

Effect of Composition and Thermal Treatment on the Natural Ageing of Aluminium-Zinc-Copper Alloys

J. Wood

THE aluminium-zinc-copper alloy designated BS L5 was one of the first aluminium casting alloys used in the United Kingdom. The first specification was issued before or during the First World War and for many years the alloy was widely used for the production of sand castings for the automotive industry, e.g. engine sumps and blocks. With the introduction of the aluminium-silicon and aluminium-silicon-copper alloys, which had superior casting properties, the use of alloys of the BS L5 type declined.

The L5 specification permitted the use of virgin materials only, but during the 1939-45 War, an emergency specification was introduced which permitted the use of secondary materials. This specification, designated LAC 113, was later superseded together with BS L5, by the General Engineering+Specification BS 1490, LM. 3.

LM. 3 alloy is susceptible to natural ageing to give considerable increases in hardness and tensile strength after periods of a few weeks*. This increase in strength is obtained at the expense of ductility, and, in some castings, difficulties were encountered in this respect as it was impossible to rectify distorted castings after a few days' ageing. It was noted that the ageing effect varied from casting to casting, and it was suspected that this effect was due to differences in composition. Another factor which could affect the rate of ageing was the thermal history, either during cooling after casting, or subsequent heat treatment. In an attempt to ascertain the relative importance of the various factors it was decided to carry out a series of experiments to determine (a) the effect of composition, (b) the effect of thermal treatment on the rate of ageing.

Mr. J. Wood, Assistant Chief Metallurgist, International Alloys Ltd., Aylesbury, Bucks., U.K.

* An aluminium-zinc-magnesium alloy, developed in U.S.A. under the trade name "Frontier 40E" has been introduced as an alloy capable of giving high strength by ageing, without the need for heat treatment. This alloy, which is specified in the U.K. as DTD 5008, has minimum specified tensile properties for sand cast test bars as follows: tensile strength 14 tons/sq in, elongation 4% on 2". This alloy conforms to a much more stringent composition range than the LM. 3 alloy discussed here.

The effect of composition

The specified composition ranges of the two obsolete specifications BS 3L5 and LAC 113 are given in the following table, together with the ranges for the current BS 1490 LM. 3 alloy.

	Cu %	Mg %	Si %	Fe %	Mn %	Ni %	Zn %	Pb %	Sn %	Ti %
BS 3L5										
Min.	2.5	—	—	—	—	—	12.5	—	—	—
Max.	3.0	—	0.7	0.8	—	—	14.5	0.10	—	0.20
LAC 113										
Min.	2.5	—	—	—	—	—	9.0	—	—	—
Max.	3.5	0.10	1.0	1.0	0.3	0.3	13.0	—	—	—
BS 1490										
Min.	2.5	—	—	—	—	—	9	—	—	—
Max.	4.5	0.10	1.3	1.0	0.5	0.5	13	0.3	0.2	—

The elements which were expected to have the most marked effect on the ageing properties were magnesium and silicon. Although zinc has some effect, it seemed unlikely that variation within the range of 9 to 13% would have any appreciable effect. Melts were therefore prepared with varying amounts of the elements—magnesium and silicon. In addition, the effect of minor impurities was also investigated and a number of melts were made up from pure aluminium and pure alloying components or from secondary materials, in the latter case, with the impurity contents normally found in this alloy.

The series of melts planned were as follows:

Melt	Make-up	Magnesium %	Silicon %
A	Pure	nil	0.1
B	Pure	nil	0.5
C	Pure	nil	1.3
D	Pure	0.1	1.3
E	Secondary	nil	0.5
F	Secondary	0.1	0.5
G	Secondary	0.2	0.5

The actual compositions of the melts are given in Table I below.

Melt A was prepared using high purity aluminium to give a low silicon content. The content is obviously much lower than the values obtained in commercial production, but is included in this series to determine the effect of variation in silicon content.

The procedure adopted for each melt was as follows: the charge consisting of aluminium ingot and the usual hardeners, was melted down in a plumbago crucible in an oil-fired furnace. The melt temperature was not allowed to rise above 800°C, and was reduced to 750°C for the addition of magnesium. The melt was then degassed using a proprietary degassing compound of the hexachlorethane type, the quantity used being about 1% of the charge weight. The melt was then allowed to stand for a period of 15 to 20 minutes, whilst the temperature dropped to the casting temperature of 690–700°C. From each melt, a number of test bars were cast into A.I.D. pattern vertical sand moulds. The bars were cast 1" diameter and were machined to 0.564" diameter (0.25 sq in section area) for testing. In this group of tests, the test bars were allowed to cool to room temperature in the mould before stripping.

