AGEING CHARACTERISTICS OF SOME TERNARY AND QUATERNARY ALLOYS BASED ON INDIAN COMMERCIAL ALUMINIUM

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ABSTRACT

A systematic study has been made of the ageing characteristics of five ternary and four quaternary alloys prepared from Indian commercial aluminium having upto 1.0 % of impurities, chiefly iron and silicon.

Following a preliminary study of ternary alloys containing either silicon and magnesium or zinc and magnesium, Hardness/Ageing Time curves have been obtained at regular temperature intervals between room temperature and 250°C for 4 alloys containing 4-6 % zinc and 2-3 % magnesium. The influence of 0.5 % manganese and 1.0 % copper on the ageing characteristics of two selected Al-Zn-Mg alloys has also been studied at a suitable ageing temperature. Tensile strength and elongation values have been determined in all cases prior to and after a standard ageing treatment. The results indicate the possibility of producing high-strength casting alloys by the addition of zinc and magnesium to Indian aluminium, but further additions have to be tried to develop wrought alloys comparable to the commercial 75 S alloy in mechanical properties. The ductility of the alloys studied is slightly impaired by the impurities in Indian aluminium, but the latter do not affect the ageing process in these alloys in any marked way.

INTRODUCTION

The production of aluminium has been steadily increasing in recent years in India, but has not been able till now to meet the rapidly growing national demand for the metal. The present annual consumption in the country is estimated at 45,000 tons and is expected to increase to 75,000 tons within the next two or three years. The production in 1960 has, however, been only 17,000 tons and although the Third Five Year Plan envisages a production of 75,000 tons per annum by 1966, the country will have to depend heavily on imports for many years to come. A good percentage of the present demand is for age-hardenable, high-strength aluminium alloys indispensable for the aircraft and transportation industry. This is bound to increase in coming years, but unfortunately no concerted effort seems to have been made by either the aluminium industry or the metallurgical research organisations to explore the possibilities of producing these important as well as expensive alloys from indigenous materials. India is thus entirely dependent on foreign countries for these strategic alloys and this dependence will continue for many more years in the absence of development work in this field. As systematic preliminary investigations are indispensable for fruitful future developments in this sphere, the present studies were undertaken of the ageing characteristics of some alloys of selected composition prepared from Indian commercial aluminium.

The most widely used age-hardenable, high-strength aluminium alloys contain copper upto 5 % by weight as the principal alloying element, but recently alloys containing zinc and magnesium upto a total 10 % by weight have come into prominence. In fact, the commercial alloys 75 S and D.T.D. 687 containing 5 – 6 % zinc and 2 – 3 % magnesium as the chief alloying elements claim to be the strongest and most easily machinable of commercial aluminium alloys, although they are somewhat inferior to the aluminium-copper alloys from the point of view of formability, weldability and susceptibility to stress corrosion cracking. In view of India's very limited resourcess of copper and also of the steadily growing importance of alloys of the Al-Zn-Mg type, the present studies were confined to aluminium alloys without any or with very small percentages of copper.

Although investigations in the field of Al-Zn-Mg alloys have been on the increase in recent years[1-7], it is not yet possible to predict the effects of the impurities in Indian commercial aluminium on the ageing behaviour of such alloys. The virgin aluminium produced by Indian Aluminium Company, the largest producers of aluminium in India, is 99.0 to 99.7% pure, the impurities comprising mainly of iron and silicon. Investigations elsewhere[4] seem to suggest that these impurity elements may have a beneficial effect on resistance to stress-corrosion cracking of Al-Zn-Mg alloys, but the effects of the Fe-Si combination in Indian aluminium on the ageing characteristics of the latter are yet to be clearly understood. It has to be borne in mind in this connection that iron affects the age-hardening process in Al-Cu alloys in a most adverse way, even if present in very small quantities. Reliable data on the ageing behaviour of some aluminium alloys containing zinc and magnesium at different ageing temperatures have been published in the recent past[1-3]. There is ample scope and urgent need for further systematic investigations in this field. As for the actual ageing mechanism in such alloys, X-ray and electron-optical studies have again been undertaken only in the last few years[5-7]. Correlations between mechanical properties, matallographic characteristics and X-ray data are yet to be attempted for the age-hardening alloys of these compositions. The investigations reported here, which constitute the first phase of a comprehensive programme of research on these alloys, are thus of interest not only to the Indian metallurgical industry, but also to the world of metallographers unravelling the mysteries of precipitation phenomena in aluminium alloys.

