Having considered the effects of precipitation on the strength of the grain boundaries, it is now necessary to discuss the effect of manganese on the grain size of aluminium alloys.

The Effect of Manganese on Grain Size

The binary constituent Al_6Mn, the metastable phase, G, and also the ternary compound T($Al_{12}CuMn_2$), have a tendency to precipitate in an extremely finely dispersed form on annealing at temperatures around 450 to 550°C. This finely dispersed phase is termed U-constituent. Its behaviour, occurrence and some peculiarities have been discussed in the previous section, while dealing with the constitution of the binary Al-Mn system.

The work of Z. JEFFRIES (1916, 1919) established the main features of grain growth in the presence of a dispersed second phase. JEFFRIES found that if various amounts of thoria were added to fine-grained tungsten, the grain growth was practically inhibited up to a certain annealing temperature. When this temperature was exceeded, extremely large grains developed abruptly from the fine-grained matrix. Such a coarsening temperature was later found by GROSSMANN (1934) in the case of certain steels, while it was known that in other steels grain growth was gradual and without inhibition and abrupt coarsening. Some work on aluminium additions to steels showed that the direct cause of inhibition and coarsening of grain-size in aluminium-killed steels was a fine dispersion of aluminium oxide (SIMS, 1945; BAIN, 1939)

Systematic work on the effect of finely-dispersed U-constituent led BECK et al. (1949) to the following conclusions.

1) The finely dispersed aluminium-manganese compound has a considerable inhibiting effect on grain growth. When specimens initially containing dispersed phase are annealed at temperatures below the solvus point, continuous grain growth takes place until a definite ultimate grain size is reached. The ultimate grain size is essentially independent of prior deformation, but it increases with increasing annealing temperatures and decreasing manganese contents.

2) If the specimens are annealed at a temperature just below the solvus point, where part of the compound slowly redissolves and noticeable coalescence of the remaining compound takes place, extremely large grains are formed by discontinuous grain growth, after an incubation period of the order of 55 days.

3) If the specimens are annealed at a temperature where the compound redissolves relatively quickly, continuous grain growth, typical of single phase aluminium alloys, takes place.

4) Continuous grain growth stops when the maximum average grain size is of the order of specimen thickness.

Discontinuous grain growth or coarsening is not limited by this effect; the whole specimen may be converted into a large single grain with only scattered residual small grains embedded in it.

Thus it is evident that the additions of manganese affect the grain size and grain growth considerably. The present work is based on the tensile measurements of specimens, therefore it will be worthwhile considering briefly the influence of grain size on the mechanical properties in general.

It was suggested by BRAGG (1942), on purely theoretical grounds, that the yield strength is inversely proportional to the grain diameter. This suggestion was found consistent with the experimental results. More recent investigators have found that the yield strength is proportional to the square root of the grain diameter (PETCH, 1953; STROTCH, 1955). BALDWIN (1958) suggested that yield strength may be proportional to the inverse of the cube root of the grain diameter: the graph of this relation was a straight line which passed through the origin in many cases.

CHAPTER II

EXPERIMENTAL

A small portion of the ingot of each alloy remaining from CHITTY'S work, was used in the present investigation. The analyses of the materials used are given in the first section of the present investigation.

It was decided to use flat test-pieces for the tensile measurements, so that the maximum number could be obtained from the limited amount of material available. It was necessary to have sufficient test-pieces to study the effects of ageing over a range of times from 0 to 120 days, in order to cover the various stages of ageing. Unfortunately, it was not possible to obtain an adequate number of test-pieces in every case.

Previous Treatment of the Ingots

After casting, the alloys were annealed for 48 hours at 490°C, in an air-circulating furnace. The ingots were subjected to hot pressing to reduce them 90% in total thickness. This served the purposes of:

1) Giving a suitable grain-size.

2) Breaking down the dendritic structure and giving a

homogeneous structure.

3) Shortening the annealing periods and thus avoiding the large grain sizes.

The alloy samples, as received, were in the form of bars of approximately 1 inch sq. cross-section.

It was found necessary to press these bars before they could be rolled to give sheets of desired thickness as the rolling mill available in the laboratory could not roll passes over ⅜ inch.

Description of the Press

The die-blocks fitted on the face of a 150-ton hydraulic press were heated by gas jets.

Ingots were sandwiched between two mild-steel plates of 0.375 inch thickness and pressed between the dieblocks to effect a reduction in the thickness by extrusion, and also by flattening. Between each pressing operation, the die faces and the mild-steel plates were well lubricated with a suspension of graphite in oil.

Pressing of the Alloys

All the alloys investigated were pressed at a temperature of 490°C, in order to avoid any damage to the alloys by melting the eutectic. The alloys were heated in an air-circulating resistance furnace, with the temperature

controlled to $\pm 2^{\circ}C$.

The die-blocks were heated to $400^{\circ}C$. They were not heated to a higher temperature because:

1) Mild-steel die blocks are not suited for use at higher working temperatures.

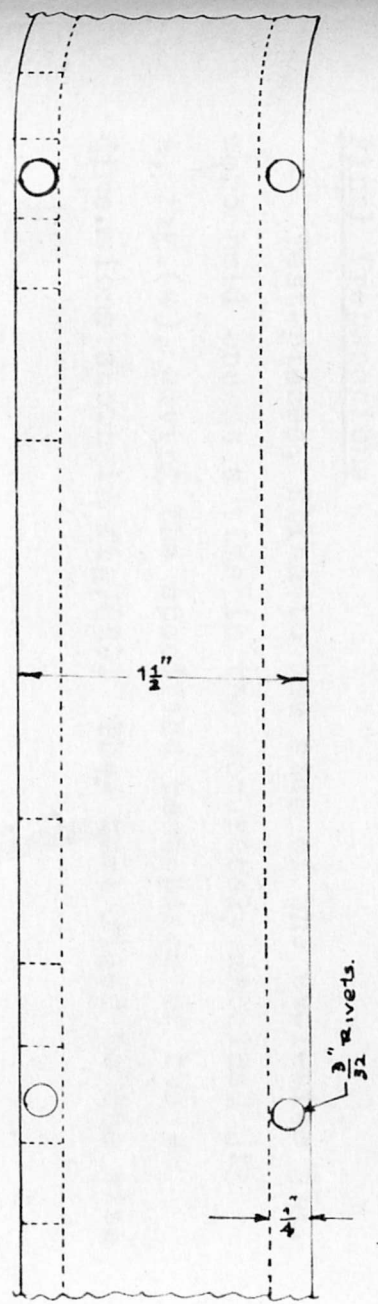
2) Heat generated due to the mechanical work may raise the temperature of the alloys and melt the eutectic.

It was found necessary to anneal the ingots between the stages of pressing at $490^{\circ}C$, for at least half an hour. The final thickness of the plates was of the order of 3/8".

Rolling

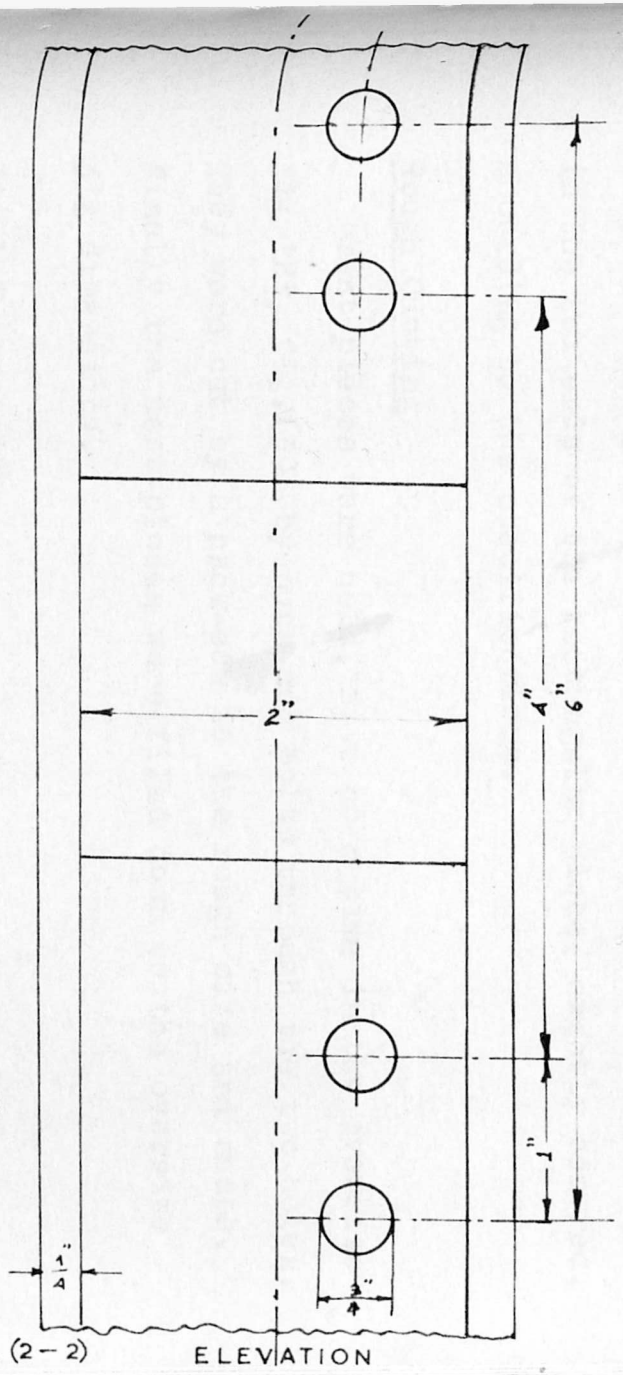
Plates of 3/8" thickness were annealed for half an hour at $490^{\circ}C$, and then passed through the lubricated rolls in stages.

1) Rolled to a thickness of 5/16".
2) Rolled to 1/4" thickness.
3) Reheated.
4) Rolled to 3/16".
5) Second pass, giving 1/8" plate.
6) Reheated.
7) Rolled to 3/32".
8) Rolled to 1/16".
9) Repassed at 1/16" after cooling to give a uniform

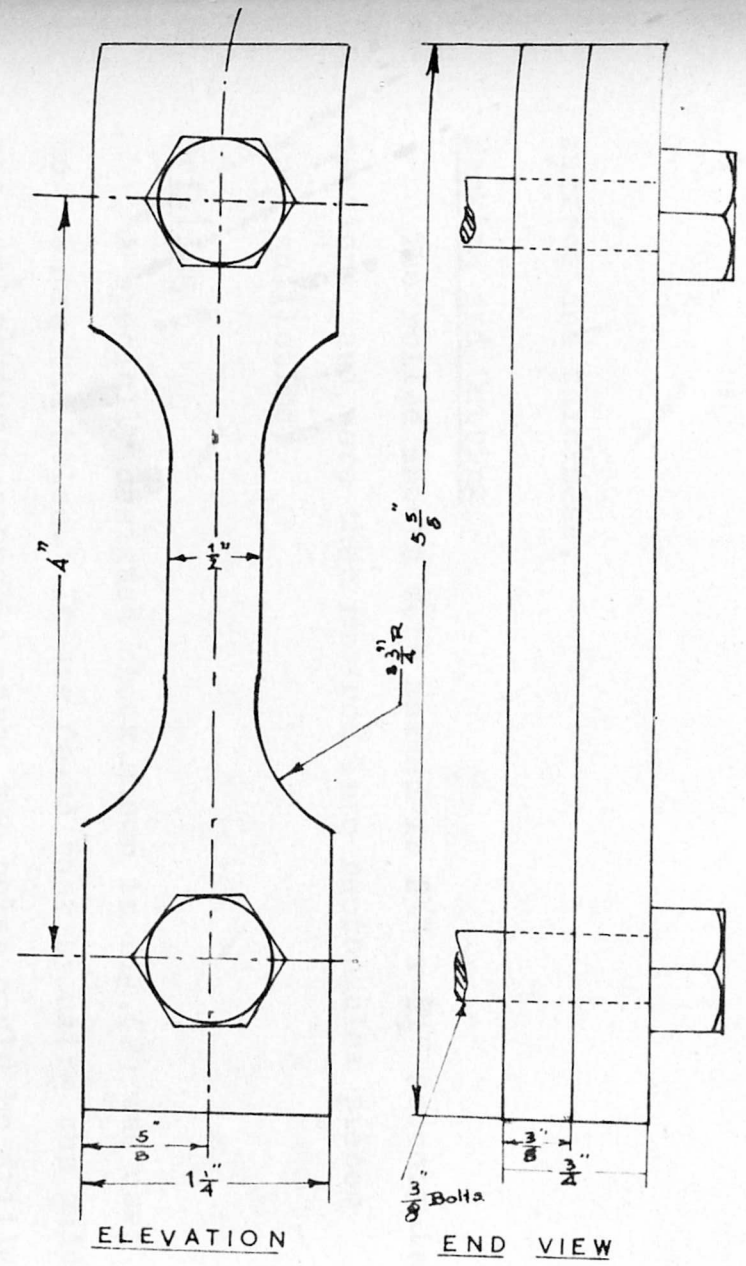


END VIEW

FIG. (2 — 2)



ELEVATION



ELEVATION

END VIEW

FIG. (2 — 3)

surface and thickness.

Marking and Cutting

The rolled sheets were marked in 1¾" x 6¼" rectangular sections, and were then sheared into rectangular pieces in a guillotine.

Drilling

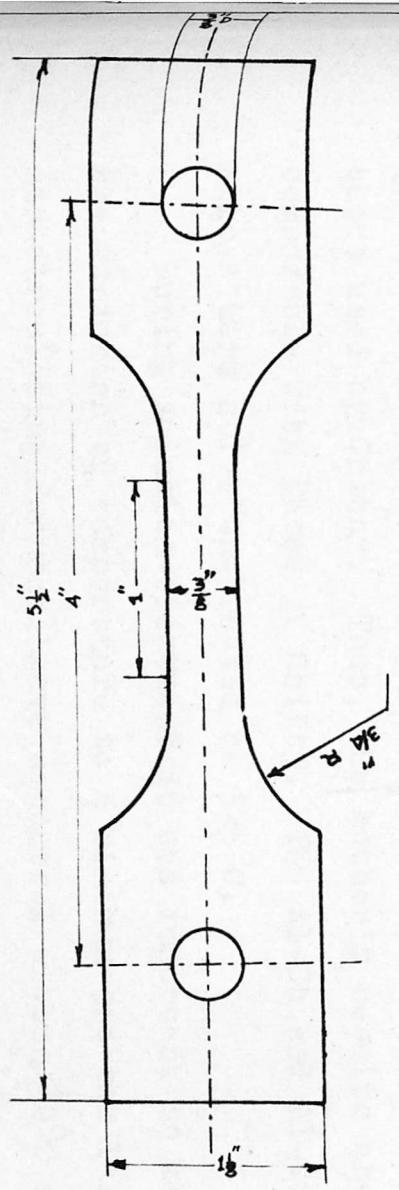
A specially designed block shown in fig.(2) was used to centre the holes. It was found that by using the guide bar, and taking reasonable care, two holes could be drilled in the two ends of the rectangular piece, exactly centred, according to the specifications.

Rough Cutting

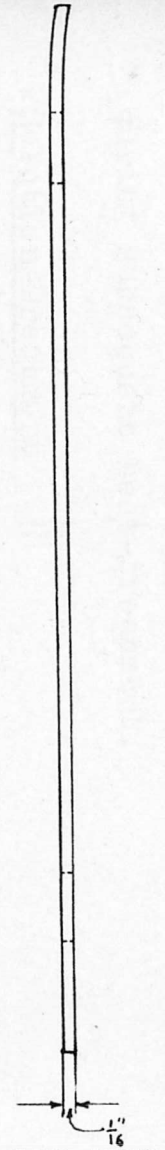
Test pieces were held, five at a time in the oversize jig 'B', fig.(3), by nuts and bolts through the two holes. They were cut by a hack-saw to the rough size and shape. Finally the test-pieces were filed down to the oversize jig dimensions.

Final Preparations

Test-pieces, filed to the size of the over-size jig, were held one at a time in the accurately machined jig A, fig.(4), giving the specified test-piece of the dimensions shown in fig.(5). They were filed to the size

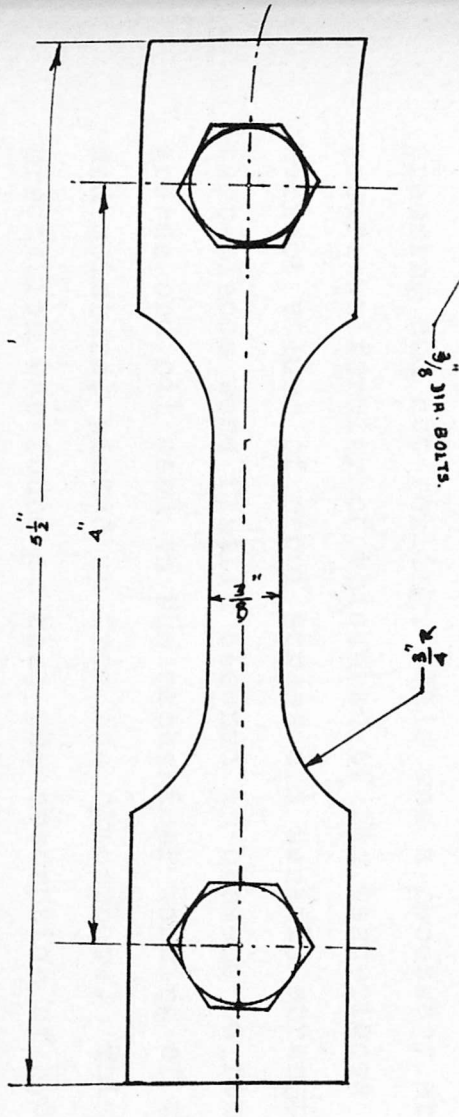


ELEVATION

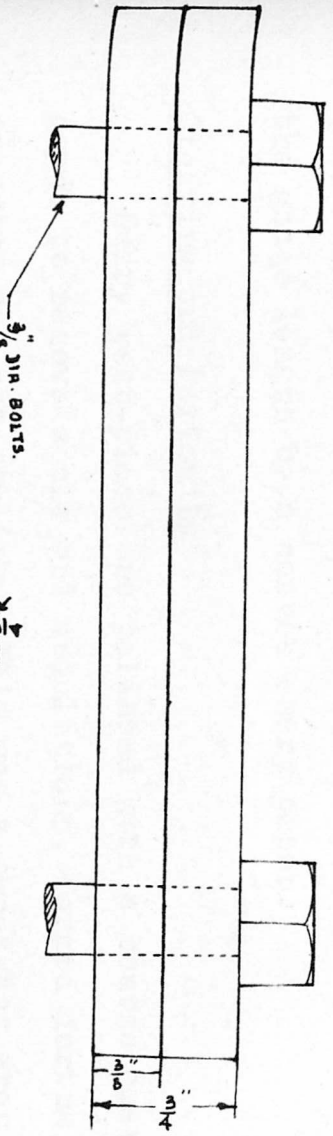


END VIEW

FIG. (2—5)



ELEVATION



END VIEW

FIG. (2—4)

of the jig 'A' and then polished at the radii and along the gauge length by a coarse emery paper.

Cleaning and Polishing

Every test-piece was polished with a coarse emery paper to remove scale and undulations, formed during hot pressing and hot rolling. This was a necessary step to ensure uniformity of thickness of the test-pieces to yield correct values of proof stress and tensile strength. The test-pieces were finally cleaned in benzene to remove grease and oil used in the mechanical working of the ingots and moisture, picked up from the atmosphere. This precaution was found to keep the absorption of hydrogen to a minimum and very little, or no, blistering occurred during subsequent heat-treatment.

Solution-Treatment

The temperatures used for the solution-treatment were those used by Chitty. Thus, the author's results are comparable with those of Chitty. The Al-Cu and Al-Cu-Mn alloys were solution-treated at 525°C.

During solution-treatment it was important to keep the variation of temperature to a minimum and the large air-circulating furnace, gave a control within $\pm 2^{\circ}C$ of the desired temperature. The test-pieces were individually

suspended on wires from bars, to avoid any warping and to facilitate quenching.

Time of Solution-Treatment

Following the procedure used by CHITTY, the test-pieces were solution-treated for a minimum time of 48 hours.

Quenching

Hanging the test-pieces individually facilitated quenching, and an efficient quench could be obtained by immersing the test-pieces individually in a large water-tank at a temperature of 20 $\pm$1°C.

Ageing Treatment

The investigation was aimed at studying the effects of ageing by means of measurements of elongation, 0.1% proof stress and tensile strength of samples aged at different temperatures. However, the number of test-pieces was hardly sufficient to study the effects of ageing at one temperature only. It was decided, therefore, to use a temperature of 130°C, which was the intermediate temperature used by CHITTY for ageing.

Storage and Transport

After quenching, the test-pieces were stored in melting ice, to inhibit the ageing at room-temperature.

Ageing Ovens

Ageing was carried out by suspending the specimens in an oil bath by means of steel wires. The oil bath was contained in an air-circulating oven which had a small hole cut in the top. This allowed specimens to be inserted or removed without opening the door of the oven, which would lower its temperature. These air-circulating ovens gave a temperature control within $\pm 1^{\circ}C$.

Cleaning

The test-pieces were cleaned by cotton wool moistened with benzene and then wiped by a dry cloth.

Tensile Testing

A Hounsfield tensile testing machine was used in conjunction with a dial-gauge extensometer, giving a minimum extension measurement of 1/20,000". The arrangement of the test-piece fitted with the dial gauge is shown in fig.(6). The screws A and B of the dial gauge gripped the tensile test piece and marked the gauge length of 1 inch. The loads were applied by manually operating the handle.

The measurements of percentage elongation, 0.1% proof stress and tensile strength were made in the usual way.

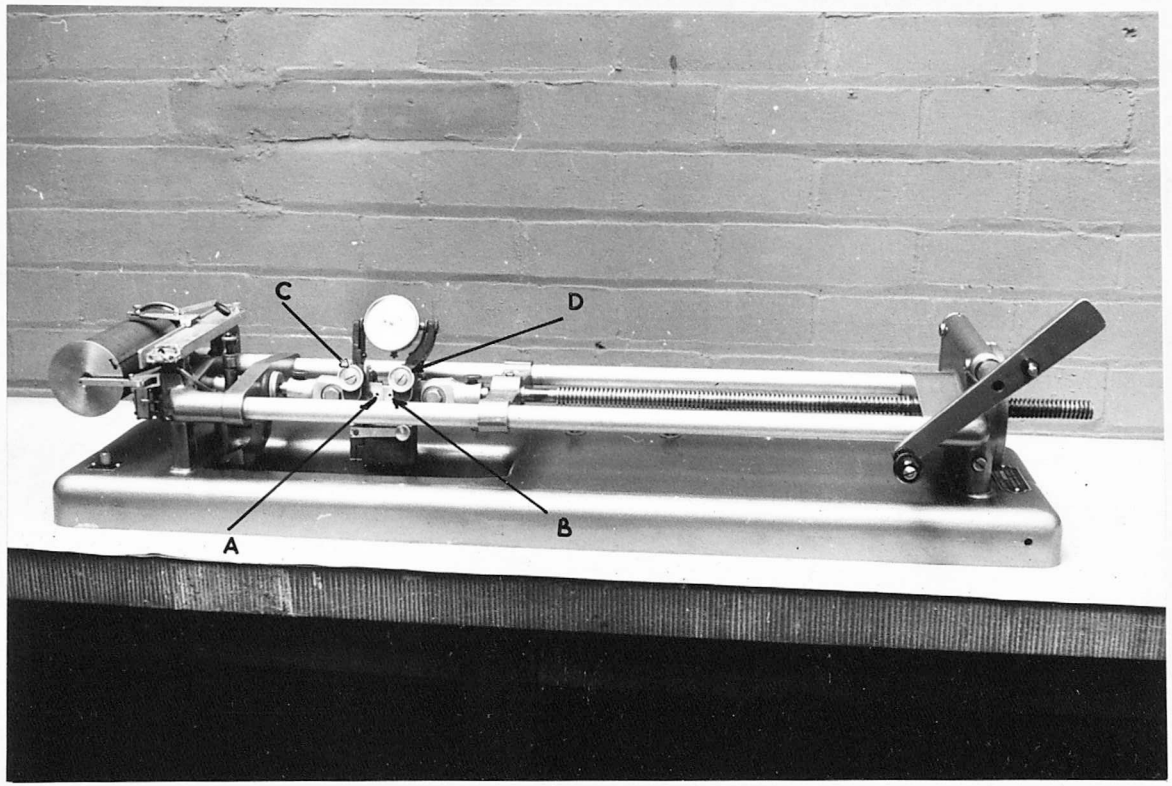


FIG (2 - 6) THE TENSILE TESTING MACHINE & THE EXTENSOMETER

Precautions

In the earlier tests, uneven tightening of the dial-gauge screws on the test-piece and slight looseness in the screws C and D (fig.2 - 6) gave faulty stress-strain curves. However, once this fault was detected, care was taken in subsequent tests to avoid it. Although this fault altered the values of Young's modulus, it appeared that proof stress values were not appreciably affected. The points derived from the faulty stress-strain curves are marked with the letter F on the ageing curves.

The accuracy for the 0.1% proof stress measurements may be taken as $\pm$0.5 tons/sq. in. In the case of the values for tensile strength, the accuracy is probably less; especially in the vicinity of the peak there was an appreciable scatter. It is most probable that this was caused by the intercrystalline fractures (figs.2 - 36, 37). However, this did not alter the general form of the ageing curve and therefore approximate values for tensile strength have been obtained. The accuracy for the percentage elongation may be taken as $\pm$2 .

CHAPTER III

RESULTS - DISCUSSION - CONCLUSIONS

THE SYSTEM ALUMINIUM-COPPER

Previous Work

An investigation on the changes in tensile properties of aluminium-copper alloys was carried out by GAYLER and PRESTON (1940). The tensile strength of these alloys was found to reach a maximum value in approximately the same time as the hardness, while the percentage elongation decreased. FINK and SMITH (1936) heat-treated an alloy containing 5.17% Cu at 160°C. An increase of about 80% in the yield strength and a decrease from 18 to 2.5% in the elongation were observed. FINK, SMITH and WILLEY (1940) quenched an alloy containing 4% Cu into water at 25°C, and aged it at 100°C. They measured the mechanical properties of this alloy; it gave two peaks, one just after beginning the ageing treatment and the other after 400 hours. They attributed the presence of the first peak to the precipitation which occurred more rapidly in the regions plastically deformed during quenching. The

second peak did not seem to have reached its maximum point within the times for which the treatment was carried out. Samples of three alloys containing 2, 3 and 4% copper, respectively, were also quenched and aged at room temperature. The yield strength/ageing curve for the 4% Cu alloy showed two stages, while those for the 2 and 3% Cu alloys exhibited only a single stage. It was concluded that the increase in the percentage of copper,

1) increased the peak value on the yield strength/ageing curve,

2) shortened the time to reach a maximum,

3) increased the quenched-yield strength.

Systematic investigations of the age-hardening characteristics of binary Al-Cu alloys have been made by several authors.

HUNSICKER (1940) reported the general effects on the age-hardening of increasing copper: they may be summarised as follows:

1) Increased hardness in the as-quenched condition.

2) Shortening of the incubation period.

3) Increased ageing rate.

4) Increased hardening capacity.

5) Increased rate of softening beyond the maximum.

The results of the recent investigations by HARDY

(1951) and CHITTY (1955) are reported in detail, particularly with regard to the ageing temperature used in the present work, and the discussion of the results.

1) Hardness / Ageing Curves 130 °C

At very short ageing times, most of the alloys showed a slight drop in hardness from the values of the quenched specimens; this was associated with the relief in quenching stresses. The incubation values became progressively longer for alloys of lower supersaturation. The initial rise for alloys with 3 - 4.5% Cu could be represented as a straight line at an angle to the logarithmic time base. The end of the initial rise was followed by a period of nearly constant hardness for the alloys with 3.5 - 4.5% Cu. The second incubation, which preceeded the rise to peak-hardness, occurred after very similar ageing times for these alloys.

The time to peak-hardness was generally independent of composition over the range 3.0 - 4.5% copper. The aluminium-2% Cu alloys showed only a single-stage rise to a peak hardness value at a much longer time.

2) Concentration/Hardness Relationships (fig.2 - 8)

The hardness of the quenched alloys exhibited a linear relationship with concentration, over the range

Analysis of Ageing Curves of Binary Aluminium — Copper Alloys (Hardy & Chitty)

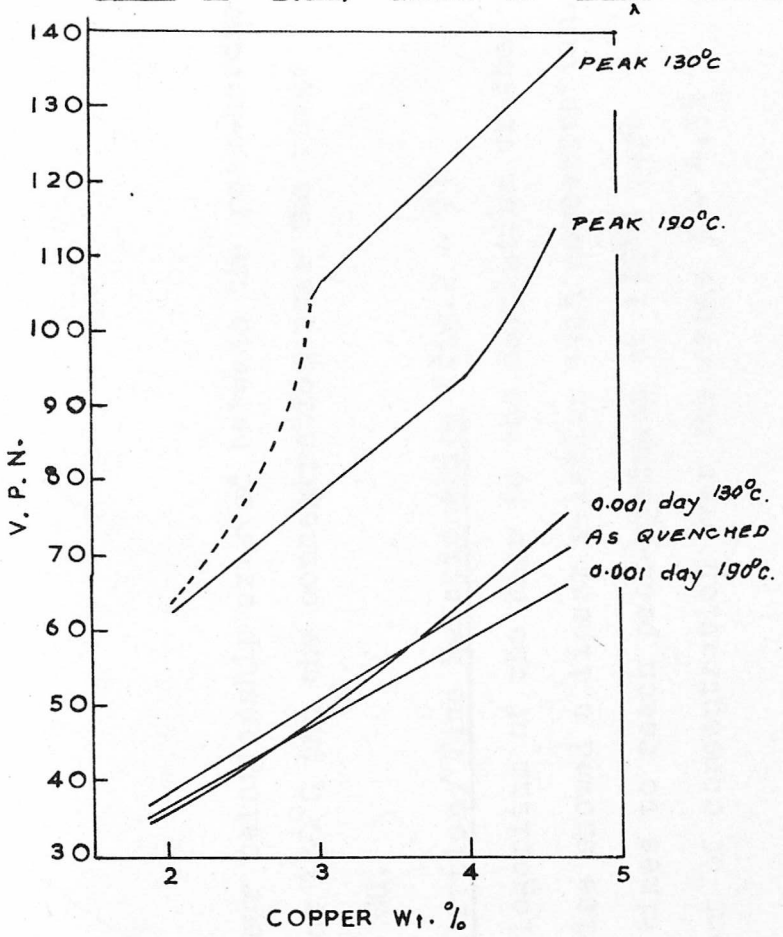


Fig.(2-8)- Concentration / Hardness Relationships

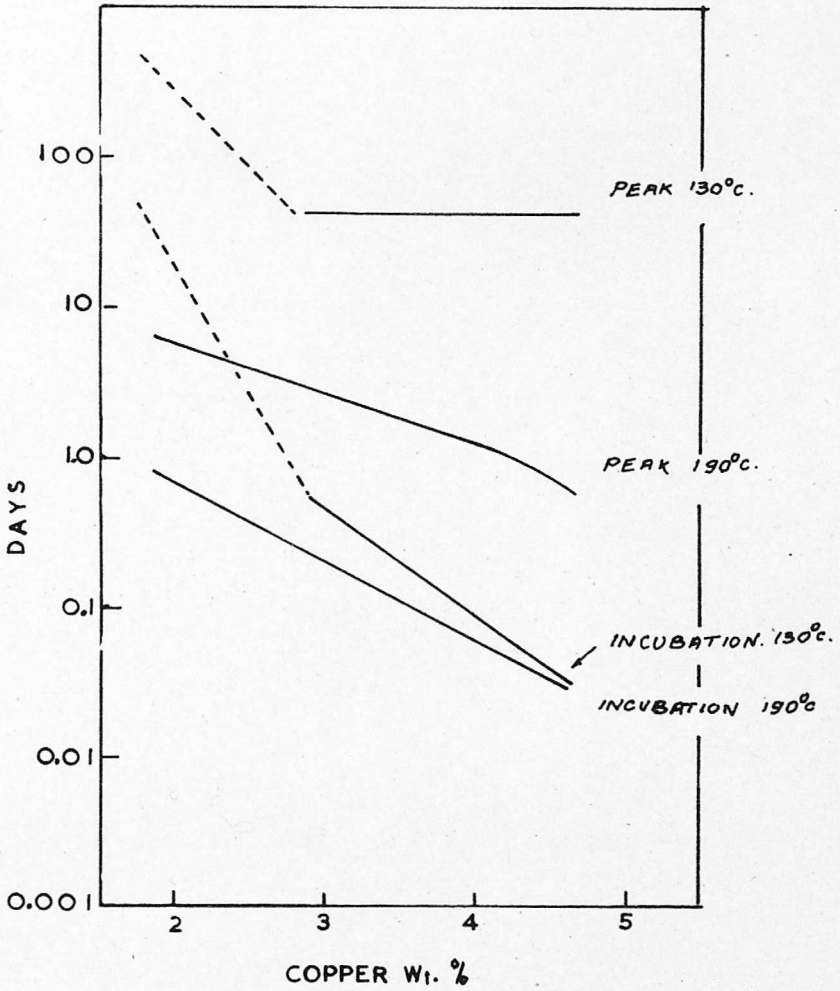


Fig.(2—9)- Concentration / Time Relationships

examined.

A linear relationship existed between the peak-hardness attained at 130°C and the concentration over the range 3 to 4.5% Cu.

3) Concentration/ Time Relationships (fig.2 - 9)

The logarithm of the time to the completion of the initial rise showed a linear relation with concentration.

The times to reach peak-hardness at 130°C were independent of concentration over the range 3 - 4.5% copper.

RESULTS

Two alloys were studied from the system aluminium-copper. The analyses are given below.

Alloy No.	% Cu	% Si	% Fe
2	4.25	0.001	0.001
3	2.92	N.A.	N.A.

(N.A. - not analysed)

Microscopical examination of samples of both alloys quenched from 525°C showed a single-phase structure.

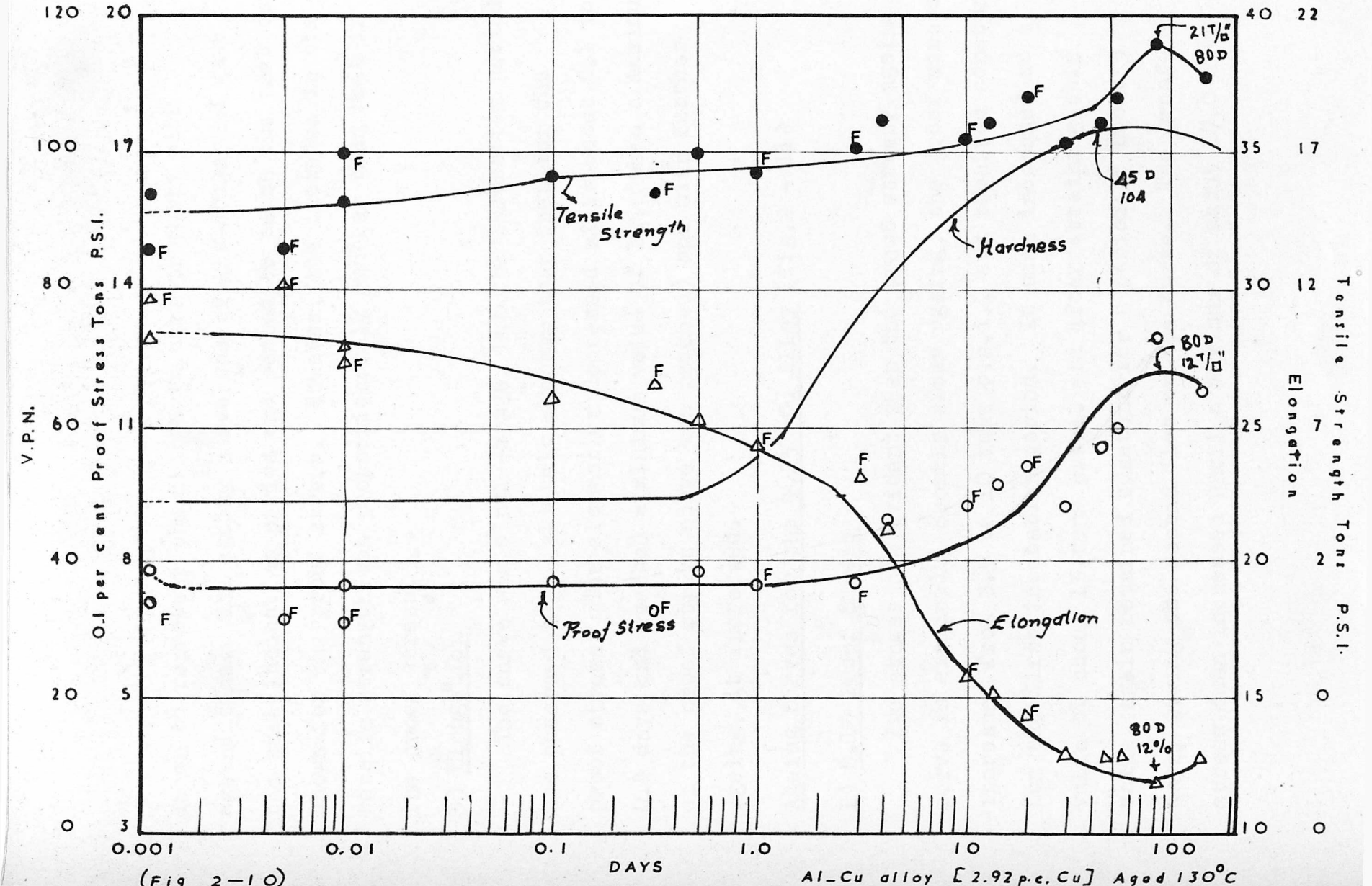
Ageing Curves for the 2.92% Cu Alloy (fig.2 - 10)

1) 0.1% Proof Stress -

The 2.92% Cu alloy showed a single-stage ageing curve. After a short time of ageing, the proof stress fell from 7.5 to 7.1 tons p.s.i. and then remained constant until the incubation value was reached in 1.0 day. The proof stress then increased to a maximum of about 12 tons p.s.i. between 70 to 100 days. Further ageing reduced the proof stress.