The bars were tested for 0.1% proof stress (yield stress), tensile strength, elongation % on 2" gauge length, and Brinell Hardness at ageing periods up to 20 days.

The values obtained are plotted in the graphs in Fig. 1. Each point represents the average of two or three test bars. For comparison, the specified tensile properties for BS 1490 LM.3 alloy, sand cast test bars are 9 tons per sq in minimum, the elongation is not specified as it is expected to be low, i.e. below 2%. From these graphs comparing the magnesium-free melts A, B, and C, it is clear that the initial properties in U.T.S. and proof stress are similar. The low silicon alloy (A) starts at a comparatively high value for elongation. All alloys age harden to some extent, the rate of ageing being dependent on the silicon content. The first points on the graph refer to material which was tested about 6 hours after casting. Melt A with very low silicon content shows very slight ageing effect, the increase in hardness is less than 10 Brinell units, compared with an increase of 30 for the melts with 0.5 and 1.3% silicon. The increase in hardness is accompanied by an increase in tensile strength and proof stress and with a reduction in elongation.

Owing to the small amount of age hardening the graph for alloy A in some cases crosses the graphs for alloys B and C.

When the magnesium is present, the hardness and strength after six hours are higher and the values after 12 days ageing are somewhat higher than for magnesium-free material. We have not examined whether the magnesium containing alloys have also higher hardness between 0 and 6 hours after casting.

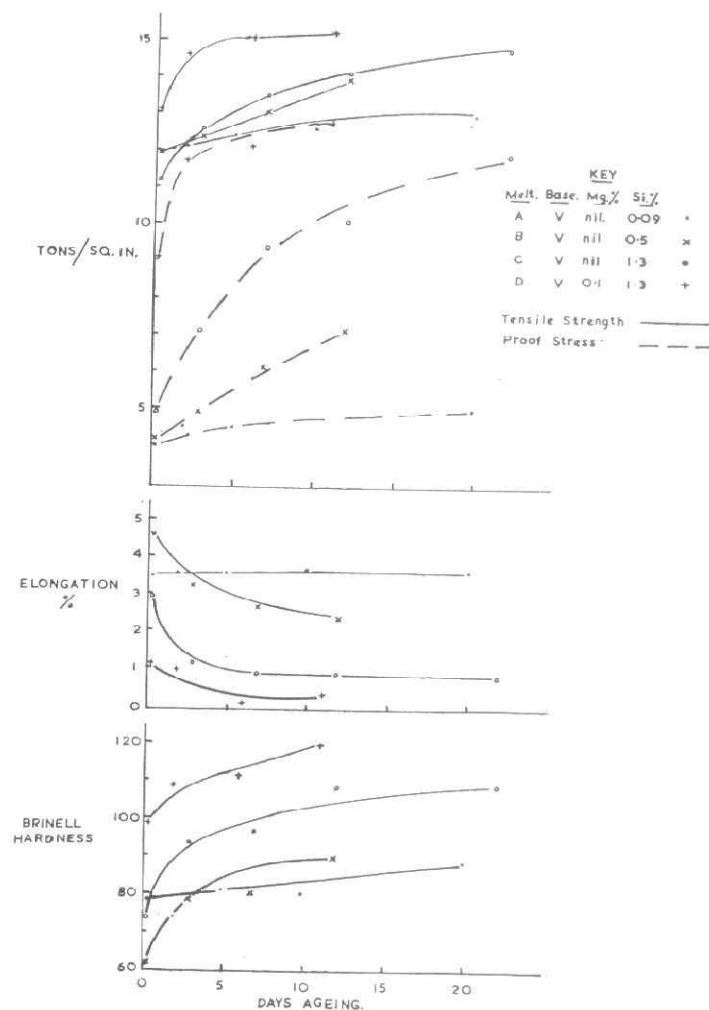


Fig. 1.