EXPERIMENTAL PROCEDURE

Preparation of alloys: The compositions of the alloys studied are given in Table 1. Barring the commercial 75 S alloy, they were prepared from *Indal* aluminium of 99.0 % purity (0.4 – 0.5 % Fe; 0.3 – 0.4 % Si; rest Cu, Mg, Mn, Pb and Ni) and the concerned pure metals. The required quantities of aluminium and other additions for a two-pound casting of each alloy were melted in a graphite crucible in an electrical resistance furnace. For 75 S, a sheet of the commercial alloy was cut to pieces weighing two pounds and then melted like the other alloys. Low-melting metals like zinc and magnesium were wrapped in aluminium foil and added to molten aluminium to avoid losses due to oxidation and volatalisation. Cryolite was used as flux and the melt was degassed before pouring with the solid degassant, Hexachloroethane. The alloys were cast into cylindrical steel moulds of 0.75″ diameter, homogenised at 400°C for about 12 hours, hot-forged to the maximum possible extent and finally annealed for two hours at 300°C. The rods were then machined to a diameter of 0.5″ and cut into specimens of 0.4″ thickness. The alloys were chemically analysed to ensure that the contents of zinc, magnesium, etc., given in Table I, were accurate to ± 0.1 % by weight.

TABLE I

Composition of Alloys subjected to Ageing Studies

No. of Alloy	Percentage by weight of alloying elements					
	Zn	Mg	Cu	Mn	Si	Cr.
1	......	2.0	......	......	4.0	......
2	4.0	2.0	......	......	......	......
3	5.0	2.5	......	......	......	......
4	6.0	2.5	......	......	......	......
5	6.0	3.0	......	......	......	......
6	5.0	2.5	......	0.5	......	......
7	6.0	2.5	......	0.5	......	......
8	5.0	2.5	1.0	......	......	......
9	6.0	2.5	1.0	......	......	......
10 (75S)	5.1-6.1	2.1-2.9	1.2-2.0	0.1-0.3	<0.5	0.15-0.40

Heat Treatment: The alloys were solution-treated at 460 ± 5°C (at 480 ± 5°C for Alloy No. 1 only) for two hours in a Heraeus Muffle Furnace and then quenched in cold water. Ageing treatments were carried out in oil baths whose temperatures could be controlled to within ± 1°C with the aid of a bi-metallic thermostat working in conjunction with a hot wire vacuum switch. Besides room temperature, 100°, 150°, 200° and 250°C were chosen for the study of ageing characteristics.

Mechanical Testing: The Vickers Pyramidal Hardness Tester with a load of five kgms. was used for the determination of hardness immediately after solution heat treatment and after different ageing times, till softening set in. Five hardness readings were taken and the average was determined for the hardness value in every case. Occasionally duplicate specimens were used to check the results. Tensile specimens were prepared from each alloy and the tensile testing was conducted in a Hounsfield Tensometer immediately after solution heat treatment and again after ageing at 100°C to peak hardness. The tensile tests also were repeated in many cases to ensure reliable results.

Metallographic Studies: The influences of homogenizing, solution heat treatment and ageing at different temperatures were studied in each case with the aid of metallurgical microscopes after grinding, polishing and etching with an aqueous solution containing 25% HNO_3 and 2% HF.

EXPERIMENTAL RESULTS

General: The data obtained from the present investigations are given in Figures I to XI and Table II. The results pertain to one Al-Si-Mg alloy, four Al-Zn-Mg alloys, two Al-Zn-Mg-Mn alloys, two Al-Zn-Mg-Cu alloys and the commercial 75 S alloy. Two more Al-Si-Mg alloys were studied in the initial stages, but as comparison between them and the Al-Zn-Mg alloys showed the clear superiority of the latter from the point of view of mechanical properties on ageing, later detailed investigations were confined to alloys containing zinc and magnesium.

Ternary Alloys: As illustrated by the data for an Al – 4% Si – 2% Mg alloy in Table II, controlled additions of silicon and magnesium are also capable of effecting an appreciable improvement in the mechanical properties of Indian aluminium through age-hardening. The two other alloys studied *viz.*, Al – 2% Mg – 1% Si and Al – 1% Si – $\frac{1}{2}$% Mg, reached maximum hardness values of only 70 and 105 VPN respectively. Such ternary alloys age quicker than the Al-Zn-Mg alloys, but attain peak hardness and tensile strength values far lower than the latter.