2) Tensile Strength -

The tensile strength plots showed considerable scatter, but with certain approximating, a curve could be



(Fig 2—10)

Al–Cu alloy [2.92 p.c. Cu] Aged 130°C

drawn to represent the change in this property with ageing time. The ageing curve was single-stage and gave the same incubation period and period to reach the peak as shown for the proof stress. However, the increase in the tensile strength was proportionately smaller than that in the proof stress.

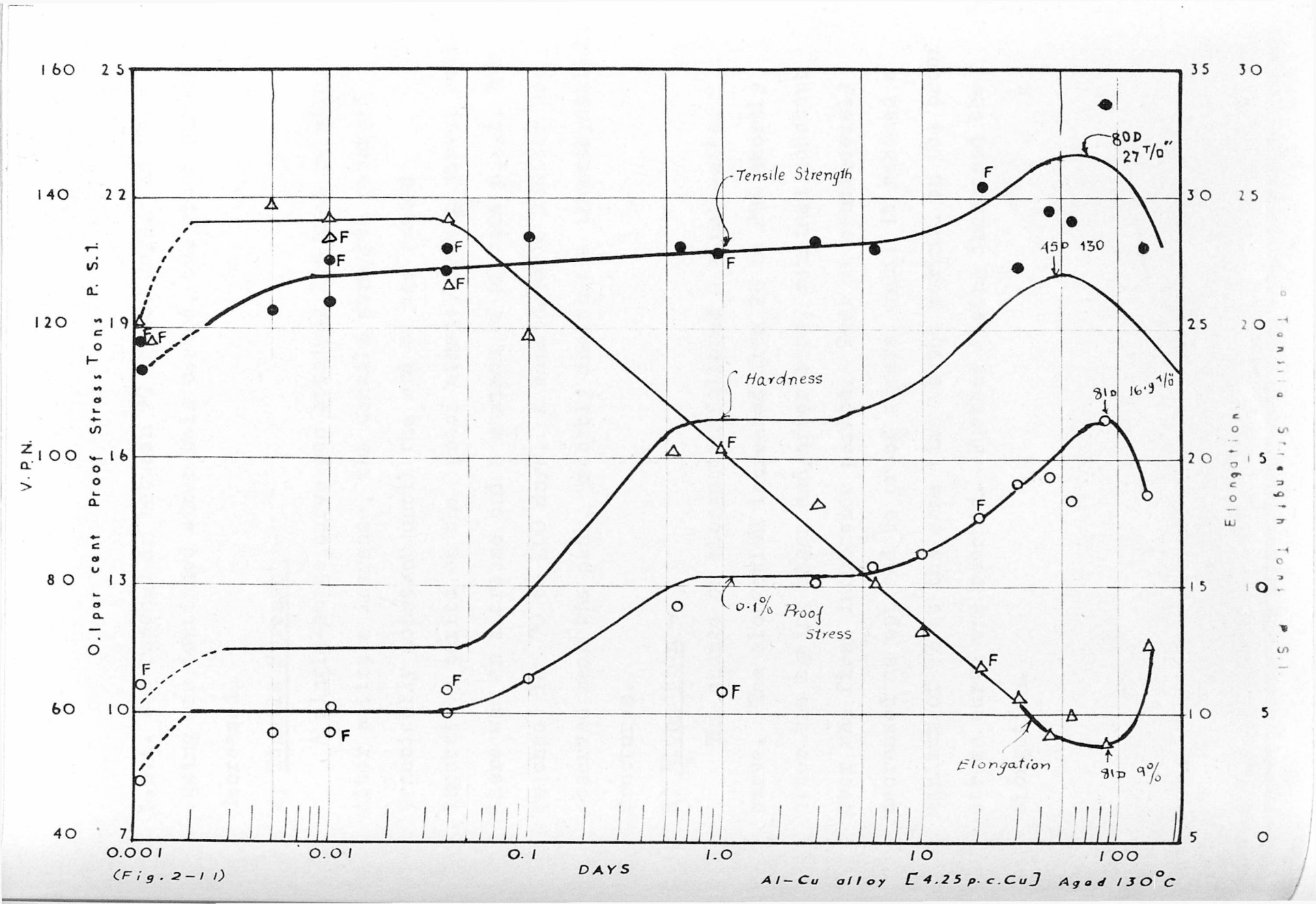
3) Elongation

The curve was single-stage, but the incubation period was observed to be slightly shorter than that for the proof stress. The elongation decreased after about 0.1 to 0.4 days and reached a minimum value of 12% (when a maximum on the proof stress curve was reached) and with further ageing, it increased.

Ageing Curves for the 4.25% Cu Alloy (fig.2 - 11)

1) 0.1% Proof Stress -

Two stages are evident when the proof stress/ ageing curve is examined. Shortly after ageing, the proof stress increased from 8.5 to 10 tons p.s.i., and remained constant for the first incubation period. It then increased to a value of about 13 tons p.s.i. and after attaining this value, again remained constant for a period of about 5 days, giving the second flat on the curve. The proof-stress then increased until a maximum of about 17.0 tons


160
140
120
100
80
60
40
V.P.N.
25
22
19
16
13
10
7
0.1 per cent Proof Strass Tons P. S. I.
35
30
25
20
15
10
5
0
Tensile Strength Tons P.S.I.
Elongation
Tensile Strength
Hardness
0.1% Proof Stress
Elongation
80D 27 T/0"
150 130
81D 16·9 T/0"
81D 9%
F
0.001
0.01
0.1
1.0
10
100
DAYS
(Fig. 2-11)
Al-Cu alloy [4.25 p.c. Cu] Aged 130°C

p.s.i. was reached in between 70 to 100 days. As the ageing was continued after this period, the proof stress decreased.

2) Tensile Strength -

A single-stage curve was obtained for this relation. After a little increase, the tensile strength remained practically constant until the end of the second incubation period on the proof stress / ageing curve; then there was an increase and a maximum of 26 tons p.s.i. was reached in 70 to 100 days. A considerable scatter was observed near the peak, probably due to the intercrystalline fractures.

3) Elongation -

The change of elongation followed a single-stage curve. The elongation increased from 25 to 28% shortly after the ageing began and, after that, remained constant over the first incubation period. Then it continuously decreased as opposed to proof stress, until it reached a minimum of 9% at the same time as the maximum on the proof stress curve was reached. Further ageing increased the elongation.

THE SYSTEM ALUMINIUM-COPPER-MANGANESE

Previous Work

FINK, SMITH and WILLEY (1940) quenched samples of three alloys of the Al-Cu-Mn system from 525°C and aged them at room temperature. The alloys contained 4 percent copper and 0.25, 0.5 and 1.0 percent manganese, respectively. Dilation, electrical resistance and yield strength curves all indicated that 0.25 per cent manganese had no appreciable effect upon the ageing of binary Al-Cu alloys, but the addition of 0.5 to 1 per cent Mn distinctly reduced the extent of ageing. They found that up to 0.25 per cent, all the manganese was in solid solution and it seemed that the diffusion of manganese was so sluggish that, at the ageing temperatures, it did not participate in the precipitation. The ternary compound, "T", is formed at manganese contents above 0.25% and this depletes the solid solution of copper. This would explain the decrease in the precipitation hardening at room temperature. However, no explanation was given as to why 1% Mn had no greater effect than 0.5% manganese.

SHARMA (1947) reported that the addition of manganese to a binary 4.4% Cu alloy, formed the ternary compound and this reduced the effective copper content, which

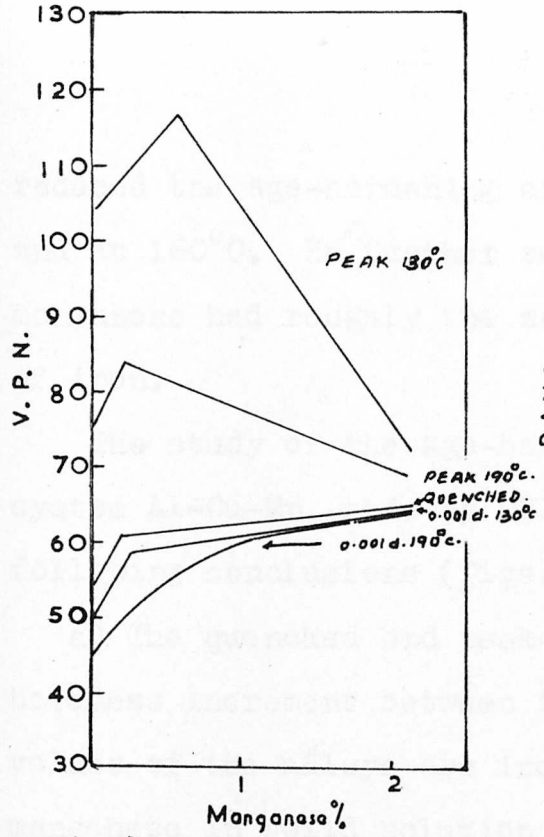


Fig (2-12)- Concentration/Hardness

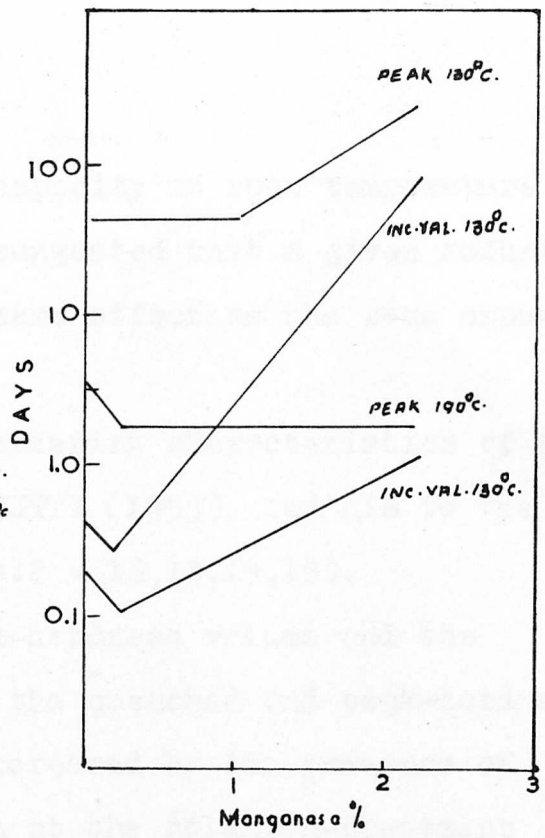


Fig (2-13)- Concentration/Time

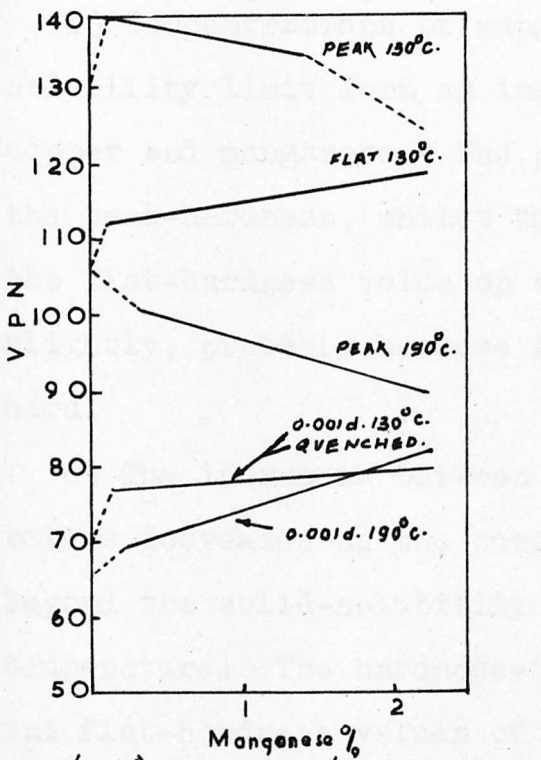


Fig (2-14)- Concentration/Hardness

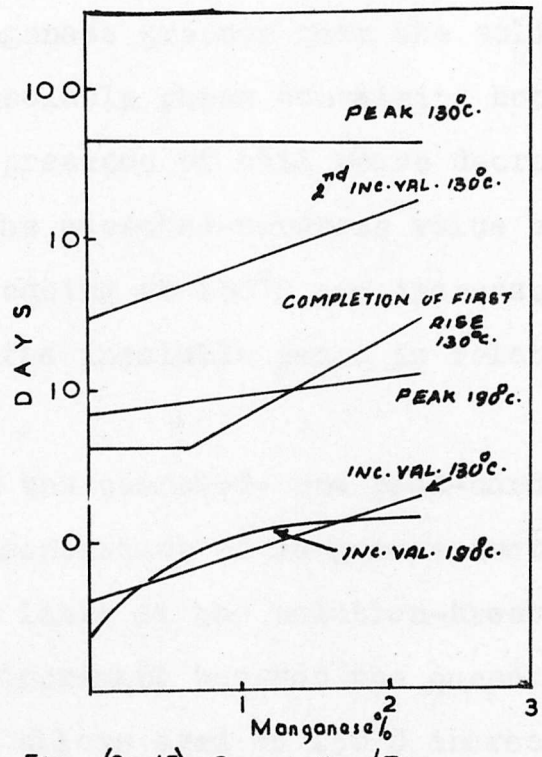


Fig - (2-15)- Concentration / Time

Analysis of Ageing Curves of Aluminium Alloys with 3% Cu (2-12, 13) & 4.5% Cu (2-14, 15) Containing Manganese (Chitty)

reduced the age-hardening capacity at room temperature and at 160°C. He further suggested that a given amount of manganese had roughly the same effect as the same amount of iron.

The study of the age-hardening characteristics of the system Al-Cu-Mn, made by CHITTY (1955), led him to the following conclusions (figs.2 - 12,13,14,15).

a) The quenched and peak-hardness values and the hardness increment between the quenched and peak-hardness values of the alloys are increased by the presence of manganese in solid solution at the solution-treatment temperature.

b) Concentrations of manganese greater than the solid-solubility limit form an insoluble phase containing both copper and manganese. The presence of this phase decreases the peak-hardness, whilst the quenched-hardness value and the flat-hardness value on ageing at 130°C are increased slightly, probably because the insoluble phase is relatively hard.

c) The increment between the quenched- and peak-hardness values decreases as the concentration of manganese increases beyond the solid-solubility limit at the solution-treatment temperature. The hardness-increment between the quenched- and flat-hardness values of alloys aged at 130°C increases

ANALYSIS OF AGEING CURVES OF ALLOYS WITH 3.0% COPPER CONTAINING Mn

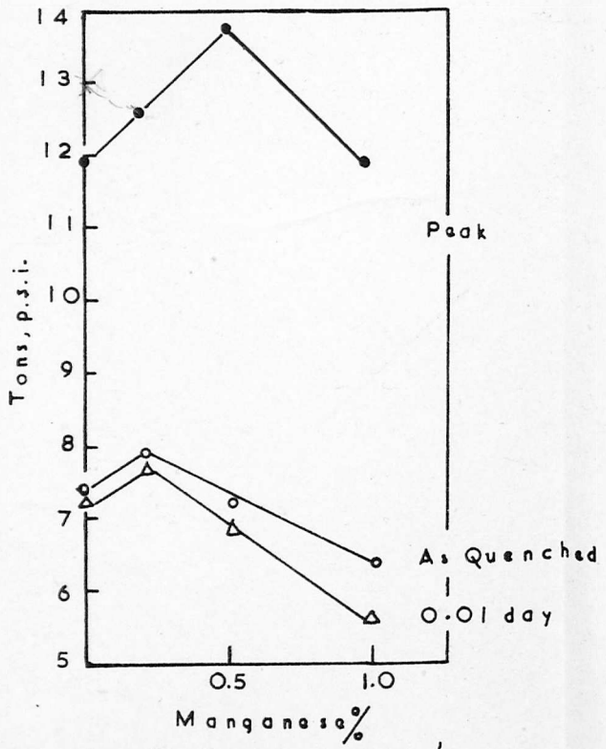


Fig.(2–19)–Concentration / 0.1 p.c. Proof Stress Relationships

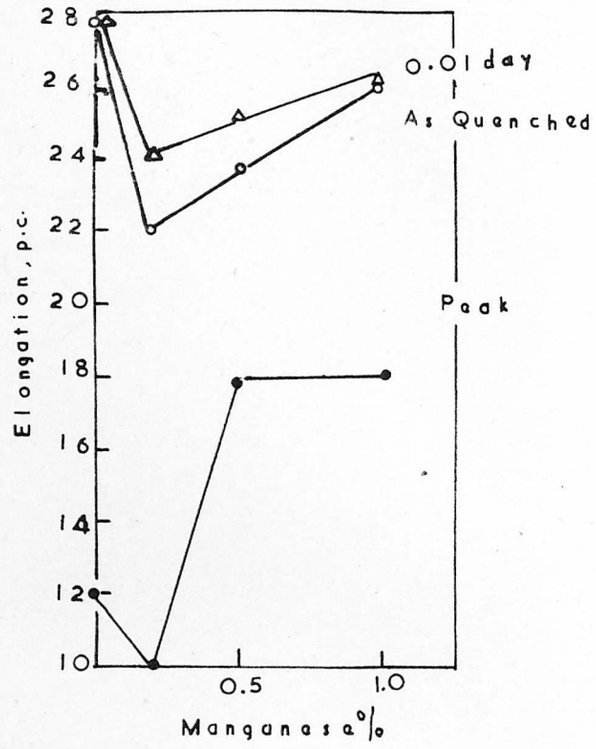


Fig.(2–21)–Concentration / Elongation per cent Relationships

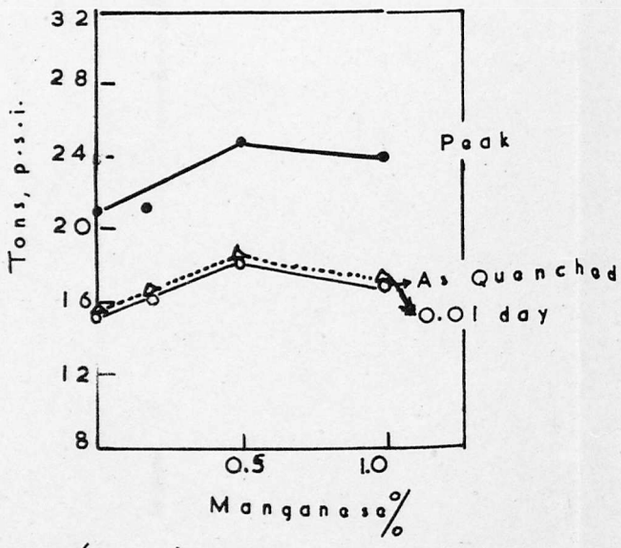


Fig.(2–20)–Concentration / Tensile Strength Relationships

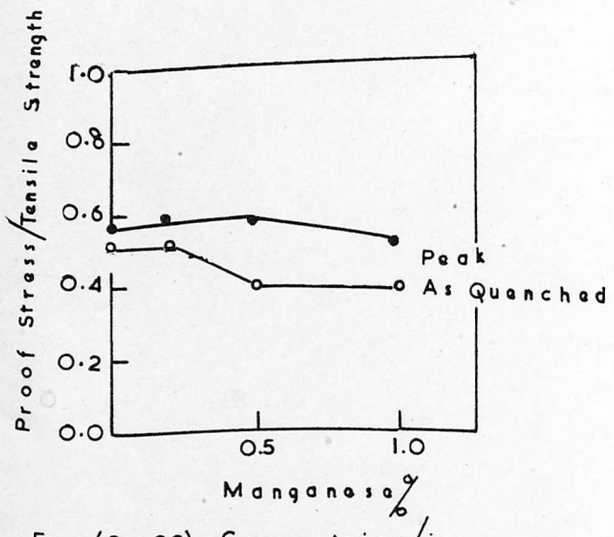
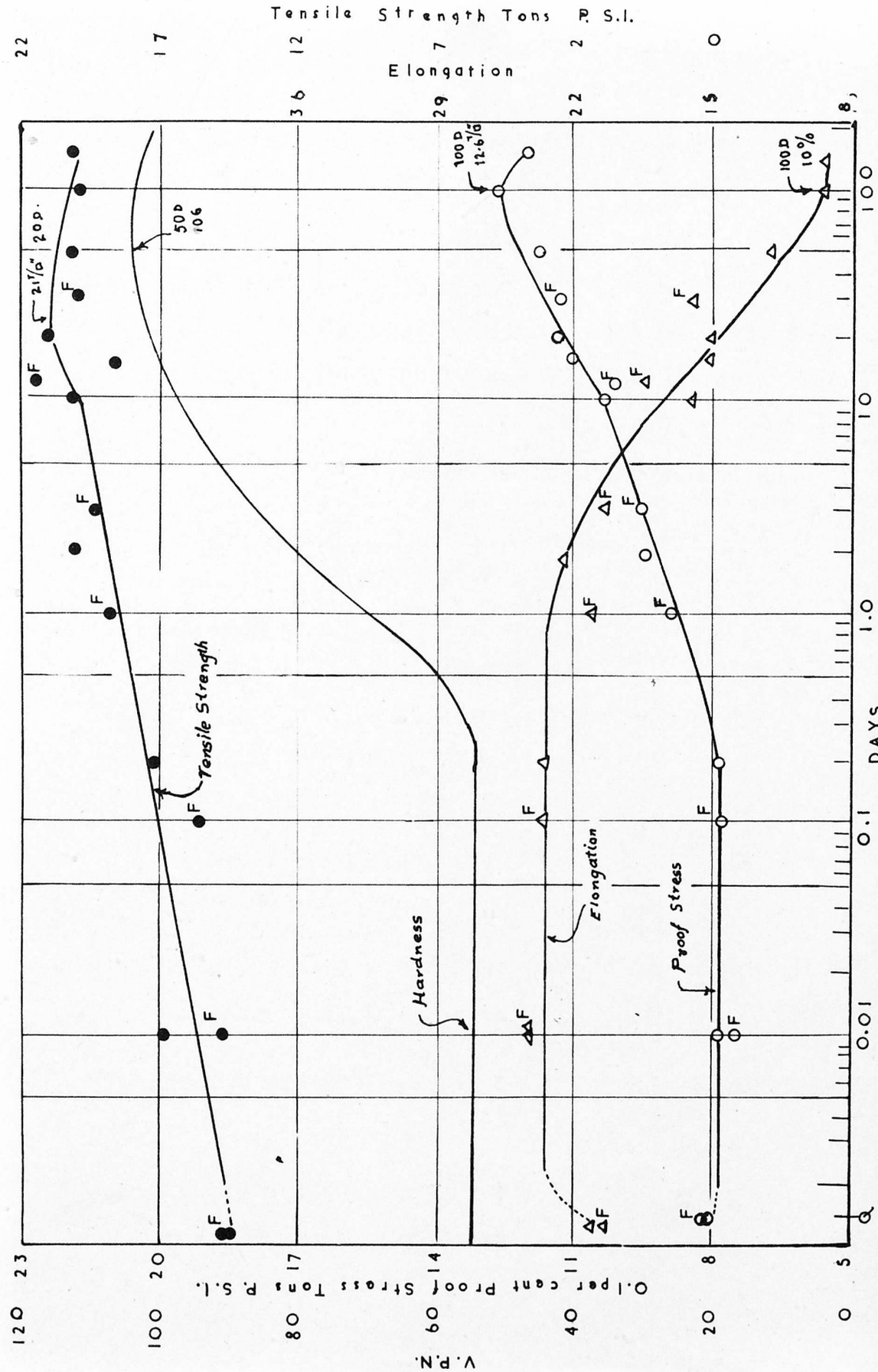


Fig.(2–22)–Concentrion / Proof Stress / T. S. Relationships



(Fig 2–16)

slightly with increased manganese concentration.

RESULTS

In the present work, seven alloys containing various amounts of manganese at nominal contents of 3.0 and 4.5% copper were studied (as described previously, these alloys were made by CHITTY, 1955).

The analyses are given below.

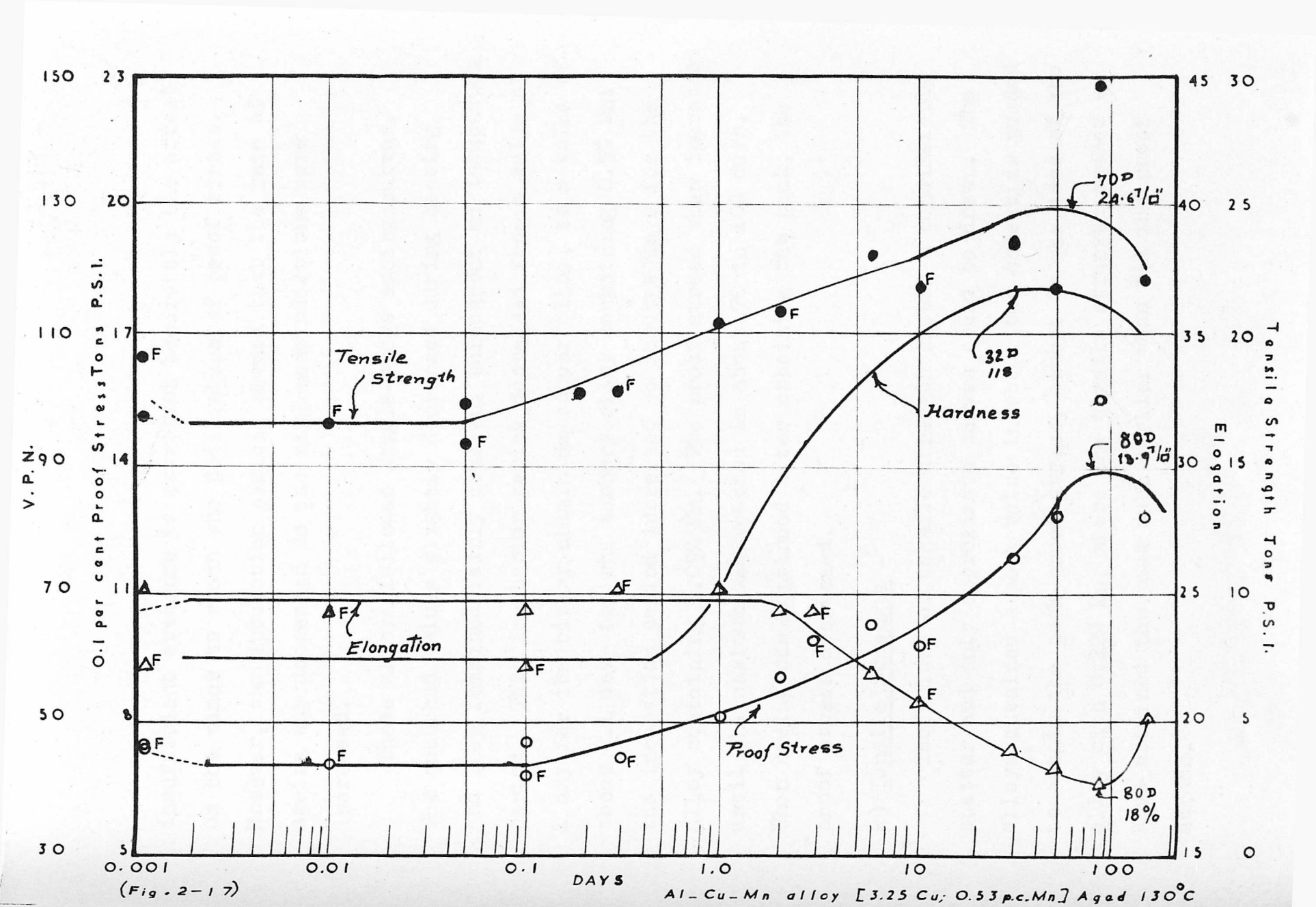
Alloy No.	% Cu	% Mn	% Fe	% Si
32	3.05	0.22	N.A.	N.A.
33	3.25	0.53	N.A.	N.A.
34	2.95	1.05	N.A.	N.A.
28	4.60	0.21	N.A.	N.A.
29	4.60	0.52	N.A.	N.A.
30	4.60	1.05	N.A.	N.A.
31	4.50	1.90	0.006	0.002

Microscopical examination of the solution-treated and quenched specimens showed the structures in all the alloys to be α-(solid solution) + T($Al_{12}CuMn_2$).

Ageing Curves for the 3% Cu Alloys (figs.2 - 16,17,18)

1) Proof Stress -

Ageing was slower and the proof stress attained was lower as the manganese content exceeded 0.5%; there was

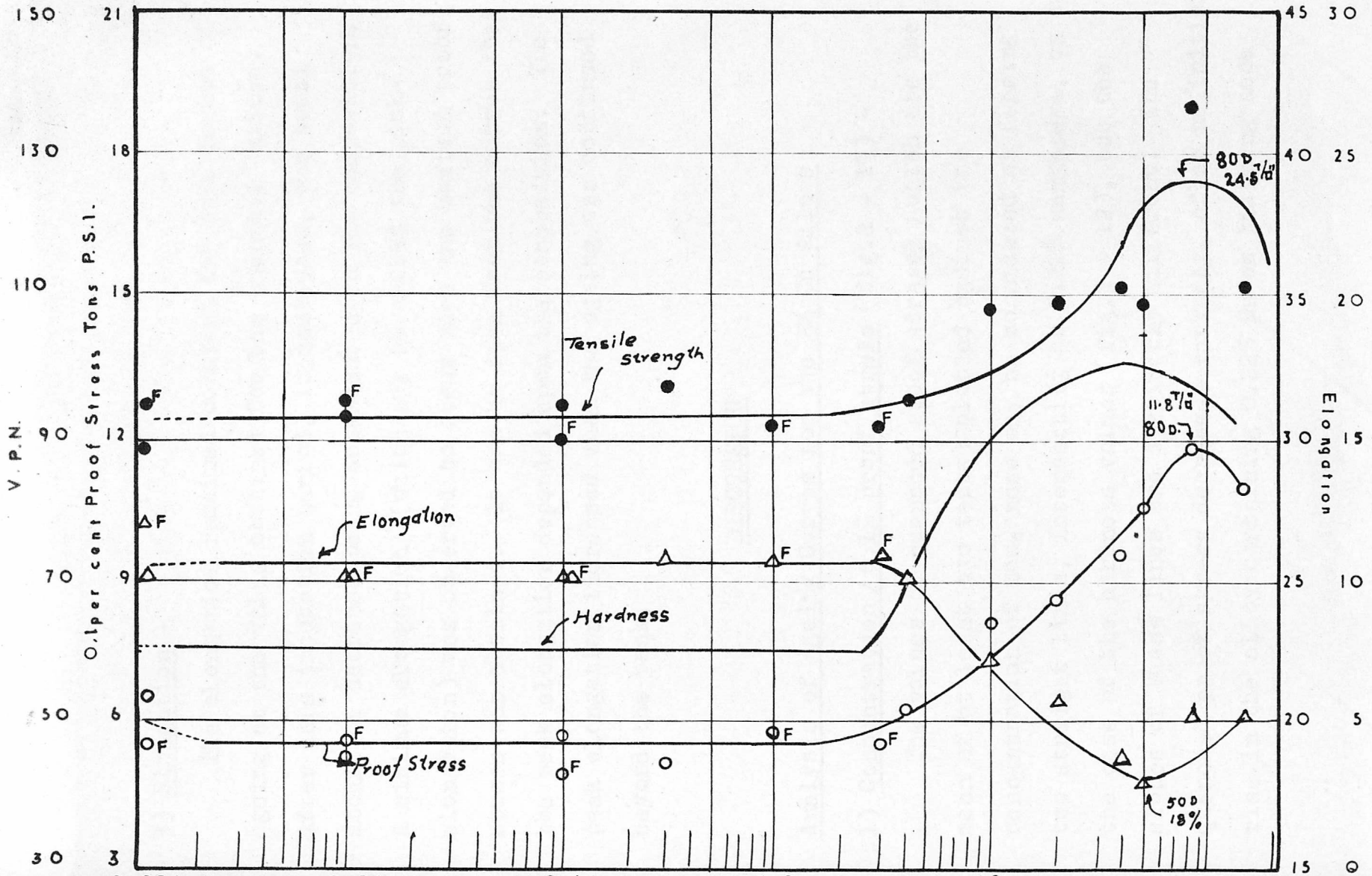

150 23
130 20
110 17
90 14
70 11
50 8
30 5
V.P.N.
0.1 per cent Proof Stress Tons P.S.I.
45 30
40 25
35 20
30 15
25 10
20 5
15 0
Tensile Strength Tons P.S.I.
Elogation
70D 24·6 T/□"
32D 118
Hardness
80D 19·9 T/□"
80D 18%
Tensile Strength
Elongation
Proof Stress
F
0.001
0.01
0.1
1.0
10
100
DAYS
(Fig. 2-17)
Al-Cu-Mn alloy [3.25 Cu; 0.53 p.c. Mn] Aged 130°C

insufficient evidence to establish accurately the effect on the times to reach the peak values of proof stress. However, the incubation periods showed that the rate of ageing was decreased as the manganese additions were increased.

These alloys followed single-stage ageing curves. The quenched values slightly decreased during heating, and then remained fairly constant throughout an incubation period. This incubation period decreased from a value of 1 day for the binary aluminium-copper alloy, to a value of about 0.1 day for the ternary alloy containing 0.5% Mn; the incubation period increased to about 4 days for the alloy containing 1.05% Mn. The proof stress then increased until the maximum was reached in about 70 to 100 days. When ageing was continued after attaining the peak, the proof stress decreased.

2) Tensile Strength -

The values of tensile strength showed a considerable scatter and only approximate curves could be drawn. The alloys attained a peak value in about the same time needed to attain the peak proof stress, except in the case of the alloy with 0.22% Mn, where the tensile strength seemed to have attained the peak much earlier than did the proof stress.



(Fig. 2–18)

Al–Cu–Mn alloy [2.95 p.c.Cu ; 1.05 p.c.Mn] Aged 130°C

3) Elongation -

The elongation remained constant for some period of ageing at the value obtained for the quenched alloys. After this incubation period, it decreased, the total amount of decrease being dependent upon the composition. A minimum elongation (which may be called the peak-elongation) was observed to occur when the maximum proof stress was attained. It can be seen from the curves that the peak elongation depended upon the composition. The peak elongation increased when the ageing was continued beyond the peak.

DISCUSSION

Analysis of Ageing Curves for the 3% Cu Alloys

1) Concentration / 0.1% proof stress (fig.2 - 19) -

The values of quenched proof stress (which are the mean of at least two tests) plotted against the concentration of manganese may be considered as forming two straight lines, intersecting at 0.22% manganese, as in the case of the hardness values (fig.2 - 12), but the slopes of these lines are distinctly different. The quenched proof stress decreases markedly, after an initial rise in the alloy containing 0.22% Mn as the manganese

percentage is increased beyond this limit, whereas the hardness increases. This also holds for the proof stress values attained after ageing for 0.01 days. It seems probable from these curves that the depletion of the solid solution in copper content, by the formation of the T-phase, has a considerable effect on the proof stress in the as-quenched condition and that the dispersed phase in these alloys, which was thought to be responsible for the increased hardness beyond 0.22% Mn, has a proportionately negligible effect on the proof stress. However, the value of the proof stress for the 0.5% manganese alloy seems to be inconsistent with this idea, because the effective copper content (fig.2 - 31) of this alloy was not reduced beyond 3%, thus this result seems anomalous and no explanation is apparent.