TABLE I

Melt	Cu %	Mg %	Si %	Fe %	Mn %	Ni %	Zn %	Pb %	Sn %
A	3.02	0.02	0.09	0.60	0.02	0.02	12.96	0.02	0.02
B	3.00	0.02	0.48	0.67	0.02	0.02	11.40	0.02	0.02
C	3.10	0.02	1.37	0.68	0.02	0.02	11.70	0.02	0.02
D	3.06	0.10	1.30	0.66	0.02	0.02	12.10	0.02	0.02
E	2.81	0.02	0.48	0.57	0.30	0.27	10.50	0.02	0.18
F	2.81	0.10	0.51	0.60	0.30	0.30	10.60	0.02	0.20
G	2.83	0.20	0.46	0.57	0.30	0.29	10.50	0.02	0.22

For the secondary base material (Fig. 2, alloys E, F, G) the effect of magnesium content is again clearly shown. The type of make-up, i.e. pure or secondary, does not appear to have much effect on the mechanical properties after ageing (compare graphs for melts B and E).

These results showed the extent to which LM. 3 alloys of the pure or secondary types age harden at room temperatures. The ageing effect is in agreement with that reported by Herenguel and Chaudron¹ for wrought alloys of similar composition, although the final hardness values found are much higher than those given by these authors, e.g. for 0.1% magnesium they obtain a maximum hardness of 70 compared with 110 in these tests. The ageing increases strength and hardness but reduces elongation to very low values, in some cases less than 0.5%. This may be a disadvantage in practice. In the production of castings, it is sometimes impossible to avoid distortion either as a result of stresses set up during cooling in the mould or as a result of stripping from the mould,

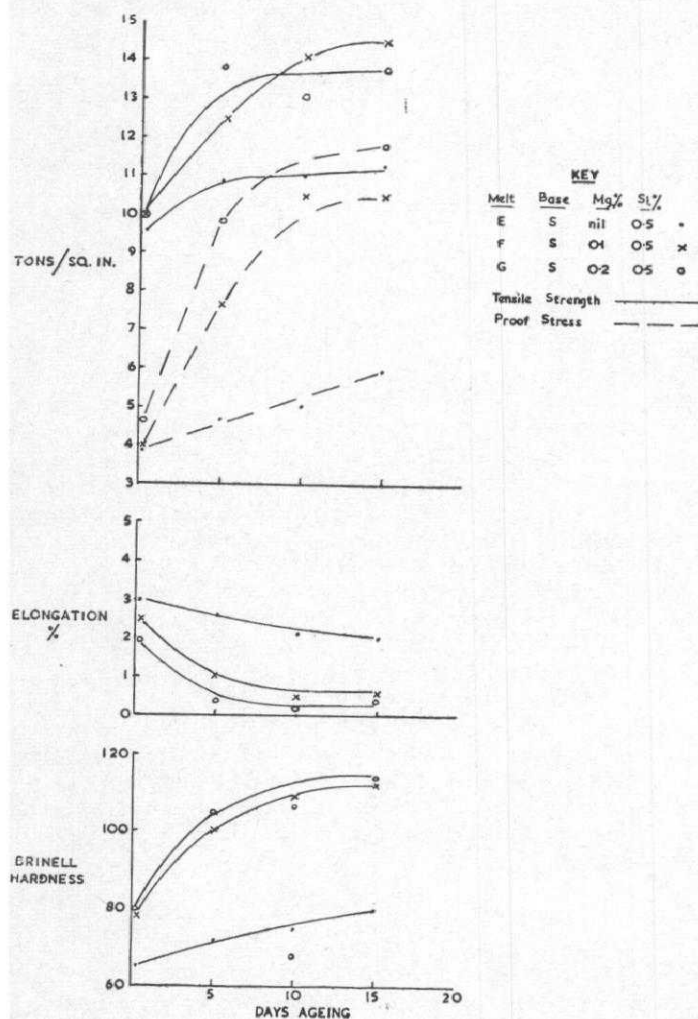


Fig. 2.

particularly when the casting is still very hot. If the castings are allowed to age for a few days before rectification is attempted, this operation becomes much more difficult. The relatively small difference between proof stress and tensile strength means that much greater forces would be required to give permanent deformation, and this force may sometimes exceed the tensile strength, causing the cracking of casting.

In the normal aluminium casting alloys, it is possible to carry out a stabilising treatment by heating the castings to a temperature between 200° and 300°C for several hours. It was therefore decided to determine if stabilising treatment would help in preventing age hardening. It is known that the aluminium-zinc-copper alloys behave somewhat differently from the aluminium-copper-magnesium and aluminium-silicon-magnesium alloys in this respect, but it was considered that stabilising treatment at 250°C should result in some improvement.*

Stabilising treatment was carried out for periods of 4, 8 and 16 hours, this treatment being applied to bars cooled to room temperature in the mould, as in melts A-G.

