CANADA

AGEING BEHAVIOUR OF Al-10% Mg CASTING ALLOYS AT ROOM TEMPERATURE AND UP TO 150°C (300°F)

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AGEING BEHAVIOUR OF Al-10% Mg CASTING ALLOYS AT ROOM TEMPERATURE AND UP TO 150°C (300°F)

by

W. A. Pollard*

ABSTRACT

The ageing and related phenomena of the Al-10% Mg casting alloy, at room temperature and up to 150°C (300°F), have been studied by tensile testing and metallographic examination over periods of up to six years.

In alloys containing more than about 10.2% Mg aged at room temperature, a slow but continuous increase in strength occurs at least up to five years. However, at 50°C (122°F) and above, this age-hardening does not occur, but precipitation is observed first at grain boundaries, with no change in properties, and then in Widmanstaetten form within grains, accompanied by rapid embrittlement. Reversion of the room temperature aged material occurs above 50°C (122°F).

The results are discussed in terms of recent work on the Al-Mg alloys and of recent theories of age-hardening.

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Direction des mines

Rapport de recherches R 120

COMPORTEMENT AU VIEILLISSEMENT, À LA TEMPÉRATURE DE LA PIÈCE ET JUSQU'À 150°C (300°F), DES ALLIAGES DE FONDERIE DE COMPOSITION Al-10% Mg

par

W.A. Pollard

RÉSUMÉ

Le vieillissement et autres phénomènes associés, d'un alliage d'Al-10% Mg, à la température ambiante et jusqu'à 150°C (300°F), ont fait l'objet d'études sous forme d'essais de tension et d'examens métallographiques pendant des périodes allant jusqu'à six ans.

Dans les alliages qui contiennent plus qu'environ 10.2 p. 100 de magnésium et qui ont vieilli à la température de la pièce, il se produit une lente mais continuelle augmentation de la résistance au moins durant cinq ans. Par contre, à partir de 50°C (122°F), ce durcissement ne se produit pas, mais on observe d'abord une précipitation à la limite des grains, sans changement dans les propriétés, et ensuite un changement de la forme Widmanstaetten à l'intérieur des grains accompagné de fragilisation rapide. La réversion des matériaux vieillis à la température de la pièce se produit à une température supérieure à 50°C (122°F).

Les résultats sont étudiés à la lumière des derniers travaux sur les alliages d'aluminium-magnésium et des récentes théories sur le durcissement par vieillissement.

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INTRODUCTION

The Al-10% Mg alloy is unusual among high strength aluminum casting alloys in that it is used in the solution treated condition. Although it has been widely recognized that strengthening occurs on ageing at room temperature, optimum properties are usually assumed to be attained without age-hardening.

As freshly quenched from the solution treatment temperature, the alloy is capable of showing high strength with unusually high ductility for an aluminum casting alloy. However, the supersaturation of magnesium is very high (the solid solubility falls from 15.35 at 450°C (842°F) to 1.9% at 100°C (212°F)(1)) and, at room and slightly elevated temperatures, structural and property changes occur that may be harmful not only to the mechanical properties but also to the resistance of the alloy to stress corrosion. This behaviour of the alloy has been one of the causes for the limitations of its use in recent years.

The object of the work reported here was to determine the property and structural changes that occur on ageing at room and slightly elevated temperatures, with a view to possible improvements in these properties of the alloy.

PREVIOUS WORK

Most of the investigations of precipitation in the binary Al-Mg system have been carried out on wrought alloys. In the Al-10% Mg alloy, attention has been directed almost exclusively to reactions that occur above about 100°C (212°F). At these temperatures, grain boundary precipitation occurs rapidly but there are no mechanical property changes until visible Widmanstaetten precipitation is present(2, 3). The precipitate is a transition lattice of the equilibrium precipitate Al_3Mg_2(3, 4). The effect of the Widmanstaetten precipitation is to cause an increase in hardness and yield strength and a severe reduction of elongation.

As will be shown, property changes at room temperature do not occur in alloys containing less than about 10.2% Mg. Even above this, changes are comparatively slow.

There has been no published work showing tensile property changes on room temperature ageing of wrought alloys of this type. However, Dahl and Detert(8), and Cordier and Detert(9), have shown that changes in resistivity and density occur in the Al-10% Mg alloy in the form of wire at 20°C (68°F), after air cooling or water quenching from the solution treatment temperature. Cordier and Detert(9) interpret their results in terms of vacancy-assisted zone formation. They also observed "reversion" above 50 °C (122 °F), which they presume is due to the instability of the zones above this temperature. Recently, Panseri et al(10) have also shown evidence of clustering in aluminum alloys containing up to 7% Mg, by electrical resistivity measurements. These results will be further discussed later.

The effect of room temperature ageing on the cast alloy has been reported by many investigators(12, 13, 14, 15). They show that the ultimate strength and yield strength increase and the elongation falls, and that these changes continue for many years.

There has been no investigation reported of the possible structural changes in the alloy that produce these property changes.

EXPERIMENTAL PROCEDURE

Materials

Most of the work reported was carried out on Alcan 350 alloy, supplied by the Aluminum Company of Canada Limited. This material usually contains about 10% magnesium, 0.1% silicon, 0.1% iron, and 0.005% beryllium. The actual compositions of the melts used are given in Table 1.

In some tests melts were made up from super-pure aluminum (99.99 Al Min), with additions of pure magnesium, titanium (from Al-5% Ti master alloy), and beryllium (from Al-5% Be master alloy). Compositions of these melts are also given in Table 1. The purpose of the beryllium

TABLE 1

Chemical Analysis Results - Composition (per cent)

Melt No.	Mg	Si	Fe	Ti	Be	Source
820	10.1*	0.08	0.22	0.009	0.004	Ingot
870	11.4	<0.01	0.04	n.d.	0.006	Super-pure
871	10.4*	0.03	0.06	0.09	0.004	Super-pure
878	10.7	0.02	0.06	0.07	0.003	Super-pure
884	10.2*	0.08	0.22	0.003	0.004	Ingot
983	10.8	0.06	0.11	0.007	-	Ingot
992	10.9	0.10	0.12	0.003	0.003	Ingot
996	10.6	-	0.003	n.d.	-	Super-pure
997	11.2	-	0.010	n.d.	-	Super-pure
333	10.9	n.d.	0.002	-	0.005	Super-pure
352	10.8	0.01	0.008	0.04	0.005	Super-pure

*These values are for samples taken from the grips of test bars. (See page 5.)

additions to these alloys is to reduce the rate of oxidation of the magnesium in the melt and to minimize metal/mould reaction when the alloy is cast in green sand moulds.

Both macro- and micro-segregation of magnesium occur in castings of Al-10% Mg alloys. In the present work the presence of macro-segregation resulted in uncertainty as to the actual composition of specimens tested. Thus, in horizontally cast test bars it has been shown(15) that variations of up to about 1% Mg can occur between the centres and ends of the bars. Most of the results given in Table 1 were obtained from analysis samples taken from the "gauge lengths" of test bars, although for some early melts only "grip" values were available. In these melts it can be assumed that the "gauge length" compositions were about 1.5% Mg higher than the values given.

Casting and Heat Treatment

Most of the material used in this work was melted in carbon-bonded silicon carbide crucibles. Degassing was accomplished by flushing with chlorine or nitrogen or both. A reduced pressure gas test was used to check the efficiency of degassing.

Cast-to-shape test bars of the "Dow" type* were used for the bulk of the experimental work. Wrought material was rolled from 6 in. x 4 in. x 1 in. chill cast slabs. The slabs were solution heat treated and

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[*] Test bars according to U.S. Federal Specification QQ-M-56 (1950), p. 6, Figure 1A.

cold rolled, usually with one intermediate anneal, to 0.125 in. thick sheet. Tensile specimens were taken parallel to the direction of rolling and re-solution heat treated before testing.

For most of the work the solution heat treatment used was that recommended by the Aluminum Company of Canada Limited, that is, twenty hours at 435 °C (815 °F), cool to 395 °C (743 °F) in thirty minutes, quench into boiling water and hold for ten minutes, then cool in air to room temperature. However, some ageing tests were done on bars quenched according to the method recommended by the Aluminum Company of America(17), that is, twenty hours at 435 °C (815 °F), cool to 395 °C (943 °F) in thirty minutes, quench in boiling water to the "knee" of the cooling curve, and then cool in air to room temperature. The object of this "delayed" quench is to improve the stress corrosion resistance of the alloy. Some tests were also done on bars quenched in cold water.