The values of peak proof stress however, lie on two lines intersecting at 0.5% manganese. This point of intersection should, in fact, represent the solid-solubility limit of manganese in the aluminium-3% copper alloy, and to be in agreement with the data, should occur at about 0.25% manganese. This discrepancy can be explained by a consideration of the plot of effective copper contents of these alloys against the manganese precentages. It may be seen from the fig.(2 - 31) that

the effective copper content of the alloy containing 0.5% manganese was, in fact, slightly higher than that of the 0.22% manganese alloy. The amount of manganese beyond the solid solubility limit, therefore, had not depleted the matrix below a value of 3% copper. This fact, coupled with the smaller grain size (fig.2 - 33) of the alloys containing 0.5 or higher percentages of manganese, leads to the explanation.

2) Concentration / Tensile Strength (fig.2 - 20) -

The plots of tensile strength against the concentration are formed by two straight lines intersecting at 0.5% manganese, in the as-quenched and partially- and fully-aged alloys.

From general considerations, it would seem that as the amount of solute elements in the solid solution decreases, the quenched- and peak-values of tensile strength should decrease. However, it may be seen, in the case of the 1.0% manganese alloy, that the peak tensile strength of this alloy was greater than that of the 0.22% manganese or basic binary alloy. As discussed in the first chapter of this section, while reviewing the literature, manganese beyond the solid solubility limit decreases the grain size. The grain boundary area is thus increased and the concentration of the precipitate at the grain boundaries



Fig.(2-33)

COMPOSITION: 4.25% Cu
TREATMENT: Solution-treated at 525°C and quenched.
REMARKS: Transcrystalline fracture (large grains)
ETCHANT: 30% H_2SO_4, 30% HNO_3, 0.5% HF; 30 secs.
x 50

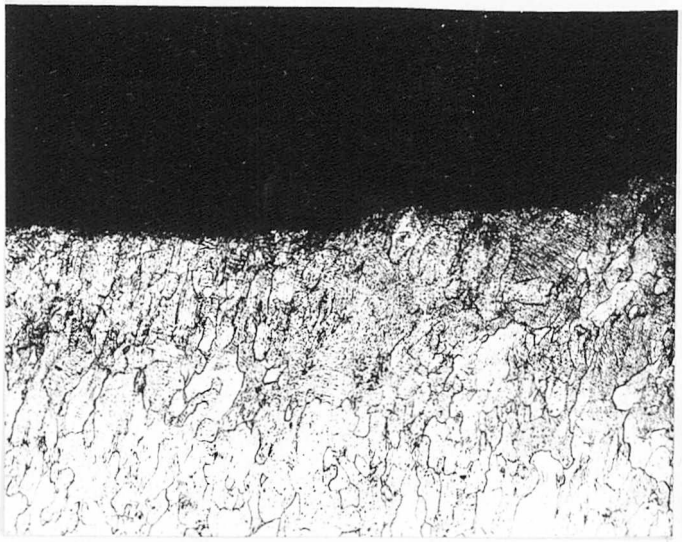


Fig.(2-34)

COMPOSITION: 4.6% Cu, 1.05% Mn
TREATMENT: Solution-treated at 525°C and quenched.
REMARKS: Transcrystalline fracture (Irregular and small grains)
ETCHANT: 30% H_2SO_4, 30% HNO_3 and 0.5% HF; 30 secs.
x 50.

should decrease. The suggestion made by GEISLER (1949) that the grain boundary precipitation may not affect the yield strength but allow fracture at lower tensile stress and thus affect the actual value of tensile strength, seems an adequate explanation of the behaviour of the 1.0% manganese alloy, as compared with other alloys.

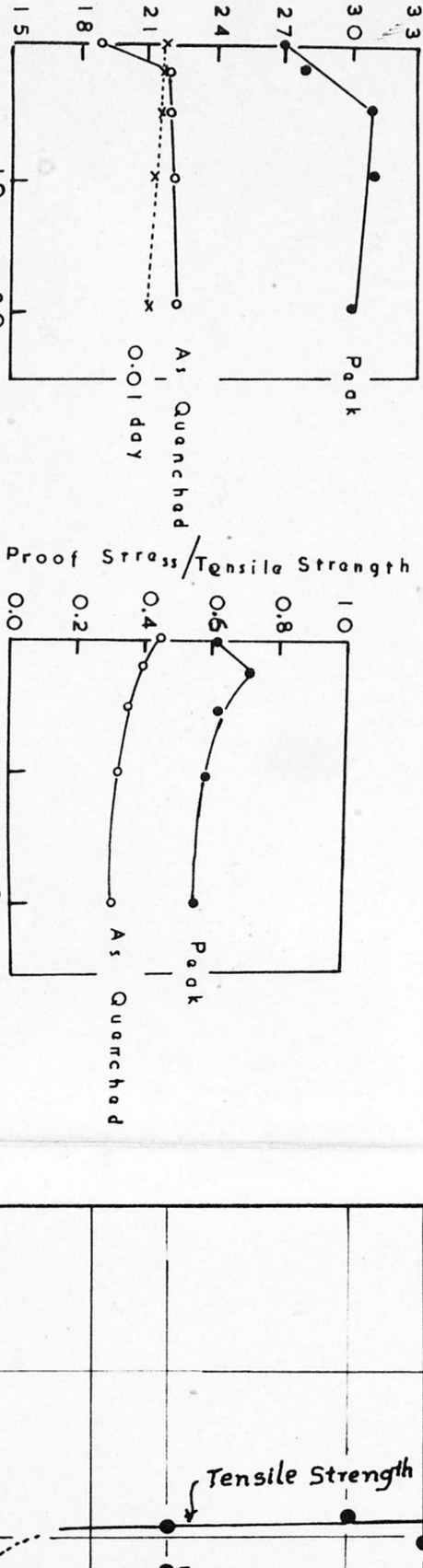
3) Concentration / (Proof Stress/Tensile Strength) fig.(2-22)

It may be seen that this relationship is dependent upon the composition more in the as-quenched than in the fully-aged condition. Following the observations of DIX (1945), it may be expected that the ratio should increase appreciably from the value for the as-quenched to that of the fully-aged alloys. However, in the case of the present series of alloys, only a small increase was observed. Possibly the increase in the tensile strength is proportionately higher in the purer alloys, as compared with that of the commercial grade.

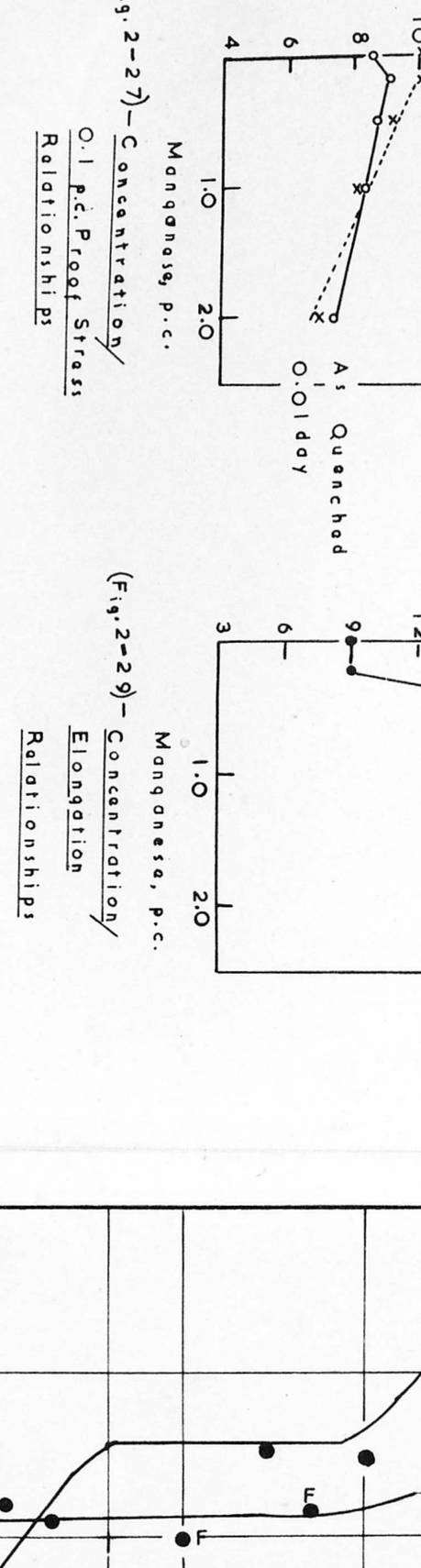
4) Concentration / Elongation (fig.2 - 21) -

The plots of elongation against the concentration of manganese in the as-quenched condition form two lines intersecting at 0.22% manganese; this holds also for the alloys aged for 0.01 day.

When the peak-elongation values are considered, it



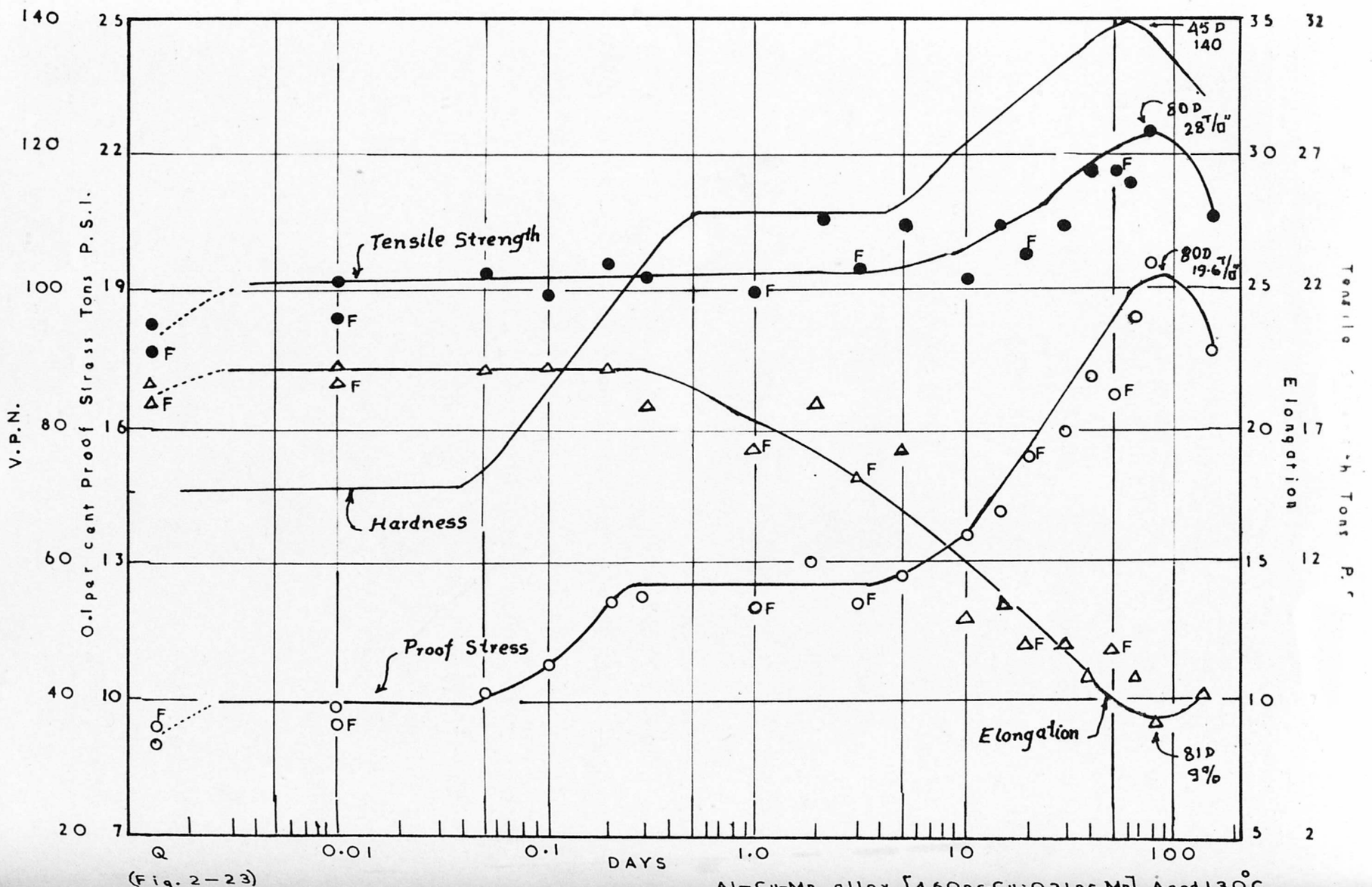
(Fig. 2-27)— Concentration/0.1 p.c. Proof Stress Relationships



(Fig. 2-29)— Concentration/Elongation Relationships

(Fig. 2-28)— Concentration/Tensile Strength Relationships

(Fig. 2-30)— Concentration/Proof Stress/T.S. Relationships



(Fig. 2-23)

Al-Cu-Mn alloy [4.60 p.c. Cu; 0.21 p.c. Mn] Aged 130°C

can be seen that the elongation first decreases from a value of 12% for the binary, to a value of 10% for the 0.22% manganese alloys; then it increases suddenly to a value of 18% for the 0.5% manganese alloy, and approximately the same value is obtained for the 1.0% manganese alloy.

The relationships will be discussed at a later stage.

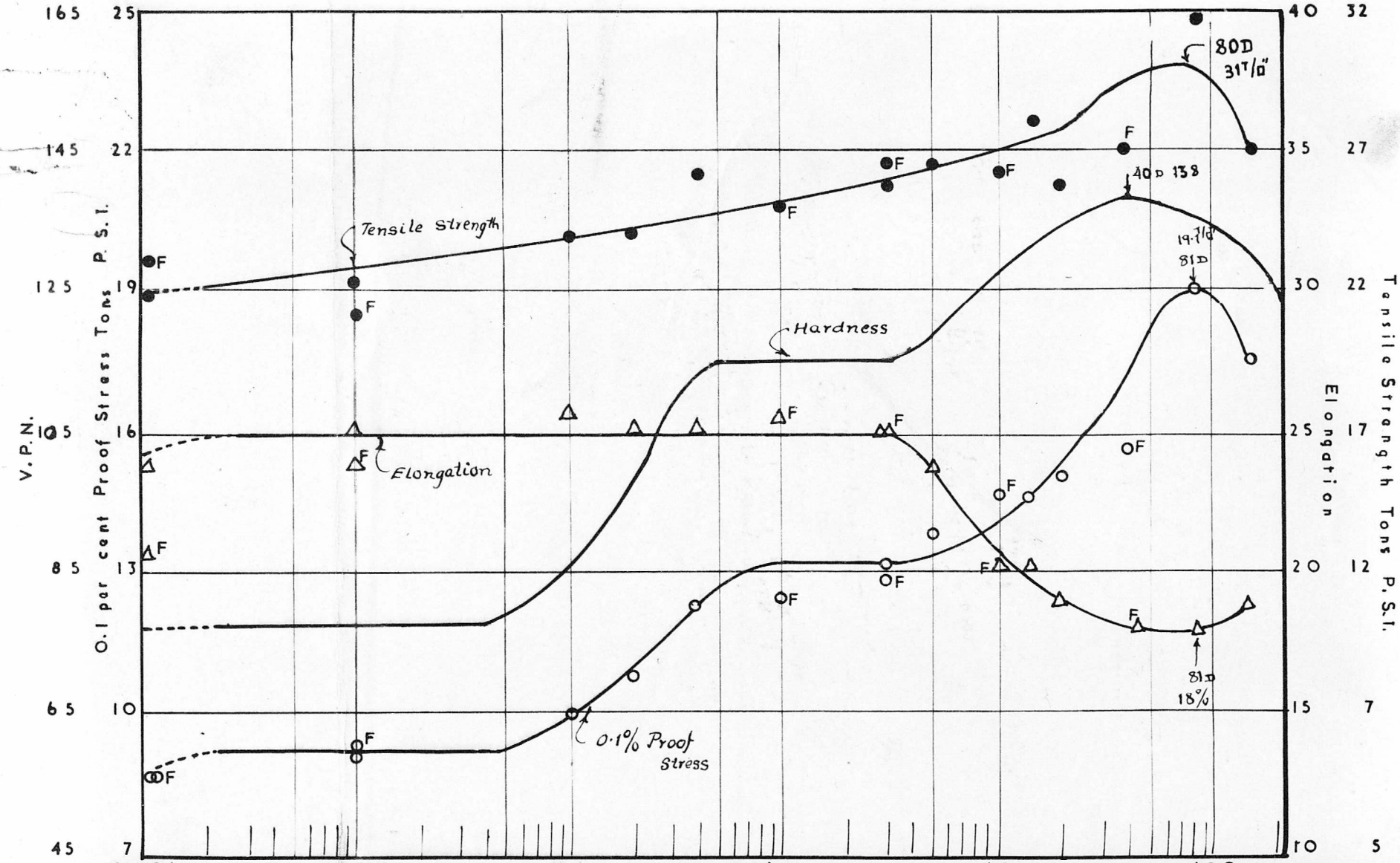
RESULTS

Ageing Curves for the 4.5% Copper Alloys (figs.2 - 23,24, 25,26)

0.1% Proof Stress -

These alloys showed two-stage ageing curves. In the case of the 0.21 and 0.5% manganese alloys, shortly after ageing, there was a slight increase in the proof stress, whilst a slight decrease occurred in the case of the 1.0% manganese alloys. The first incubation period seemed to be independent of the manganese content and this period was found to be approximately 0.05 day , as for the binary alloy.

The proof stress increased after the first incubation period and reached a steady value, which was dependent upon the manganese content; the alloy with 0.21% manganese reached a value of about 12.5 tons p.s.i.,



(Fig. 2-24)

Al_Cu_Mn alloy [4.60 Cu; 0.52 pc. Mn] Aged 130°C

whilst the 0.5 and 1.0% manganese alloys reached a value of about 13.4 tons p.s.i. (These values are the mean of several tests as shown by the points on the curves). The proof stress remained constant for about 5 days for all the alloys and then increased to a peak value of about 20.0 to 16.50 tons p.s.i., as the manganese was increased from 0.21 to 1.9%.

Tensile Strength -

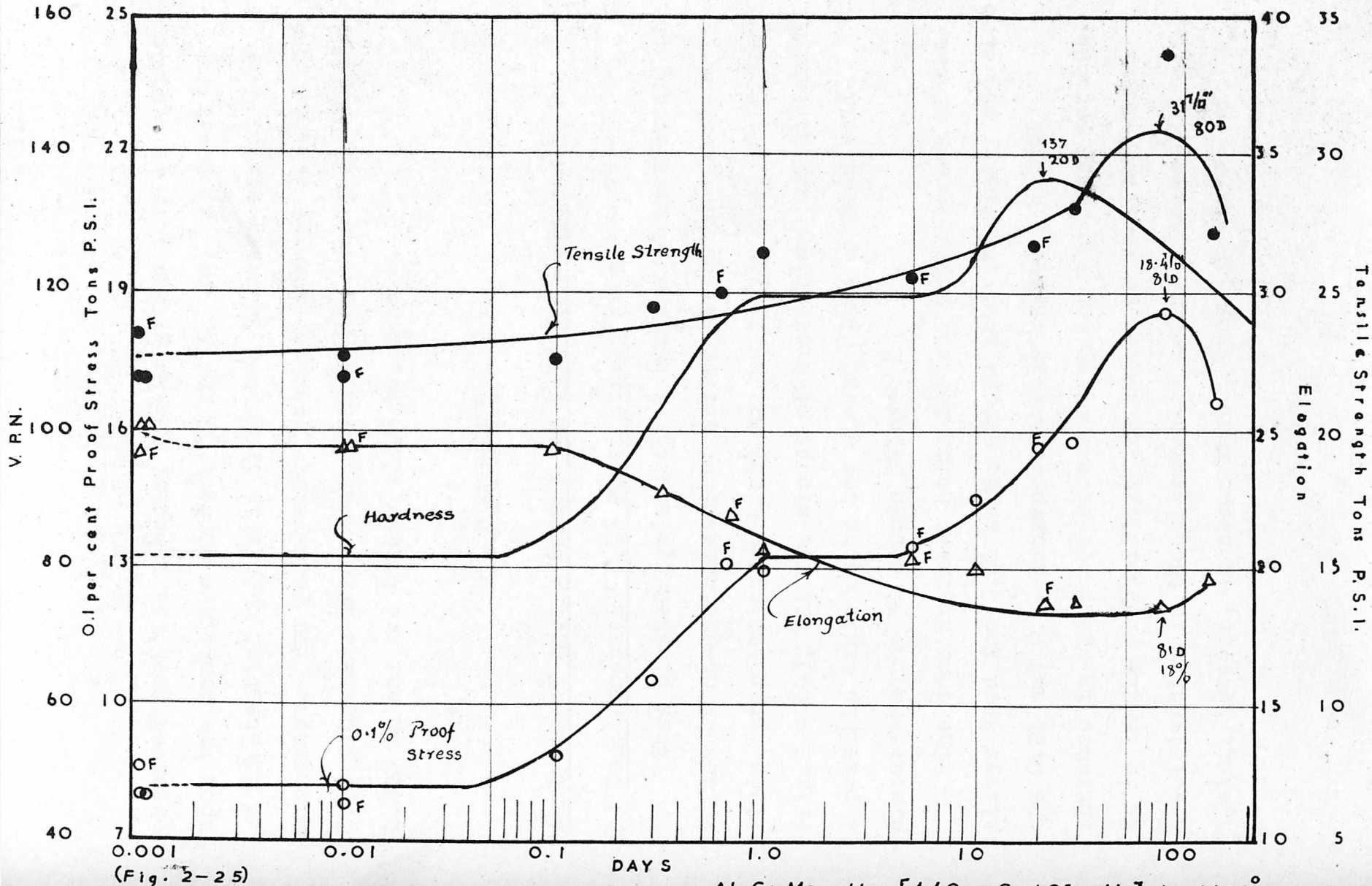
There was a considerable scatter as found in the previous series, but the curves were drawn with approximations. It will be seen from these curves that, in some cases, they do tend to show two stages; however, due to the lack of experimental points the stages are not very distinct.

The tensile strength increased as the ageing was continued, and reached a maximum in about the same time as the proof stress.

Elongation -

The elongation decreased with ageing and did not show any evidence of two stages. The peak was reached within about the same time as for the tensile strength and proof stress.

However, as found in the previous series, it was



(Fig. 2-25)

Al-Cu-Mn alloy [4.60 p.c. Cu; 1.05 p.c. Mn] Aged 130°C

observed that the decrease in elongation largely depended upon the manganese content of the alloys, but there was no substantial change in the total decrease beyond 0.5% manganese. The peak-values obtained for the 0.5, 1.0 and 1.9% manganese alloys were much higher than those for the 0.21% Mn and the binary 4.25% Cu, alloys.

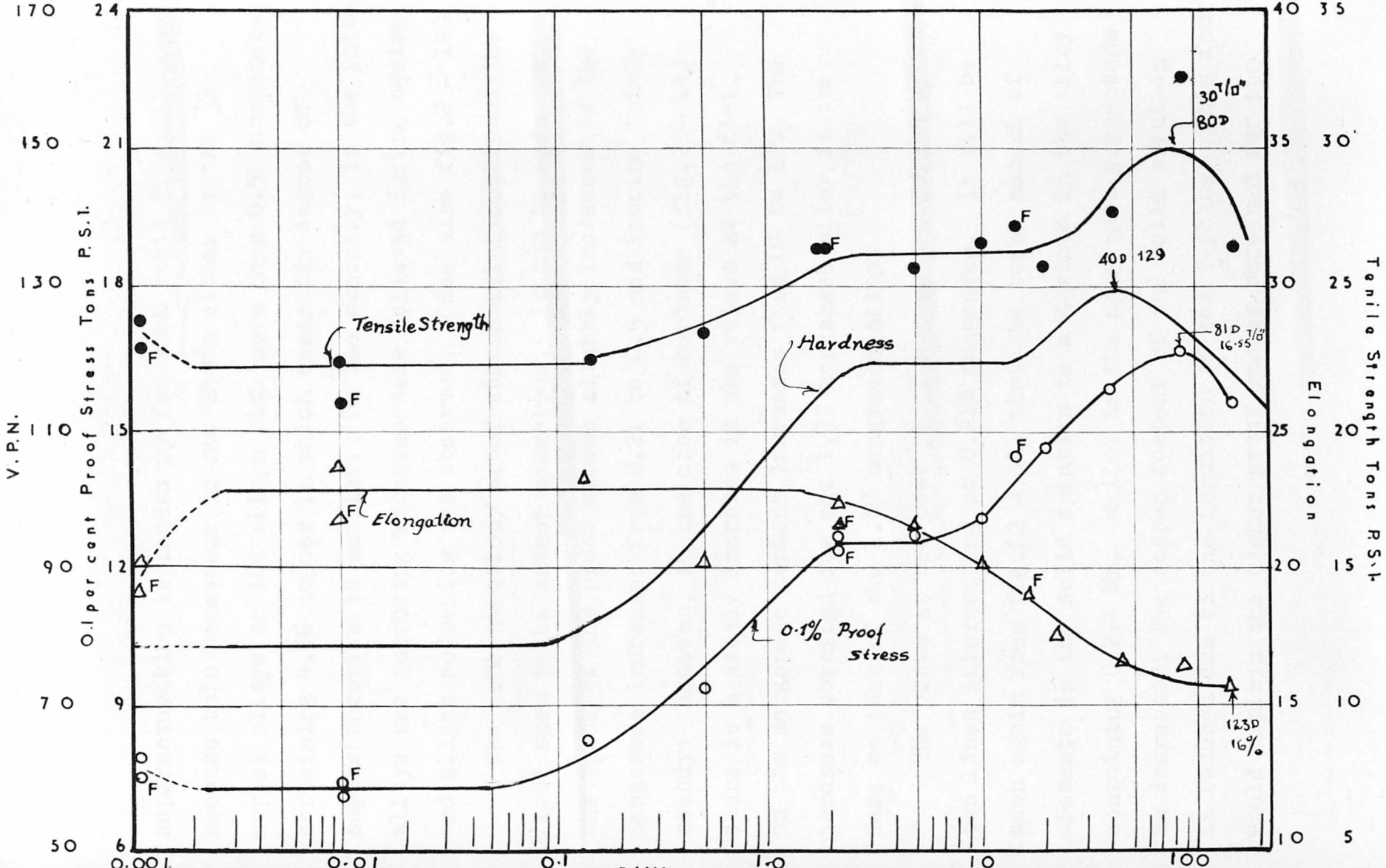
DISCUSSION

Analysis of Ageing Curves for 4.5% Cu Alloys

1) Concentration/ 0.1% Proof Stress (fig.2 - 27)

When plotted against the manganese concentration, the values of as-quenched proof stress lie on two straight lines intersecting at 0.21% Mn, as in the case of hardness (fig.2 - 14), but the slopes of these lines are different. A possible explanation has already been offered while discussing the 3% copper alloys.

The same argument holds for the proof-stress of the alloys aged for 0.01 days, except that the binary and also the 0.21 and 0.5% manganese alloys showed a slight increase in the proof stress on ageing for short periods. It is in all probability, the effect of localised rapid precipitation in the plastically deformed areas during ageing; however, it seems that a very high degree of



(Fig. 2–26)

Al–Cu–Mn alloy [4.50 p.c. Cu; 1.90 p.c. Mn] Aged 130°C

supersaturation is necessary for such rapid precipitation, because this behaviour is not shown either by the 3% copper alloys or the alloys with more than 0.5% manganese, containing 4.5% copper in which cases the degree of supersaturation is smaller. On the contrary, in the latter alloys the quenching stresses were relieved during ageing and slight softening was observed. (See also fig.2 - 19).

The concentration/ proof stress relationshipsat the 'flat' seem to be rather anomalous. It can be seen that the value of the proof stress slightly increases as the manganese increases from 0.21 to 0.5 and remains fairly steady: however, in the case of hardness (fig.2 - 14) there is a steady increase in the values at the flat, as the manganese content increases from 0% to 1%. The hardness obtained for the 1.9% manganese alloy is the same as that of the 1.0% manganese alloy.

The plots at the peak proof stress are formed by two lines intersecting at 0.21% manganese. It will be seen again from fig.(2 - 32) that the total amount of elements in the solid solution is a maximum in the alloy containing 0.21% Mn, whilst as the manganese percentage is increased, the copper content of the solid solution is reduced due to the formation of the T-phase. This fact would explain the higher proof stress obtained for the

alloy containing 0.21% manganese, and a subsequent decrease as the manganese percentage is increased. However, even on this basis, an alloy containing 1% manganese should have a lower proof stress than the 4.25% copper alloy, because the effective copper content of this alloy is about 4.0% only. The slightly higher values of the proof stress of these alloys may be accounted for, by the consideration of the smaller and irregular grain size of the alloys containing more than 0.5% manganese (fig.2 -33, 35, 37)

2) Concentration/ Tensile Strength (fig.2 - 28)

In the as-quenched condition, the plots of the tensile strength against the concentration of manganese show that the tensile strength increased as the manganese percentage increased from 0 to 0.21% and then remained fairly constant up to 1.90%.

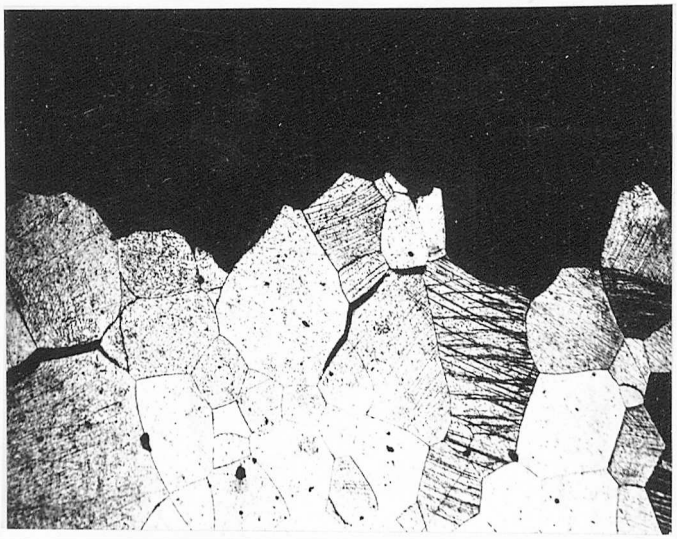
This can be explained by considering the relation of the tensile strength to the strength of the grain-boundary. It seems that in general, the fracture strength and the tensile strength depend on the strength of the grain-boundary rather than that of the matrix. In the case of these alloys, the photomicrographs (figs.2 - 33 to 37) show that as the manganese additions were increased, the grain size became smaller and the grain-boundaries very

irregular; therefore, it is natural to expect that the alloys with higher manganese would give higher tensile strength as compared with alloys with little or no manganese, although, with higher manganese contents the matrix is depleted more in copper. The curve for the alloys aged for 0.01 day may be explained on the same lines.

In the case of the relations between the tensile strength and the concentration at the peak, it can be seen that there was a considerable difference in the tensile strengths of the binary aluminium-4.25% Cu, the ternary 0.21% manganese and those of the alloys containing more than 0.5% manganese.

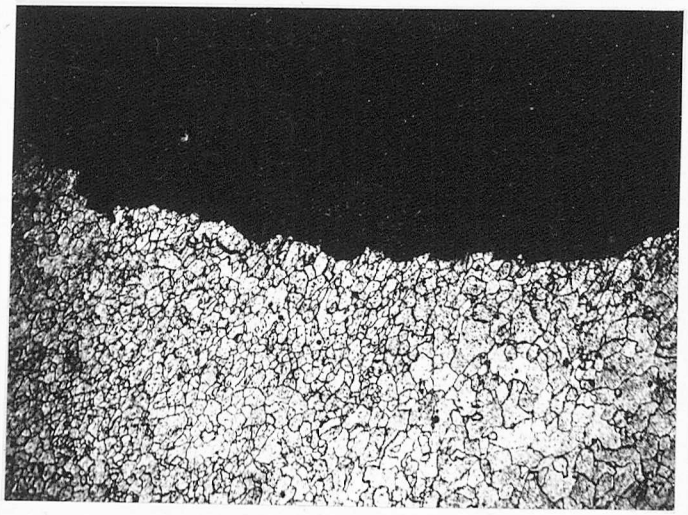
The review of the literature has shown that the occurrence of a continuous precipitate at the grain boundaries tends to favour intercrystalline fractures, while if the network of the precipitate is not continuous the susceptibility to intercrystalline fractures is reduced.

Figs.(2 - 36,37,38) show that, as the manganese content of the alloys increased to or beyond 0.5%, the fractures obtained tended to be more on the side of transcrystalline in nature, while the alloys with 0.21 or less manganese showed a coarser grain size and a pronounced tendency to



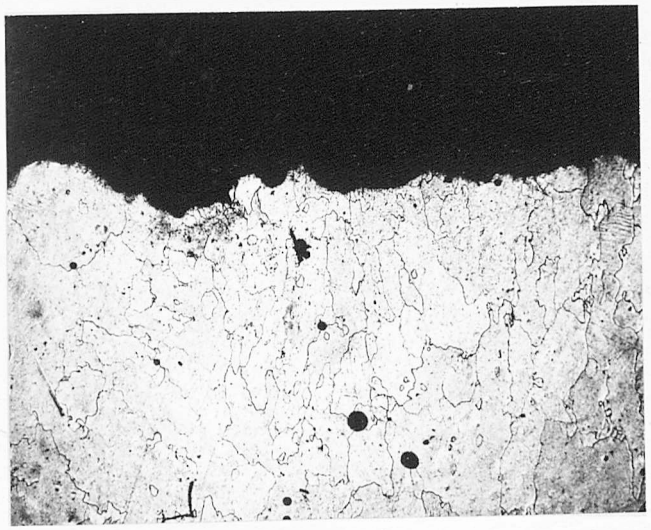
Fig(2-35)

COMPOSITION: 4.6%Cu, 0.22%Mn
TREATMENT: Solution-treated at 525°C and aged at 130°C for 80 days.
REMARKS: Inter-crystalline fracture (large grains)
ETCHANT: 30% H_2SO_4, 30% HNO_3 and 0.5% HF. 30 secs. x 50.



Fig(2-36)

COMPOSITION: 4.6%Cu 0.5% Mn
TREATMENT: Solution-treated at 525°C and aged at 130°C for 80 days.
REMARKS: Inter-mediate fracture. (small grain size)
ETCHANT: 30% H_2SO_4, 30% HNO_3 and 0.5% HF. 30 secs. x 50.



Fig(2-37)

COMPOSITION: 4.6% Cu 1.05% Mn
TREATMENT: Solution-treated at 525°C and aged at 130°C for 80 days.
REMARKS: Inter-mediate fracture, (Irregular grains, slightly coarsened)
ETCHANT: 30% H_2SO_4, 30% HNO_3 and).5% HF 30 secs. x 50.

intercrystalline fractures. It is therefore probable, in higher manganese alloys that,

i) due to the smaller grain size the grain boundary area increases, and thus the concentration of the precipitate along the grain boundary is reduced.

ii) The reduction in the localised precipitation further reduces the extent of the denuded zone, and also the degree of denudation.

iii) the U-constituent supplies alternative sites for the precipitate, and thus reduces its concentration along the grain boundaries.

These factors seem to have so much effect on the tensile strength that the alloy containing 1.9% manganese which has, in fact, an effective copper content of about 3.6% only (fig.2 - 32) showed a higher tensile strength than the alloy containing 4.6% Cu and 0.21% Mn. (The difference between the modes of fractures and the grain size is worthy of note).

3) Concentration / (Proof stress/Tensile Strength)

The ratio of proof stress to tensile strength is seen to decrease with increasing concentration, for the alloys in the as-quenched condition. The ratio increases from about 0.4 for the quenched alloys to about 0.6 for the fully-aged alloys. However, the alloy with 0.21%

manganese showed a slightly higher increase in this ratio, suggesting that the difference between the proof stress and tensile strength was less for this alloy. Its effect on the elongation is quite important, which will be discussed below.

4) Concentration / Elongation (figs.2 - 29, 2 - 21)

In the as-quenched condition, the elongation decreases from the value of about 25% for the binary alloy to about 22% for the 0.21% manganese alloy; it then increases to a value of about 25% for the 1% manganese alloy and again decreases to about 20% for the 1.9% manganese alloy. Similar behaviour is exhibited by the 3% copper alloys. Both results can be explained on the same principles and, for this reason, they have been grouped together.