Another factor which can affect the ageing characteristics of an alloy is the rate of cooling after casting. In the tests described above, the test bars were allowed to cool to room temperature in the mould. However, in commercial practice, castings may be removed from the mould at higher temperatures. A few tests were therefore made on the effect of rate of cooling and test bars were removed from the mould when the metal temperature was 300°C, in other cases at 100°C and the remainder allowed to cool to room temperature in the mould as before. The temperature of 300°C was considered to be the highest at which moulds would be stripped in practice. The nominal compositions of the three melts used for these tests were:

Melt	Make-up	Magnesium%	Silicon%
A	Pure	nil	0.1
H	Secondary	nil	0.5
J	Secondary	0.07	0.5

Ageing tests in this series were carried out over a period of 80 days; in the case of the bars cooled to room temperature in the mould, the proof stress, tensile strength, elongation and Brinell Hardness were measured, but for the bars cast under different cooling conditions, the age hardening was followed by hardness determinations only.

The results of these tests are shown in Figs. 3 and 4. Fig. 3 gives the graphs for the change in mechanical properties of mould cooled bars, and Fig. 4 the relationship between hardness and ageing time for bars subjected to various treatments. In Fig. 4, graphs are shown only for bars cooled to room temperature in

* Since these tests were concluded Hug³ has found that a temperature of 200°C would possibly have been more suitable for the stabilising treatment.

the mould and bars removed from the mould at a temperature of 300°C. There is very little difference between the values for these two treatments. The bars removed at 100°C were so similar in properties with regard to these two conditions that the results have not been plotted. The third graph for each melt represents hardness values for 8 hours, stabilisation treatment at 250°C.

It was found that stabilising treatment for 4 and 16 hours gave almost identical results, and therefore only the results for 8 hours' treatment have been shown.

Considering the graphs in Fig. 3, it can be seen that in magnesium containing alloys (melt J), ageing is rapid and the maximum hardness is obtained after 20 days. The properties attained with 0.1% magnesium after 80 days, ageing are: 0.1% proof stress 14 tons/sq in, tensile strength 15 tons/sq in, elongation $\frac{1}{2}$ -1%, Brinell Hardness Number 120. For magnesium-free materials, the alloy with 0.5% silicon gives properties after the same period as follows: 0.1% proof stress 10 tons/sq in, tensile strength 14 tons/sq in, elongation 1%, Brinell Hardness Number 110. The low silicon, magnesium-free material has greatly reduced ageing characteristics and although the tensile strength is reasonably high, the hardness and proof stress do not rise appreciably. The values after 80 days are

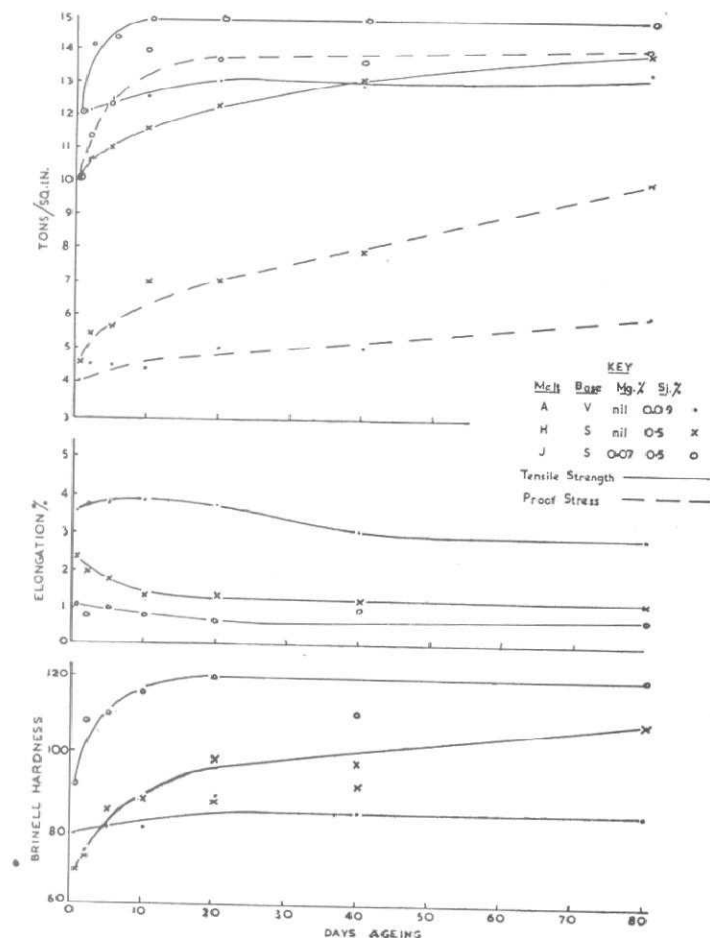


Fig. 3.