Ageing Conditions

Ageing at temperatures of 50 °C (122 °F) and above was carried out in ovens in which the temperature was controlled to about ± 2 °C (± 3.6 °F). Most of the room temperature ageing was done in an air-conditioned room at 22 °C (71.6 °F), although failures of equipment caused brief excursions to higher temperatures.

TENSILE TEST RESULTS

The changes in the alloys with ageing at various temperatures were followed by means of tensile tests. It was found that hardness changes were not large enough to provide a sufficiently sensitive indication of ageing. Also, considerable scatter in hardness results was obtained, probably owing to the porosity in most of the cast bars.

Of the parameters determined in the tensile test, probably the yield strength was the most useful in the present work as it provides a reasonably sensitive measure of ageing and is relatively insensitive to casting defects.

The ageing behaviour at various temperatures, as shown by changes in tensile properties of a typical melt, is illustrated in Figures 1 to 3.

Ageing at Room Temperature

At room temperature (approximately 25 °C ± 5 °C (77 °F ± 9 °F)), the ultimate strength and 0.2% yield strength of an alloy containing about 10.5% Mg increase from about 50 kpsi and 26 kpsi to about 65 kpsi and 45 kpsi, respectively, in five years. The room temperature ageing behaviour is shown in more detail in Figures 4 to 6, which give ageing curves for a number of Al-10% Mg melts of various compositions, purities,

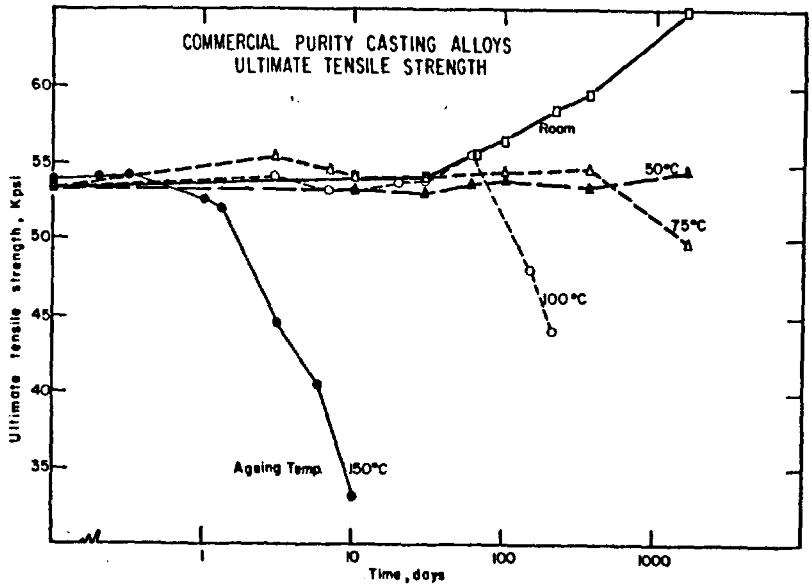

Figure 1. Variation of ultimate tensile strength with time at various temperatures for a commercial purity Al-10% Mg-type alloy (Melt 884).

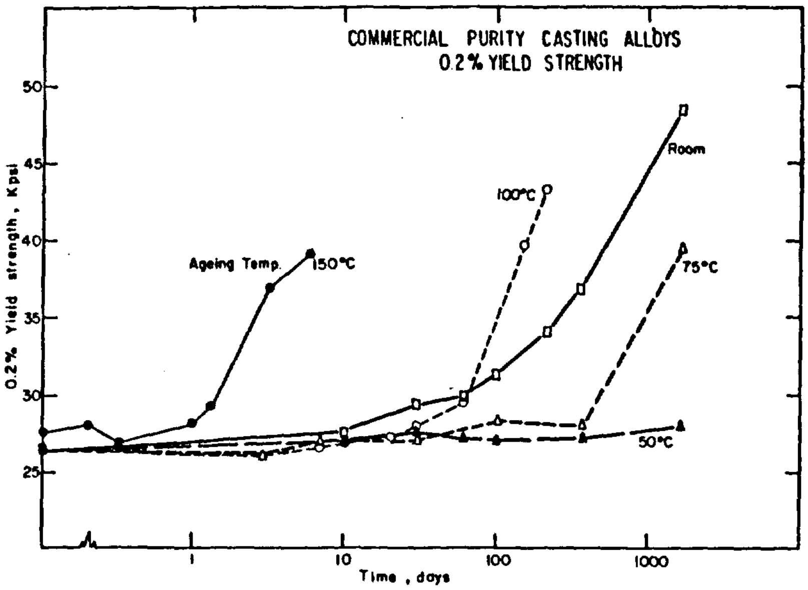

Figure 2. Variation of 0.2% yield strength with time at various temperatures for a commercial purity Al-10% Mg-type alloy (Melt 884).

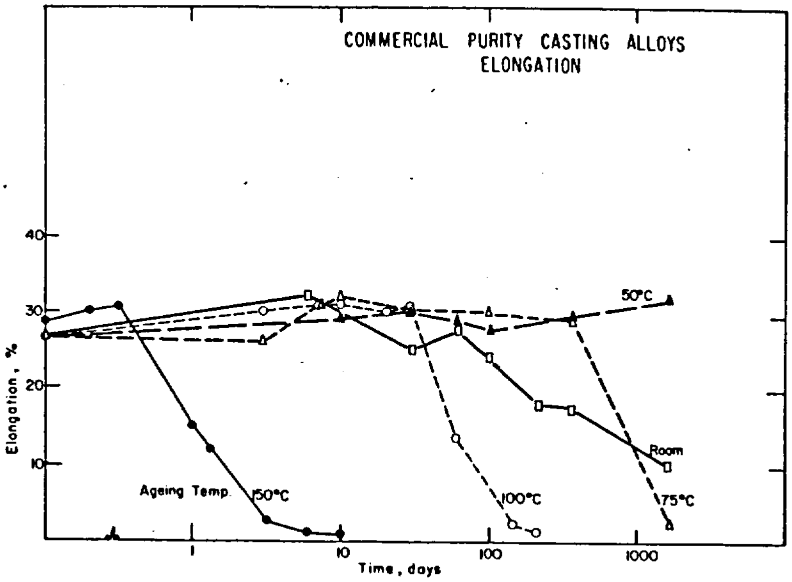

Figure 3. Variation of per cent elongation with time at various temperatures for a commercial purity Al-10% Mg-type alloy (Melt 884).

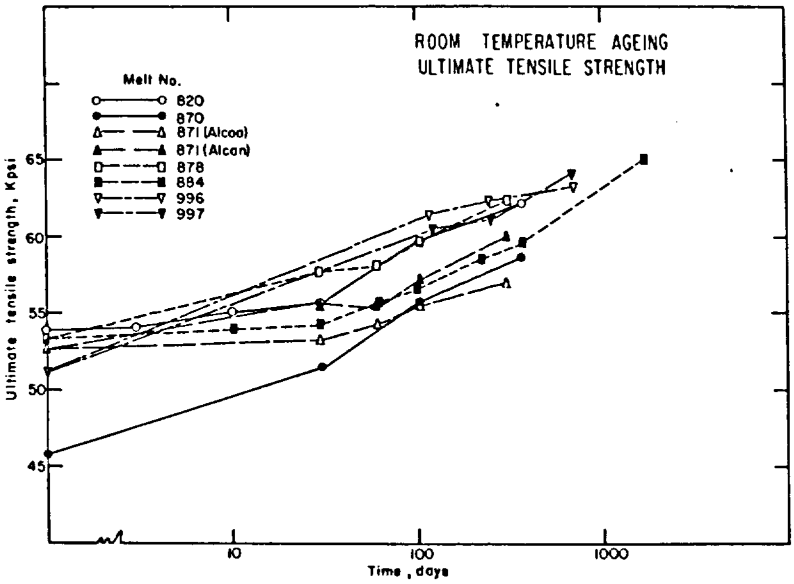

Figure 4. Variation of ultimate tensile strength with time at room temperature for various Al-10% Mg-type alloys.