The Hardness/Ageing Time curves of Al-Zn-Mg alloys (Figs. I to V) display the following general characteristics:

(*a*) There is a definite "incubation period" before the increase in hardness begins. This period varies from a few seconds to a few hundred minutes and decreases with increase in alloying content as well as ageing temperature. The Al – 4% Zn – 2% Mg alloy takes about five hundred minutes to show any appreciable increase in hardness at room temperature, after solution heat treatment, but the Al – 6% Zn – 3% Mg alloy starts hardening within seconds even at 100°C.

(*b*) There is a continuous increase in hardness after the incubation period till the peak hardness is attained. Although there is an appreciable

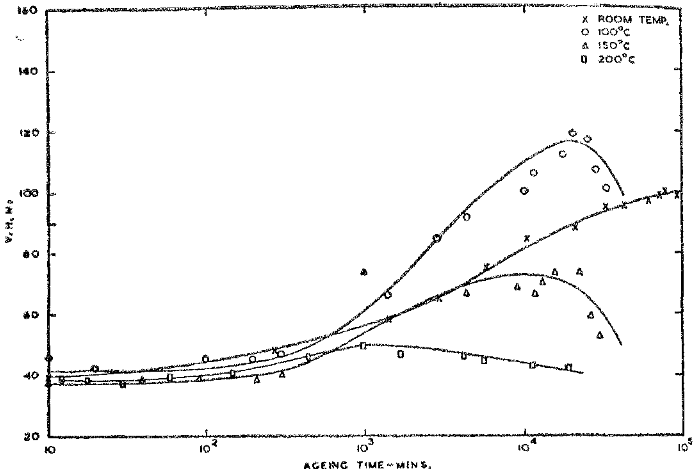

FIG. I
Hardness/Ageing Time curves for Alloy 2 (2 % Mg—4 % Zn—Al)

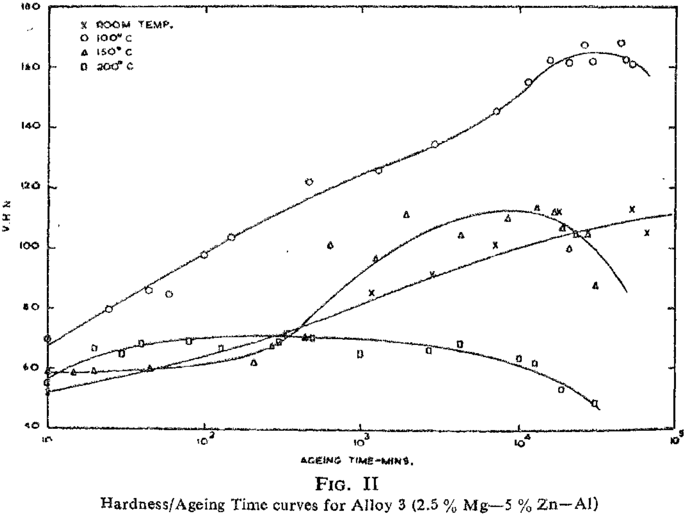

FIG. II
Hardness/Ageing Time curves for Alloy 3 (2.5 % Mg—5 % Zn—Al)

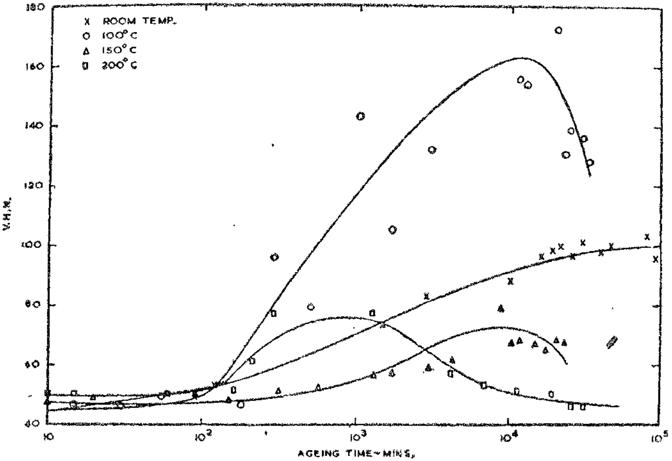

FIG. III

Hardness/Ageing Time curves for Alloy 4 (2.5 % Mg—6 % Zn—Al)