In the case of the alloys with 0.21% manganese, nearly all the amounts of the alloying elements will be in solid solution and thus, as compared with the binary alloys, these ternary alloys would have more lattice stresses.

Now considering the elongation as the total deformation along the longitudinal axis by slip, in highly-stressed lattices the slip becomes more and more difficult and consequently, the ternary alloys with about 0.2% manganese should show lower elongation.

The behaviour of the 3 0% Cu-0.5% Mn alloy in the quenched condition, seems to be rather anomalous at first sight, because this alloy also contains approximately the same amount of the elements in the solid solution, as that of the 0.22% manganese alloy of the same series; (unfortunately, the copper % of this alloy was found to be 3.25% and, therefore, this alloy actually contains 3% copper and 0.2% manganese in the solid solution): however, considering the figs.(2 - 20) and (2 - 19), it can be seen that the difference between the proof stress and tensile strength for the 0.5% Mn alloy was appreciably greater than that for the 0.21% manganese alloy.

Now, if the tensile test is considered it will be seen that the elongation depends mainly upon the amount of plastic deformation that a specimen will undergo before fracture. The elastic strain may be neglected for practical purposes. The plastic deformation is set up when the elastic strain ceases, i.e. when the proof stress is passed, the specimen starts deforming plastically and continues until the tensile strength is reached, and thus the total elongation, to some extent, would depend upon the difference in the proof stress and the tensile strength. A further elongation occurs during necking, but often it does not contribute appreciably towards the total

elongation, except in cases where the elongation is very small and the gauge lengths are comparable with the amount of necking. However, in the alloys tested, it was found that there was very little necking and therefore its effect on the elongation measurements is not significant.

HOLLOMAN and JAFFE (1947) suggested that the elongation depends more on the rate of strain-hardening than on the difference between yield and tensile strength.

The rate of strain-hardening can be assessed from the slope of the stress-strain curve, between the proof stress and tensile strength; the greater the slope the greater the rate of strain-hardening.

In the present case, it was found that slopes of the stress-strain curves between the proof stress and tensile strength, for both the 0.21 and 0.5% manganese alloys were substantially the same. It may, therefore, be said that the higher value of elongation for the 0.5% Mn alloy is due to the increased tensile strength.

The values of elongation for the alloys aged for 0.01 days may be explained on the same basis, except that, due to the relief in quenching stresses they may give slightly higher elongation.

As the manganese content of these alloys increases, the solid solution is depleted in copper by the formation

of the T-phase, and the lattice stresses are further reduced and higher values for elongation, as obtained in the present work, may be expected.

The alloy containing 1.9% manganese and 4.5% copper, however, showed a lower value, though the matrix is depleted in copper to a considerable extent. It seems perhaps, that the effect of the finely dispersed T-phase beyond a certain amount, exceeds the lattice-relief effect due to depletion, and thus inhibits the slip, consequently giving lower values for the elongation.

The values of the elongation of the fully-aged alloys, when plotted against the concentration form two groups:

1) The binary and 0.20% manganese ternary alloys, giving lower values of around 9 to 10% elongation.

2) Alloys with higher manganese, giving higher values of elongation around 16 to 18%.

1) As already stated, the continuous network of the precipitate prevents the slip from passing through the grain boundaries. It allows pile-up of the dislocations along the grain boundaries, and leads to strain-hardening. The denuded zones along the grain-boundaries are subjected to a state of hydrostatic pressure and before any appreciable deformation takes place, the specimens fracture by intercrystalline failures.

2) As compared with the (fig.2 - 33,35) above case, the alloys with higher manganese contents have a smaller grain size and irregular grain boundaries. This will lead to a more uniform precipitation during the ageing. Manganese may be providing the alternative sites for nucleation and thus may be reducing the extent of the precipitate at the grain boundary. This ultimately amounts to a reduction in the denuded zones and increased strength of the grain boundaries.

The network of the precipitate would not be continuous as found in the binary aluminium-copper or the ternary 0.22% manganese alloys, and this would permit the slip to pass from one grain to another. These different factors ultimately give an increased deformation and hence the increased elongation.

Concentration / (Hardness/Proof Stress) fig.(2 - 38) -

It is generally assumed that there is a close relation between the proof stress and hardness, and, therefore, an attempt has been made to see whether this idea is applicable to the alloys tested in the present work.

In the as-quenched condition, there is a steady increase in this ratio, for both the 3 and 4.5% copper alloys. With increasing manganese, the proof stress

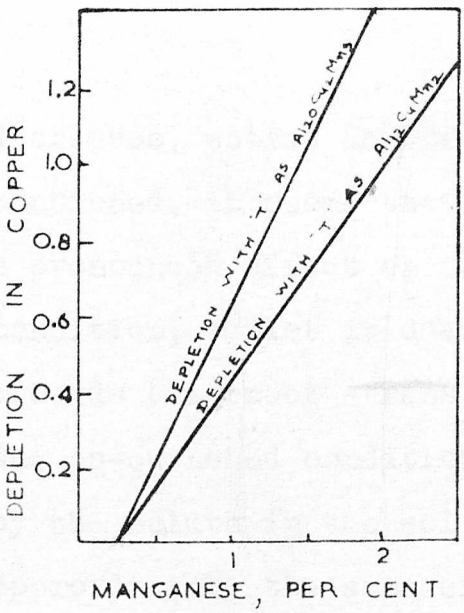
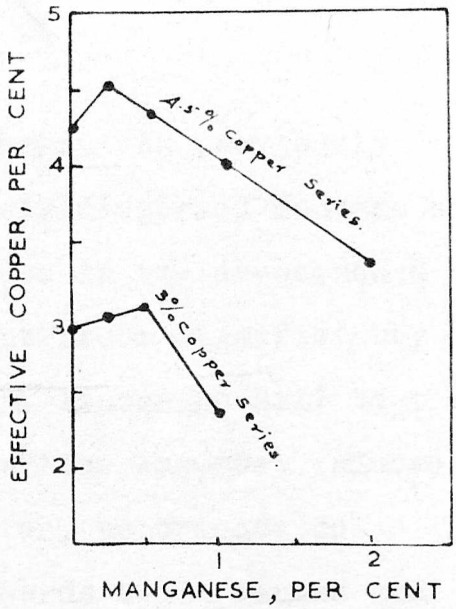


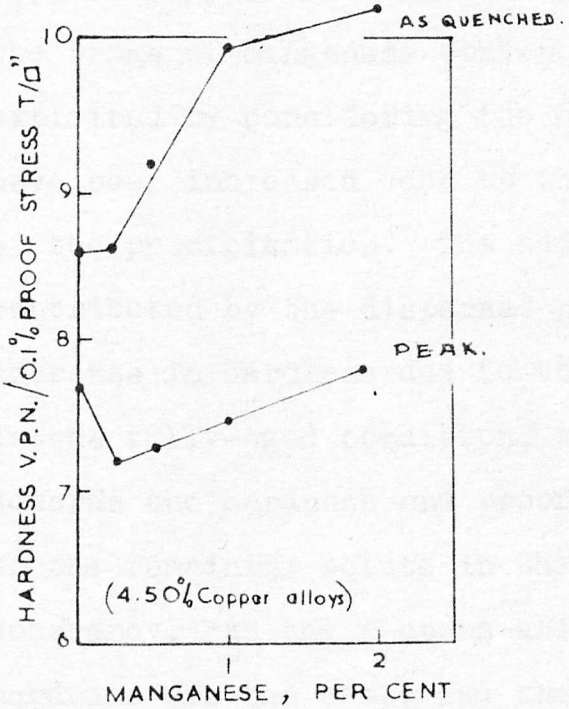
FIG.(2 – 32) – CONCENTRATION/ DEPLETION

(Assuming the Mn solubility to be 0.25% in all the ternary alloys used in the present work)



FIG(2 – 31) – CONCENTRATION/ EFFECTIVE COPPER%

(The plots showing the effective copper per cent of the alloys used in the present investigation)



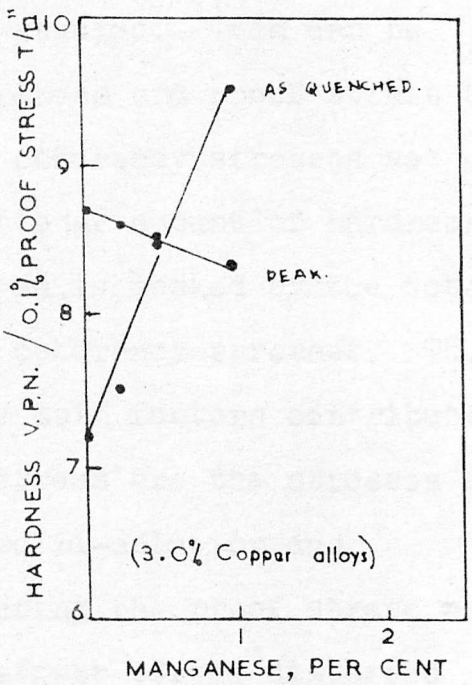


FIG (2 – 38) – CONCENTRATION / (HARDNESS / 0.1% PROOF STRESS) RELATIONSHIPS

decreases, whilst hardness increases. As previously mentioned, it seems that the finely dispersed T-phase has a pronounced effect on the hardness in the as-quenched condition, whilst it does not contribute significantly towards the proof stress. Perhaps it can be said that in the as-quenched condition, the lattice stresses induced by the solute in the solid solution, contribute to approximately the same extent towards the hardness and proof stress, but an additional contribution towards the hardness can be provided by the dispersed phases.

In the fully-aged condition, for both the 3 and 4.5% copper alloys, the ratio is approximately constant over the range of manganese contents studied. This can be explained by considering the hardness and proof stress to have been increased due to the coherency stresses set up by the precipitation. The additional amount of hardness contributed by the dispersed phase is masked by the total increase in hardness due to the coherency stresses. Thus, in the fully-aged condition, the main factors contributing towards the hardness and proof stress are the stresses due to the remaining solute in the solid-solution and coherency. As the factors affecting the proof stress and hardness are the same, and the effect of the dispersed phases is masked, there is a proportionate increase in

both these properties of the alloys.

In the fully aged condition, the proof stress may be expressed in a simple form as follows:

$$\text{Proof stress}_{\text{tons}}\text{ s.i.} \simeq \frac{\text{Hardness V.P.N.}}{11.8 - (\text{Effective \% Cu} + 0.2)}$$

(0.2% being the solid solubility of Mn).

This relation is approximate and may be taken as valid only over the compositional range studied.

Thus, it will be seen from the above equation that, if only the % amounts of the elements in the solid solution (in the present case effective copper content and 0.2% manganese being the amounts dissolved at the solution treatment temperature) are taken into account, it may be possible to correlate hardness with proof stress, in both as-quenched and fully-aged conditions. As a generalisation, this principle might apply to any aluminium alloy.

CONCLUSIONS

1) The ageing characteristics of the aluminium-copper and aluminium-copper-manganese alloys as studied by the measurements of 0.1% proof stress, tensile strength and percentage elongation, correspond closely with those obtained by the hardness measurements.

2) The effect of dispersed phases on the 0.1% proof stress of these alloys seems to be negligible as compared with their effect on the hardness. However, they may have some effect on the elongation of the as-quenched alloys and quite a considerable one on that of the fully-aged alloys.

3) The ratio of proof stress/ tensile strength is greater in the fully-aged than in the as-quenched condition.

4) Manganese affects the grain shape and grain size considerably and gives higher ductility. However, its effect beyond the addition of 1.0% seems to be rather detrimental even on the elongation.

5) The times to reach the maxima on the ageing curves for hardness, proof stress, tensile strength and elongation seem to be different.

6) No constant relationship exists between the hardness and proof stress in the as-quenched condition, but it may be possible to express proof stress in terms of hardness in the fully-aged condition.

SECTION III

EFFECT OF MANGANESE ADDITIONS ON THE AGEING CHARACTERISTICS OF THE TERNARY ALUMINIUM-COPPER-MAGNESIUM ALLOYS

CHAPTER I

PREVIOUS WORK

General

The effects of manganese additions on the age-hardening characteristics of the ternary aluminium-copper-magnesium alloys have been studied. It will be necessary to briefly summarise the age-hardening characteristics of the aluminium-copper-magnesium system, before attempting an analysis and a correlation of the quaternary system.

The age-hardening characteristics of the binary aluminium-copper alloys and the aluminium-copper-manganese alloys have been summarised in the second section of this thesis.

Age-hardening Properties of the System Aluminium-Copper-Magnesium

MERICA, WALTENBERG and SCOTT (1919) suggested that magnesium was of minor importance in the hardening of Duralumin, and the main agent was $CuAl_2$. However, ROSENHAIN et al. (1921), HANSON and GAYLER (1921), GAYLER (1922, 1923) and others pointed out that the hardening of aluminium-copper alloys was inadequate to explain that of the Duralumin.

DIX, SAGER and SAGER (1932) found that the addition of 0.5% magnesium to aluminium-copper alloys, slightly reduced the solid solubility of copper in aluminium, but that the form of the solubility curve was not greatly altered, so that magnesium would not be expected to influence the ageing of aluminium-copper alloys to a marked extent. GAYLER (1923), stated that at 400°C, copper is practically insoluble in aluminium in the presence of magnesium and that alloys of aluminium with low percentages of copper and magnesium do not age-harden after quenching from 400°C. She found that some alloys, containing less than 2% magnesium and more than 1% copper age-hardened after quenching from 400°C. However, the aluminium used was of 99.6% purity (0.2% Si) and it is suggested that this effect is due to the influence of Mg_2Si, which must have been present in the alloys.

PETROV (1938) found that the hardness of quenched alloys increased almost linearly with increase in magnesium content, whilst that of alloys with 4, 3 and 2% copper, respectively, aged at room temperature, increased markedly as the magnesium content was raised from zero to 0.04%; beyond this value the effect was less marked. He also discovered that the age-hardening capacity of aluminium-copper alloys at room temperature, destroyed by

the presence of iron is completely restored by as little as 0.03% magnesium.

ARCHER (1926) suggested that magnesium in such small quantities would not take part in the age-hardening but perhaps help the diffusion of copper through the lattice by expanding it. The explanation was found inadequate. In connection with the suggested effect of silicon, GAYLER and PRESTON (1932) found that, though the silicon content was extremely low, an addition of 0.5% magnesium to a 4% copper alloy improved its age-hardening at room temperature.

Thus magnesium may be said to have a duplicate role; of restoring the age-hardening capacity to the iron-containing commercial aluminium-copper alloys, and of raising the hardness of pure binary alloys, presumably by the formation of the phase S (PETROV, 1938).

The formation of the compound S in Al-Cu-Mg alloys also accounts for the observation that the high-purity Al-Cu-Mg alloy containing 1% copper and 0.5% magnesium, hardens considerably at room temperature, whilst neither the 1% copper alloy nor the 0.5% magnesium alloy hardens either at room temperature or at elevated temperature.

There seems to be little doubt that the room temperature ageing is caused by the formation of 'S' and

$CuAl_2$; at higher temperatures, however, the same mechanism does not occur.

Most of these workers used aluminium containing enough iron and silicon to affect the results. However, recently, HARDY (1954-55) has carried out systematic work on the ternary alloys of high purity, having copper: magnesium weight ratios of 7:1 and 2.2:1. His results are summarised as follows:

1) Ageing at 30°C -

For a given percentage of copper, the alloys with more magnesium aged more rapidly and reached a higher hardness value. The rise in hardness was practically complete after 10 days; only slight or no change occurred in the next 950 days.

2) Ageing at 110°C -

Alloys with a Cu:Mg ratio of 7:1 showed clear evidence of three-stage ageing curves at the higher super-saturation, for example, the alloys containing 3.4 and 3.55% copper hardened very considerably either during heating to the ageing temperature or within the first few minutes. A fairly flat portion up to about 15 mins. was succeeded by a steady rise, with a further flat portion extending from one to twenty days. The final rise to peak hardness was completed after some two to three

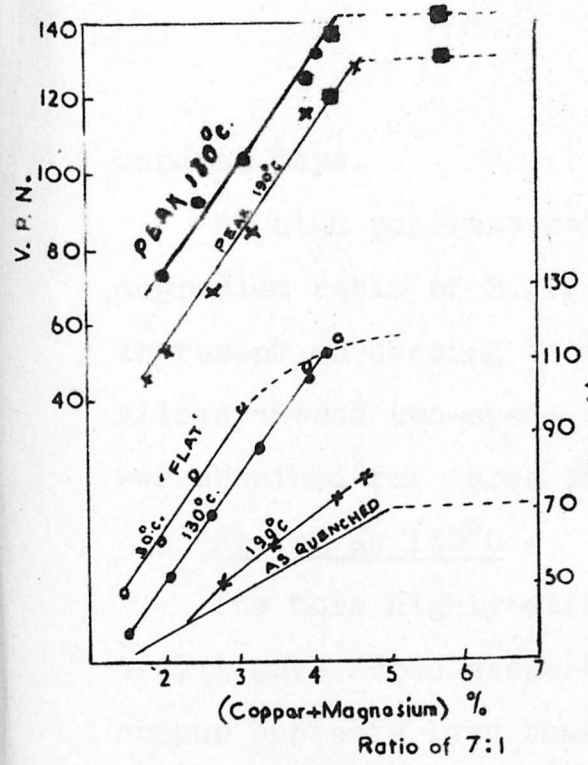


Fig (3–1) – Concentration / Hardness

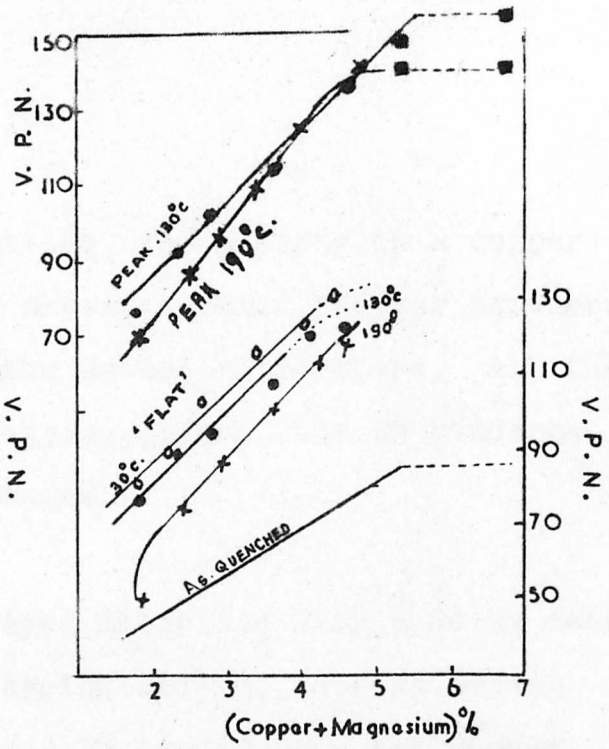


Fig. – (3 – 3) – Concentration / Hardness

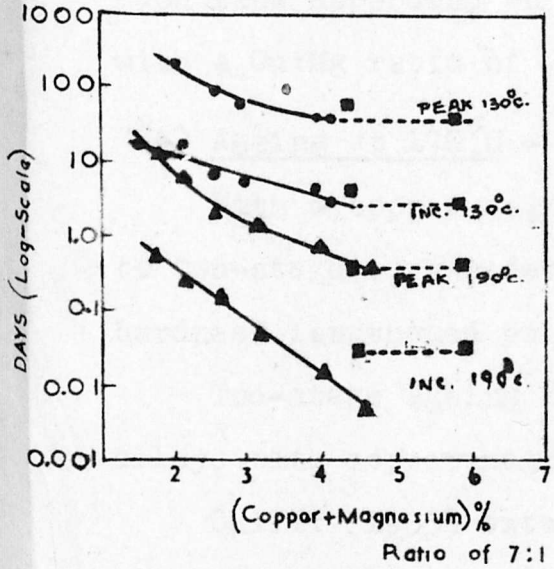


Fig (3–2) – Concentration / Time

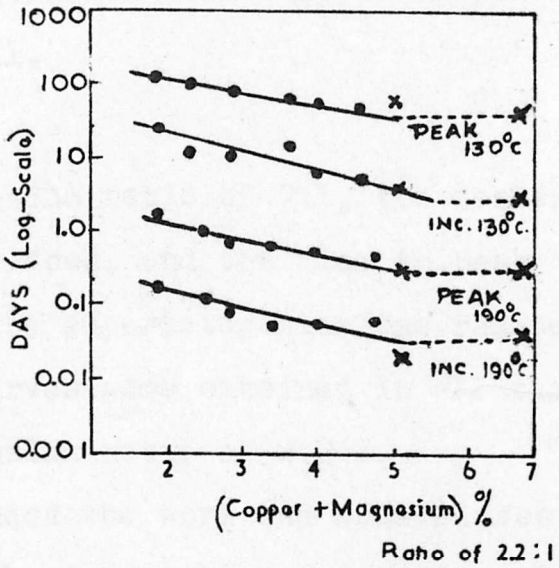


Fig (3.– 4) – Concentration / Time

ANALYSIS OF AGEING CURVES OF ALLOYS WITH COPPER & MAGNESIUM

(Hardy & Chitty)

hundred days.

At high supersaturations, the alloy with a copper:magnesium ratio of 2.2:1 showed a still greater hardness increment on heating to the ageing temperature. All these alloys showed two-stage ageing curves, but no evidence was obtained for three stages.

3) Ageing at 130°C -

The more highly-alloyed materials with a Cu:Mg ratio of 7:1 gave three-stage ageing curves. Alloys having copper contents less than 2.7% showed only two stages.

Only one flat occurred in the ageing curves of the 2.2:1 series. In the alloys with 3.1 and 2.7% copper, the first stage of hardening was almost completed during, or shortly after heating. The time to peak hardness was much less dependent on concentration than in the alloys with a Cu:Mg ratio of 7:1.

4) Ageing at 190°C -

With a copper-magnesium ratio of 7:1, the tendency to two-stage curves decreased, and the time to peak hardness lengthened as the supersaturation was reduced.

Two-stage ageing curves were obtained in all the alloys with copper:magnesium ratio of 2.2:1.

CHITTY (1955) extended the work and studied a few other ternary alloys with copper:magnesium ratios of

7:1 and 2.2:1. As HARDY, he found that:

1) The quenched-hardness, peak-hardness and hardness increment values of the binary alloys were increased considerably by magnesium.

2) At ageing temperatures of 130°C and 190°C, alloys with Cu:Mg ratio of 2.2:1 showed two-stage ageing in which the first stage is extremely rapid. Alloys with a Cu:Mg ratio of 7:1 exhibited three-stage ageing curves at 130°C, and two-stage ageing at 190°C.

The results of these authors are summarised in the fig .(3 - 1, 2, 3, 4).

CHAPTER II

EXPERIMENTAL

GENERAL

Age-hardening characteristics were studied by hardness measurements on wrought and heat-treated aluminium alloys of the quaternary system aluminium-copper-magnesium-manganese. It was therefore necessary to have ingots as free from metallurgical defects as possible. A careful procedure of melting and casting of alloys using high purity materials was employed.

MATERIALS AND CRUCIBLES USED

A detailed description of the materials, crucibles, method of lining and the durability of lining has been given in the experimental part of the first section. Similar materials, crucibles and linings were used in the present investigation, except that the crucibles were larger in size.

MELTING FURNACE

Melting was carried out in a gas furnace having a circular chamber with tangential jets which could melt the charge quickly.

PRODUCTION OF INGOTS

It was necessary to produce sound ingots free from gas cavities, folds, shrinkage, and non-metallic inclusions, the impurities from other sources being prevented by using high purity materials.

PRECAUTIONS TAKEN

(a) Mould Design

The mould was designed by CHITTY (1958) which gave very satisfactory results. It was of circular cross-section tapering towards the bottom end, and had a capacity of 3.5 lbs. of aluminium and an average diameter of 2.5 inches. The mould was machined from mild steel, and the bottom was made to screw on to the body of the mould to facilitate the removal of ingots. The walls were made thin to reduce solidification rate, but a thickness of 0.25 inch was allowed in order to stand repeated heating up to 600°C. without warping.

The mould was supported in the water jacket by means of steel bars, and rested on an extension of the water jet inlet at the bottom. The cooling jacket was formed of welded mild steel sheet, having a central water inlet at the bottom, so that water produced a cooling of the ingot from the bottom upwards. There was an outlet for water at the top of the cooling jacket.

The use of a mild steel mould gave ingots which were free from extraneous non-metallic inclusions. However, oxide inclusions were a possibility and the care taken to avoid them is discussed below.

SURFACE QUALITY

The tenacious oxide film on the surface of the liquid metal folds, while the mould is filling, and envelopes the liquid metal preventing it from conforming with the shape of the mould surface. To prevent the formation of folds due to the above possibility, the metal was introduced very slowly into the tilted mould.

A second type of defect arises from the liquid metal being thrown on the mould walls, where it solidifies and forms into globules. These globules are enveloped by the liquid metal but sometimes are not remelted. To avoid such folds the mould was pre-heated to a temperature of 550°C.

The other possible surface defect was the presence of inclusions of aluminium oxide. In ordinary practice fluxes are used but in the present case no such flux could be used due to the fear of contamination. However, it was found that if the stream of the molten metal was not broken while pouring, this defect could be minimised.

GAS POROSITY

Liquid aluminium dissolves hydrogen, but it is rejected on solidification and thus gas cavities are formed. However, in an ingot solidifying unidirectionally the rejected gases travel in the direction of the solidification front.

(1) In the present case the mould design and the cooling system gave unidirectional solidification from the bottom towards the top, and much of the gas escaped from the surface of the ingot.

(2) Heating time in the furnace was minimised by preheating the crucible and the charge.

(3) The tenacious oxide film was disturbed as little as possible to prevent adsorption from the atmosphere.

DEGASSING

The above precautions were found to be inadequate to avoid all the gas cavities. Nitrogen was therefore used to de-gas the metal. It was dried by passing through concentrated sulphuric acid, and then up a drying column of anhydrous calcium chloride and silica gel. A carbon tube was used to introduce nitrogen into the melt. The de-gassing was carried out for about 3 minutes.

POURING TEMPERATURE

A pouring temperature 50°C above the liquidus point of the alloy was found to be quite satisfactory.

MELTING AND CASTING PROCEDURE

A weighed quantity of aluminium was added to the pre-heated crucible and the gas supply was turned off when the aluminium was in a molten state. The weighed amounts of master alloys were then added and the charge was stirred. Magnesium was introduced last and held below the surface by a carbon rod until it melted. This avoided the possibility of burning magnesium. The charge was stirred and the melt de-gassed with nitrogen as described. The surface of the melt was skimmed and the melt was cast into the mould. The water was turned on after casting. A little of the molten alloy was retained in the crucible to feed the pipe.

HOMOGENIZING

All the ingots were annealed for 48 hours at 490°C in an air-circulating furnace and were furnace cooled.

MACHINING

The ingots were machined to give uniform billets of round section. It was found that if the ingot surface was machined before working the surface defects could be minimised. This also served the purpose of removing the inverse segregations.

WORKING OF THE ALLOYS

It was necessary to break down the as-cast structure to obtain consistent results. The ingots were therefore subjected to pressing and rolling.

PRESSING AND ROLLING

All the ingots were hot-pressed and hot-rolled. The description of the press has already been given in the experimental part of the second section.

The ingots were pre-heated to a temperature of 450°C and were then pressed in various stages to a thickness of $\frac{3}{8}$" between the heated die-blocks of the hydraulic press. The $\frac{3}{8}$" plates were heated for an hour at 450°C and were rolled to a thickness of 0.20".

PREPARATION OF SPECIMENS

After hot-working the plates were sheared and the pieces were numbered. These smaller pieces were marked to give the required hardness specimens of approximately 0.80" x 0.20" x 0.30" dimensions. The rectangular pieces were cut by the band-saw. Before cutting, a hole was drilled at one end of each specimen to facilitate handling in the subsequent operations.

SURFACE PREPARATION

The rectangular test-pieces were found quite satisfactory to give five or six hardness impressions. Before solution treatment each specimen was ground on a 400-grade silicon carbide paper and was given a final rub on a wax-pad containing 302-grade alumina subsequent to solution treatment and ageing.

HARDNESS TESTING

All the hardness testing was done with a 10 kg. load on a Vicker's machine. It was found that four to five impressions gave a consistent mean value.

All the hardness values reported are the mean of 4 such impressions made on each specimen in the case of the ageing curves at 21 and 130°C, and the hardness values reported for quenched specimens and for hardness-ageing curves at 190°C. are the mean of 8 such impressions made on two different specimens, 4 impressions being made on each of them.

SOLUTION TREATMENT

The purpose and the choice of the solution-treatment temperature have been discussed in the first section of the thesis. The solution-treatment of all the specimens was carried out at 500°C in an air-circulating furnace of the electrical resistance type, giving a control of $\pm$ 2°C.

The solution treatment was of minimum duration of 48 hours. Sometimes specimens were left in the furnace for longer times, e.g. 8 to 10 days, but this is not thought to lead to any significant difference in results.

The specimens were hung on steel wires and were separated from each other by insulating beads, in order to facilitate quenching. The steel wires carrying the specimens were placed inside an aluminium box covered with a lid. The temperature of the furnace was checked periodically by a chromel-alumel thermo-couple introduced permanently into the furnace.

QUENCHING

Quenching was carried out in a large water tank, the temperature being maintained at $20 \pm 1^{\circ}C$ to get uniform results. The specimens were agitated in the water during quenching to obtain an efficient quench.

AGEING TREATMENT

Ageing was carried out at three different temperatures.

1) $21^{\circ}C$. (Room Temp.)

2) $130^{\circ}C$.

3) $190^{\circ}C$.

These temperatures were used to obtain results comparable with those of previous workers, and for the same reasons as given by them. (HARDY, 1953-54, CHITTY, 1958.)

EXPERIMENTAL APPARATUS FOR AGEING

(1) 21°C - The ageing treatment was carried out by placing the specimens in containers floating in a water bath thermostatically controlled at 21±1°C. Heating was done by an electric light bulb with an "on-off" switch controlled by the thermostat. The water-bath was provided with a cooling jacket which was used to bring down the temperature to 21°C whenever the room-temperature rose above 21°C.

(2) 130°C and 190°C.

The ageing was carried out at these temperatures by suspending the specimens in an oil bath by means of steel wires. The oil bath was heated in an air-circulating oven, which had a small hole at the top to facilitate the removal of the specimens without cooling the oven. The temperature was controlled to within ± 1°C.

STORAGE

The specimens were quenched from the solution-treatment temperature and were transferred to a bath of melting ice to inhibit the ageing at room-temperature before testing or transferring to the ageing oven. The maximum time of the specimens in the storage bath was not more than one hour, and it was found that during this time there was no significant difference in the hardness (SMITH, 1958.) The same procedure was carried out for the specimens aged at different temperatures while being stored for the hardness testing.

PRESENTATION OF HARDNESS/AGEING CURVES

The hardness/ageing curves were obtained by plotting the hardness (V.P.N) as ordinate and time (days) on a logarithmic scale as abscissa.

THE SCOPE OF THE INVESTIGATION

In all, fifteen alloys were cast and they were analysed for copper, magnesium and manganese by the British Aluminium Co. Ltd. Two of them were analysed for iron and silicon to check the impurities.