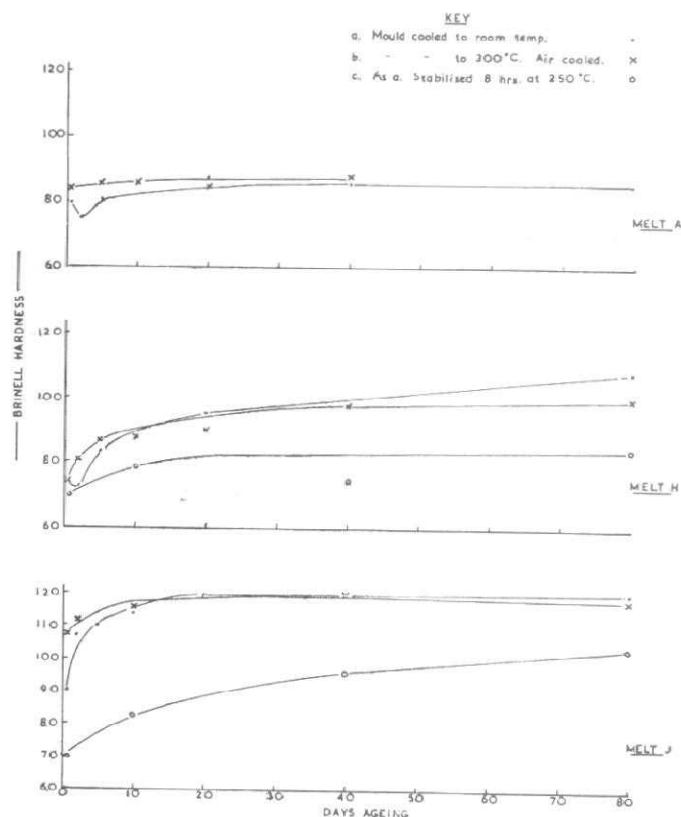


Fig. 4.

as follows: 0.1% proof stress 6 tons/sq in, tensile strength 13 tons/sq in, elongation 3%, Brinell Hardness Number 85.

Referring to Fig. 4, it appears that cooling rate after the casting has no effect on ageing behaviour, in the range of cooling conditions investigated. Stabilising treatment for 8 hours at 250°C reduces the initial hardness and although the shape of the ageing curves for stabilised material is similar to that for non-stabilised material, the hardness after 80 days is about 15-20 Brinell units lower for stabilised material. It cannot be concluded that elongation will be higher for stabilised material, compared with non-stabilised as the stabilising treatment may give over-ageing effects. It is probable that stabilising tests at other temperatures and times would give better results, and produce a condition where ageing does not take place, but no attempt was made in this limited investigation to explore the effect of other conditions (see footnote on page 101).

Conclusions

It has been shown that the aluminium-zinc-copper alloys age harden at room temperature to give increase in strength and hardness and reduction in ductility. The element having the most profound effect on ageing

is magnesium and with a content of 0.1% the alloy age hardens relatively quickly. These properties are of course desirable for applications where rigidity is important. The silicon content has also been found to be of importance, and with very low contents of this element (less than 0.1%) the ageing effect is much reduced. There is some evidence, however, to indicate that silicon is a desirable element from the point of view of casting properties.

The rate of cooling of the test bar has been found to have little effect on ageing within the range of conditions expected to occur in normal sand foundry practice. Stabilising heat treatment at a temperature of 250°C for periods of 4 to 16 hours results in a reduction in hardness initially and after ageing for 80 days, but does not completely inhibit ageing. It is probable that stabilising treatments under other conditions of temperature and time would prevent age hardening.

Acknowledgement

This work was carried out in the laboratories of International Alloys Ltd., and the author wishes to acknowledge the permission of the Directors of this company for publication of this paper.