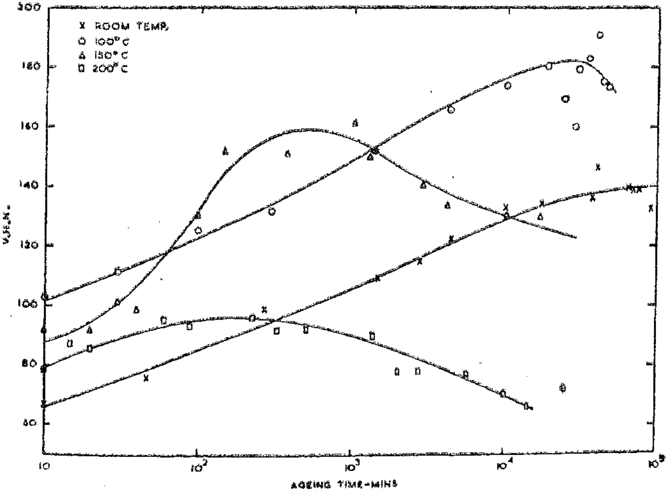

FIG. IV

Hardness/Ageing Time curves for Alloy 5 (3 % Mg—6 % Zn—Al)

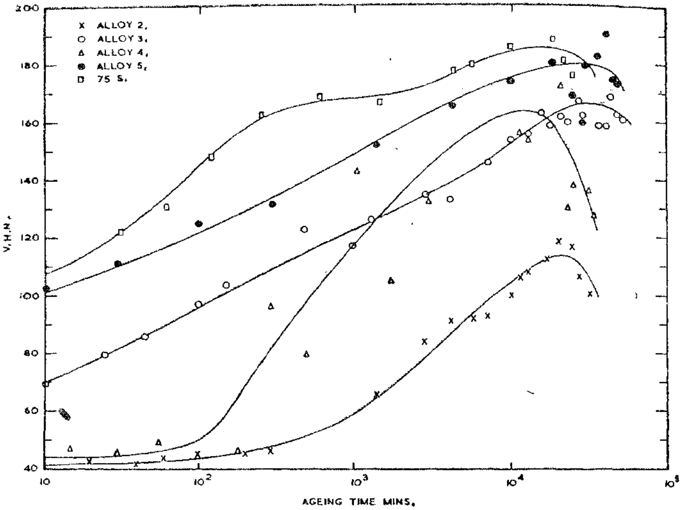

FIG. V

Hardness/Ageing Time curves at 100°C (Ternary Alloys)

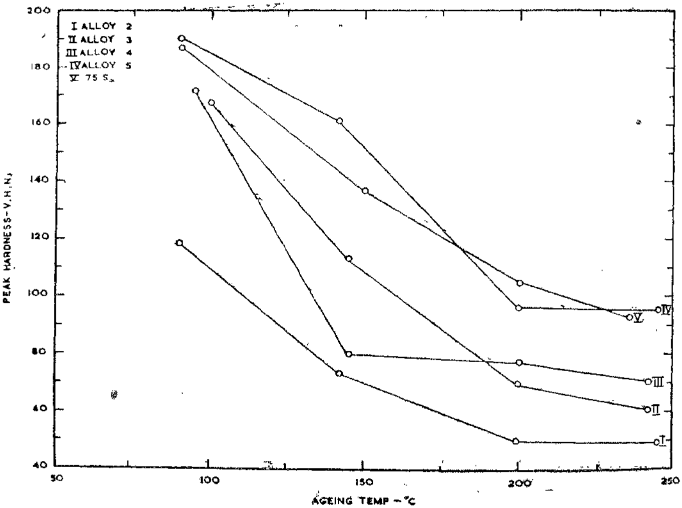

FIG. VI

Peak Hardness/Ageing Temperature relationships (Ternary Alloys) scatter of the hardness values in some cases with reference to the curves shown in figures I to V, the increase in hardness is definitely without intermediate peaks or changes of slope in the Hardness/Ageing Time curves. As shown in Fig. VI, the peak hardness is higher for lower ageing temperatures and higher alloying contents. The maximum hardness is reached in a few hours at 200°C and 250°C, in a few days at 100° and 150°C and only after many weeks or months at room temperature.