These alloys may be divided into five series of fixed copper and magnesium contents and varying manganese contents. These were:

I.	1.	3.0%	copper	0.50%	magnesium	0.2%	manganese
	2.		"		"	0.6%	"
	3.		"		"	1.2%	"
II.	4.	3.0%	copper	1.5%	magnesium	0.2%	manganese
	5.	"		"		0.6%	"
	6.	"		"		1.2%	"
III.	7.	3.7%	copper	1.5%	magnesium	0.2%	manganese
	8.	"		"		0.6%	"
	9.	"		"		1.2%	"
IV.	10.	4.5%	copper	0.5%	magnesium	0.2%	manganese
	11.	"		"		0.6%	"
	12.	"		"		1.2%	"
V	13.	4.5%	copper	1.5%	magnesium	0.2%	"
	14.	"		"		0.6%	"
	15.	"		"		1.2%	"

The chemical composition and the structure of the alloys after the solution treatment were as follows:-

	COMPOSITION					
	Cu	Mg	Si	Fe	Mn	STRUCTURE
1	3.12	0.60	-	-	0.22	α + T (Traces)
2	3.03	0.60	-	-	0.63	α + T
3	3.06	0.54	-	-	1.17	α + T
4	2.95	1.58	-	-	0.20	α + T
5	2.97	1.58	-	-	0.62	α + T
6	3.02	1.50	-	-	1.29	α + T
7	3.69	1.49	-	-	0.22	α + T
8	3.50	1.49	-	-	0.60	α + T
9	3.60	1.49	0.0065	0.0075	1.26	α + T
10	4.31	0.55	-	-	0.22	α + T + θ
11	4.29	0.52	-	-	0.62	α + T + θ
12	4.35	0.50	-	-	1.28	α + T + θ
13	4.35	1.53	-	-	0.20	α + T + θ + S
14	4.41	1.49	-	-	0.57	α + T + θ + S
15	4.40	1.56	0.0030	0.0035	1.29	α + T + θ + S

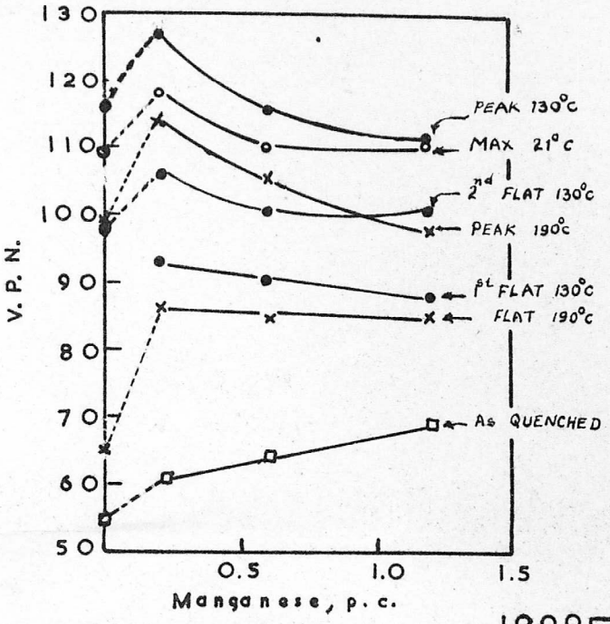


Fig.(3-14) Concentration/Hardness Relationships

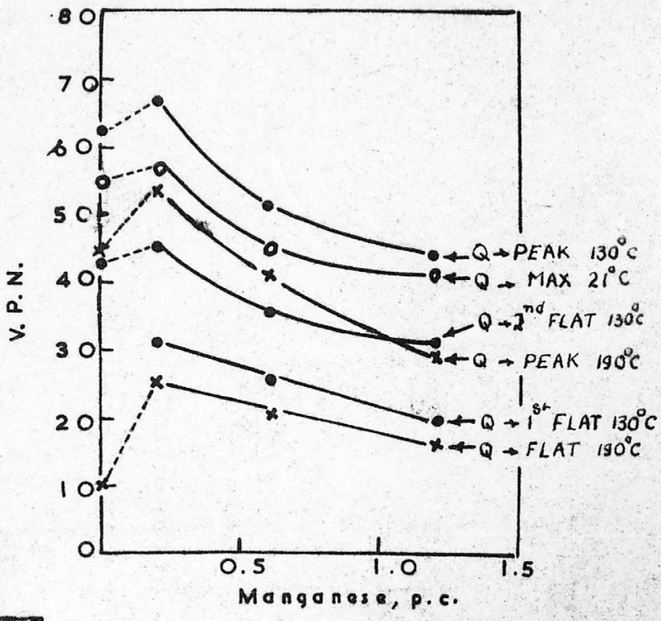


Fig. (3-15) Concentration/Hardness-Increment Relationships

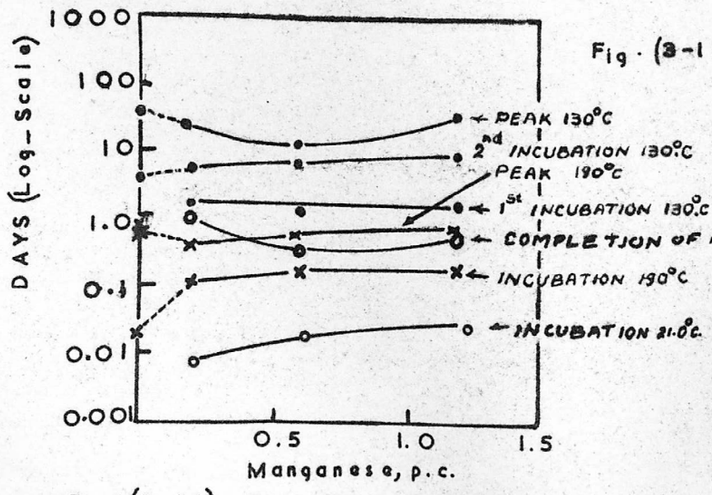
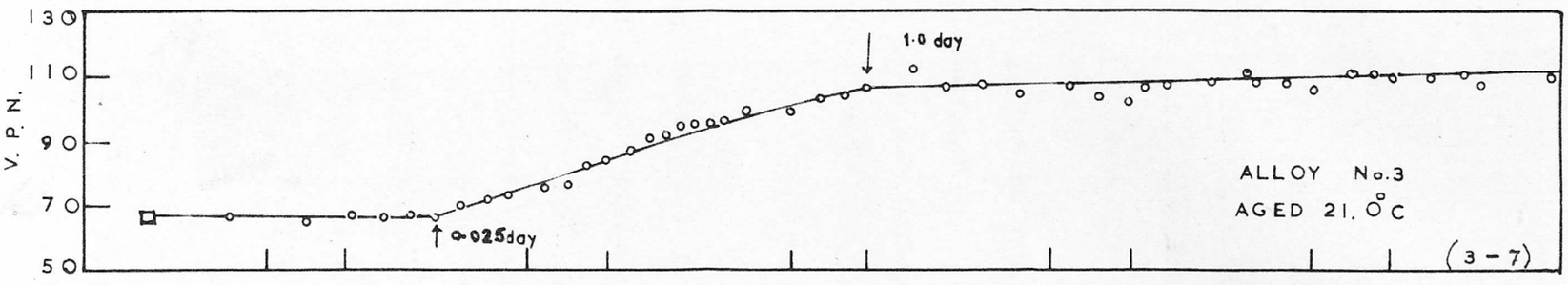
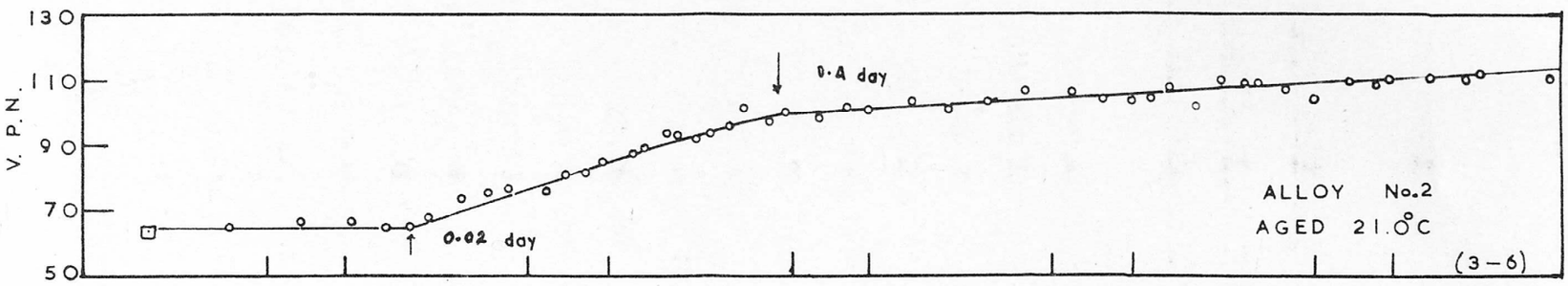
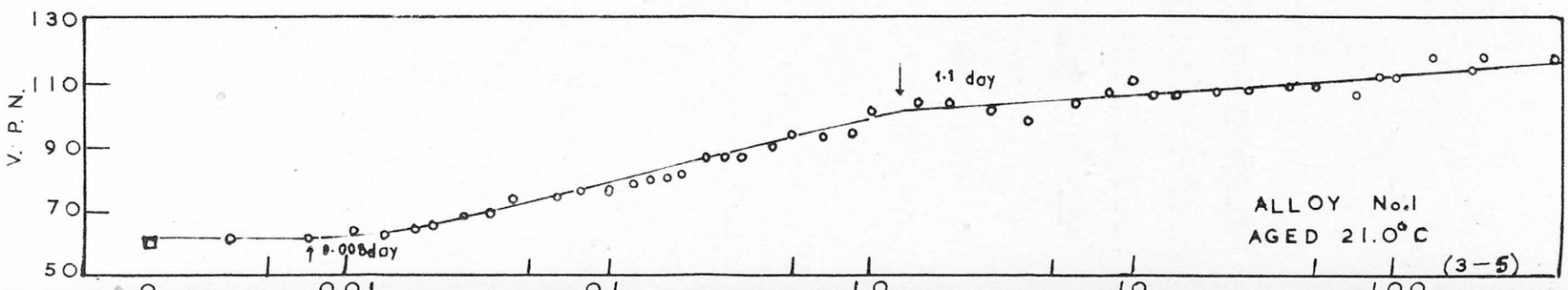


Fig. (3-16). Concentration/Time Relationships

ANALYSIS OF AGEING CURVES OF ALLOYS WITH 3% COPPER & 0.5% MAGNESIUM CONTAINING MANGANESE







CHAPTER III

RESULTS, DISCUSSION AND CONCLUSIONS

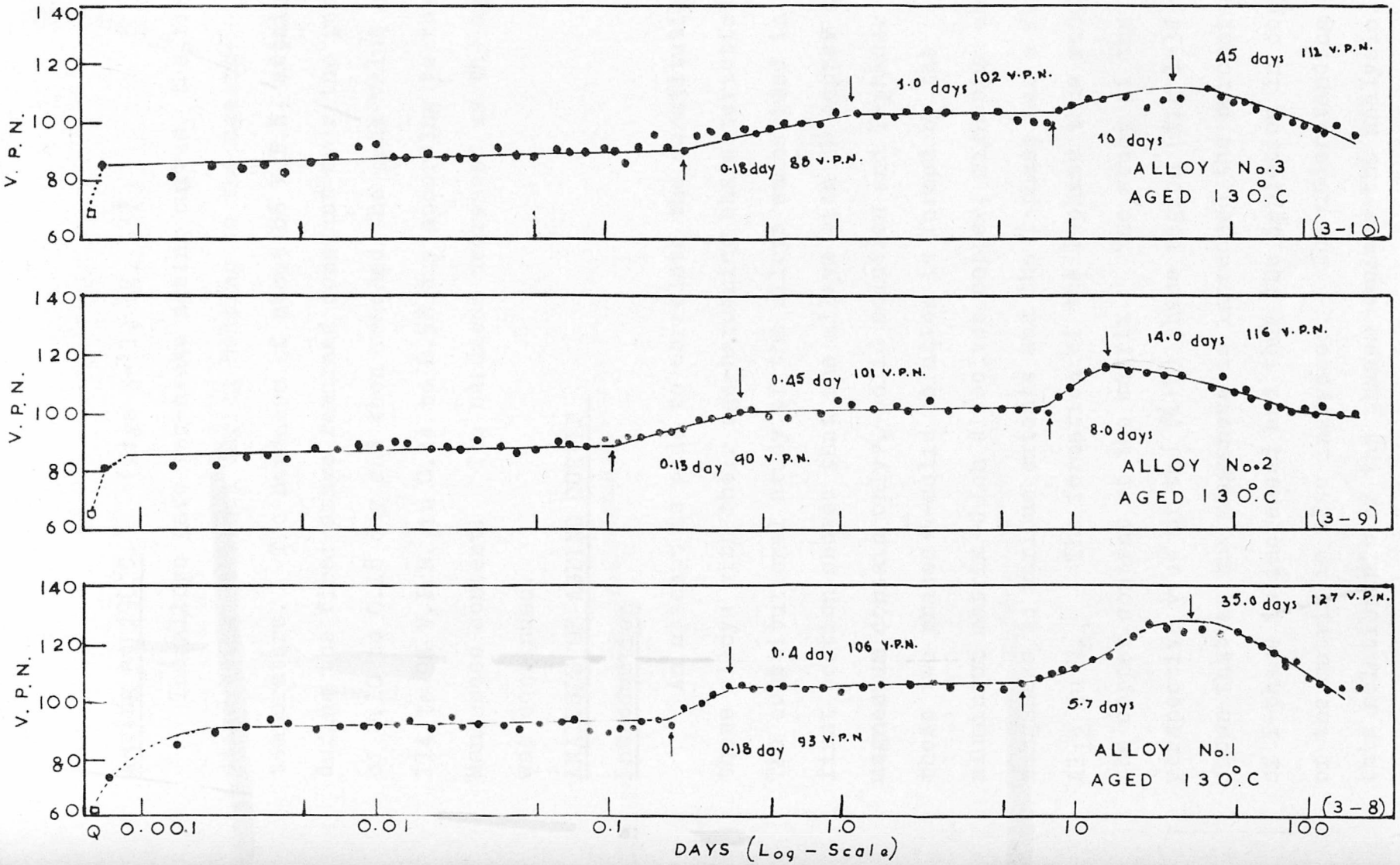
Hardness/Ageing Curves for Alloys with 3% Cu and 0.5% Mg containing 0.2, 0.6 and 1.2% manganese respectively.

Ageing at 21.0°C. (figs.3-5, 6, 7)

These alloys exhibited a single-stage curve. After a short incubation of 10 to 25 minutes the hardness increased to about 110 V.P.N. in times ranging from 0.4 to 1.1 day, and then showed a slight increase over the period of 480 days.

Ageing at 130°C. (figs 3-8, 9, 10)

Three-stage curves were obtained of which the first stage was reached during heating to the ageing-temperature. The hardness of about 93 to 88 V.P.N. attained during this time remained constant up to about 0.18 day, and after this incubation increased to 106 to 101 V.P.N. in 0.4 to 1 day. This value of hardness which remained constant for the period of 5.7 to 10 days increased to 127 to 112 V.P.N. in 14 to 45 days and then decreased on further ageing.


140
120
100
80
60
V. P. N.
45 days 112 V.P.N.
1·0 days 102 V.P.N.
10 days
0·18 day 88 V.P.N.
ALLOY No.3
AGED 130°C
(3-10)
14·0 days 116 V.P.N.
0·45 day 101 V.P.N.
8·0 days
0·15 day 90 V.P.N.
ALLOY No.2
AGED 130°C
(3-9)
35·0 days 127 V.P.N.
0·4 day 106 V.P.N.
5·7 days
0·18 day 93 V.P.N
ALLOY No.1
AGED 130°C
(3-8)
Q 0·001
0·01
0·1
1·0
10
100
DAYS (Log - Scale)

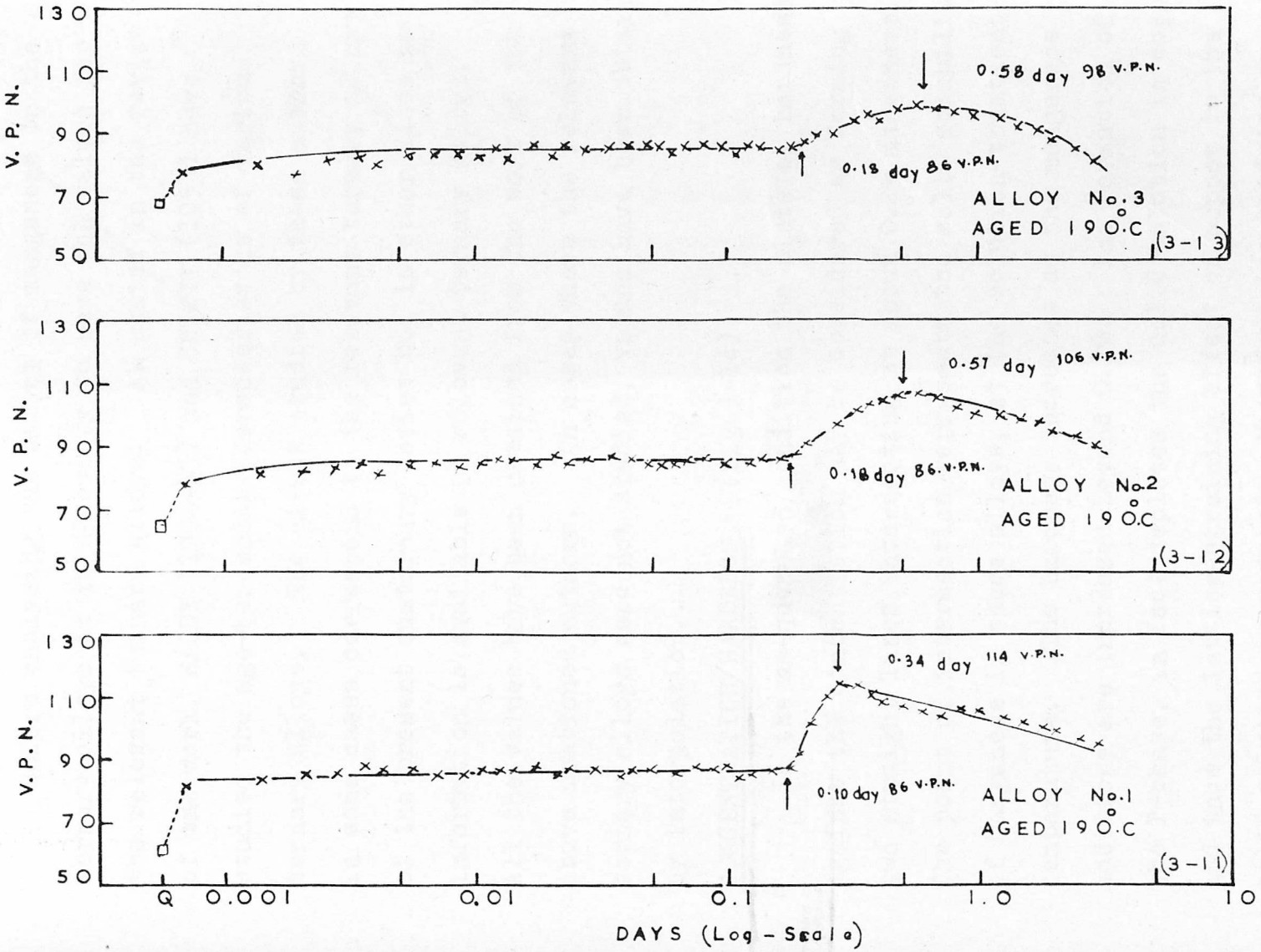
Ageing at 190°C. (figs 3-11, 12, 13)

The alloys gave two-stage ageing curves, the first stage being attained during heating to the ageing-temperature. The hardness of about 86 V.P.N. attained during the first stage remained constant over the period of 0.10 to 0.18 day and then reached the peak value of 114 to 98 V.P.N. in 0.34 to 0.58 day according to the Manganese content. The hardness decreased as the ageing was continued.

ANALYSIS OF AGEING CURVES

Introduction

An attempt is made to correlate the constitution of these alloys with their age-hardening characteristics. The constitutional study of the alloys summarised in the first section showed that the alloys with 3% copper and 0.5% magnesium contain only α-solid solution and T-phase. Of these two phases α-solid solution is formed by the aluminium matrix which dissolves copper, magnesium and manganese to various extents and the T-phase has a formula Al_{12} Cu Mn_2. The formation of the T-phase thus reduces the copper content of the matrix. The study of the perspective view of the (α+T) phase region (fig 1-34) has shown that as the manganese is increased the percentage of T-phase is increased and thus the depletion in copper of the matrix is also increased. The understanding of this relationship of the phases assists the analysis.


130
110
90
70
50
V. P. N.
0.58 day 98 V.P.N.
0.18 day 86 V.P.N.
ALLOY No.3
AGED 190°C
(3-13)
0.57 day 106 V.P.N.
0.18 day 86 V.P.N.
ALLOY No.2
AGED 190°C
(3-12)
0.34 day 114 V.P.N.
0.10 day 86 V.P.N.
ALLOY No.1
AGED 190°C
(3-11)
Q
0.001
0.01
0.1
1.0
10
DAYS (Log - Scale)

Before analysing the effect of manganese on the ternary alloys it is necessary to have the values for the relevant ternary alloys. As stated in the review of the work, HARDY (1954-55) and CHITTY (1955) have studied the age-hardening characteristics of various ternary alloys. The alloys studied by these authors in some cases correspond to the relevant ternary alloys of the present quaternary series but in other cases no information is available on relevant ternary alloys. All the values have been obtained from the work of the above mentioned authors. In cases where the relevant ternary alloys were not studied, values have been obtained by interpolation.

CONCENTRATION/HARDNESS (fig 3-14)

In the as-quenched condition the plots of hardness against the concentration may be considered as forming two straight lines intersecting at about 0.2% manganese. The point of intersection represents the solid solubility of manganese in these alloys, at the solution-treatment temperature. The hardness increases as the manganese additions are increased beyond 0.2%. The formation of the T-phase, in fact depletes the solid solution in copper, and thus the lattice-straining effect of copper in the solid solution is reduced; therefore the hardness on adding more than 0.2% manganese, should decrease. The T-phase is presumably very hard and increases the hardness

by its presence in the matrix, thus the hardness values attained on adding more than 0.2% manganese are actually the results of the counter-balancing effect of these two processes.

The peak-hardness at 130 and 190°C, the maximum hardness at 210°C and 2nd flat-hardness at 130°C, gave a curved and a straight line intersecting at about 0.2% manganese. The increased hardness of the 0.2% manganese alloy is due to the increased amounts of alloying elements in the solid solution; but as the manganese content is increased beyond 0.2%, the matrix is depleted in copper, and hence there is a reduction in the hardness. However, the hardness of the 1.2% manganese alloy is not as low as expected from the straight-forward depletion effect; and therefore the plots, instead of giving straight lines gave curved lines. This behaviour of the ternary aluminium-copper-manganese alloys was reported by FINK, SMITH, and WILLEY (1940) and has been referred to in the review of the literature in the second section of the thesis. These authors did not offer any explanation.

An attempt will now be made to suggest a tentative explanation. It is probable that, because of the sluggishness in diffusion, as the manganese content of these alloys is increased, manganese in an amount greater than the equilibrium solubility may be held in solid solution. This manganese would then participate in the precipitation and thus give a higher value of hardness.

Thus, although the effect of depletion in copper is increasing proportionately with increasing manganese the increased manganese content in the solid solution may contribute towards balancing the decreased hardness.

Another interesting point is provided by the flat-hardness at 190°C. It will be seen that the hardness of the quaternary alloys as compared with that of the ternary alloy is strikingly greater than in the other plots. It is possible that the precipitating phase at 190°C at the end of the first stage is nucleated by the T-phase. (Probable mechanism is discussed later.) Thus, the growth of the precipitating phase is hastened and at a given stage the size of the precipitate is greater. The precipitating phase will be G.P. Zones (Cu and Mg) and as there is no information available on the lattice of this phase, no analysis can be made.

CONCENTRATION/HARDNESS INCREMENTS (fig 3-15)

The plots of the increments from the as-quenched to peak and to 2nd flat-hardness at 130°C, and as-quenched to maximum hardness at 21.0°C are each formed of a straight line and a curved line intersecting at about 0.2% manganese. It will be seen that the difference in the increments of the 0.2% manganese and the ternary alloys is very little; it seems therefore, that the manganese is dissolved to a very little extent and naturally does not contribute appreciably to the precipitation process.

However, the curved portions substantiate the idea put forward in the analysis of the concentration/hardness relationships.

It will be seen that although the total hardness in the partially - or fully-aged conditions is not affected to an extent, expected from the depletion effect, the increments from the quenched hardness are markedly reduced as the manganese concentration is increased. It can, therefore, be said that manganese beyond 0.2% decreases the age-hardening capacity.

Thus the total hardness in the quenched condition is due to the cumulative effect of the solid-solution and dispersion hardening whilst that in the partially - or fully-aged conditions is due to the additive effect of the remaining solid solution, coherency stresses and the dispersion hardening.

CONCENTRATION/TIME RELATIONSHIP - (fig. 3-16)

The plots of the logarithms of incubation periods against concentration show that in general with the addition of 0.2% manganese the incubation value is slightly increased, but on further addition of manganese there is very little or no increase in this value. Assuming that 0.2% is the solid solubility of manganese in these alloys, the fact suggests that manganese may be participating in the precipitation process, and therefore as the manganese is sluggish in diffusion the incubation periods are slightly lengthened.

As the manganese content of these alloys is increased beyond 0.2%, the degree of supersaturation of copper should decrease and therefore the incubation periods should be longer, but this is not shown by the experimental results; there seems to be an accelerating effect.

This is well-brought out by the plots of the logarithmic times necessary to reach the peak at 130°C and to complete the initial rise at 21.0°C. These plots are shown by smooth curves, and it will be seen that the 0.6% manganese alloy shows the shortest periods necessary to reach the peak at 130°C, and to complete the initial rise at 21.0°C.

It seems that the T-phase may be providing nucleation sites for the phase precipitating at the third stage on the hardness/ageing curve at 130°C. According to BAGARYATSKY (1948), the sequence of precipitation in the ternary aluminium-copper-magnesium alloys is:-

$$\text{G.P. (Cu + Mg)} \text{ on } \{100\}_{Al} \longrightarrow$$
$$\text{S' platelets on } \{021\}_{Al} \text{ and } \{035\}_{Al} \longrightarrow \text{S.}$$

It will be seen that in general the times to reach the peak at 130°C for all the quaternary alloys are decreased by the formation of the T-phase. It is of interest to consider if the T-phase could have any possible effect on the phases precipitating at the stage of the ageing just before the peak.

The metastable equilibrium products in these alloys can either be S' platelets as stated by BAGRYATSKY or

G.P.Zones [2], just prior to reaching the peak. In the alloys containing enough magnesium the entire metastable product may be of S' platelets ultimately giving an (α+S) structure, but in the case where the ratio of Cu: Mg. is high some amount of G.P.zones [2] or θ' would precipitate along with S', and thus the ultimate structure would be (α+θ+S).

BAGARYATSKY claimed that the S' phase is orthorhombic with a' = 4.04, b' = 9.04 and c' = 7.2 Å, providing a matching between the (100)S' and $(021)_{Al}$. Now looking at the structure of the T-phase it will be seen that according to PETRI (1938) it also crystallises in orthorhombic symmetry with a = 7.69 b = 24.06 and c = 12.48 kX. It is probable that there is a fit between the (001) S' and (100)T. Even if the metastable product is G.P. [2], a reasonable fit is available; the structure of G.P.[2] is reported as tetragonal with a = 4.04 and c = 7.6. to 7.9 A^{o} (depending upon the time of ageing) by GUINIER (1950) and SILCOCK et al (1953-54). These lattice parameters of G.P.[2] and the T-phase suggest that there is likely to be matching between $(001)_{\theta'}$ and $(100)_{T}$

The time necessary for the 1.2% manganese alloy to reach the peak at 130°C again increases. This can be explained by considering the total effect of depletion and nucleation on the time to reach the peak. The 1.2% manganese alloy is depleted in copper to such an extent that the nucleation effect is masked by the former process and therefore as a result of these two opposing processes

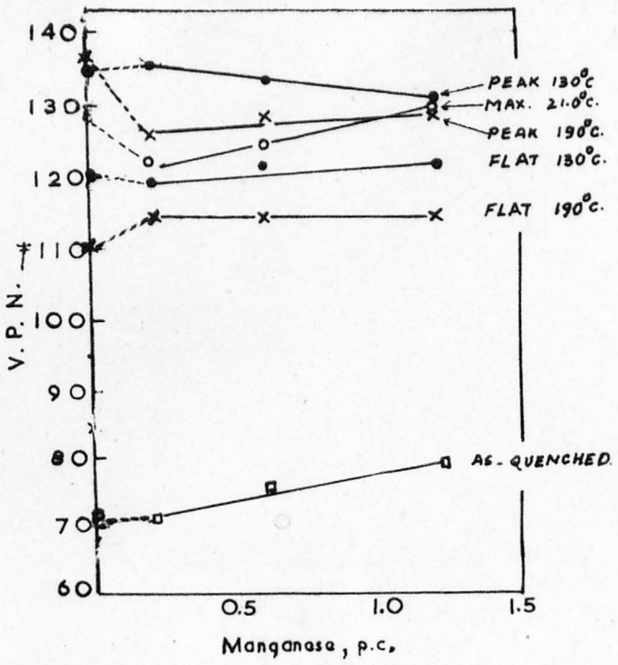


Fig (3–26) - Concantration / Hardness Relationships

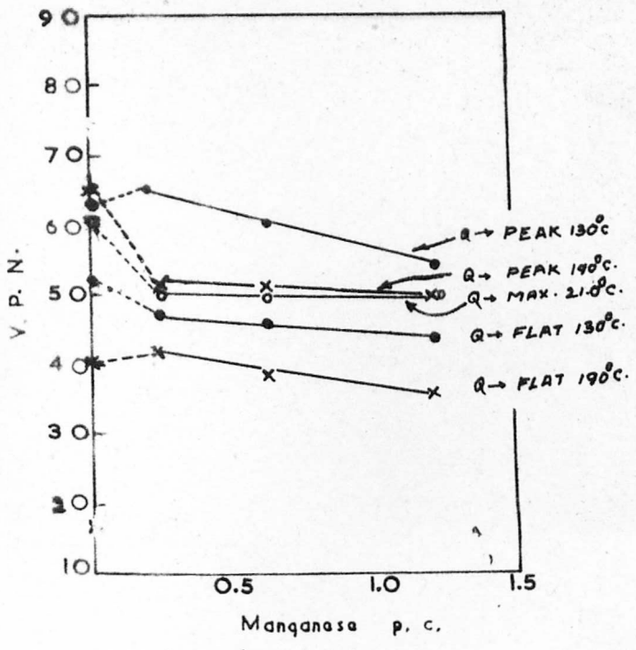


Fig (3–27) — Concantration / Hardness — Incremant Relationships

(* Value taken from CHITTY'S work)

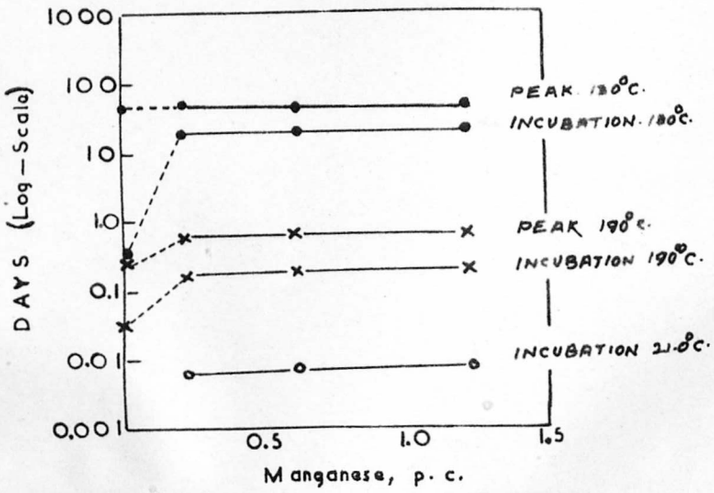
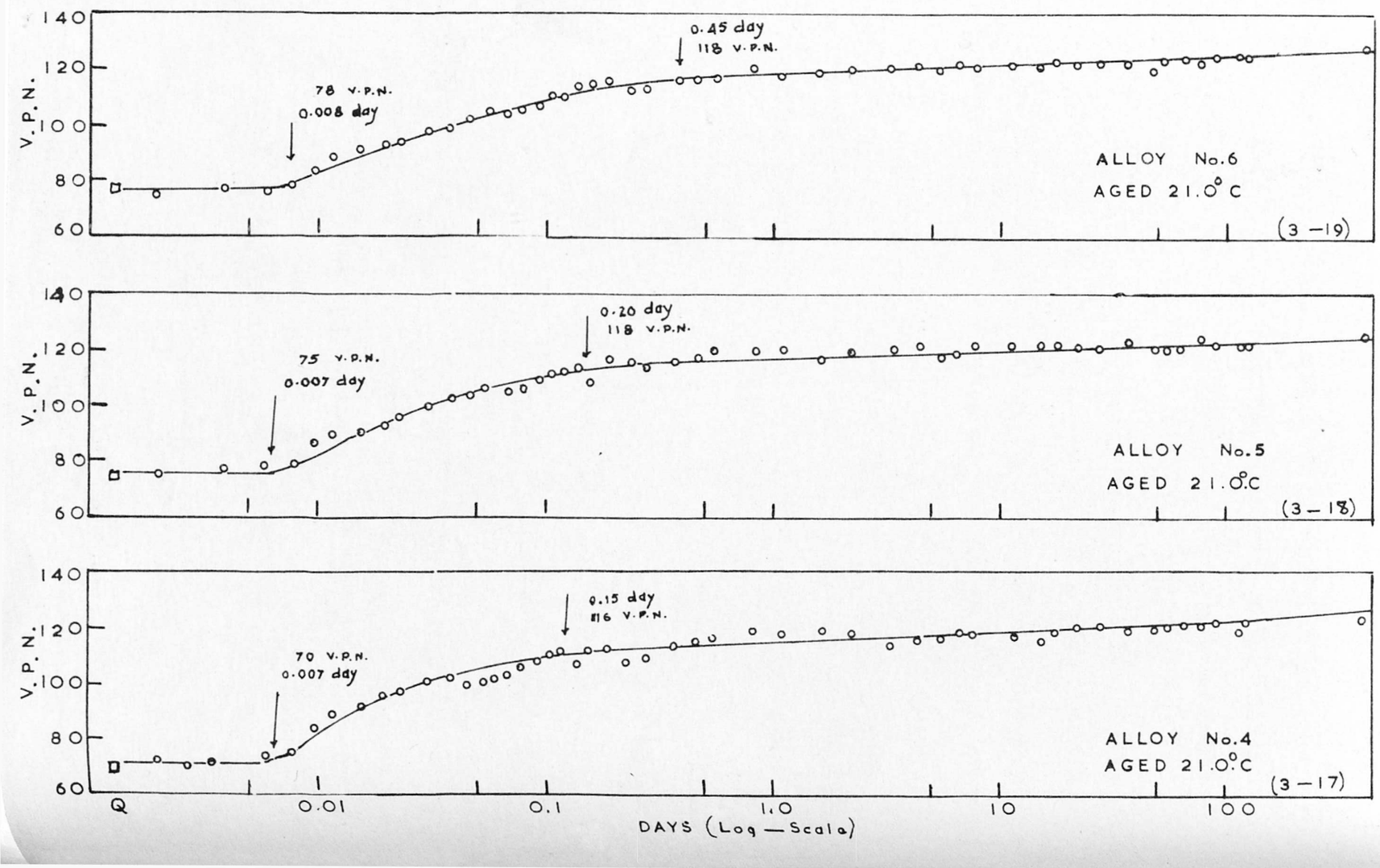


Fig (3–28) — Concantration / Time Relationships

ANALYSIS OF AGEING CURVES OF ALLOYS WITH 3.0% COPPER & 1.50% MAGNESIUM CONTAINING MANGANESE



the time to reach the peak for this alloy increases.

Hardness/ageing curves for alloys with 3.0% Cu. and 1.5% Mg. containing 0.2, 0.6 and 1.2% Mn respectively -- Ageing at 21.0°C. - (figs. 3-17, 18, 19).

For all the alloys single-stage curves were obtained, with short incubation periods of between 15 to 20 minutes. The quenched hardness remained constant over this period and then increased to about 118 V.P.N. in 0.15 to 0.45 day. Very little further increase in the hardness was found to occur on ageing for 480 days.

Ageing at 130°C - (figs 3 - 20, 21, 22).

The curves showed two stages, of which the first was completed during heating to the ageing-temperature. The hardness of about 122 V.P.N. attained during the first stage remained practically constant up to 15 to 20 days and then increased to 136 to 131 V.P.N. in 40 to 50 days; this hardness decreased with further ageing.

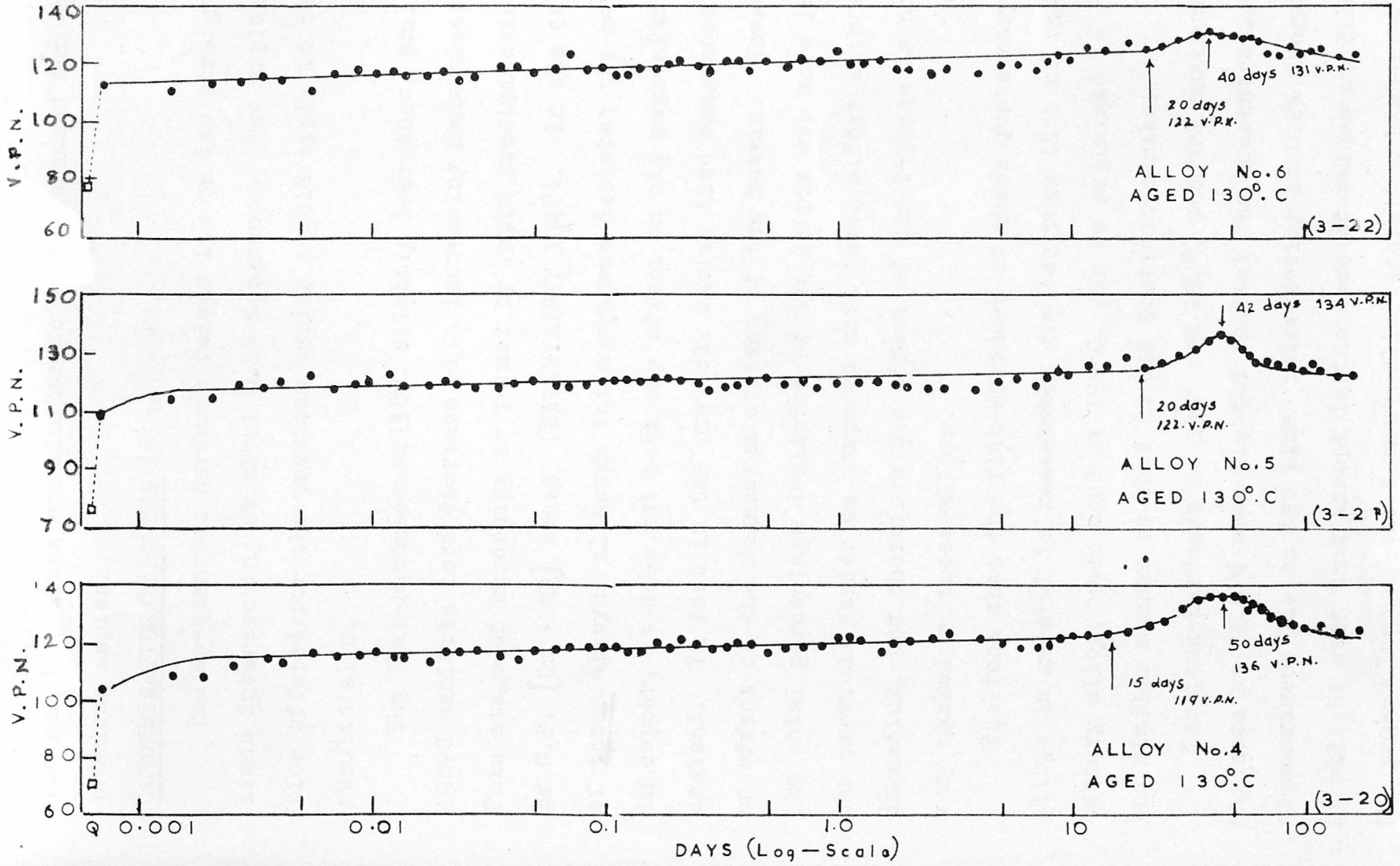
Ageing at 190°C. - (figs. 3-23, 24, 25).

All the hardness/ageing curves were two-stage. The as-quenched hardness increased to about 114 V.P.N. during heating to the ageing temperature, which constituted the first stage, and then remained constant over the incubation period of about 0.30 day. The peak-hardness of 124 to 128 V.P.N. was reached in about 0.5 day.

ANALYSIS OF AGEING CURVES

Introduction. -

These alloys contained 3%copper and 1.5% magnesium and their structure was (α+T). The effect of manganese on


V.P.N.
140
120
100
80
60
40 days 131 V.P.N.
20 days
122 V.P.N.
ALLOY No.6
AGED 130°.C
(3-22)
V.P.N.
150
130
110
90
70
42 days 134 V.P.N.
20 days
122. V.P.N.
ALLOY No.5
AGED 130°.C
(3-21)
V.P.N.
140
120
100
80
60
50 days
136 V.P.N.
15 days
119 V.P.N.
ALLOY No.4
AGED 130°.C
(3-20)
0
0·001
0·01
0.1
1.0
10
100
DAYS (Log—Scale)

the solid solution was similar to that discussed for the previous series.