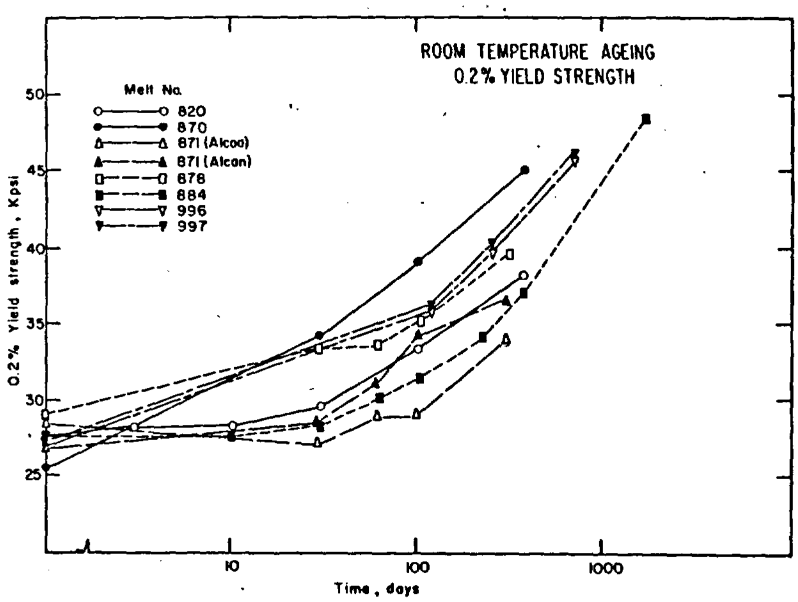

Figure 5. Variation of 0.2% yield strength with time at room temperature for various Al-10% Mg-type alloys.

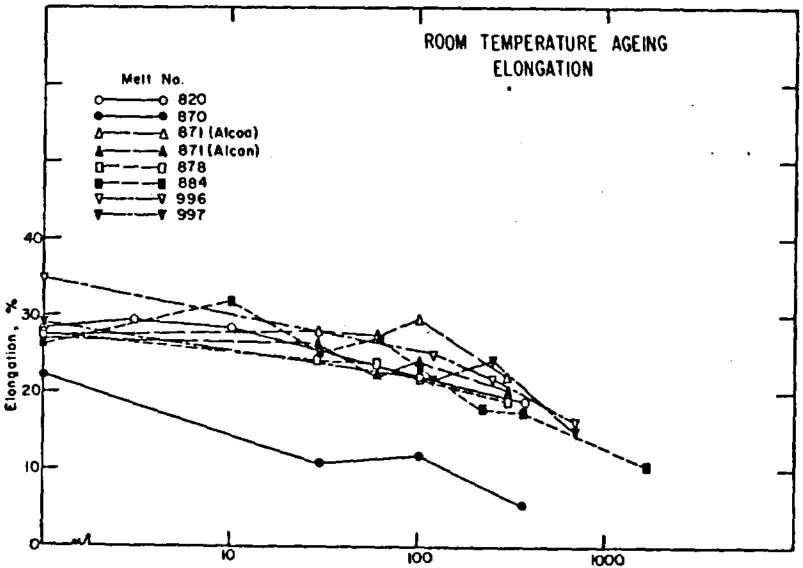

Figure 6. Variation of per cent elongation with time at room temperature for various Al-10% Mg-type alloys.

etc. (see Table 1). It will be seen that the changes in mechanical properties are similar for the various alloys, although actual values vary considerably.

The elongation of all alloys falls continuously during ageing at room temperature (see Figure 6).

Reference to Table 1 will show that most of the alloys included in this work contained more than about 10.5% Mg as determined on samples taken from the gauge lengths of test bars. However, some bars with lower magnesium contents have been tested after storage in the T4 condition for a number of years. Although complete ageing curves are not available, these results have shown that alloys containing less than about 10.2% Mg do not show changes in tensile properties on ageing at room temperature. Owing to the marked and somewhat variable segregation that occurs in the alloy it is not possible, in cast material, to fix the limiting composition precisely, but experiments on wrought alloys, in which segregation of magnesium can be minimized, have shown approximate agreement with this figure, 10.2% Mg. When the magnesium content is above this value there is a trend for the rate of ageing at room temperature to increase with increasing magnesium content, although many inconsistent results are obtained (see Figures 4 to 6) owing, presumably, to the complicating effects of macro- and micro-segregation of magnesium in the test bars, and to variations in grain size, impurity content, porosity, etc.

Ageing at 75 °C, 100 °C and 150 °C (167 °F, 212 °F and 302 °F)

At temperatures of 75 °C (167 °F) and above, the mechanical property changes are markedly different from those that occur at room temperature (see Figures 1 to 3). There is an initial period in which no property changes occur. This period decreases with increasing ageing temperature, so that at 75 °C (167 °F) it is from one to five years and at 150 °C (302 °F) about twelve hours.

The yield strength then begins to increase and at the same time the elongation falls rapidly. The ultimate tensile strength first tends to increase slightly and then falls. In a relatively short time the elongation is very low (about 1%) and the ultimate and yield strengths are about equal.

Ageing at 50 °C (122 °F)

In most alloys tested at 50 °C (122 °F), no mechanical property changes occurred for ageing periods up to about five years.* This behaviour was also observed by Van Ewijk(13), who noted an apparent inconsistency in his ageing results at 50 °C (122 °F) as compared with those at 30 °C (86 °F).

Effect of Ageing at 75 °C and 50 °C (167 °F and 122 °F) on Subsequent Ageing at Room Temperature

It was found that if solution treated bars were given ageing periods at 50 °C (122 °F) and 75 °C (167 °F), subsequent ageing at room temperature was retarded. A commercial purity melt was studied (Melt 992 - see Table 1). Bars were treated for seven, twenty-one and ninety days at 50 °C (122 °F) and 75 °C (167 °F) and then aged at room temperature for

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* An exception noted to the usual ageing behaviour, Melt 870, is referred to in the Appendix.

periods up to 1820 days. These pre-treatments were well within the incubation periods at these temperatures. The results (tensile 0.2% yield strength) are shown in Figure 7. It will be seen that the treatments at 50°C (122°F) and 75°C (167°F) reduced the rate of room temperature ageing in the early stages but after about a year the rate of ageing increased -- in some cases it actually exceeded that of the untreated bars.

The accelerating effect of the pre-treatment at 50°C (122°F) should be accepted with caution, inasmuch as

(a) there was wide variation between duplicate tests and

(b) a check on another melt (983), which had pre-treatments of ninety days at 50°C (122°F) and 75°C (167°F), showed no accelerating effect.

However, there seems to be no doubt that room temperature ageing can occur after pre-treatments at the higher temperatures and that its onset is delayed by such pre-treatments.

Effect of Treatment at Higher Temperatures After Ageing at Room Temperature - Reversion

It was found that if test bars that had been aged at room temperature were then treated for comparatively short times at temperatures above 50°C (122°F), the tensile properties tended to return to those of the freshly solution treated material.