(*c*) There is a softening of the alloy after the attainment of peak hardness, but this process is slow at lower ageing temperatures and practically undetectable at room temperature.

On the basis of the above observations as well as the findings of earlier workers[1, 3], ageing for 10 days at 100°C was chosen as an ideal treatment for comparing the influence of ageing on mechanical properties of the Al-Zn-Mg alloys. The results in Table II and the curves in Figure V bring out the marked and steady increase in tensile strength and hardness with alloying content as well as the decrease in ductility to a minimum value in aged alloys.

Quaternary Alloys : As copper and manganese are present in commercial high-strength Al-Zn-Mg alloys, a study was undertaken of the effects of small

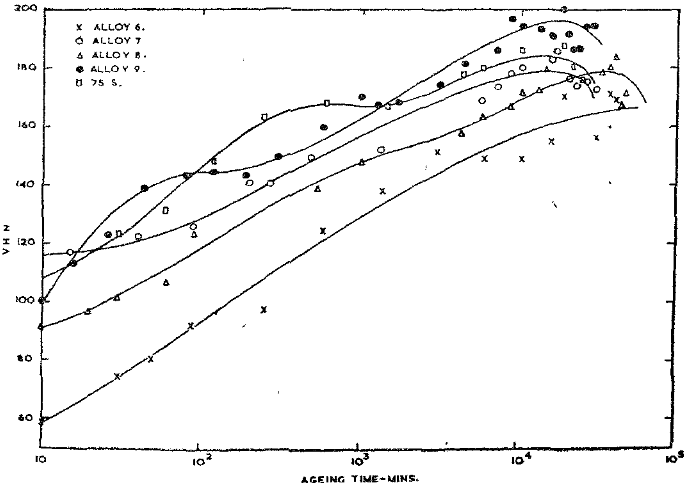

FIG. VII

Hardness/Ageing Time curves at 100°C (Quaternary Alloys) percentages of these two elements on the ageing characteristics of two selected Al-Zn-Mg alloys at 100°C. Fig. VII and Table II show the Hardness/Ageing Time curves and peak mechanical properties respectively for two alloys containing 0.5% manganese, two alloys containing 1.0% copper and the commercial 75 S alloy.

TABLE II

Influence of Ageing on the Mechanical Properties of Alloys listed in Table I

S. H. T.: Solution Heat Treated *i.e.* soaked at 460°C for two hours and quenched in cold water

Aged: Aged at 100°C for 10 days after solution heat treatment

No. of Alloy	Conditions	Ultimate Tensile Strength (psi)	Hardness (VPN)	% Elongation
1*	S.H.T.	22,100	46	15
	Aged	30,200	108	6
2	S.H.T.	23,100	40	25
	Aged	42,000	122	8
3	S.H.T.	24,200	48	17
	Aged	44,800	168	2
4	S.H.T.	24,500	51	13
	Aged	48,400	176	1
5	S.H.T.	25,300	62	8
	Aged	57,800	190	1
6	S.H.T.	24,400	58	14
	Aged	45,200	171	2
7	S.H.T.	24,600	59	10
	Aged	47,800	180	1
8	S.H.T.	24,700	58	10
	Aged	49,200	184	2
9	S.H.T.	24,600	57	7
	Aged	57,500	203	2
10 (75S)	S.H.T.	30,800	82	12
	Aged	68,400	190	3

* Alloy No. 1 was solution-treated at 485°C and aged for only 5 days at 100°C.