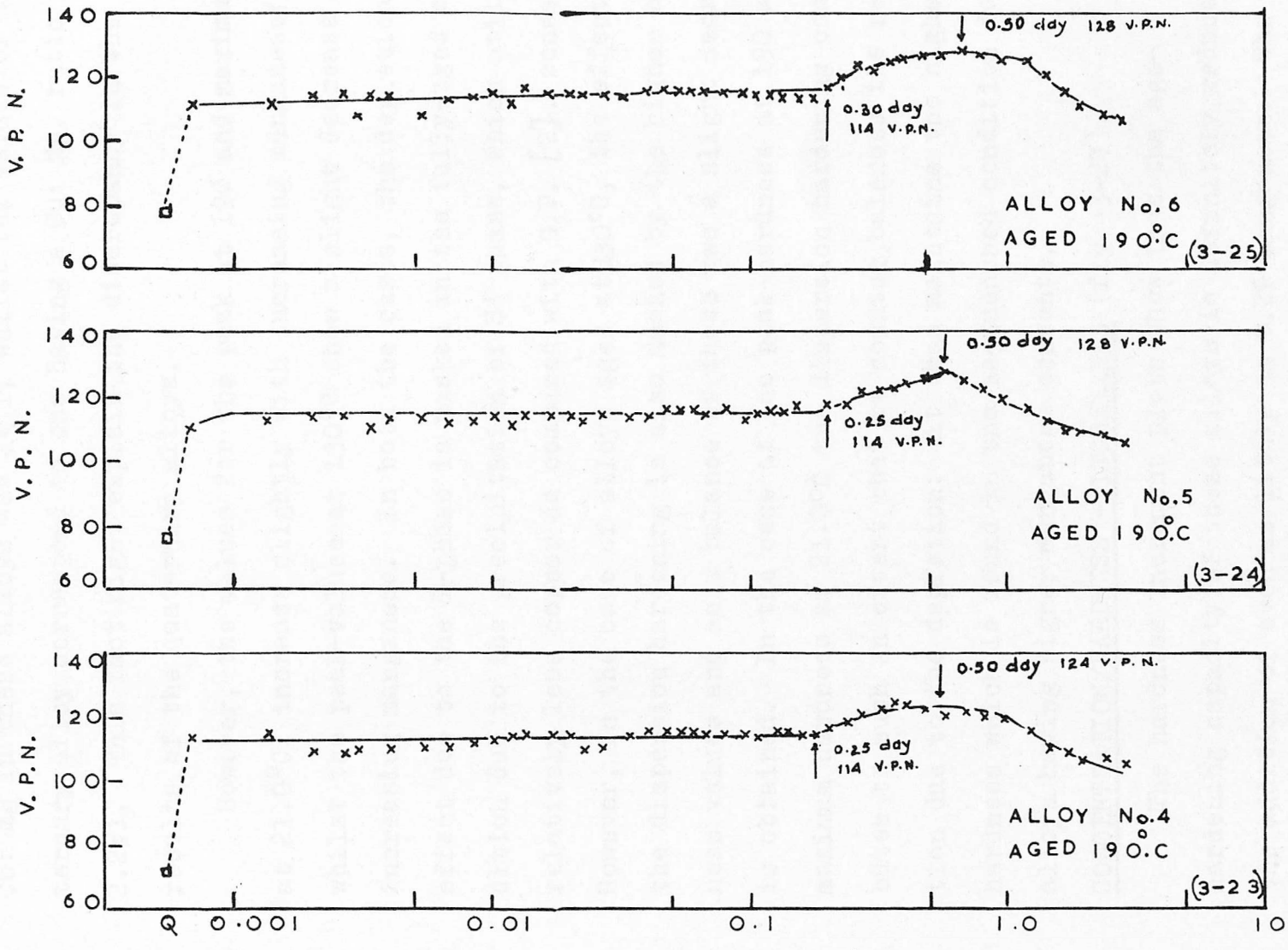
CONCENTRATION/HARDNESS (fig. 3-26).

The as-quenched hardness values lie on two straight lines intersecting at about 0.2% manganese. The explanation offered for the previous series should apply to these results also.

The flat-hardness at 130°C slightly increases, while at 190°C exhibits less decrease with increasing manganese. This stage of hardening is formed by rapid precipitation of G.P. [Cu + Mg] Zones (BAGARYATSKY 1948). In the case of these alloys, although the manganese depletes the matrix in copper, it does not have any effect on its magnesium content. In fact in the previous series also manganese had no effect on the magnesium content of the matrix. However, the total percentage depletion of the matrix was more in the previous series as compared with these alloys with 1.5% magnesium, and therefore the effect of the T-phase is not very marked on these alloys.

The fact that the flat-hardness of these quaternary alloys in general is ~~remarkably~~ greater than that of the ternary alloy, when aged at 190°C, can be explained in the similar manner to that in the previous series.

The peak-hardness at 130° and 190°C and the maximum hardness at 21.0°C when plotted against the concentration of manganese lie on two lines intersecting at 0.2% manganese. It will be seen that except in the case of values at 21.0°C, the peak-values of the ternary alloy exhibit a higher hard-


140
120
100
80
60
V. P. N.
0.50 day 128 V.P.N.
0.30 day
114 V.P.N.
ALLOY No. 6
AGED 190°C
(3-25)
140
120
100
80
60
V. P. N.
0.50 day 128 V.P.N.
0.25 day
114 V.P.N.
ALLOY No. 5
AGED 190°C
(3-24)
140
120
100
80
60
V. P. N.
0.50 day 124 V.P.N.
0.25 day
114 V.P.N.
ALLOY No. 4
AGED 190°C
(3-23)
0 0.001 0.01 0.1 1.0 10
DAYS Log - Scale

ness than that of the 0.2% manganese alloy. The ratio of Cu: Mg in these alloys was 2: 1, whilst the values of the ternary alloy correspond to one having a Cu: Mg. ratio of 2.2:1. This fact might explain the discrepancy in the results of the quaternary alloys.

However, the values for the peak at 190 and maximum at 21.0°C, increase slightly with increasing manganese; whilst the peak-values at 130°C show a slight decrease with increasing manganese. In both the cases, the depletion effect due to the T-phase is masked in the fully-aged condition due to the precipitation of S' phase, which utilises relatively less copper as compared with G.P. [2]. zones. However, in the case of alloys aged at 130°C, the effect of the dispersion hardening is also masked by the higher hardness values and as a balance of these two a slight decrease is obtained. In the case of the peak-hardness at 190 and maximum hardness at 21.0°C the dispersion hardening contributes to such an extent that it counter balances the reduction due to the depletion; it thus maintains the higher hardness which is found in the as-quenched condition for alloys having higher manganese contents.

CONCENTRATION/HARDNESS - INCREMENTS (fig. 3-27).

The hardness increment plots show that the age-hardening capacity of these alloys is definitely reduced by the addition of even as little as 0.2% manganese. The possible reasons are (1) that the values quoted for the ternary alloy are not of the exactly corresponding one, or (2) that the solubility of manganese in these alloys is

less than 0.2%. The isothermal at 500°C in the system aluminium-magnesium-manganese (fig. 1-13) shows that the solubility of manganese decreases rapidly with increasing magnesium contents; therefore the suggestion that the solubility of manganese may be less than 0.2%, seems a possible answer to the decreasing capacity to age-harden.

However, the hardness increment plots of the flat-hardness at 190°C are an exception to the other curves, and a possible mechanism of the increased rate of hardening at this temperature has already been suggested while analysing the previous series.

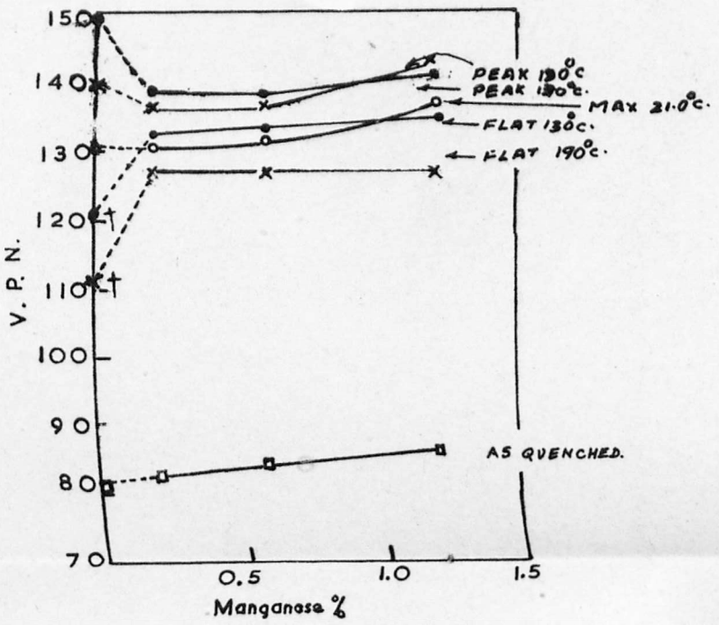
CONCENTRATION/TIME - (fig 3-28).

The plots of the logarithmic times for incubation at 130 and 190°C and for the peak at 190°C, lie on two straight lines intersecting at about 0.2% manganese. As suggested previously, the small amount of manganese dissolved in the solid solution may be participating in the precipitation process, and due to the sluggishness of diffusion of manganese these periods are lengthened. However, no evidence of increased rate of precipitation, as observed in the previous series, for the 0.6% manganese alloy is obtained. It is probable that with a higher degree of magnesium supersaturation the precipitation process is not favoured by the alternative nucleation sites provided by the T-phase.

It is pointed out in the foregoing analysis that both S' and G.P[2] zones have a direction which can fit with the lattice of the T-phase; but from the observations on these

alloys containing higher magnesium contents it seems that a better matching is obtained with G.P.[2] zones than with S' platelets. It has already been explained that at the stage just prior to the peak both G.P.[2] zones and S' will be precipitating as metastable products (HARDY 1954-55). In cases where the supersaturation of magnesium is high enough to form only S' platelets no G.P.[2] zones will precipitate. In these alloys the ratio of Cu: Mg. was 2:1 and therefore all the precipitate would be formed of S' platelets, and therefore the nucleation discussed previously may not be so marked in its effect on the ageing process.

As the manganese is increased beyond 0.2% the times are independent of the manganese concentration. This suggests that the decrease in the rate of ageing due to the depletion in the copper content of the solid solution is balanced by the magnesium content. Magnesium does not form any compound with manganese in these alloys, and therefore the magnesium content of the solid solution remains unchanged. The same holds for the alloys with 0.5% magnesium; however, in alloys with 1.5% magnesium the percentage decrease in the solute elements of the solid solution due to the T-phase will be appreciably less. It has been observed by previous workers that for the binary aluminium copper alloys containing more than 3% copper (fig. 2-9), the ternary aluminium-copper- manganese alloys containing 3 and 4.5% copper (fig 2- 13,15) and also for the ternary aluminium-copper-magnesium alloys with more than 4 (Cu + Mg)% (figs 3 - 2,4) the times to reach the peak



Fig(3–38) – Concentration / Hardness Relationships

(†-Values taken from CHITTY'S work)

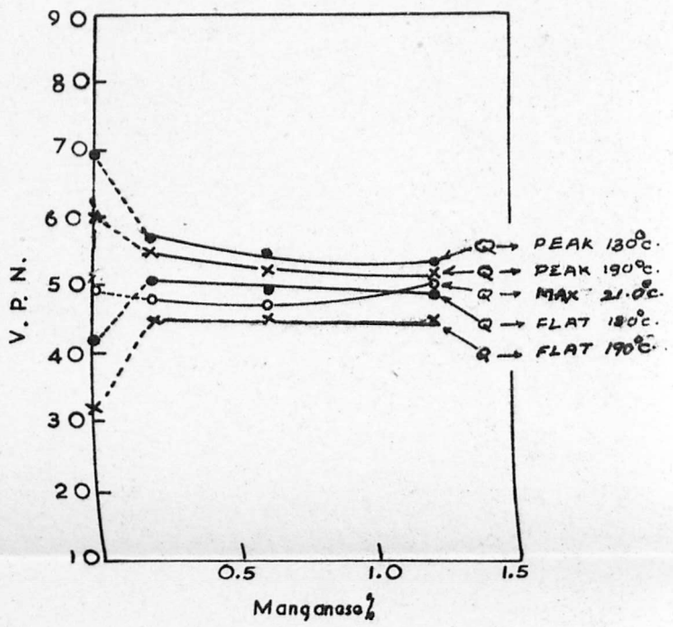


Fig (3 – 39) – Concentration / Hardness – Increments Relationships

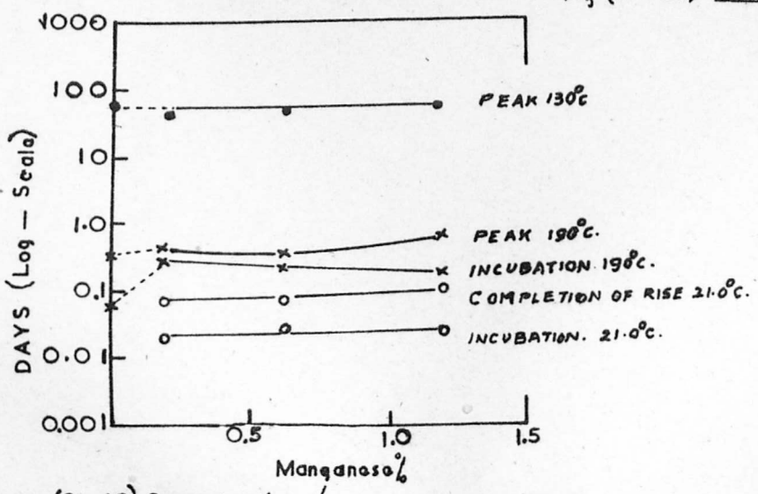
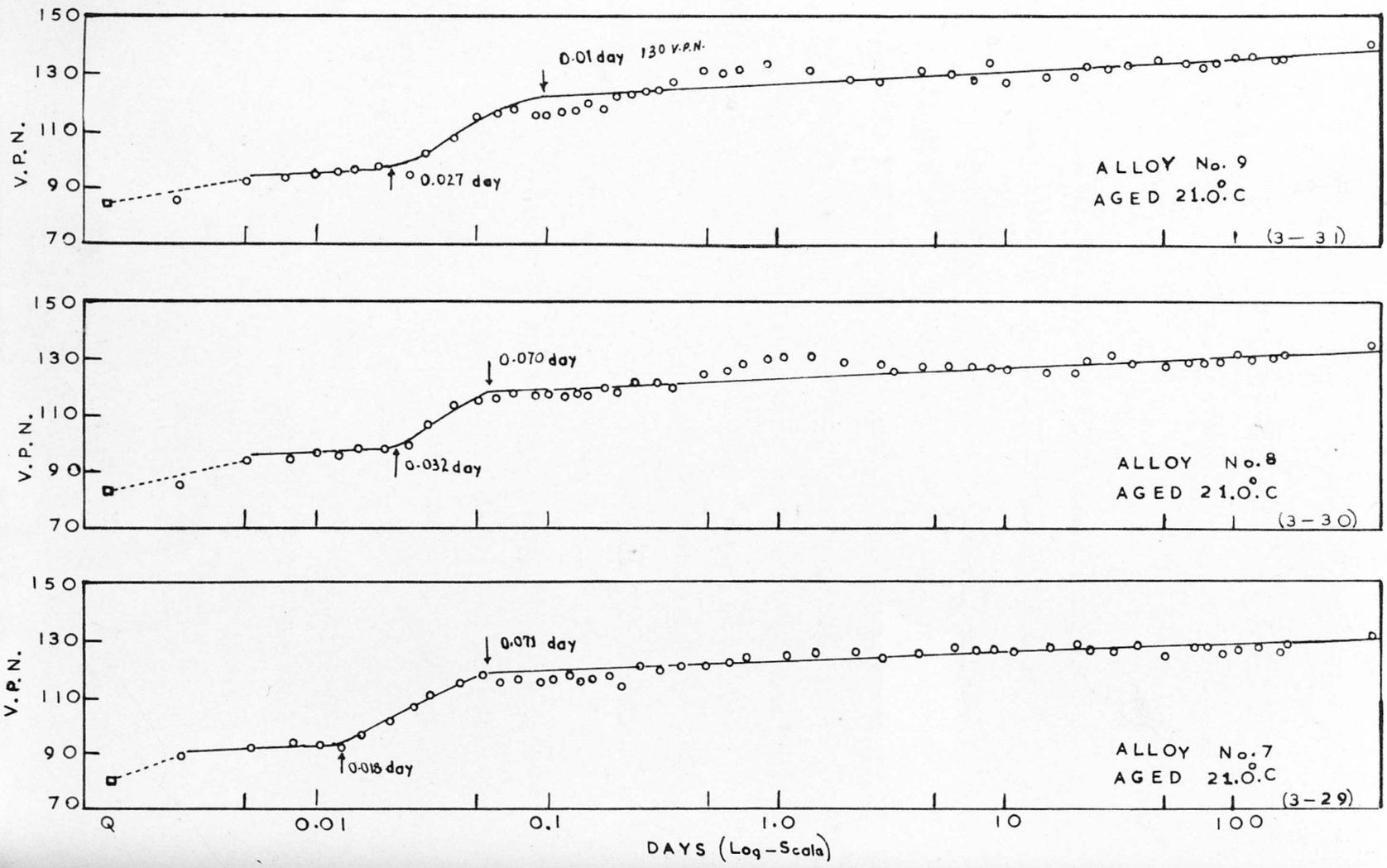


Fig (3–40) – Concentration / Time Relationships

ANALYSIS OF AGEING CURVES OF ALLOYS WITH 3.70% COPPER & 1.5% MAGNESIUM CONTAINING MANGANESE.



at 130°C are generally independent of the composition. These observations seem to hold for these quaternary alloys also.

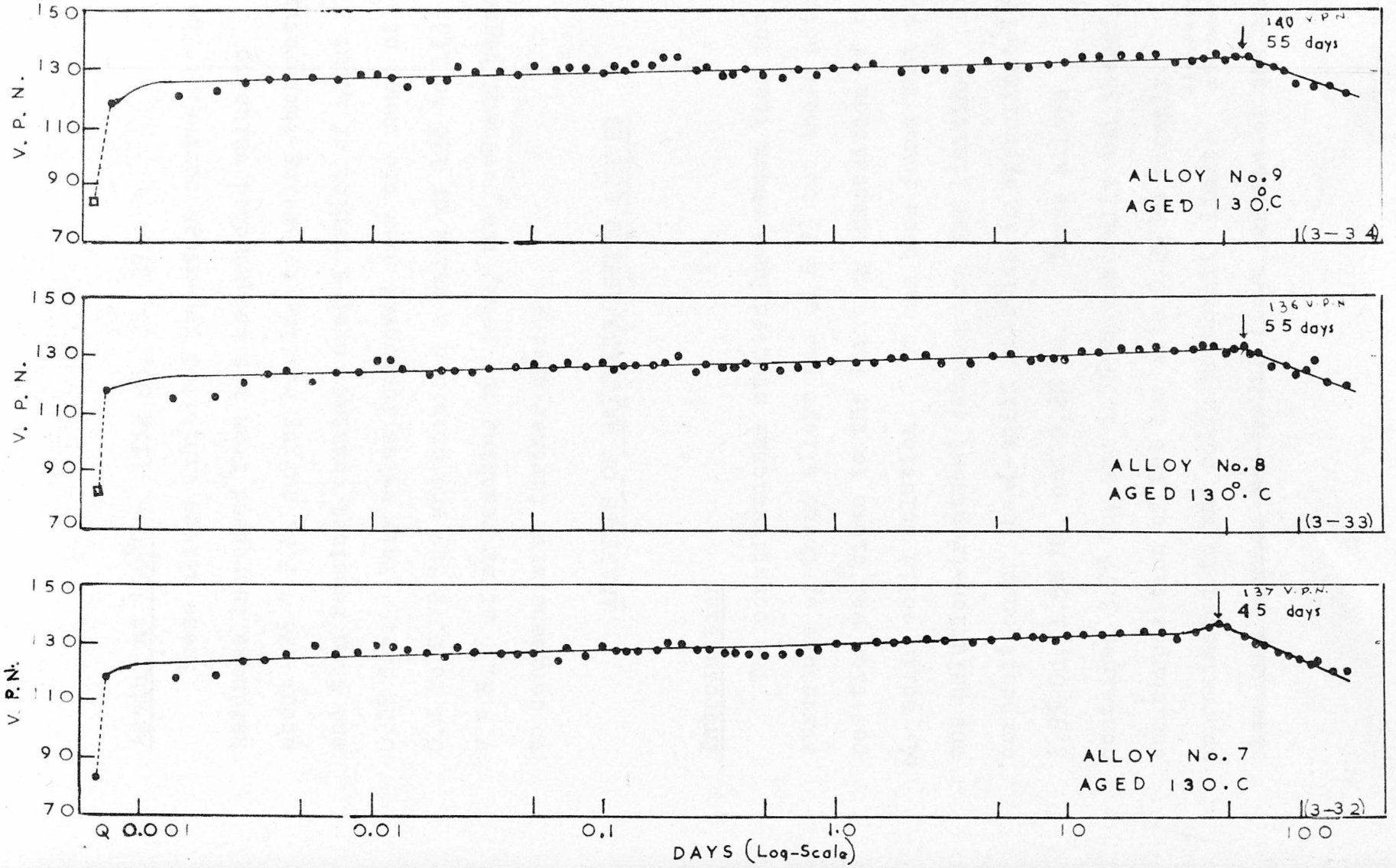
Hardness/Ageing Curves for Alloys with 3.7% Cu and 1.5% Mg containing 0.2, 0.6 and 1.2% manganese

Ageing at 21.0°C - (figs. 3 - 29, 30, 31)

The as-quenched hardness of these alloys increased slightly and then remained constant for 20 to 30 minutes. After this incubation period the hardness increased to 126 to 130 V.P.N. in about 0.1 day. There was very little further increase in the hardness over the period of 480 days.

Ageing at 130°C - (figs. 3 - 32, 33, 34)

Two-stage curves were obtained for all the alloys. The as-quenched hardness increased to about 126 to 130 V.P.N. during the times of heating to the ageing-temperature. The value steadily increased, although the change was very small, for about 40 days, and after about 45 to 53 days the hardness started falling. The peak was not very marked but an approximate value of about 135 to 140 V.P.N. has been reported from the curves as the best compromise.


150
130
110
90
70
V. P. N.
140 V.P.N.
55 days
ALLOY No. 9
AGED 130°C
(3-34)
136 V.P.N.
55 days
ALLOY No. 8
AGED 130°. C
(3-33)
137 V.P.N.
45 days
ALLOY No. 7
AGED 130. C
(3-32)
Q 0.001
0.01
0.1
1.0
10
100
DAYS (Log-Scale)

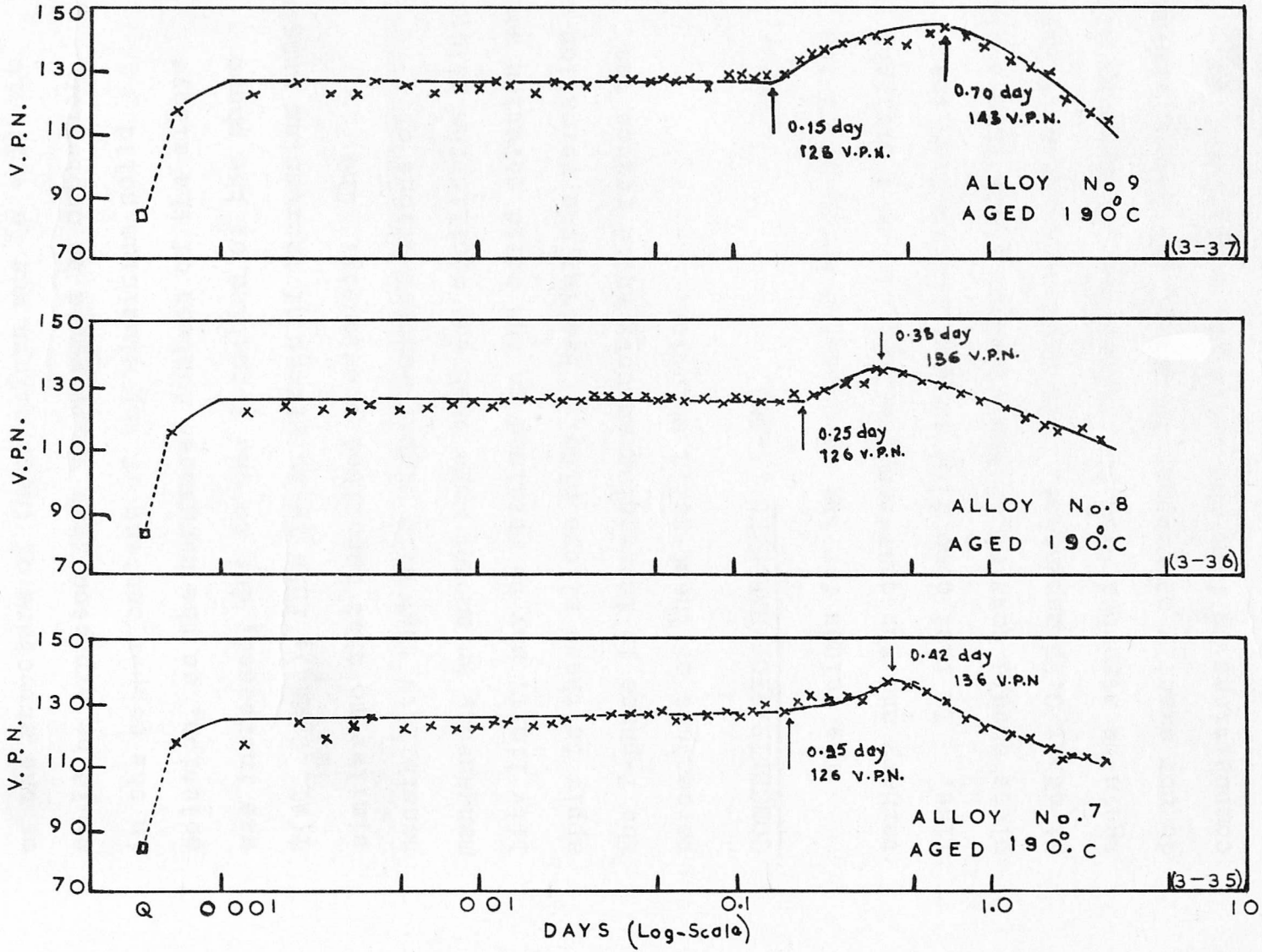
Ageing at 190°C - (fig 35, 36, 37)

These alloys exhibited two-stage curves. The hardness increased from the as-quenched value to about 126 V.P.N. during heating to ageing-temperature and then remained constant over a period of about 0.25 day. This value increased over the range of 0.4 to 0.72 day and attained a value of 136 to 143 V.P.N. After reaching the peak, the hardness began to decrease with further ageing.

ANALYSIS OF HARDNESS/AGEING CURVES

Introduction

The constitutional studies have shown that the structure of these alloys was (α & T) but their actual position was close to the limiting composition of the α- solid solid solution. It has been found that at the solution-treatment temperature the limiting composition of the α-solid solution is approximately 3.9% Cu, 1.5% Mg. and 0.2% Mn. These alloys contained 3.7% Cu, and 1.5% Mg nominally and therefore the composition of the one with 0.2% Mn closely approximated to the solid solubility limit. ~~It has also been pointed out in the first section of the thesis~~ However,


150
130
110
90
70
V.P.N.
0·15 day
126 V.P.N.
0·70 day
143 V.P.N.
ALLOY No 9
AGED 190°C
(3-37)
0·38 day
136 V.P.N.
0·25 day
126 V.P.N.
ALLOY No.8
AGED 190°C
(3-36)
0·42 day
136 V.P.N
0·25 day
126 V.P.N.
ALLOY No.7
AGED 190°C
(3-35)
0·0001
0·001
0·1
1·0
10
DAYS (Log-Scale)

as the structure of these alloys was (α + T), it would be expected that there would be depletion in the copper content of the aluminium solid solution, as the manganese content of the alloys was increased, due to the formation of the phase T($Al_{12}CuMn_2$); this is an effect of increasing manganese similar to that described previously. The possibility that with higher concentrations of manganese, an amount more than the equilibrium solubility limit, may be retained in the solid solution would apply to these alloys also. Besides, the formation of the T-phase in increasing amounts would reduce the percentage of the α-solid solution.

CONCENTRATION/HARDNESS (3-38)

The values for the as-quenched hardness of the ternary and the quaternary alloys lie on a straight line. In fact according to the constitution the plots should consist of two straight lines intersecting at about 0.2% manganese. In this connection it may again be stressed that the values for the ternary alloys do not exactly correspond to one of the exact relevant compositions to form the basis for comparison, and that the solubility of manganese in the alloys with

1.5% Mg may probably be even less than 0.2%.

Regarding the suggestion that with higher manganese concentration, unexpectedly higher amounts of manganese may be held in the solid solution, it can be said that in alloys with lower manganese contents the equilibrium solubility may be reached more readily as compared with those containing higher manganese. On this assumption the as-quenched values should give curved lines, but in fact appear to give a straight line. This is most probably due to the fact that the lattice straining effect due to slightly higher manganese content of the alloys with 1.2% manganese is being counterbalanced by the reduction in the amount of hard T-phase.

The flat-hardness values at 130 and 190°C lie on two straight lines intersecting at about 0.2% manganese. There is an appreciable increase in the flat-hardness of the quaternary alloys as compared with that of the ternary alloy. The general explanation has already been given for the sudden increase in the flat-hardness values of the quaternary alloys when aged at 190°C; a similar explanation is applicable to these flat-hardness values.

The peak-hardness values at 130 and 190°C and the

maximum hardness values at 21.0°C lie nearly on a straight line. However, the values for the 1.2% manganese alloy are slightly higher and therefore the portion between the value for the 0.6 and 1.2% manganese is drawn slightly curved for the plots at 21 and 190°C. As explained in the introductory paragraph the alloy with 1.2% manganese would retain more manganese in the solid solution as compared to the 0.2 and 0.6% manganese alloys. The slightly higher manganese content of the solid solution did not exhibit an appreciable effect on the quenched-hardness, but definitely shows to some extent on the peak-hardness values. It is natural to expect this kind of behaviour because the lattice straining effect due to a certain amount of element in the solid solution, is generally less than its effect due to coherency stresses.

CONCENTRATION/HARDNESS - INCREMENTS (Fig 3 - 39)

The hardness-increments from quenched to flat at 130 and 190°C, when plotted against manganese concentration form two straight lines intersecting at about 0.2% manganese. It will be seen that, although the solubility of manganese seems to be very small the

capacity to age-harden at the first stage during heating is increased by the introduction of manganese.

The hardness-increments from the as-quenched to peak at 130 and 190°C lie approximately on straight lines sloping towards the concentration axis. Considering quenched to peak increments the age-hardening capacity of these alloys is seen to be slightly reduced by increasing manganese. Considering the depletion effect on the aluminium solid solution due to the increasing manganese content, a greater reduction in age-hardening capacity than actually observed would be expected. The explanation for this behaviour of the alloys of this series is not apparent. The increment plots for the 1.2% manganese alloy substantiate the idea that with higher manganese concentrations, manganese, more than the solid solubility limit may be held in solution.

Besides, the reduction in the percentage of the α-solid ~~solid~~ solution would also have some effect in reducing the total age-hardening capacity of the alloys.

The increments from as-quenched to maximum hardness at 21°C lie on a curved line and this suggests that the 1.2% manganese alloy has a greater

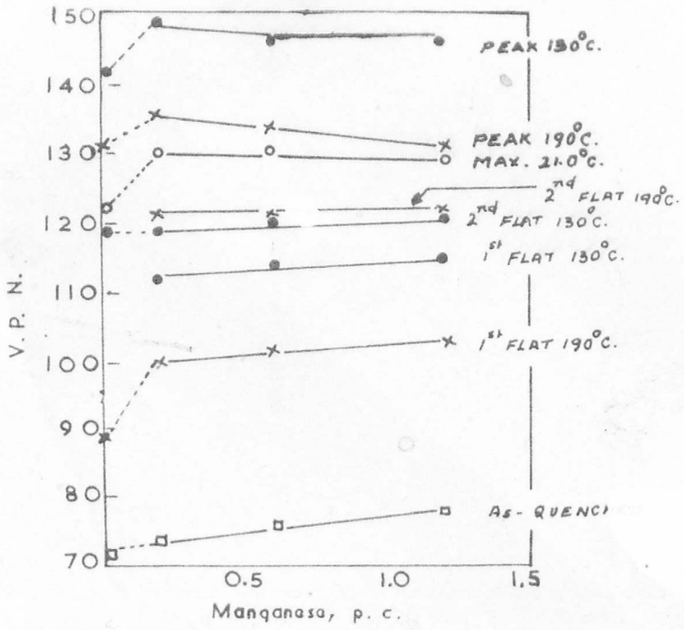


Fig. (3—50)— Concantration / Hardness Relationships

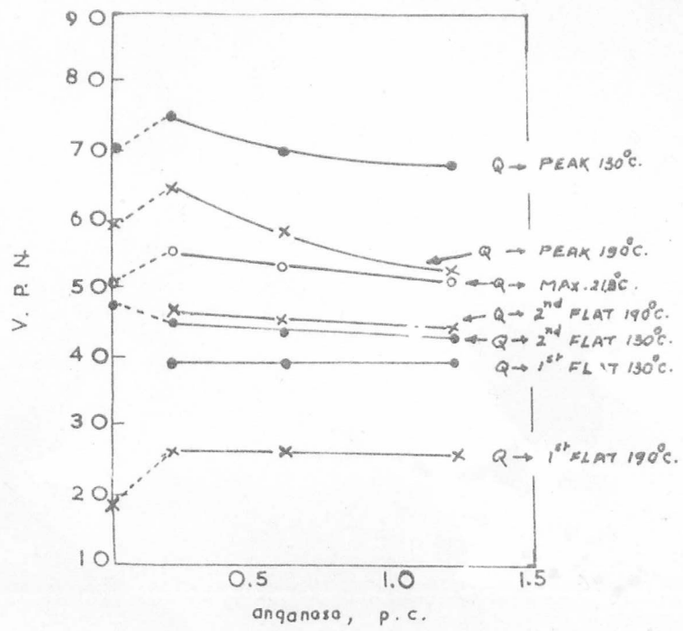


Fig. (3—51) — Concentration / Hardness—Incramant Relationships

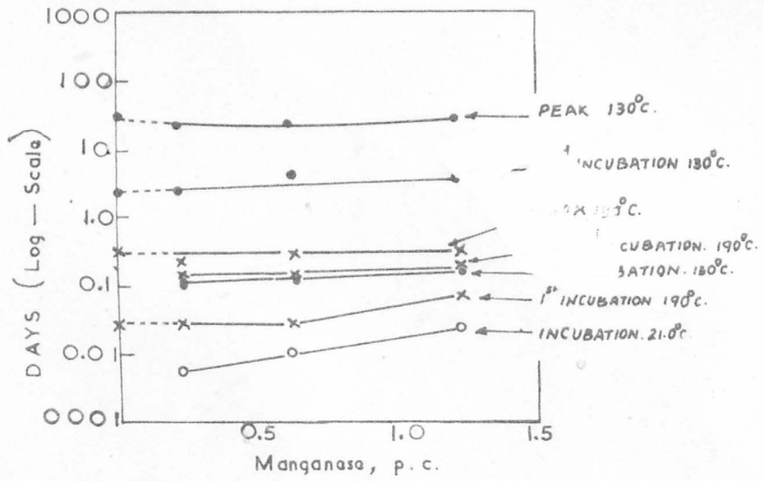
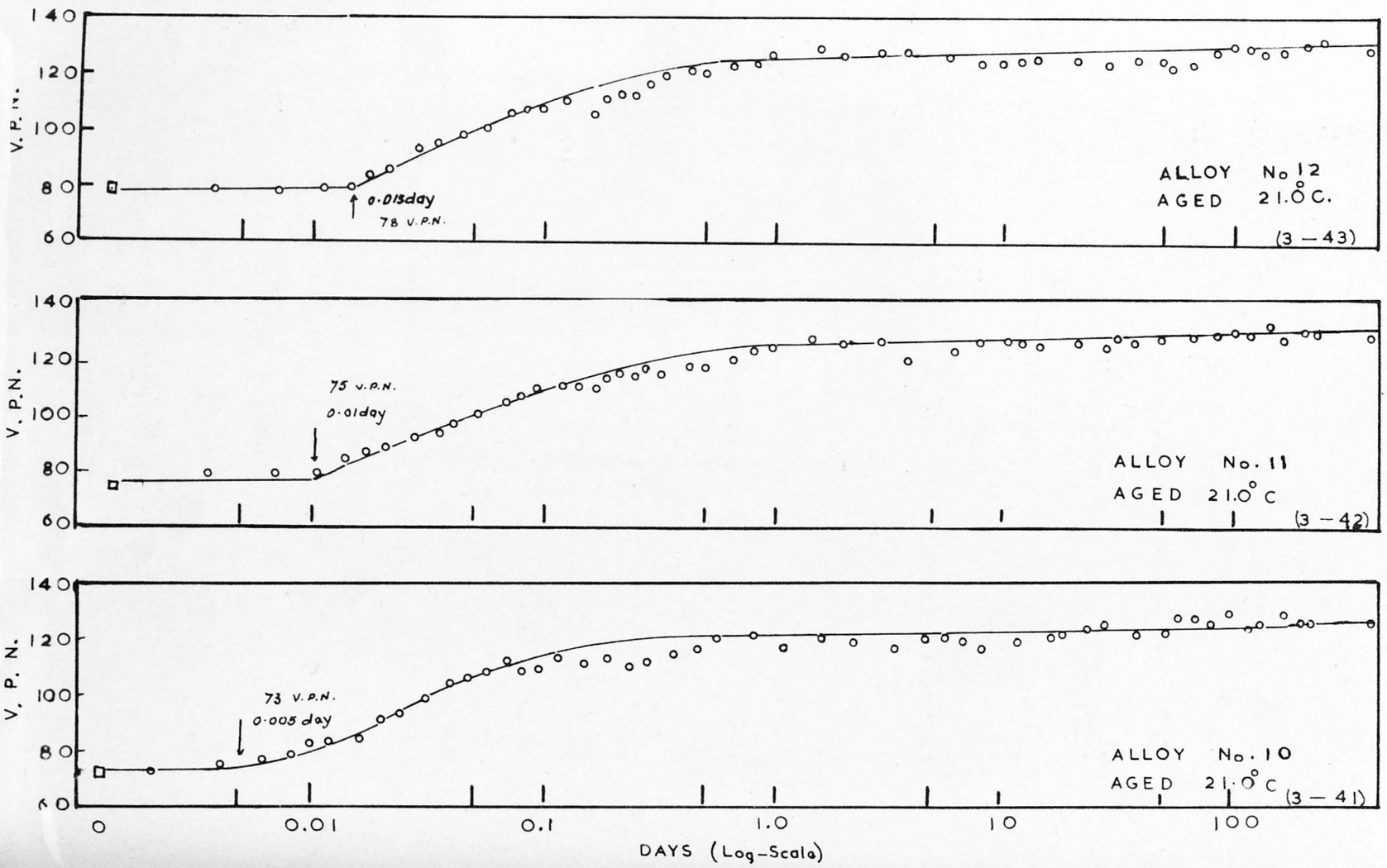


Fig. (3—52)- Concentration / Time Relationships

ANALYSIS OF AGEING CURVES OF ALLOYS WITH 4.50% COPPER & 0.50% MAGNESIUM CONTAINING MANGANESE



capacity to age-harden at this temperature. In fact, the hardness/ageing curves did not reach the peak even during 480 days.