References

1. J. Herenguel and G. Chaudron. *Revue de Metallurgie*, Vol. 41, No. 2, Feb. 1944, pp. 33-41.
2. Hiram Brown. American Foundrymen's Society Preprint, 48th Annual Meeting, 1944.
3. H. Hug., *Aluminium Suisse*, 4, pp 112-121 (July 1955).

DISCUSSIONS

Dr. B. R. Nijhawan, NML: It gives me great pleasure to introduce Mr. M. B. Shankar, Chief of the Laboratory and Metrology, Hindustan Aircraft Limited, whom I have known both personally and professionally for the last two decades. During the period since I first met him in the U. K., he has passed through varied and several specialised fields of metallurgical interests. His different assignments with the Government of India have culminated in his present important and responsible position at the Hindustan Aircraft Ltd. The subject of light metal and their alloys is of direct and fundamental interest to the Aircraft industry and the field which is thus opened up is as vast as it is complex, considered both from the academic and practical angles. As such, I wish to invite Mr. Shankar to give us an account of the different physical phenomena met with in light alloys particularly in its relationship to their age-hardening characteristics. I have no doubt that Mr. Shankar's observations in the light of his rich and specialised experiences will be of direct interest and value to the Symposium delegates.

Mr. M. B. Shankar, Hindustan Aircraft Limited, Bangalore: I thank Dr. Nijhawan for asking me to speak on the important phenomenon of ageing of light alloys.

In my explanations of different aspects during the past days, I had confined to the practical side of production, working and treatment of light alloys as pertaining to the highest quality user, the Aircraft industry. Now I would like to deal with some of the theoretical aspects of the most important phenomenon of age-hardening on which the strength and usefulness of the light alloys depend. The fundamental theory, as postulated about a quarter of a century ago seems to still hold good. But my inferences are based primarily on my experiences as a Steel-Metallurgist and now as engaged in the studies of the behaviour of several types of high strength light alloys of aluminium and magnesium in the Aircraft industry, with which I have the honour to be associated during the past few years.

The age-hardening phenomenon is one of the most important characteristics of light alloys, the usefulness of which is fully availed of in the Aircraft industry. The phenomenon becomes a complex one as we move from an alloy of one composition to another and from one degree of work and condition to another. Ageing occurs, in two different ways: (1) as a result of cold working; and (2) as a result of thermal treatment. The phenomenon of gradual hardening as a result of drastic cold working is known as strain-ageing such as is commonly observed in steels. There are a number of theories starting from Beilby up to the present-day thinking. More or less all of them have reached the conclusion that the phenomenon is due to the formation of a fine metal "debris", along the planes of easy slip, or cleavage or crystallographic planes, which has been corroborated by X-ray diffraction studies. The degree of fineness and the quantities of the "debris" have a pre-dominant influence in bringing about stiffening or tightening-up of the grains with consequent hardening of their boundaries. Therefore, the change in their hardness is to some extent a measure of the strain ageing effect. Based on the degree of straining and the "nascent" state of the "debris", there is a tendency for certain spontaneous recrystallisation with time to proceed with a fall in hardness from a maximum.

On the other hand, quench-ageing (ageing as a result of thermal treatment) though also an induced one, is entirely due to a different cause. The phenomenon is the result of gradual deposition at the room temperature of the constituents held in a solid solution in a supersaturated condition—a metastable state as a result of quenching inhibiting the precipitation of excess solute in the normal course.

The deposition of the constituents occurs along the cleavage planes, depending on certain inherent characteristics and "grain sensitiveness" in an effort to attain rapid equilibrium conditions from induced metastability. The manner and extent of precipitation depend upon: (1) the difference in solubility at the high temperature of quenching to that at the room temperature; (2) the extent of solubility of the particular alloying constituent in the base metal; (3) the temperature and time of heating for the solutionising treatment; (4) the grain size, "grain-sensitiveness" and certain inherent characteristics of the alloy. Finer grains tend to yield closer packing, thus leading to

higher hardness than initial coarse-grained structures which are determined by the degree of working, temperature and time of heating for solution treatment, as also the temperature and time of heating for precipitation (artificial ageing) treatment.

In steels, the quench-hardening or slight ageing effect is due to the formation of martensite entailing volume changes. Ageing is also observed in the case of a few non-ferrous alloys but not so generally nor conspicuously as in the case of light alloys. On precipitation treatment (artificial ageing), they exhibit higher hardness strength and better mechanical and chemical (corrosion resistance) properties by virtue of a desirable, relatively closed structure.