The behaviour may be illustrated by results obtained on a melt made from super-pure aluminum with titanium and beryllium additions (Melt 352; see Table 1 for chemical analysis). These bars, which had been aged at room temperature for 1306 days, were then treated at 75°C,

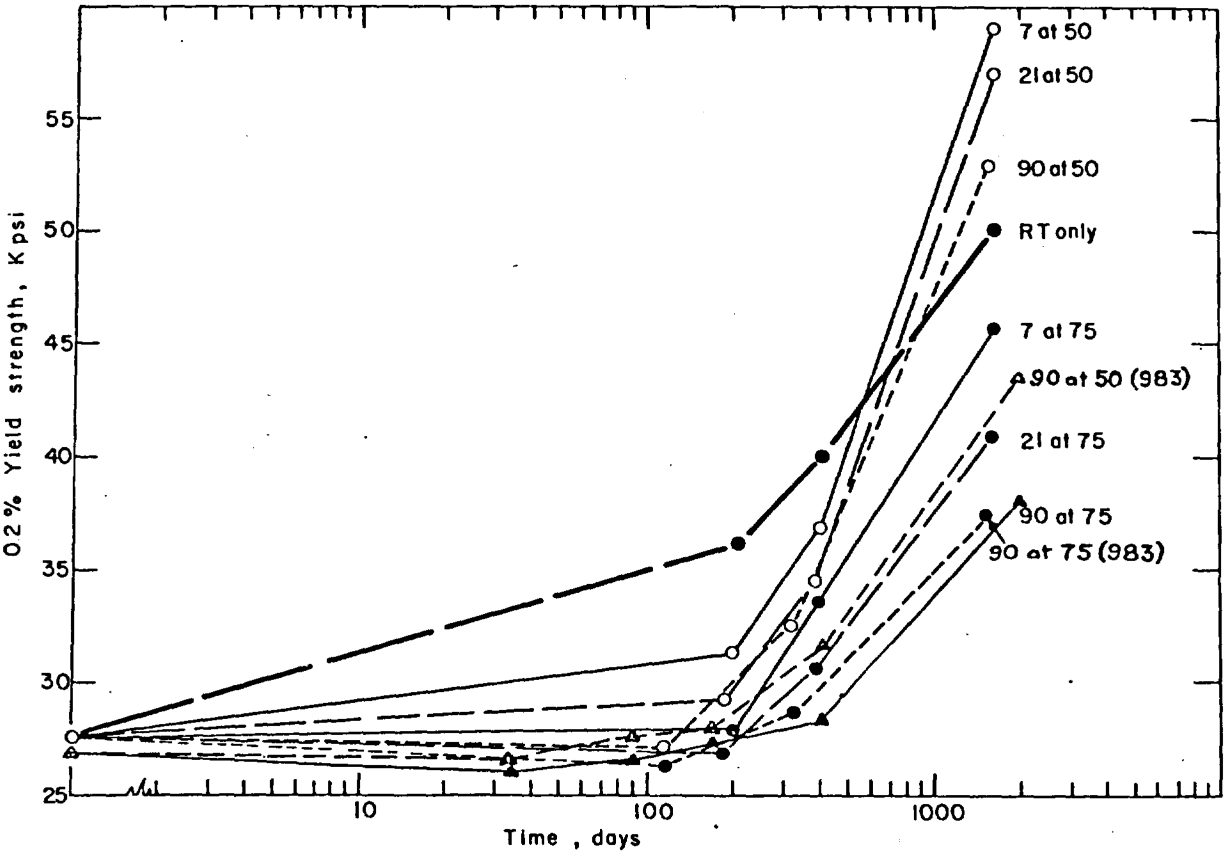


Figure 7. Effect of pre-treatment at 50 °C (122 °F) and 75 °C (167 °F) on subsequent ageing at room temperature (0.2% yield strength).

87 °C, 100 °C and 125 °C (167 °F, 188.6 °F, 212 °F and 257 °F) for various times up to twenty hours. At the three lower temperatures the treatments were done in water baths (temperature control, ± 0.5 °C (± 0.9 °F)), and at 125 °C (257 °F) in a bath of Wood's metal. After treatment, the bars were quenched into water at room temperature. The results obtained at 125 °C (257 °F) are probably the least accurate, because the time to reach temperature and to cool afterwards was a significant proportion of the treatment time. The results are given in Table 2.

The variation of the 0.2% yield strength with time at the various temperatures is shown in Figures 8 to 11. The activation energy for the reversion process was determined by plotting the reciprocal of the time for the yield strength to fall to 30 kpsi against the logarithm of the reciprocal time (see Figure 12). The slope of this line gave an activation energy of 32 kcal/g atom, which is in good agreement with an average of values of the activation energy for the diffusion of magnesium in aluminum(19) (32.2 kcal/g atom).

This relation has also been found for the reversion of other aged alloys (for example, Graf(20)) and is consistent with the re-solution of an unstable precipitated phase by simple diffusion. Slow reversion occurred at 50 °C (122 °F). For example, the yield strength of bars of similar composition and properties to those of Melt 352 (whose reversion behaviour is described above) fell from an aged value of 45.1 kpsi to 31.7 kpsi after 117 days at 50 °C (122 °F).

TABLE 2

Results of Reversion Experiments at Various Temperatures (Melt No. 352)

Treatment	Time (sec)	UTS (kpsi)	0.2% YS (kpsi)	El % in 2 in.
As Solution Treated	-	54.5	26.7	35.5
Aged 1306 days at R.T.	-	70.2	45.6	20.5
125 °C (257 °F)	120	56.4	30.1	32.0
	220	55.2	28.4	33.0
	300	54.7	27.5	n.d.
	390	54.5	27.3	33.5
	480	53.6	26.7	30.5
	600	54.7	27.0	35.0
100 °C (212 °F)	900	55.8	30.5	30.0
	1020	57.0	34.9	34.5
	1800	55.0	28.5	32.0
	3600	54.9	27.5	32.5
	5400	52.6	26.3	34.5
	7200	53.2	26.6	32.0
87 °C (189 °F)	3600	58.2	31.7	32.0
	4980	56.7	30.7	31.0
	7200	55.0	28.4	34.5
	10800	53.2	26.8	37.0
	14800	53.8	26.9	36.0
	18000	53.8	25.8	35.0
75 °C (167 °F)	7200	62.4	38.6	30.0
	14400	59.0	33.5	32.0
	25200	56.4	30.2	31.5
	25800	56.0	30.1	31.5
	63900	54.0	27.5	34.0

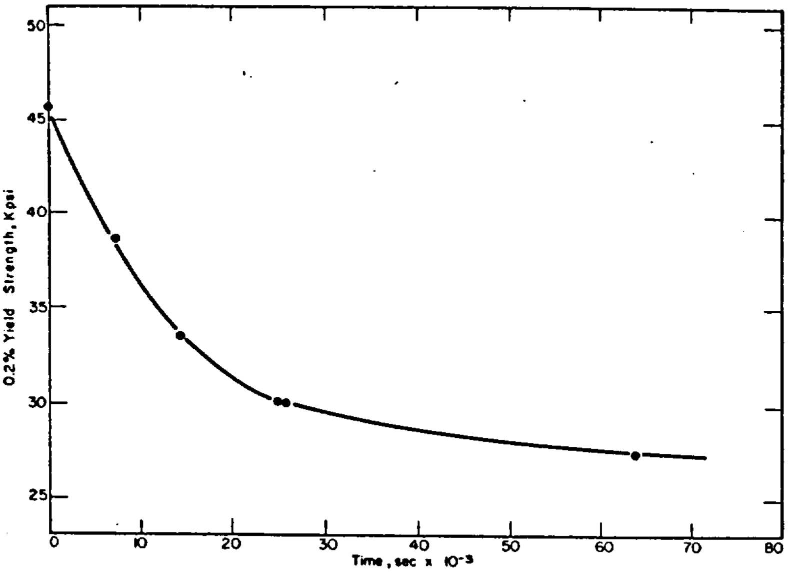


Figure 8. Reversion at 75 °C (167 °F).

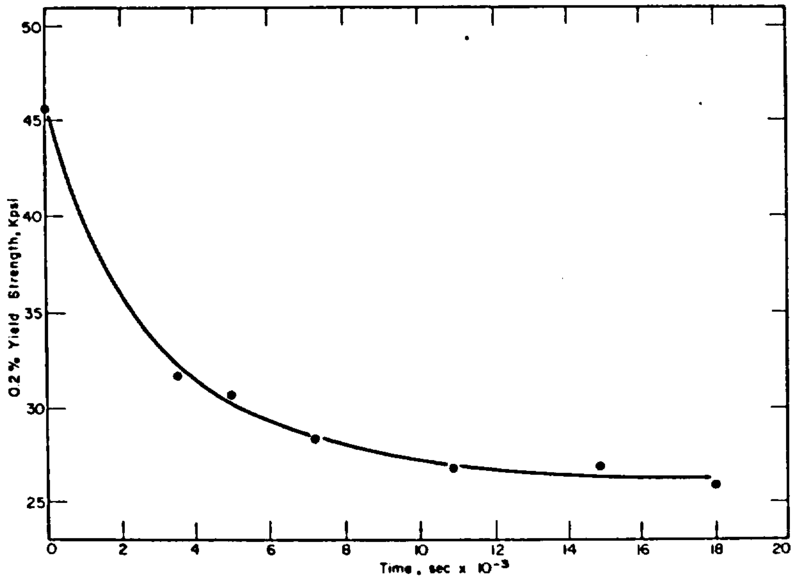


Figure 9. Reversion at 87 °C (189 °F).