CONCENTRATION/TIME (Fig 3 - 40)

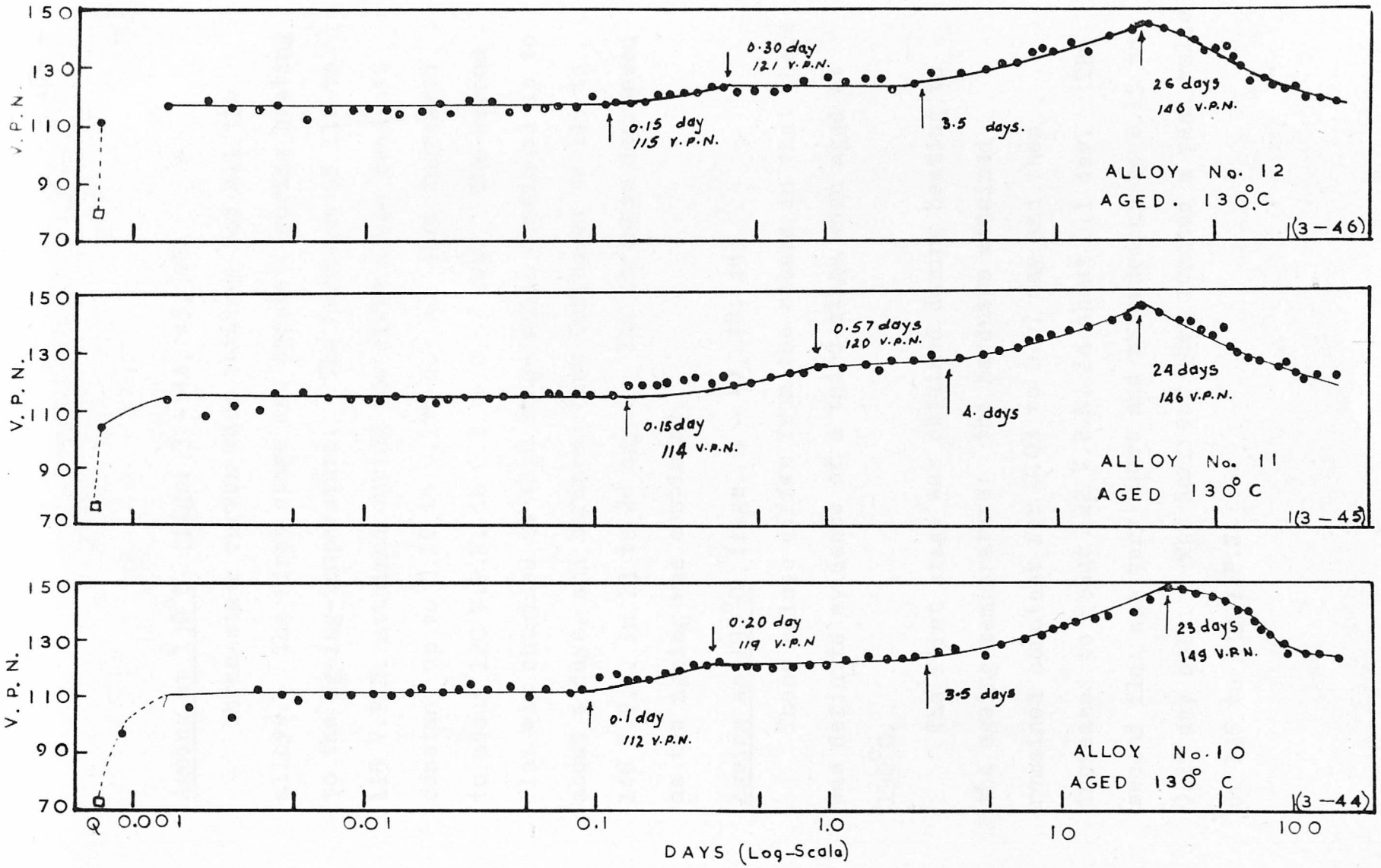
As previously stated the times to various stages are independent of composition in these alloys of higher supersaturation.

However, the logarithms of incubation periods at 190°C, when plotted against the concentration do exhibit a slight effect of shortening the time due to the nucleation provided by the T phase.

Hardness/Ageing curves for Alloys with 4.5% Cu, 0.5% Mg, containing 0.2, 0.6 and 1.2% Mn. respectively.

Ageing at 21.0°C. (figs. 3 - 41, 42, 43)

These alloys exhibited single-stage ageing curves. After short incubation periods of 10 to 20 minutes the hardness increased to about 125 V.P.N. in about 0.7 day and then increased only by 4 or 5 V.P.N. over the period of 480 days.


150
130
110
90
70
V. P. N.
0·30 day
121 V.P.N.
0·15 day
115 V.P.N.
3.5 days.
26 days
146 V.P.N.
ALLOY No. 12
AGED. 130°C
(3-46)
0·57 days
120 V.P.N.
0·15 day
114 V.P.N.
4. days
24 days
146 V.P.N.
ALLOY No. 11
AGED 130° C
(3-45)
0·20 day
119 V.P.N
0·1 day
112 V.P.N.
3·5 days
23 days
149 V.P.N.
ALLOY No. 10
AGED 130° C
(3-44)
Q
0.001
0.01
0.1
1.0
10
100
DAYS (Log-Scale)

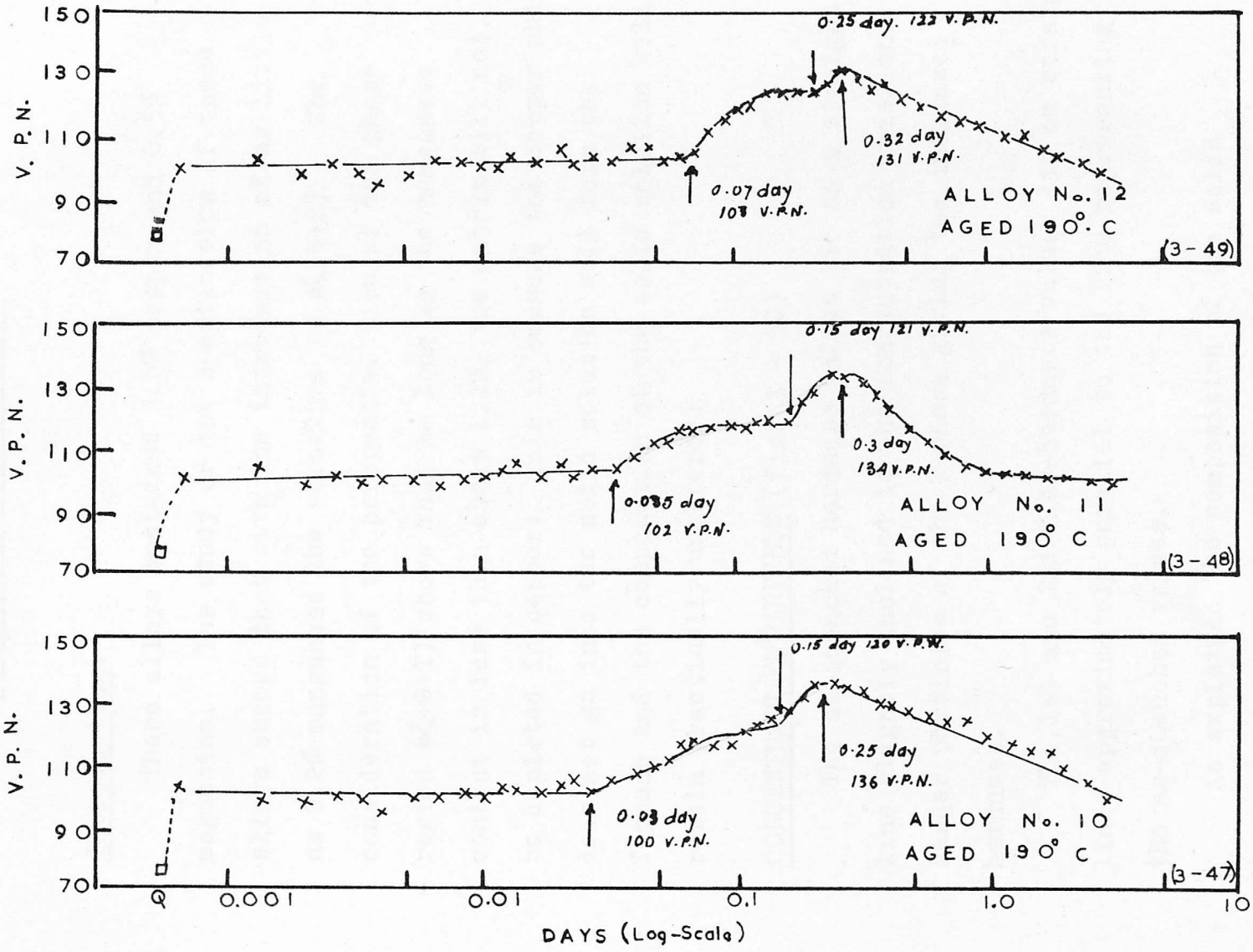
Ageing at 130°C (figs. 3 - 44, 45, 46)

Three-stage curves were obtained for all the alloys. The first stage was complete during heating to the ageing-temperature. The hardness of 112 to 115 V.P.N. attained during the first stage remained constant up to 0.10 to 0.150 day and then increased to about 120 V.P.N. in 0.2 to 0.57 day. The second flat was obtained at this stage which continued up to about 4 days, and hardness then increased to 149 to 146 V.P.N. in 23 to 26 days. The hardness decreased as the ageing was continued.

Ageing at 190°C (figs. 3 - 47, 48, 49)

These alloys differ from the others in that there was definite evidence of a third stage when aged at 190°C.

The first stage was obtained during heating to the ageing-temperature; the hardness attained remained constant for 0.03 to 0.07 day and then increased to about 122 V.P.N. in about 0.1 day. The second flat was very short and extended up to 0.15 to 0.25 day only. The hardness then reached a peak value of 136 to 132 V.P.N.


150
130
110
90
70
V. P. N.
0·25 day. 122 V.P.N.
0·32 day
131 V.P.N.
0·07 day
108 V.P.N.
ALLOY No. 12
AGED 190° C
(3-49)
0·15 day 121 V.P.N.
0·3 day
134 V.P.N.
0·035 day
102 V.P.N.
ALLOY No. 11
AGED 190° C
(3-48)
0·15 day 130 V.P.N.
0·25 day
136 V.P.N.
0·03 day
100 V.P.N.
ALLOY No. 10
AGED 190° C
(3-47)
0
0.001
0.01
0.1
1.0
10
DAYS (Log-Scale)

ANALYSIS OF AGEING CURVES

Introduction.

These alloys contained 4.5% copper and 0.5% magnesium. The study of the constitution of these alloys showed that with the introduction of as little as 0.2% manganese the structure is (α+θ+T). The consideration of the perspective view of the phase region (α+θ+T) shows that as long as the manganese content is less than about 1.2%, the matrix will not be depleted in copper; this is because the copper which does not go into the solid solution will form the T-phase and the composition of the solid solution will remain practically unaltered:

CONCENTRATION/HARDNESS (fig. 3 - 50)

The as-quenched hardness values lie on a straight line slightly inclined to the concentration axis, the harder particles of the T-phase giving the increased hardness.

The 1st and 2nd flat-hardness values lie on straight lines approximately parallel to the line representing the as-quenched values.

As explained the composition of the solid solution of these alloys remained practically constant

with increasing manganese and therefore there was very little or no change in the age-hardening capacity of these alloys. The values of peak-and maximum-hardness at 130, 190 and 21.0°C respectively form two straight lines intersecting at about 0.2% manganese. As previously suggested it seems that with 0.5% magnesium the solubility of manganese in these alloys may be about 0.2%, but may be decreasing appreciably with increasing magnesium. Although the increasing manganese does not change the composition of the α-solid solution appreciably, it forms the T-phase and thus reduces the percentage of the α-solid solution present in the alloy. This effect is quite likely to reduce the total age-hardening of the alloys with higher manganese contents. Nevertheless, the effect is not very pronounced as the percentage reduction of the α-solid solution is not appreciable.

CONCENTRATION/HARDNESS-INCREMENTS (fig 3 - 51)

The nature of the increments from the as-quenched to 1st and 2nd flat hardness curves is similar to that of the concentration/hardness curves and a tentative explanation has been suggested while analysing the concentration/hardness relationships.

The T-phase has a formula Al_{12} Cu Mn_2, and thus it will be seen that although the percentage of manganese was small the amount of the T-phase present could cause some reduction in the percentage of the α-solid solution. The hardness increments from quenched to peak at 130 and 190°C substantiate this suggestion. The plots of increments for the 1.2% manganese alloy exhibit a slightly less reduction in the age-hardening capacity due to the reduction in the percentage of α as compared with that of the 0.6% manganese alloy. This is in all probability due to higher manganese contents being retained in the solid solution in cases where higher manganese percentages are added.

CONCENTRATION/TIME (fig 3 - 52)

For all practical purposes the times to different stages on the hardness/ageing curves are independent of the concentration. This is in agreement with the observations of previous investigators on other systems.

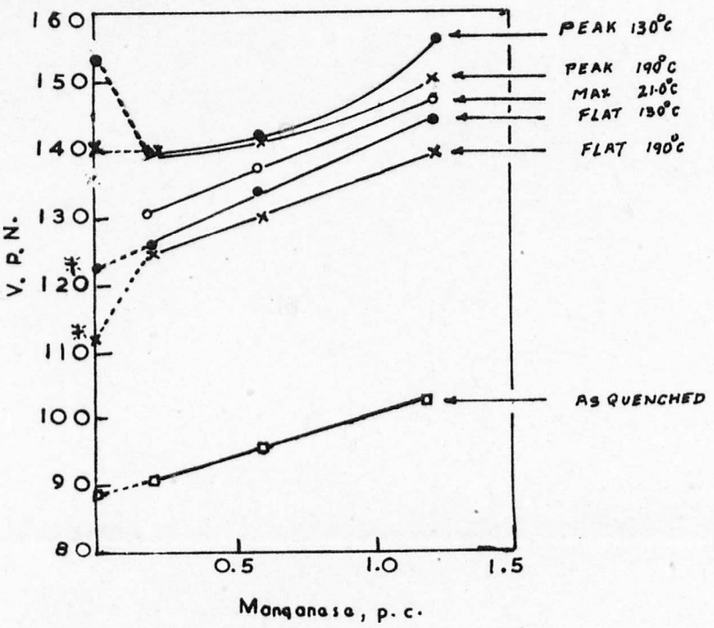


Fig. (3–62)– Concentration / Hardness Relationships

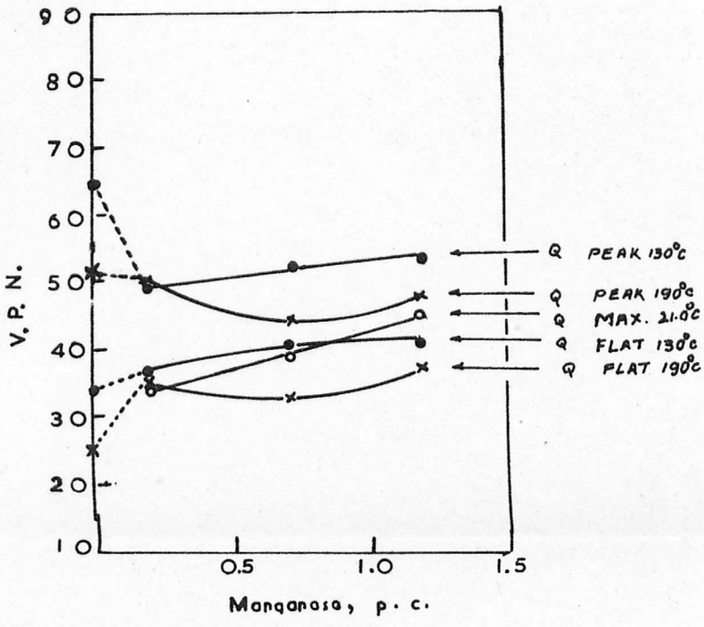


Fig (3 – 63) – Concentration / Hardness – Increment Relationships

(* Values from CHITTY's Work.)

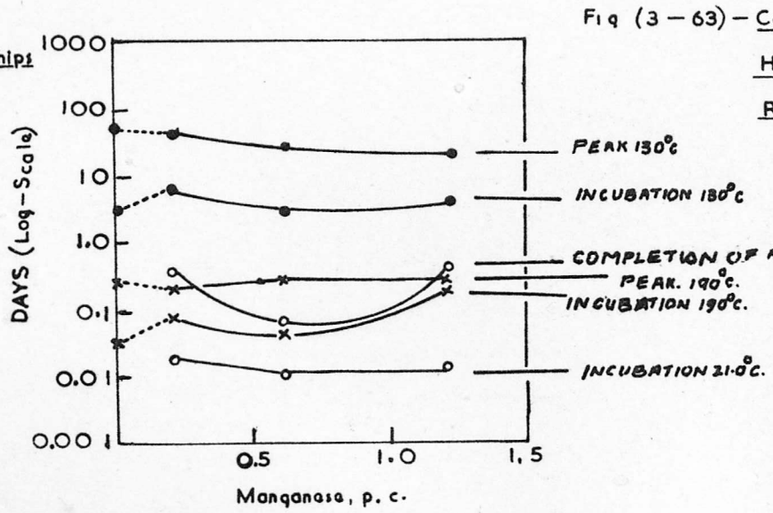
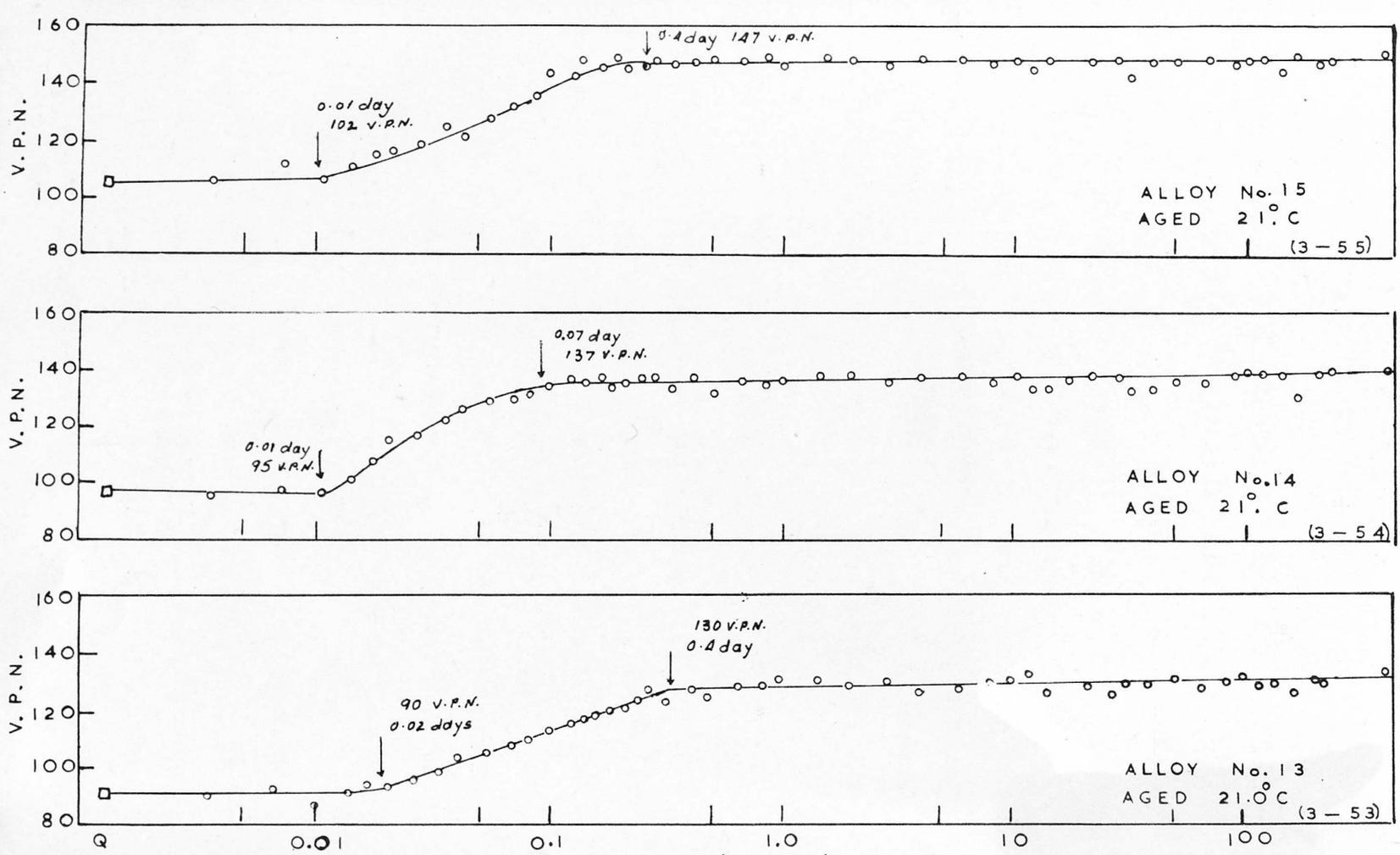


Fig (3–64) – Concentration / Time Relationships

ANALYSIS OF AGEING CURVES OF ALLOYS WITH 4.50% COPPER & 1.50% MAGNESIUM CONTAINING MANGANESE



Hardness/Ageing Curves for Alloys with 4.5% Cu, 1.5% Mg containing 0.2, 0.6 and 1.2% Mn respectively -

Ageing at 21°.0C - (figs - 3 - 53, 54, 55)

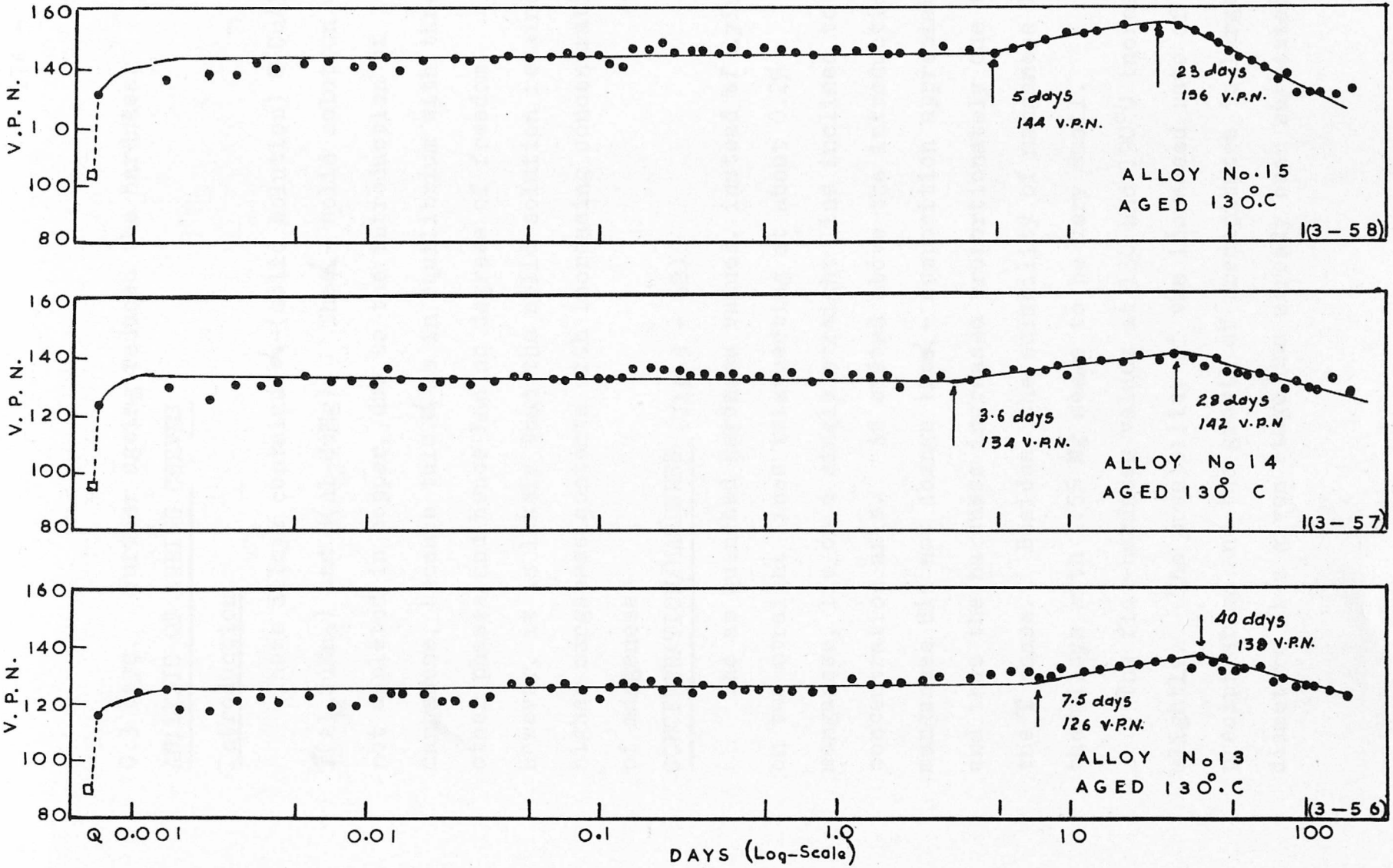
Single-stage ageing curves were obtained for all the alloys. After the incubation periods of 20 to 30 minutes the hardness increased to 130 to 147 V.P.N. in about 0.4 day. The hardness attained at the end of the increment practically remained constant for further ageing of 480 days.

Ageing at 130°C - (Figs - 3 - 56, 57, 58)

The alloys exhibited two-stage ageing curves of which the first stage was completed during heating when the hardness increased to 126 to 144 V.P.N. This hardness remained constant for 7.5 to 5 days and then increased to 138 to 156 V.P.N. in 40 to 23 days. The hardness decreased as the ageing was continued.

Ageing at 190°C - (Figs - 3 - 59, 60, 61)

For all the alloys two-stage ageing curves were obtained. The hardness increased to 126 to 140 V.P.N. during heating to the ageing temperature and then remained constant up to 0.04 to 0.2 days. The flat was followed by an increase to 140 to 150 V.P.N. in 0.2 to


160
140
120
100
80
V. P. N.
5 days
144 V.P.N.
28 days
136 V.P.N.
ALLOY No. 15
AGED 130°C
(3-58)
3·6 days
134 V·P·N.
28 days
142 V.P.N
ALLOY No 14
AGED 130° C
(3-57)
40 days
139 V·P·N.
7·5 days
126 V·P·N.
ALLOY No 13
AGED 130°. C
(3-56)
0 0.001
0.01
0.1
1.0
10
100
DAYS (Log-Scale)

0.3 days. Further ageing reduced the hardness.

ANALYSIS OF AGEING CURVES

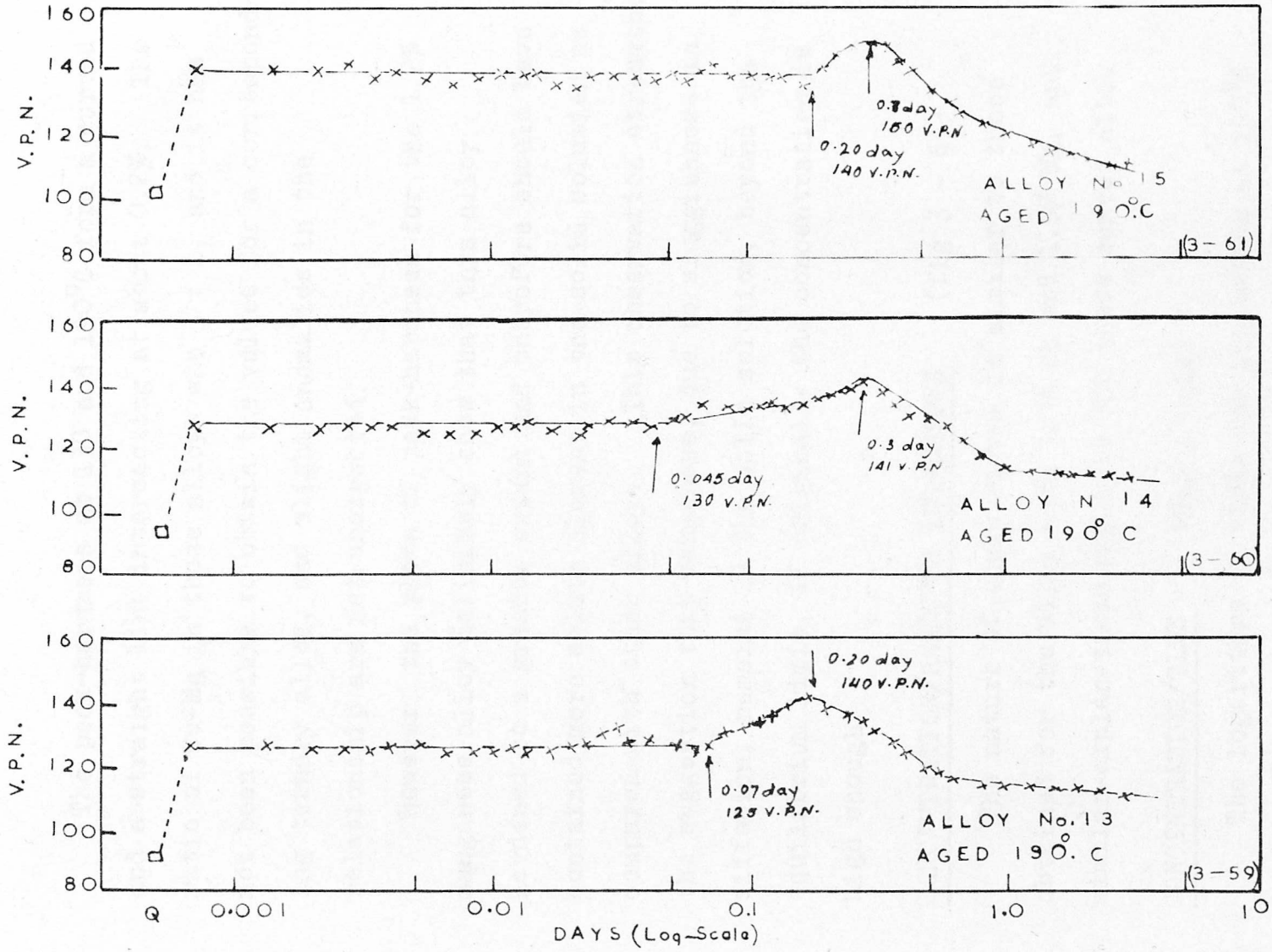
Introduction

These alloys contained α-(solid solution) O($CuAl_2$), T($Al_{12}CuMn_2$) and S(Al_2CuMg). The α- solid solution was not depleted in copper, due to the introduction of manganese, because this α is in equilibrium with three other phases and hence had no degrees of freedom. However, it is likely that the solid solution retained higher manganese contents with increasing concentration of manganese.

CONCENTRATION/HARDNESS (fig 3 - 62)

The as quenched hardness values, instead of lying on two straight lines intersecting at about 0.2% manganese, lie on a single straight line inclined to the concentration axis. As stated above the introduction of manganese did not change the α- composition appreciably and thus the hardness increased proportionately due to the T phase. Besides, the solubility of manganese in the alloys with 1.5% Mg seems to be very small.

The flat-hardness values at 130 and 190°C increased slightly. The possibility of the increased rate of precipitation and the growth of precipitates to larger diameters at a given stage has already been suggested.


160
140
120
100
80
V. P. N.
0·20 day
140 V.P.N.
0·8 day
150 V.P.N
ALLOY No 15
AGED 190°C
(3-61)
0·045 day
130 V.P.N.
0·3 day
141 V.P.N
ALLOY N 14
AGED 190° C
(3-60)
0·20 day
140 V.P.N.
0·07 day
125 V.P.N.
ALLOY No. 13
AGED 190°. C
(3-59)
Q
0·001
0·01
0·1
1·0
10
DAYS (Log-Scale)

The peak-hardness at 130 and 190°C form a curved and a straight line intersecting at about 0.2%. The ratio of Cu-Mg in these alloys was 3 : 1, and it has not been possible to obtain the values for a corresponding ternary alloy, and slight anomalies in the relationship are not unexpected.

However, the plots of peak-hardness for the 1.2% manganese alloy definitely show that this alloy hardened to a greater extent and therefore should have contained more solute element in the solid solution as compared with other alloys. This observation strengthens the suggestion that manganese, due to sluggishness in diffusion, remains in the solid solution, beyond the equilibrium limit, if originally the concentration is high enough.

CONCENTRATION/HARDNESS INCREMENTS (fig 3 - 63)

The nature of these curves is similar to those obtained for the alloy with 3.7% Cu and 1.5% Mg, and similar explanations may hold for these curves also.

CONCENTRATION/TIME (Fig 3 - 64)

The logarithms of times for incubation at 190°C and 21.0°C, suggest that nucleation effects might be hastening the ageing process. Similar curves are

obtained for the times to peak and incubation at 130°C. However, these results are slightly different from those of the alloys with 3.7% Cu and 1.5% Mg. The small discrepancy may be due to the experimental limitations.

CONCLUSIONS.

1) The quenched and peak-hardness values in general and the increments between the quenched and flat-hardness of the alloys aged at 190°C are increased by manganese in the solid solution.

2) The solubility of manganese decreases rapidly with increasing magnesium and therefore the limiting solid solubility in the quaternary system may be well below 0.2%.