As most of the papers in this Symposium had some bearing on the ageing property and with the advent of numerous new alloys into aircraft field, I considered it fitting on this occasion to touch on the several aspects of the phenomenon. I need not emphasise the urgent need for detailed studies of the ageing effects of the new alloy compositions, by X-ray diffraction and crystal studies. I understand that NML is soon going to have an X-ray diffraction unit which would help in initiating such studies.

Dr. B. R. Nijhawan, NML: We had a very illuminating account on the ageing of light alloys by Mr. Shankar and now the paper is open for discussion. To start with, I would like to know from Mr. Ved Prakash whether the work done by him in U.K. has any relationship with this paper?

Mr. Ved Prakash, NML: The work carried out by me in U.K. pertained to the study of age hardening behaviour of an aluminium-(3.8%) copper alloy of super-purity with respect to specimen size. The present work presented by me on behalf of Mr. J. Wood refers to the effect of composition and thermal treatment at the room temperature, ageing of aluminium-zinc-copper alloys. Aluminium-copper alloys of high purity on which I worked and aluminium-zinc-copper alloys discussed in this paper seem to differ with respect to the effect of impurities on their natural ageing.

Mr. M. B. Shankar, Hindustan Aircraft Ltd., Bangalore: The subject deals with castable alloy, i.e. Al-Cu-Zn series. The properties of different groups cannot be correlated because the behaviour of aluminium-copper alloys is entirely different from that of alloys of aluminium with other elements like Mg and Cu. This may be due to segregation which plays an important part in determining the properties.

Mr. Ved Prakash, NML: I really had no intention to make a comparison between the two alloys. Since the present paper dealt with the effect of impurities on natural ageing of aluminium-zinc-copper alloys in some direct or indirect fashion, I merely meant to add in reply to Dr. Nijhawan's question that alloys on which I worked were somewhat different from aluminium-zinc-copper alloys in their response to the effect of impurities on their room temperature ageing. Aluminium-copper alloys show a very slow rate of ageing when the impurities like cadmium, tin, lead or indium are present as minor constituents.

I agree with Mr. Shankar that segregation of solute

atoms play an important part in determining physical properties of age-hardening alloys. There are, however, a number of factors which determine the speed at which segregation of solute atoms takes place within the alloy. One of the factors emphasised by Hardy is the impurities present. He showed that when metals like lead, tin, cadmium or indium are present to the extent of 0.05% by weight in aluminium-copper alloys, the room temperature ageing of these alloys is markedly slowed down.

To illustrate this point, some of the tensile test results are given in Table I from his paper [Hardy, H. K., Jour. Inst. Metals, 80(1952), p. 483]. The tensile tests were carried on aluminium-4%, Copper-0.15%, Titanium alloys of high purity after ageing for 14 days at room temperature after quenching in water from 530°C.

TABLE I
*Averaged tensile test results of Al-4%, Cu-0.15%,
Titanium alloy.*

Addition %	0.1% proof stress tons/in ²	Max. stress tons/in ²	Elongation
Nil	10	18.1	18.0
0.05 Cd	7.6	13.9	22.0
0.05 In	4.8	13.9	22.5
0.05 Sn	4.35	12.8	23.0

The Table shows that the proof-stress values of the high purity alloys are greatly reduced in the presence of cadmium, indium or tin.

Mr. G. Chatterjee, Metallurgical Inspectorate, Ministry of Works, Housing and Supply, Tatanagar: As far as my knowledge goes, the age-hardening properties in aluminium-alloys can be attributed to the presence of magnesium and copper. What is the function of zinc and that, too, at such a high percentage of 10-11% in this alloy?

Mr. Ved Prakash, NML: Aluminium-zinc alloys spontaneously age harden. Zinc, therefore, causes an increase in hardness. Zinc also increases weight. Magnesium and copper present alone will not cause appreciable hardening under conditions described in the paper. Copper is added to improve casting properties of Al-Zn-alloys.

Mr. J. Wood (Author): The aluminium-zinc alloys age harden at room temperature without previous solution treatment, the rate of cooling after casting within the normal range for castings does not appear to be critical. The presence of magnesium increases the rate of ageing considerably. The effect of silicon in producing age-hardening is surprising, particularly in magnesium-free alloys.

Although copper has some effect on age-hardening properties, the effect is low compared with the effect of zinc and magnesium.