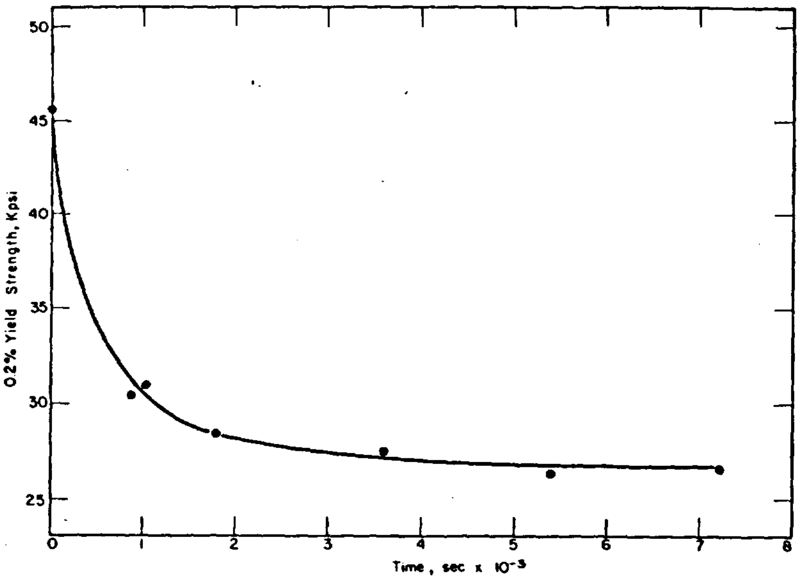


Figure 10. Reversion at 100°C (212°F).

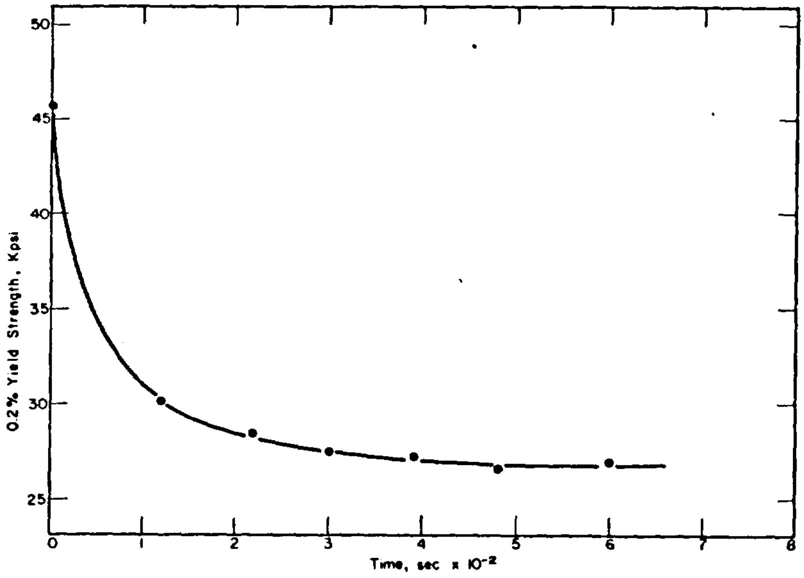


Figure 11. Reversion at 125°C (257°F).

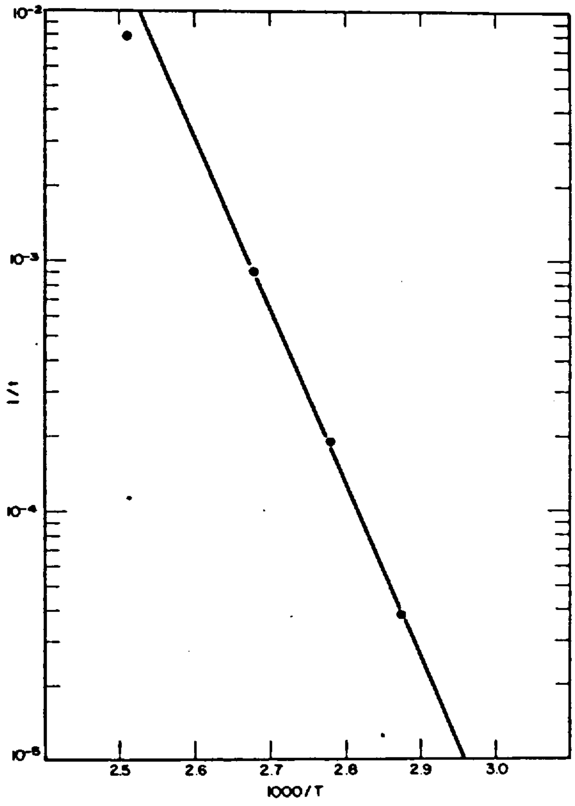


Figure 12. Reciprocal of the absolute temperature (X1000) plotted against the reciprocal of the time for the yield strength to fall, during reversion, to 30 kpsi (obtained from Figures 8 to 11). The slope of the curve gives an effective activation energy for reversion of 32 kcal/g atom.

Effect of Pre-Strain on Room Temperature Ageing

Test bars from Melt No. 333 (see Table 1) were solution treated, and half were strained in tension to a permanent set of 5%. All bars were then aged at room temperature. The results of tensile tests are shown in the ageing curves of Figure 13. It will be seen that the pre-strained bars aged at a considerably slower rate than the unstrained bars. This finding agrees with that of Van Ewijk(13).

Ageing at -46°C (-50°F)

Test bars from Melts 996 and 997 were stored at -46°C (-50°F) for 446 days and no tensile property or structural changes were detected.

OTHER EVIDENCE OF STRUCTURAL CHANGES DURING AGEING

Metallography

The normal heat treatment of the Al-10% Mg type alloys results in the complete solution of the β-AlMg eutectic present in the as-cast alloy. However, some grain boundary precipitate is always present and is presumably formed during or immediately after quenching. Impurities usually found in commercial purity material are silicon, which is present as Mg_2Si, and iron, which occurs as $FeAl_3$. In alloys containing titanium as a grain refiner, excess occurs as crystals of $TiAl_3$.

Figures 14 and 15 show structures typical of the alloy in the solution treated condition.