3) It is suggested that manganese is held in the solid solution in an amount greater than the solid solubility limit, in cases where the concentration of manganese is high. This behaviour is probably due to the sluggishness in diffusion.

4) In alloys containing α and T the solid solution is depleted in copper and hence age-hardening capacity is reduced. However, the T-phase being harder than the matrix increases the as-quenched hardness to some extent.

5) In alloys containing α, θ and T the composition of the solid solution is not appreciably altered with increasing manganese concentrations, and also the solubility of manganese is not reduced below 0.2% (as the magnesium content was only 0.5%) and therefore both the manganese in solid solution and the T-phase are found to contribute towards the hardness in the as-quenched and fully-aged conditions.

6) In four phase alloys where α exists with θ ($CuAl_2$), T(Al_{12} Cu Mn_2) and S(Al2 Cu Mg) the composition of the α-solid solution remains unaltered and in such alloys the contribution of the harder T-phase is found in both as-quenched and fully-aged conditions.

7) In general, where the composition of α-solid solution remains unaltered, the age-hardening capacity is reduced to some extent due to the reduction in the percentage of α, as a result of the formation of T-phase.

APPENDIX I

APPLICATION OF THE "FRACTIONAL NUCLEATION THEORY" TO THE PRECIPITATION HARDENING (OF THE ALUMINIUM - 4.25% COPPER ALLOY).

INTRODUCTION

In 1935 SCHEIL published a paper on the transformation of austenite. He put forward a "Fractional Nucleation Theory", which suggested that transformation from austenite to a stable product will begin when the sum of the fractional nucleation times is unity. This theory may be explained by reference to figure I.

Taking the C - curve as a basis, the incubation period in an isothermal experiment will be t seconds at a temperature T. If a specimen is held at temperature T for t' seconds (where t' is less than t) then the fractional nucleation time or "Scheil fraction" is t'/t .

Consider a specimen step quenched in accordance with the dotted line ABCDE on fig. I. The specimen remains at a temperature T_1 , for a time $\frac{1}{2}\ t_1$, thus producing a "Scheil fraction" of $\frac{1}{2}\ t_1/t_1$ or $\frac{1}{2}$. It is then rapidly quenched to temperature T_2 and held there for time $\frac{1}{2}\ t_2$;

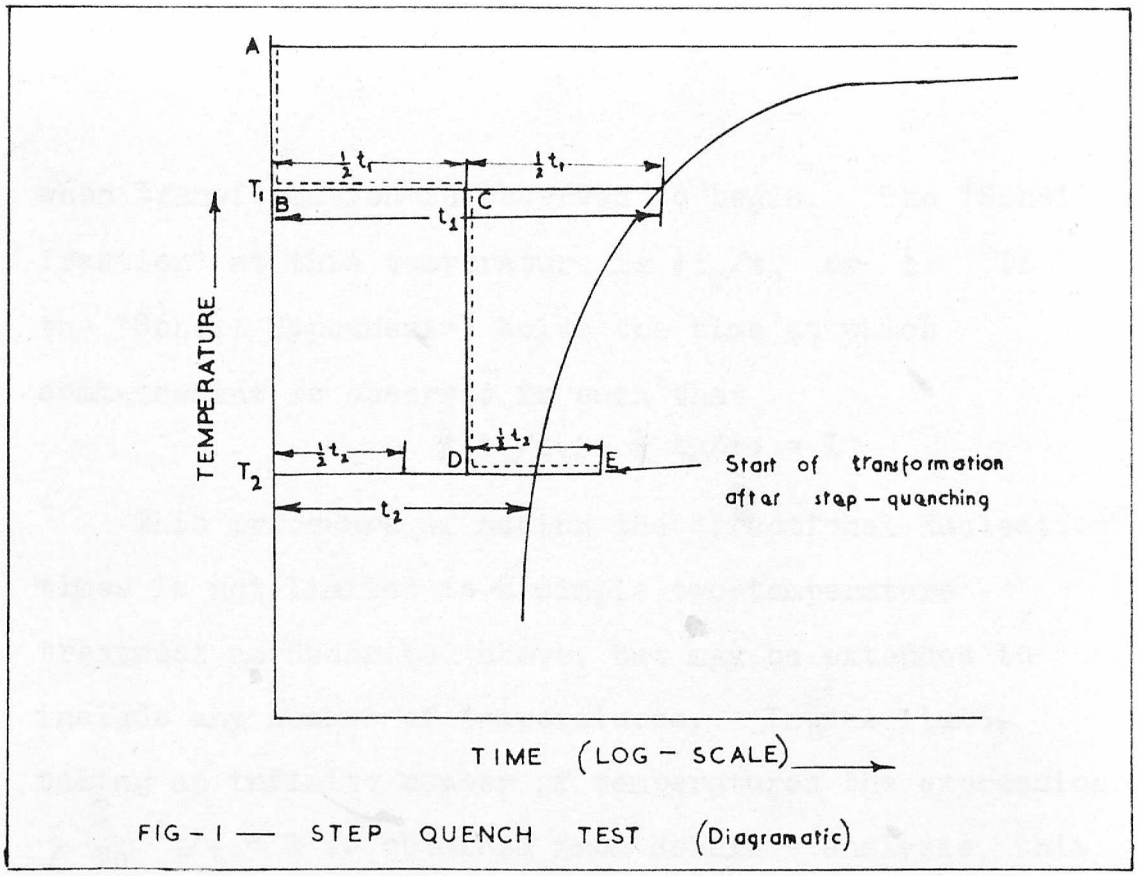


FIG – 1 — STEP QUENCH TEST (Diagramatic)

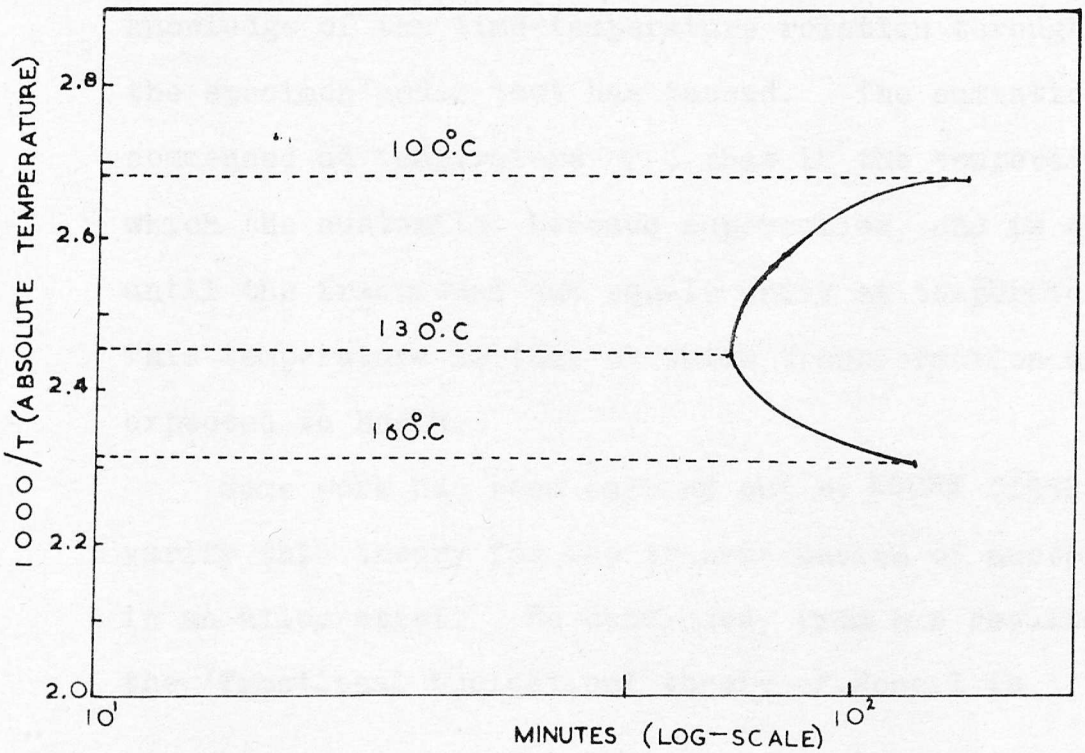


FIG – 3 –

Incubation minutes (log scale) / [1000/T (Absolute temperature of ageing)]

when transformation is observed to begin. The "Scheil fraction" at this temperature is $\frac{1}{2}t_2/t_2$ or $\frac{1}{2}$. If the "Scheil Hypothesis" holds the time at which commencement is observed is such that

$$\tfrac{1}{2}\, t_1/t_1 + \tfrac{1}{2}\, t_2/t_2 = 1$$

This procedure of adding the "fractional Nucleation" times is not limited to a simple two-temperature treatment as described above, but may be extended to include any number of temperatures. In the limit, taking an infinite number of temperatures the expression $\int_{To}^{T} t_1/t = 1$ is obtained from Scheil's analysis, this representing conditions of cooling, in which the commencement of transformation may be calculated from a knowledge of the time-temperature relation through which the specimen under test has passed. The summation is commenced at temperature T , that is the temperature at which the austenite becomes supercooled, and is continued until the fractional sum equals unity at temperature To. This temperature is that at which transformation may be expected to begin.

Some work has been carried out by MOORE (1952) to varify this theory for the transformation of austenite in an alloy steel. He concluded, from his results, that the 'fractional nucleation' theory of Scheil is

applicable to a limited extent, and that the discrepancies between predicted and observed transformation behaviour were due to the partial nucleation time spent at one temperature not having a proportional effect on subsequent nucleation at another temperature (either higher or lower than the first). However, predictions of transformation behaviour during cooling, by means of the 'Scheil theory' showed good correlation with observed transformation behaviour, and therefore it has been suggested that such a method would be useful, in works practice, in the prediction of complete or partial hardening resulting from a given heat-treatment.

The aim of the present work was to determine, whether or not the 'Fractional Nucleation' theory of Scheil is applicable to precipitation processes in the age-hardening of binary aluminium-copper alloys.

Since precipitation in age-hardening alloys is a process that follows the general rules of nucleation, it may be possible to apply the above theory. It has been shown by HARDY (1951, 1953-54) that a series of intersecting C-curves can be drawn to show the time-temperature-transformation relations in the age-hardening of binary Al-Cu alloys as determined by hardness measurements. These C-curves are comparable

to T-T-T diagrams in steel.

However, the main difference in these two processes is that in ageing, the precipitation of the stable phases occurs through metastable phases coherent with the aluminium matrix, while the austenite to pearlite decomposition is a process of straightforward nucleation of a non-coherent phase and a subsequent growth until the decomposition is completed.

EXPERIMENTAL

A binary aluminium-copper alloy prepared by CHITTY (1958) was used for the present investigation. The previous treatment which this alloy had undergone is described in the second section of the thesis. The composition of the alloy was: 4.25%Cu, 0.001%Si, 0.001%Fe and 95.74%Al (by difference).

The solution-treatment, quenching and ageing were carried out as previously described (section 11, experimental procedure).

Temperatures of Ageing.

Ageing was carried out at 100, 130 and 160°C. The purpose of choosing these temperatures was to restrict the precipitation process to the formation of G.P. [1] zones only. (HARDY, 1951). It was shown by Hardy that as the temperature of ageing is raised beyond a certain value, for a certain alloy the metastable products precipitating first may vary. The foregoing consideration

left a choice of range of temperature between 100 and 160°C for the 4.25%-Cu alloy.

Ageing Treatments.

Ageing was continued up to 8 hours in each case, but the time intervals of hardness measurements were increased once the incubation period was completed.

Four hardness measurements were done at each time and the mean values are represented by the points on the Hardness/Ageing Curves.

A smooth curve was drawn through these points and the end of the incubation was decided by a point from whence a definite and continuous tendency to give higher hardness values was found. This method was considered preferable to interpolating the sloping portion of the curve to cut the horizontal and taking the end of the incubation period as the point of intersection as has been done by previous workers.

Step-Quenching.

When a specimen was aged at temperature T, for a certain time, and was then transferred to another oven to age at temperature T_2, the treatment was known as 'step-quenching.' (A time of 50% of the incubation period was employed in the present work).

Normal Quenching.

When a specimen was quenched from a higher temperature to a lower temperature to continue the precipitation the

treatment was called 'normal quenching.'

Inverse Quenching.

When a specimen was transferred from a lower temperature to a higher temperature to continue the ageing, the treatment was called 'inverse quenching.'

In all cases care was taken to avoid delay in transferring a specimen from a bath at temperature T to one at temperature T_2. The ovens were arranged adjacent to each other, and the time of transfer was always less than 5 seconds.

RESULTS

Times for Incubation.

a) The times for the first incubation, as determined by the hardness measurements were found to vary for the different ageing temperatures. (fig. 2).

b) The times of incubation were judged to within ± 5 minutes: the incubation period at 100°C was 135 to 145 minutes, that at 160°C was 120 to 130 minutes and that at 130°C was 65 to 75 minutes. (fig. 2).

c) The logarithms of the incubation periods at 100, 130 and 160°C plotted against the reciprocal of the absolute temperatures gave a C-curve, as shown by HARDY (1951). (fig. 3).

Normal Quenching - (fig. 4)

As previously stated the alloy specimens were aged at

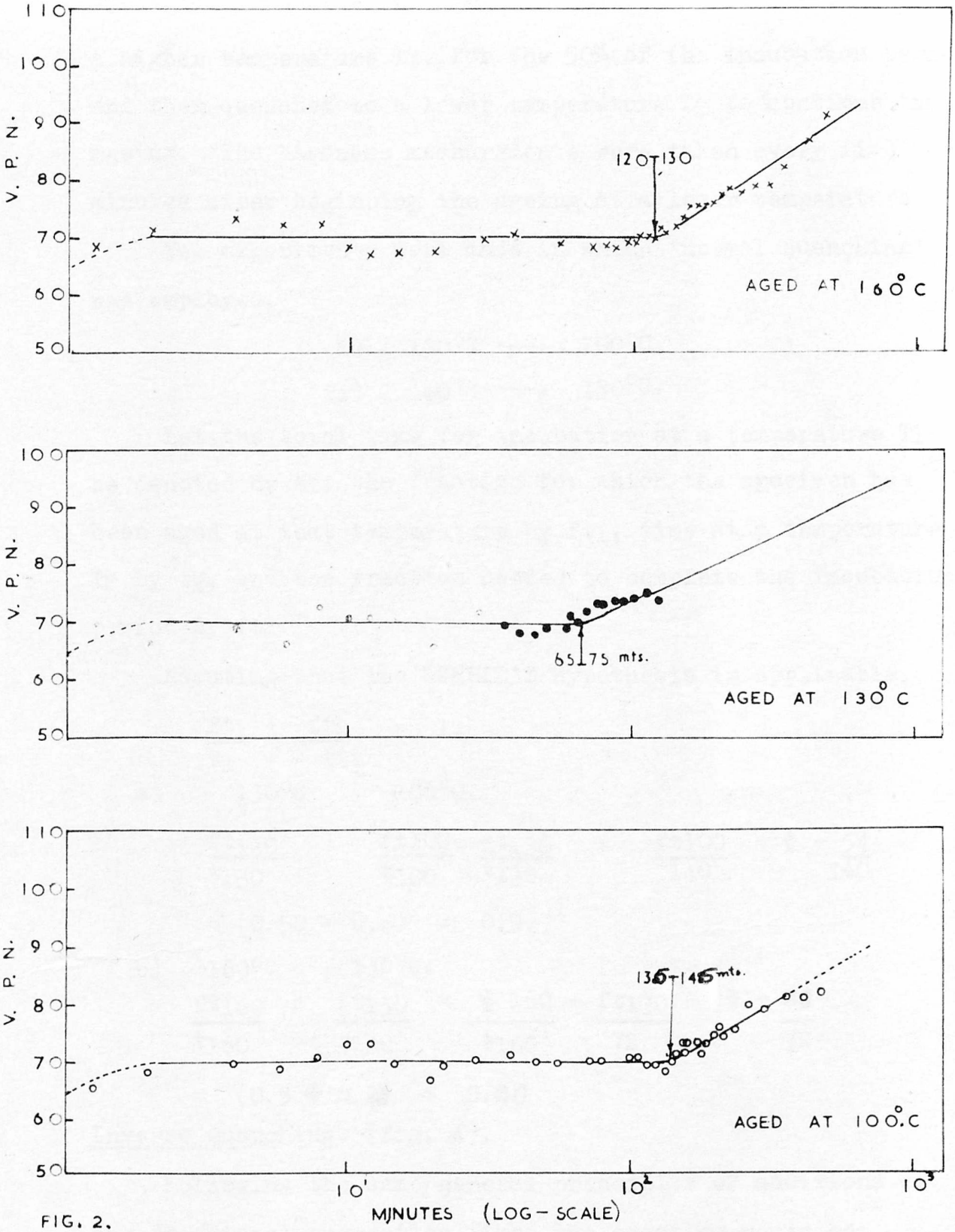


FIG. 2.

AGEING CURVES OF THE ALUMINIUM-4.25% COPPER ALLOY AGED AT VARIOUS TEMPERATURES

a higher temperature T_1, for the 50% of the incubation period, and then quenched to a lower temperature T_2 to continue the ageing. The hardness measurements were taken every five minutes after beginning the ageing at a lower temperature

Two experiments were made in which 'normal quenching' was employed.

i) $130^{\circ}C \longrightarrow 100^{\circ}C.$

ii) $160^{\circ}C \longrightarrow 130^{\circ}C.$

Let the total time for incubation at a temperature T_1 be denoted by t_1, the fraction for which the specimen has been aged at that temperature by ft_1, time at a temperature T_2 by t_2, and the fraction needed to complete the incubation period by ft_2.

Assuming that the 'SCHEIL'S hypothesis is applicable.

$$\frac{ft_1}{t_1} + \frac{ft_2}{t_2} = 1.$$

a) $130^{\circ}C$ $100^{\circ}C.$

$$\frac{ft_{130}}{t_{130}} + \frac{ft100}{t_{100}} = \frac{\frac{1}{2}t_{130}}{t_{130}} + \frac{ft100}{140} = \frac{1}{2} + \frac{54}{140}$$

$$= (0.50 + 0.4) = 0.9.$$

b) $160^{\circ}C$ $130^{\circ}C.$

$$\frac{ft_{160}}{t_{160}} + \frac{ft_{130}}{t_{130}} = \frac{\frac{1}{2}\,160}{t_{160}} + \frac{ft_{130}}{72} = \frac{1}{2} + \frac{30}{72}$$

$$= (0.5 + 0.40 = 0.90.$$

Inverse Quenching. (fig. 4).

Following the same general principles of additions of the fractional nucleation times the equation would be:

$$\frac{ft_2}{t_2} + \frac{ft_1}{t_1} = 1$$

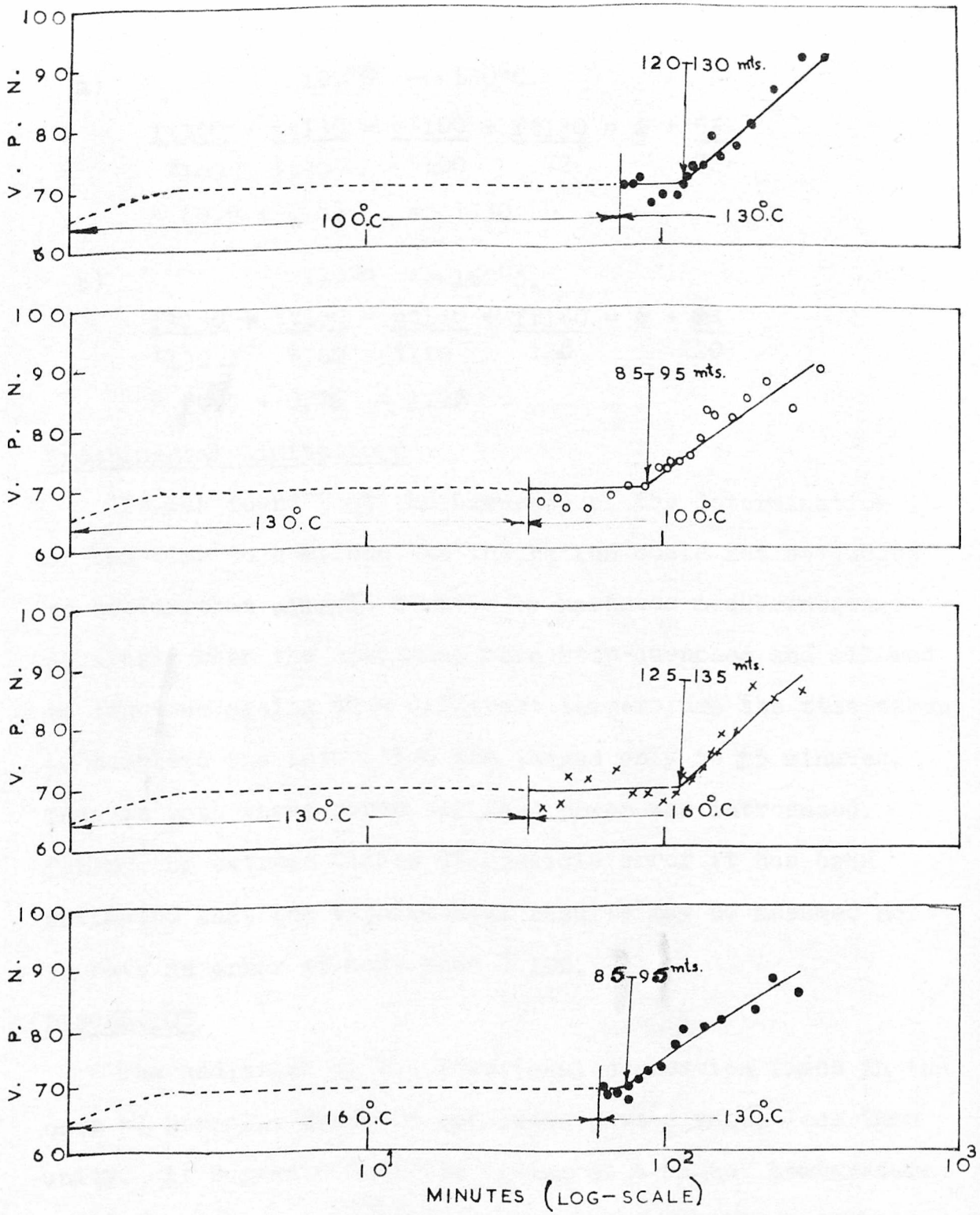


FIG. 4.

HARDNESS/AGEING CURVES OF THE NORMALLY & INVERSELY QUENCHED SPECIMENS SHOWING THE EFFECT OF STEP-QUENCHING ON THE 'FRACTIONAL NUCLEATION'

a) $100^{\circ}C \longrightarrow 130^{\circ}C$.

$$\frac{ft100}{t100} + \frac{ft130}{t130} = \frac{\frac{1}{2}t100}{t100} + \frac{ft130}{72} = \frac{1}{2} + \frac{55}{72}$$

$$= (0.5 + 0.8) = 1.30$$

b) $130^{\circ}C \longrightarrow 160^{\circ}C$.

$$\frac{ft130}{t130} + \frac{ft160}{t160} = \frac{\frac{1}{2}t130}{t130} + \frac{ft160}{125} = \frac{1}{2} + \frac{94}{120}$$

$$= (0.5 + 0.78) = 1.28$$

Experimental Limitations

It was found that the accuracy of the determination of the time to complete the incubation could not be judged to better than within ±5 minutes by hardness measurements. Similarly when the specimens were step-quenched and allowed to continue ageing at a different temperature the time taken to complete the incubation was judged only to ±5 minutes. Thus in both these processes some error was introduced. Taking the extreme limits of possible error it has been estimated that the experimental results may be assumed not to have an error of more than ± 10%.

DISCUSSION.

The additions of the fractional nucleation times in the case of normally quenched specimens gave a value less than unity. It suggests that the ageing at a higher temperature induces a state of nucleation, which is proportionately more advanced than what it would be in the same fraction of the incubation period at a lower temperature. The additions of the fractional nucleation times in the case of inversely

quenched alloys, however were greater than unity. This suggests that the growth of embryos or germ nuclei (ultimately forming the nuclei of critical radius) in a certain fraction of the incubation period at a lower temperature, is proportionately less as compared to that, at a higher temperature in the same fraction of the incubation period.

CONCLUSIONS

The 'SCHEIL hypothesis' does not appear to hold exactly to the age-hardening of the aluminium - 4.25% copper alloy. However, within experimental limitations it may be said that, in normal quenching the sums of the 'fractional nucleation' times are less than unity, whilst the additions of 'fractional nucleation' times in inversely quenched specimens are slightly greater than unity.

APPENDIX II

THE ALLOYS MADE FOR THE CONSTITUTIONAL WORK

Alloy No.	Copper wt.per cent	Magnesium wt.per cent	Manganese wt.per cent	Remarks
A.1	1.80	1.00	0.60	N.A.
A.2	2.10	2.50	0.60	N.A.
A.3	2.20	2.80	"	N.A.
A.4.	1.90	3.30	"	N.A.
A.5.	1.70	3.20	"	N.A.
A.6.	0.88	0.60	0.64	Analysed
A.7.	1.10	0.50	0.60	N.A.
A.8.	1.20	4.00	"	N.A.
A.9.	0.80	4.00	"	N.A.
A.10	2.50	2.00	"	N.A.
A.11	2.50	2.10	"	N.A.
A.12	2.67	2.25	0.60	Analysed
A.13	3.10	0.50	0.60	N.A.
A.14	3.30	0.50	"	N.A.
A.15	3.10	1.50	"	N.A.
A.16	3.10	1.80	"	N.A.
A.17	3.25	1.30	"	N.A.
A.18	3.60	1.70	"	N.A.
A.19	3.90	0.80	"	N.A.
A.20	3.75	1.30	"	N.A.
A.21	4.23	1.45	0.59	Analysed
A.22	5.00	1.80	0.60	N.A.
A.23	5.00	1.20	"	N.A.
A.24	5.00	3.50	"	N.A.
A.25	2.60	2.85	0.63	Analysed
A.26	4.75	4.50	0.60	N.A.
A.27	0.50	0.82	"	Analysed(Mg)
A.28	0.25	2.80	"	N.A.
A.29	0.35	2.80	"	N.A.
A.30	0.75	2.72	0.62	Analysed
A.31	0.30	5.00	0.60	Analysed(Mg)
A.32	0.60	5.00	"	N.A.
A.33	0.90	5.00	"	N.A.
A.34	1.50	5.05	"	Analysed(Mg)
A.35	1.80	5.05	"	Analysed(Mg)
A.36	1.58	3.95	0.62	Analysed
A.37	1.80	4.15	0.60	Analysed
A.38	2.24	3.65	0.60	Analysed
A.39	3.10	2.10	0.60	Analysed(Mg)
A.40	4.02	0.18	0.60	Analysed
A.41	4.10	0.12	"	N.A.
A.42	4.20	0.12	"	N.A.
A.43	4.35	0.43	"	Analysed(Mg)
A.44	4.05	0.28	"	N.A.
A.45	4.00	1.25	"	N.A.

(contd.)

Alloy No.	Copper wt.per cent	Magnesium wt.per cent	Manganese wt.per cent	Remarks
A.46	4.10	1.25	0.60	Analysed(Mg)
A.47	6.00	5.00	"	N.A.
A.48	6.15	2.25	0.61	Analysed
A.49	6.00	1.28	0.60	N.A.
A.50	6.00	0.84	0.60	Analysed(Mg)
A.51	5.00	2.12	"	Analysed(Mg)
A.52	3.75	1.45	"	N.A.
A.53	5.00	2.20	"	N.A.

Alloy No.	Copper wt.per cent	Magnesium wt.per cent	Manganese wt.per cent	Remarks
B.1	2.25	2.50	1.20	N.A.
B.2	1.26	0.50	1.13	Analysed
B.3	1.37	0.50	1.20	N.A.
B.4	1.60	0.50	"	N.A.
B.5	1.55	2.25	"	N.A.
B.6	1.12	2.60	"	Analysed(Mg.)
B.7	1.45	3.75	"	N.A.
B.8	1.25	3.75	"	N.A.
B.9	1.60	4.00	"	N.A.
B.10	1.75	4.00	"	N.A.
B.11	1.99	4.05	1.20	Analysed
B.12	2.25	2.90	1.20	N.A.
B.13	2.75	1.75	"	N.A.
B.14	3.10	1.50	"	N.A.
B.15	3.10	1.70	"	N.A.
B.16	3.14	1.95	1.24	Analysed
B.17	3.50	1.40	1.20	N.A.
B.18	3.70	1.55	"	N.A.
B.19	4.43	0.55	"	Analysed(Cu.)
B.20	4.9	0.47	1.20	Analysed
B.21	3.90	0.75	1.20	N.A.
B.22	4.00	1.11	1.20	Analysed(Mg.)
B.23	4.65	1.25	"	Analysed(Cu.)
B.24	5.00	1.50	"	N.A.
B.25	5.00	1.00	"	N.A.
B.26	4.35	1.34	1.20	Analysed
B.27	5.00	1.90	"	N.A.
B.28	5.00	2.10	"	N.A.
B.29	5.00	2.25	"	N.A.
B.30	4.25	2.00	"	N.A.
B.31	1.00	3.75	"	N.A.
B.32	0.20	0.52	"	N.A.
B.33	0.50	0.52	"	N.A.
B.34	0.75	0.52	"	N.A.
B.35	1.00	0.52	"	N.A.
B.36	0.30	2.28	"	N.A.
B.37	0.90	2.28	"	N.A.
B.38	0.30	5.00	1.20	N.A.
B.39	0.50	5.00	"	N.A.
B.40	0.81	5.10	1.22	Analysed
B.41	1.60	5.00	"	N.A.
B.42	1.80	5.00	"	Analysed(Cu.)
B.43	2.00	5.00	"	N.A.
B.44	2.00	3.60	"	N.A.
B.45	2.55	2.30	1.18	Analysed
B.46	2.75	2.52	1.20	N.A.
B.47	3.90	0.12	"	N.A.
B.48	4.20	0.20	"	N.A.

Alloy No.	Copper wt.per cent	Magnesium wt.per cent	Manganese wt.per cent	Remarks
B.49	4.35	0.12	1.17	Analysed
B.50	4.50	0.12	1.20	N.A.
B.51	4.45	0.14	1.18	Analysed
B.52	3.70	0.72	1.20	N.A.
B.53	3.65	1.72	"	N.A.
B.54	6.00	0.80	"	N.A.
B.55	6.02	1.21	1.18	Analysed
B.56	6.02	2.35	1.18	Analysed
B.57	6.00	2.63	1.20	Analysed(Mg.)
B.58	6.00	3.72	"	N.A.
B.59	4.00	4.00	"	N.A.

Alloy No.	Copper wt.per cent	Magnesium wt.per cent	Manganese wt.per cent	Remarks
C.1	1.70	0.50	1.80	N.A.
C.2	1.90	0.50	"	N.A.
C.3	1.55	2.25	"	N.A.
C.4	2.05	2.25	"	N.A.
C.5	1.45	3.55	"	N.A.
C.6	1.50	4.50	"	N.A.
C.7	1.70	4.50	"	N.A.
C.8	1.75	4.20	1.80	Analysed
C.9	2.18	3.90	1.80	Analysed
C.10	1.90	3.00	"	N.A.
C.11	2.35	3.75	"	N.A.
C.12	3.00	2.75	"	N.A.
C.13	3.00	2.35	"	N.A.
C.14	3.75	2.00	"	N.A.
C.15	5.25	2.75	"	N.A.
C.16	5.95	1.95	1.80	Analysed
C.17	5.00	1.60	"	N.A.
C.18	4.70	1.55	1.8	Analysed
C.19	4.50	2.50	1.8	N.A.
C.20	4.98	1.10	1.80	Analysed(Cu.)
C.21	4.75	0.60	1.80	Analysed(Cu.)
C.22	5.25	1.00	"	N.A.
C.23	1.05	5.02	1.80	Analysed
C.24	1.25	0.50	1.80	N.A.
C.25	0.75	0.50	1.80	Analysed(Cu.)
C.26	0.30	0.50	1.80	N.A.
C.27	1.00	1.80	"	N.A.
C.28	0.50	1.80	"	N.A.
C.29	0.15	1.80	"	N.A.
C.30	0.87	3.60	1.82	Analysed
C.31	0.40	5.00	1.80	N.A.
C.32	1.50	5.00	"	N.A.
C.33	1.90	5.00	"	N.A.
C.34	2.00	3.60	"	N.A.
C.35	1.85	3.75	1.65	Analysed
C.36	2.50	3.00	1.80	N.A.
C.37	3.60	1.25	1.80	N.A.
C.38	3.75	0.75	"	N.A.
C.39	4.00	0.28	"	N.A.
C.40	4.25	0.10	"	N.A.
C.41	4.50	0.28	"	N.A.
C.42	5.00	0.76	"	N.A.
C.43	5.00	1.20	"	N.A.
C.44	6.00	0.28	"	N.A.
C.45	6.00	0.60	"	N.A.
C.46	6.00	1.00	"	N.A.
C.47	6.00	1.80	"	N.A.
C.48	6.00	2.00	"	N.A.
C.49	6.00	2.18	"	Analysed(Mg.)
C.50	4.35	1.36	1.80	Analysed
C.51	4.65	1.55	1.82	Analysed
C.52	4.32	3.2	1.80	Analysed(Cu.)

Alloy No.	Copper wt. per cent	Magnesium wt.per cent	Manganese wt.per cent	Remarks
D.1	3.00	0.28	0.10	N.A.
D.2	"	0.30	0.10	Analysed(Mn)
D.3	"	0.30	0.30	N.A.
D.4	"	0.30	0.40	N.A.
D.5	3.05	1.00	0.15	Analysed
D.6	3.00	1.00	0.25	N.A.
D.7	3.18	2.10	0.09	Analysed
D.8	3.00	2.00	0.20	N.A.
D.9	3.18	2.08	0.30	Analysed
D.10	3.00	2.00	1.0	N.A.
D.11	"	2.00	2.00	N.A.
D.12	"	1.00	1.00	N.A.

Alloy No.	Copper wt.per cent	Magnesium wt.per cent	Manganese wt.per cent	Remarks
P.1	4.50	0.25	0.25	N.A.
P.2	4.68	0.26	0.45	Analysed
P.3	4.50	1.26	0.5	Analysed(Mg)
P.4	"	1.29	0.25	Analysed(Mg)
P.5	"	1.44	1.50	Analysed(Mg)
P.6	"	2.00	0.20	N.A.
P.7	"	1.90	0.50	N.A.
P.8	"	1.54	0.50	Analysed(Mg)
P.9	"	1.50	0.60	N.A.
P.10	"	1.90	2.00	N.A.
P.11	"	1.49	2.00	Analysed(Mg)
P.12	"	1.55	2.00	Analysed(Mg)
P.13	"	1.30	2.00	N.A.
P.14	"	0.60	2.00	N.A.
P.15	4.59	0.26	2.00	Analysed
P.16	4.50	0.20	2.00	N.A.
P.17	"	0.07	2.00	Analysed(Mg)
P.18	"	0.12	1.60	Analysed(Mg)
P.19	"	0.07	1.75	N.A.
P.20	"	0.25	1.75	N.A.
P.21	"	1.25	0.10	N.A.
P.22	"	0.60	2.00	N.A.
P.23	"	0.75	2.00	N.A.
P.24	"	0.20	1.80	N.A.
P.25	"	0.28	1.80	N.A.
P.26	"	0.40	1.80	N.A.

Alloy No.	Copper wt.per cent	Manganese wt.per cent	Remarks
T.1	0.50	0.60	N.A.
T.2	0.75	0.60	N.A.
T.3	1.14	0.48	Analysed
T.4	0.76	1.20	Analysed(Cu)
T.5	1.17	1.12	Analysed
T.6	1.62	1.20	Analysed(Cu)
T.7	0.75	1.80	N.A.
T.8	1.00	1.80	N.A.
T.9	1.40	1.80	N.A.
T.10	1.60	1.80	N.A.
T.11	1.91	1.80	Analysed
T.12	1.10	0.85	N.A.
T.13	1.48	1.02	Analysed
T.14	1.40	0.75	N.A.
T.15	4.20	1.20	Analysed(Cu)
T.16	4.4	1.20	N.A.
T.17	4.45	1.20	Analysed(Cu)
T.18	3.9	0.60	N.A.
T.19	4.0	0.60	N.A.
T.20	4.1	0.60	N.A.
T.21	4.2	1.80	Analysed(Cu)
T.22	4.5	1.8	N.A.
T.23	4.57	2.00	Analysed
T.24	4.5	0.02	Analysed(Mn)
T.25	4.5	0.15	N.A.
T.26	4.5	0.20	N.A.

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