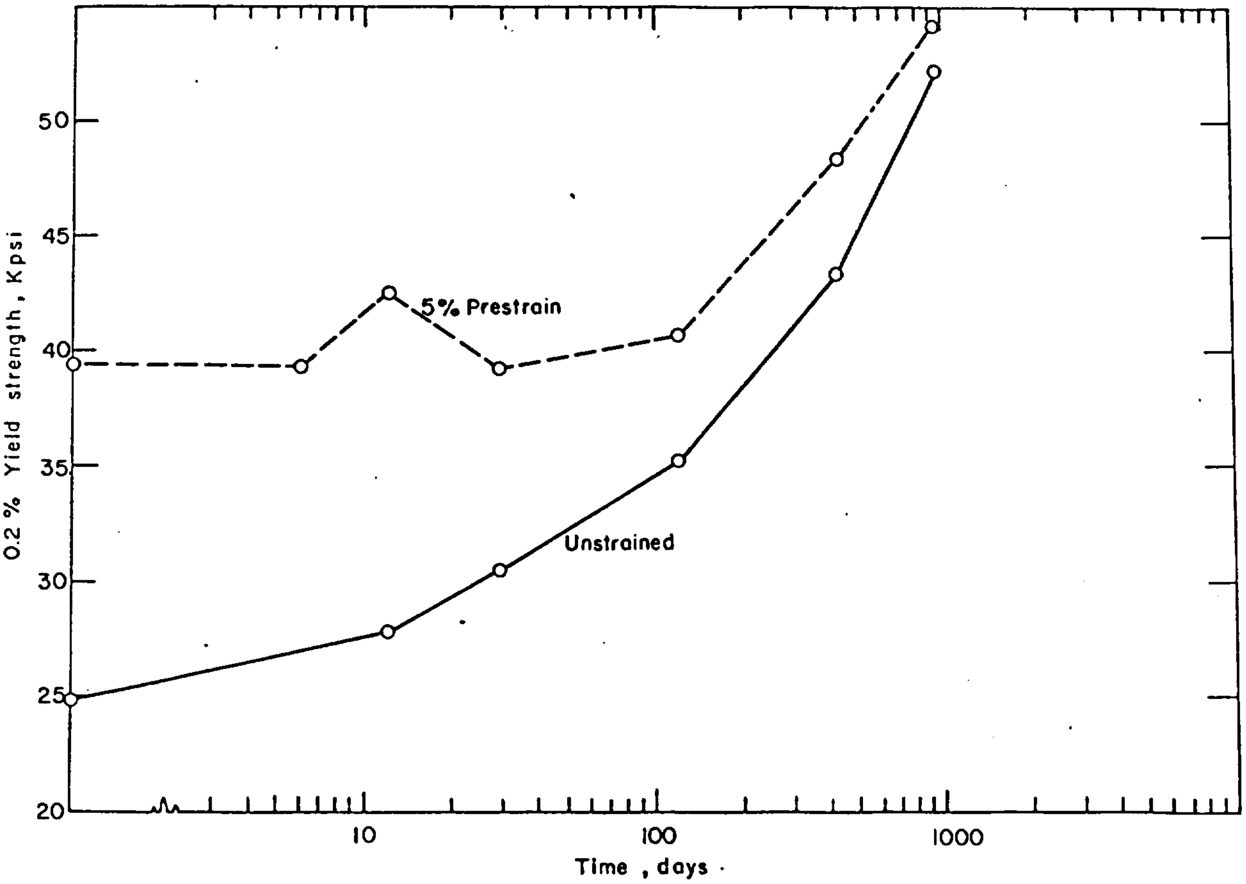
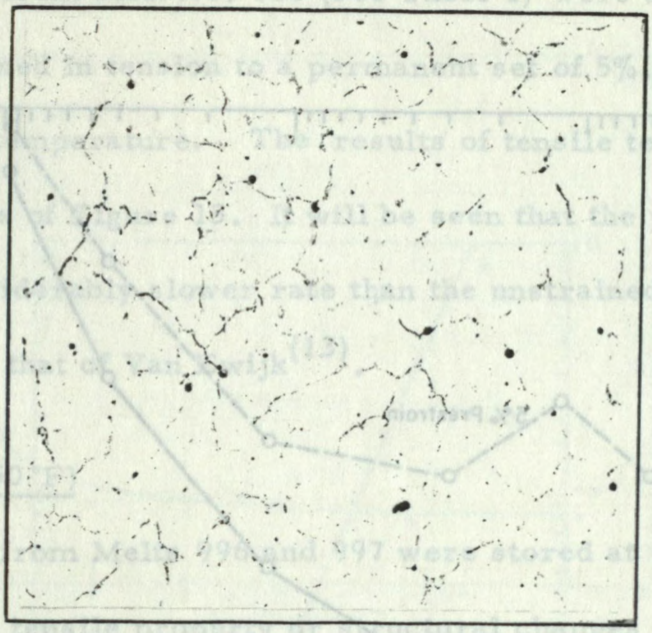
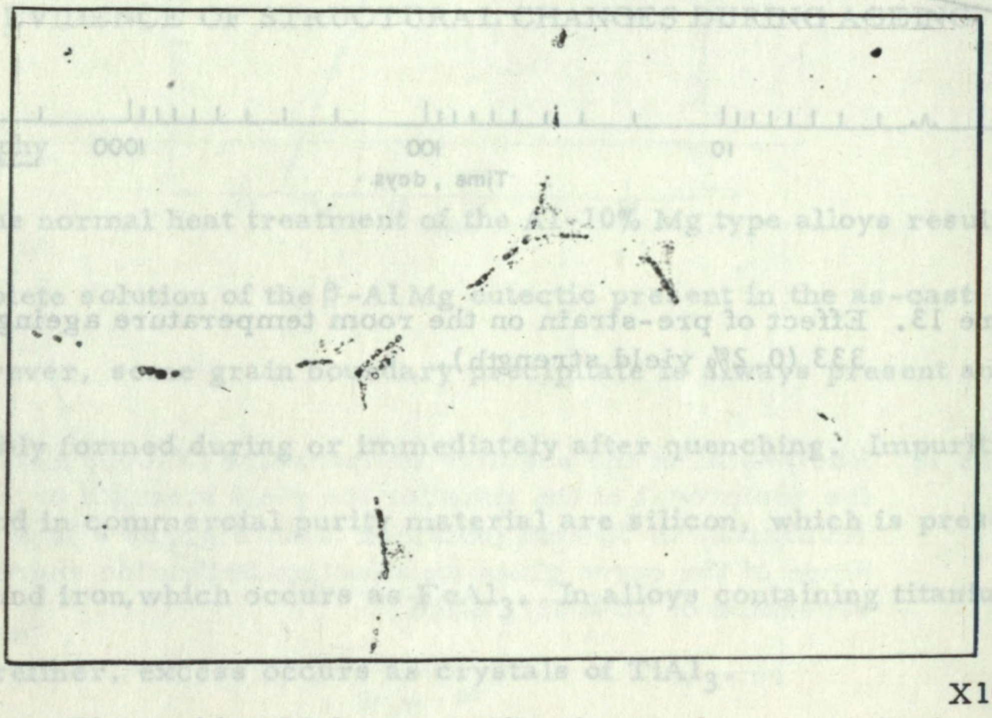


Figure 13. Effect of pre-strain on the room temperature ageing of Melt 333 (0.2% yield strength).



X100

Figure 14. Structure of Al-10% Mg-type alloy (Melt 348) in the solution treated condition (Alcan T4). Note precipitation at grain boundaries.



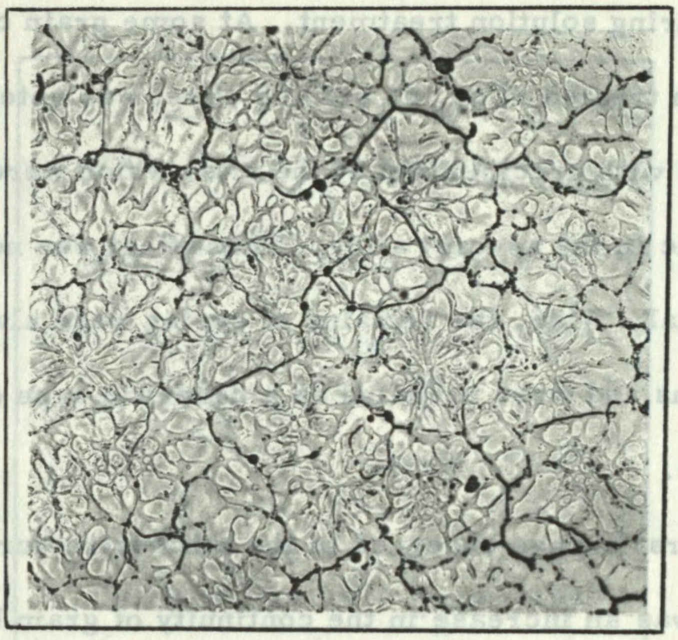
X1000

Figure 15. As Figure 14, at higher magnification to show precipitation at grain boundaries and grain corners.

There are several indications that complete homogenization is not achieved during solution treatment. At some grain corners in the freshly solution treated alloy, an etching effect was noted which seemed to be connected with precipitation at the sites which were occupied by the β-AlMg eutectic in the as-cast alloy. This effect was not observed in wrought material. Also, the remains of coring were always observed within the grains and were revealed as a dendritic-type etching pattern (see Figure 16).

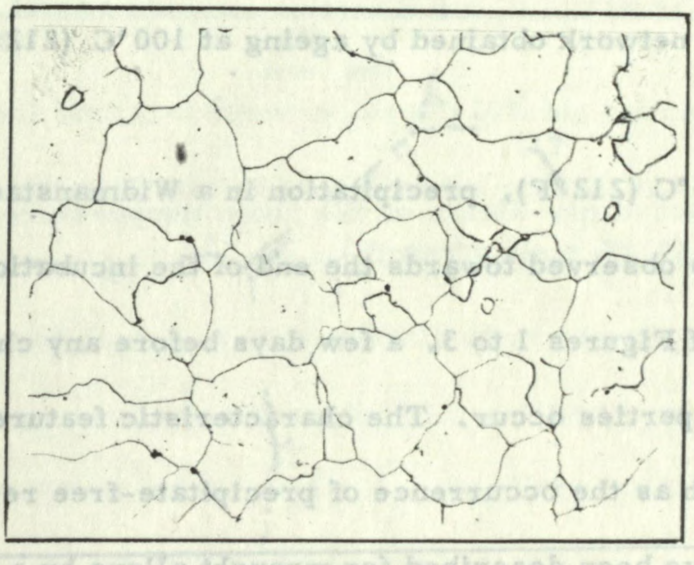
The first change observed in the microstructure of the alloy during ageing was an increase in the continuity of grain boundary precipitate. The rate of this precipitation increases with increasing ageing temperature. Thus, at 100°C (212°F) an almost continuous grain boundary network is formed after about ten hours, while at 50°C (122°F) near continuity is observed only after several months. Figure 17 shows a grain boundary network obtained by ageing at 100°C (212°F) for thirty hours.

At 100°C (212°F), precipitation in a Widmanstaetten pattern within grains is observed towards the end of the incubation period shown in the curves of Figures 1 to 3, a few days before any changes in the mechanical properties occur. The characteristic features of this precipitation, such as the occurrence of precipitate-free regions near grain boundaries, have been described for wrought alloys by a number of investigators(2, 3, 4) and the cast material appears to behave in a very similar manner.



X100

Figure 16. Sample similar to that shown in Figure 14, over-etched to show coring.



X100

Figure 17. Sample aged at 100°C (212°F) for thirty hours, showing almost continuous grain boundary network.

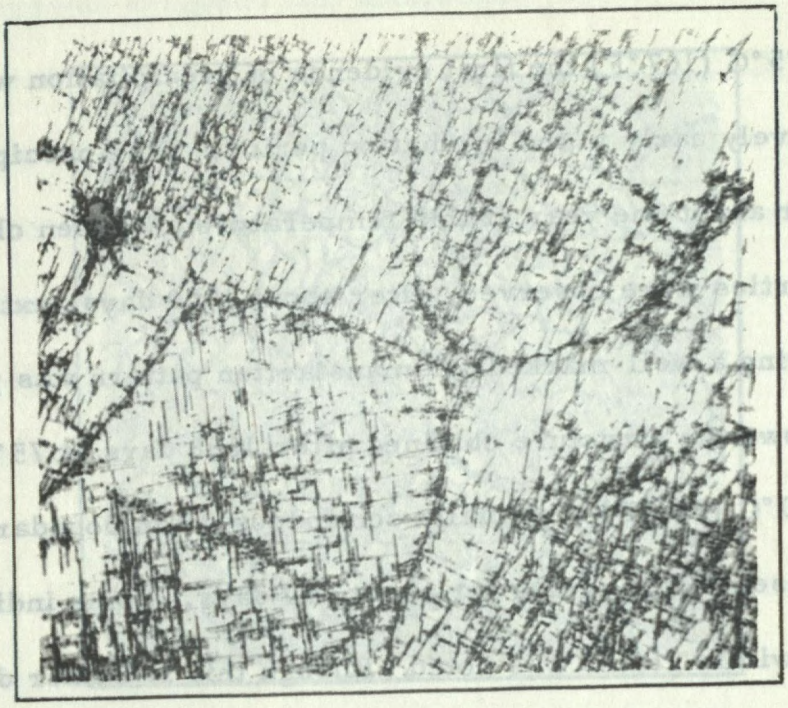
At 75°C (167°F) the first evidence of precipitation within grains occurs relatively early in the incubation period. Fine precipitation was detected after about one year at this temperature, and when changes in tensile properties were observed, after about 1000 days, extensive precipitation having a well-marked Widmanstaetten pattern was present. Figure 18 shows the structure obtained after 1658 days at 75°C (167°F).

At 50°C (122°F) a virtually continuous grain boundary network is usually present after ageing for about 300 days. Some indication of precipitation within grains was noted, although this is rather doubtful. No definite Widmanstaetten precipitation of the type observed at 75°C (167°F) has been observed at 50°C (122°F).

At room temperature the precipitate at grain boundaries becomes more continuous and somewhat thicker, but even after long periods (e.g., up to 1500 days) complete continuity is not always obtained (see Figure 19). No precipitation within grains (except that at grain corners mentioned above) has been detected in samples aged at room temperature.

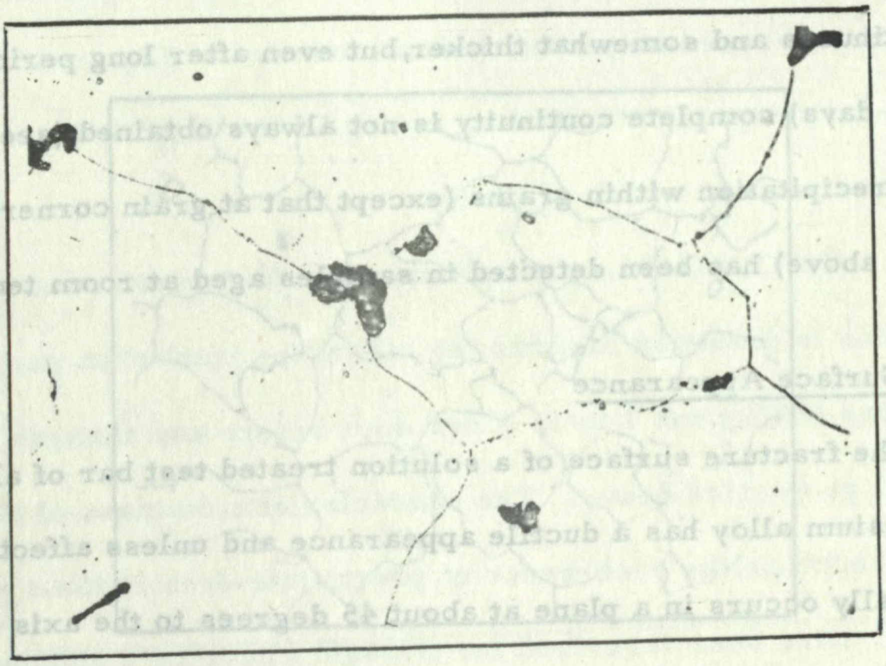
Fracture Surface Appearance

The fracture surface of a solution treated test bar of aluminum-10% magnesium alloy has a ductile appearance and unless affected by a flaw it usually occurs in a plane at about 45 degrees to the axis of the bar. The surface appears "silky" and suggests completely transgranular failure.



X1500

Figure 18. Fine Widmanstaetten precipitate obtained on ageing at 75 °C (167 °F) for 1658 days (Melt 884).



X500

Figure 19. Incomplete grain boundary network obtained after ageing at room temperature for 1658 days (Melt 884).

The appearance of the fracture surface does not change during the "incubation period" of ageing at temperatures of 75°C (167°F) and above, nor throughout the entire ageing periods at 50°C (122°F). As the ductility of the alloy decreases, the fracture becomes correspondingly rougher and tends to occur at 90 degrees to the axis of the bar. The appearance of the surface eventually becomes typically brittle and suggests intergranular failure.-

On ageing at room temperature, however, the appearance of the fracture surface changes continuously from ductile and silky to brittle and intergranular as ageing progresses. These changes are reversed when the room temperature aged alloy is treated at a higher temperature and reversion occurs.

Stress Corrosion

One serious disadvantage of the aluminum-10% magnesium type alloy is its tendency to become susceptible to stress corrosion. It is generally recognized that in the freshly solution treated condition its resistance to stress corrosion is good. However, after long periods of ageing at room temperature, or after shorter periods at somewhat elevated temperatures, it becomes extremely susceptible. It is thought that the reason for this deterioration is the formation of continuous grain boundary precipitate β-AlMg. As mentioned earlier, this occurs in the "incubation periods" observed in the early stages of ageing at temperatures of 75°C (167°F) and above. Also, in ageing at 50°C (122°F) a continuous grain boundary precipitate is gradually formed.

At room temperature the metallographic evidence for the formation of continuous grain boundary network is, as mentioned earlier, less definite, but the fact that the stress corrosion susceptibility does increase on room temperature ageing suggests that some grain boundary precipitation does occur at this temperature also.

WROUGHT ALLOYS

Although the present work was intended to elucidate the ageing behaviour of the binary aluminum-magnesium casting alloys, in view of the apparently conflicting observations on room temperature ageing(8) some tests have been done on wrought alloys containing various magnesium contents. It was found that alloys containing more than about 10.2% Mg aged at room temperature in a similar manner to the cast material.

The ageing behaviour of wrought alloys at 100°C (212°F) as shown by other investigators(2, 10) is similar to that of the cast alloys in the present work. It seems probable that this similarity would also apply at intermediate temperatures.

DISCUSSION

Although the ageing of the Al-10% Mg casting alloys at room temperature is widely known and has been mentioned in the literature many times, there has, so far as is known, been no published work that has drawn a clear distinction between the room temperature ageing and the ageing which occurs in these alloys at higher temperatures.

In the present work it has been shown that, above a critical magnesium content (about 10.2%), both wrought and cast aluminum-magnesium alloys show pronounced tensile property changes on ageing at room temperature whereas at 50°C (122°F) no such changes occur.

At room temperature, considerable increases in the ultimate tensile and yield strengths occur, along with a gradual decrease in elongation, but these changes are slow, and, as there appears to be no indication of an end-point in the process, castings of the alloy must be expected to become stronger and more brittle indefinitely. For this reason, the room temperature ageing of the alloy cannot be considered beneficial.

In passing, it may be pointed out that a short treatment (approximately 20 min at 100°C (212°F)) will restore the tensile properties of an aged casting to the original "as-quenched" values, by the reversion process mentioned earlier.

A more serious consequence of long ageing periods, both at room and slightly elevated temperatures, is the increase in susceptibility to stress corrosion, which is probably caused by the precipitation of β-AlMg at the grain boundaries. This precipitate cannot, unfortunately, be reverted by the treatment mentioned above and, in fact, reversion treatment at 100°C (212°F) only accelerates the grain boundary precipitation.

In general, ageing at 50°C (122°F) produces no tensile property changes. However, the occurrence of grain boundary precipitation suggests that all of the observations, so far, have been within the "incubation period" and that if tests at this temperature were carried on for very long periods, the type of phase separation observed at 75°C (167°F) and higher would occur (that is, Widmanstaetten precipitation within grains) and the associated tensile property changes would be observed.

At 50°C (122°F) and above, reversion of room temperature aged bars has been shown to occur. Complete recovery of the solution treated properties is obtained and the effective activation energy of the process has been shown to be the same as that for diffusion of magnesium in aluminum.

These results suggest that the precipitate or pre-precipitate responsible for the room temperature age-hardening is unstable and redissolves above about 50°C (122°F).

The precipitation which is characteristic of higher temperatures, but which probably occurs slowly even at room temperature, appears to take place independently of that which causes the "room temperature" ageing. As the "higher temperature" type of precipitation occurs only at grain boundaries in the early "incubation" period, and does not cause mechanical property changes, solution of the "room temperature" pre-precipitate results in the tensile properties reverting completely to those of the solution treated alloy.

It should be pointed out that the reversion of this alloy is not "complete" in the sense that a homogeneous solid solution is obtained, as is the case, for example, when an aluminum-copper alloy containing G.P. zones or Θ is reverted(22). In aluminum-copper alloys a parallel to the present conditions occurs (see Ref.11, p.284) "..... if an alloy containing Θ'' (G.P.2) and Θ' is reverted, the Θ'' will dissolve but the Θ' will grow rapidly. However, since the volume fraction of Θ' is small it has no effect on the strength of the reverted alloy." In the present case the phase that precipitates at reversion temperatures (grain boundary β') also appears to have no effect on the strength of the alloy.

It is possible to interpret some of the results of this investigation in the light of recent ideas in age-hardening theory as follows.

Recently, two papers have given evidence of zone formation in aluminum-magnesium alloys. Cordier and Detert(9) (continuing earlier work of Dahl and Detert(8)) and Panseri et al(10) have postulated, from electrical resistivity changes, that clustering occurs in supersaturated alloys of this type. Cordier and Detert used an alloy containing 9.88% Mg and Panseri et al examined alloys containing up to 7% Mg. Both of these groups observed the reversion of clusters above about 50°C (122°F). This is in close agreement with the present work and strongly suggests that the "room temperature" ageing is due to the presence of zones of the same type as those responsible for the resistivity changes.

These clusters or zones form rapidly on ageing at room temperature but after a certain size further growth is much slower. As aluminum-magnesium alloys containing less than about 10.2% Mg do not show hardening at room temperature, it is presumed that below this critical supersaturation the zones either never grow large enough or their volume fraction or degree of dispersion is insufficient to cause strengthening.

The diffusion of solute atoms to form clusters and zones occurs by the migration of vacancy-solute atom pairs, and it has been shown(6) that in aluminum-magnesium alloys the vacancy-magnesium atom binding energy is particularly high. The growth of zones is also thought to be controlled by the vacancy flux (Ref. 11, p. 178), so that the significance of the "critical" magnesium content (10.2%) may be connected with the number and distribution of excess vacancies as well as with the supersaturation of magnesium. In this connection it has been found(23) that as the magnesium content of binary aluminum-magnesium alloys is increased (up to 8.2 at %) the number of vacancies absorbed on helical dislocations or dislocation loops decreases, and it is considered (Ref. 11, p. 188) that this indicates that more vacancies remain in solid solution than in the more dilute alloys. This would presumably make more vacancies available for zone growth.

The results of room temperature ageing after pre-treatments at 50 °C (122 °F) and 75 °C (167 °F) (see Figure 7) give further evidence that the "higher temperature" and "room temperature" ageing processes are independent of each other. If the precipitation occurring at 50 °C (122 °F) or 75 °C (167 °F) were a later stage (or "over-ageing") of that at room temperature, re-ageing at room temperature would not be expected. The effect of the pre-treatments in retarding the room temperature ageing might be explained by the reduction of supersaturation of magnesium or by the elimination of some excess vacancies. However, it is more difficult to explain the subsequent rapid hardening, which appears to be at least as rapid as that of the bars that were not pre-treated.

The effect of pre-strain on room temperature ageing (see Figure 13), which is confirmed by the results published by Van Ewijk(13), agrees with the hypothesis that zone formation is responsible for the strengthening, as cold work usually increases the rate of nucleation of an intermediate precipitate (see Ref. 11, p. 275) but has generally been found to decrease the rate of zone formation(24). The effect of cold work is thought to be due to the dislocations that are introduced, acting as additional sinks for migrating vacancies.

CONCLUSIONS

It has been shown that both cast and wrought aluminum-magnesium alloys containing more than about 10.2% Mg age harden at room temperature, and that this process is independent of the precipitation normally associated with the aluminum-magnesium alloys and which predominates at temperatures above about 50°C (122°F).

The tensile properties of a room temperature aged alloy can be restored to the as-quenched properties by a reversion treatment above about 50°C (122°F).

The characteristics of the room temperature ageing are consistent with a pre-precipitation of the G.P. zone type, and early indications of the formation of such zones in aluminum-magnesium alloys have recently been reported by other workers.

The phase separation characteristic of higher temperatures -- i.e., precipitation of a form of the equilibrium precipitate Al_3Mg_2, first at grain boundaries and later in a Widmanstaetten pattern within grains -- appears to occur at all temperatures (above room), although below 75°C (167°F) only the grain boundary form has been observed in the ageing times so far employed. This precipitation is not subject to reversion, and although in the grain boundary form it has no effect on tensile properties it is believed to be the cause of the increased susceptibility to stress corrosion, which was observed with these alloys after long ageing periods.

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APPENDIX

Anomalous Behaviour Noted at 50°C (122°F)

One exception to the usual ageing behaviour at 50°C (122°F) should be mentioned: Melt No. 870 appeared to age at 50°C (122°F) in the same way as at room temperature, although at 75°C (167°F) it behaved in the same manner as did other melts.

No apparent reason could be found for this anomalous behaviour but, assuming that there was no gross experimental error, such as incorrect ageing temperature, it would seem that the ageing behaviour at 50°C (122°F) is sensitive to factors that are not immediately apparent from the present work.

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