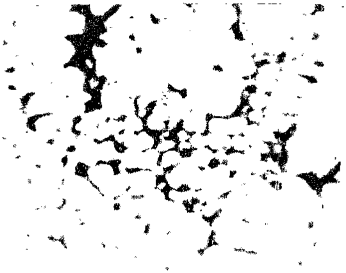

FIG. VIII
Alloy No. 5; Homogenized × 250

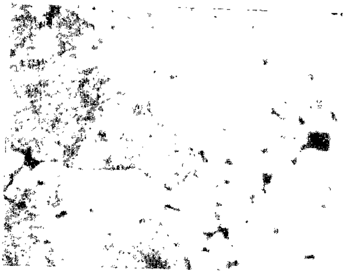

FIG. IX
Alloy No. 5; Solution Heat-treated × 250

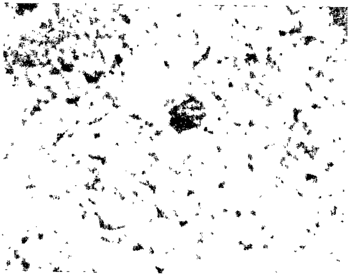

FIG. X
Alloy No. 5; Overaged at 200°C × 250

FIG. XI
75 S Alloy; Aged for 20 minutes at 200°C × 350

Manganese does not seem to have any noticeable effect on the ageing behaviour of the ternary alloys, but copper seems to modify the Hardness/Ageing Time curves of these alloys by accelerating the initial rate of increase of hardness, introducing a change of slope due possibly to the superimposition of two ageing processes and leading to a greater peak hardness. The Al – 6 % Zn – 2.5 % Mg – 1.0 % Cu alloy shows even a higher hardness than 75 S under identical ageing conditions, but its tensile strength and elongation values are slightly inferior to those of the latter.

Microstructure: Some precipitation was found to occur along the grain boundaries in all Al-Zn-Mg alloys during the solution heat treatment, although the precipitate could be easily detected only in alloys of higher Zn-Mg content (Figs. VIII and IX). This precipitate could be identified as the ternary phase $(Al, Zn)_{49} Mg_{32}$ from the available data on the etching characteristics of different phases in Al-Zn-Mg alloys[6,8]. Further precipitation during ageing could not be followed microscopically, although there seemed to be an increase of the grain-boundary precipitate on ageing at 100°C and above. In the over-aged and softened alloys (Fig. X), evidence for precipitation within the grains was available, but no conclusions could be drawn regarding the precipitation mechanism. Occasionally a Widmanstaetten pattern of the precipitate was noted in the 75 S alloy (Fig. XI).

CONCLUSIONS

(*a*) It is possible to produce age-hardenable alloys from Indian commercial aluminium by addition of silicon and magnesium. Such Al-Si-Mg alloys are inferior to the Al-Zn-Mg alloys in mechanical properties, but may find suitable application as casting alloys of moderate strength. Increase of Si-Mg content in such alloys does not lead to any proportional improvement of the mechanical properties on ageing.

(*b*) High-strength, age-hardenable alloys may be produced from Indian aluminium by controlled additions of zinc and magnesium. Indian aluminium has a tensile strength of about 13,000 psi and a hardness of VPN 20. These values can be increased to about 58,000 psi and VPN 190 respectively by the addition of 6 % zinc and 3 % magnesium and a carefully planned ageing treatment. The ductility of Indian aluminium suffers markedly by this alloying and ageing, and further Zn-Mg additions may well be expected to lead to brittle alloys, as has been reported by earlier workers[2].

(*c*) The Hardness/Ageing Time curves are of the same type for Al-Zn-Mg alloys prepared from Indian aluminium as for these ternary alloys studied elsewhere[1,4]. They are generally characterised by an incubation period, a gradual increase to maximum hardness and a final softening. The increase in hardness is very striking, being of the order of at least 200 % in every case.

(*d*) The addition of 0.5 % manganese does not effect the ageing characteristics of the Al-Zn-Mg alloys in any marked way, as concluded by an earlier investigation[1].

(*e*) The addition of 1.0 % copper improves the rate of increase of hardness as well as the peak hardness in Al-Zn-Mg alloys and also leads to the superimposition of two distinct ageing processes. These effects are not perhaps surprising, as copper by itself confers precipitation hardening characteristics on aluminium, but they have not all been reported by previous workers[1, 7]. Earlier evidence on the influence of copper on peak hardness is conflicting, but the modification of the ageing process leading to a change of slope in the Hardness-Ageing Time curves of Al-Zn-Mg-Cu alloys as well as the 75 S alloy seems to have been just overlooked by the earlier workers.

(*f*) All the Al-Zn-Mg and Al-Zn-Mg-Cu alloys prepared from Indian aluminium for present studies offer promise as high-strength casting alloys. The Al – 6 % Zn – 2.5%Mg – 1 % Cu alloy especially is comparable to the well-known 75 S alloy in all mechanical properties except ductility in the solution heat-treated condition. The ductility, which is perhaps impaired by the impurities in Indian aluminium, may be restored by trying other additions besides copper and manganese. It is re-assuring, however, that the general ageing process is not so adversely affected in these alloys by the presence of iron, as in Al-Cu alloys.

(*g*) The increase in hardness is obviously due to sub-microscopic precipitation in Al-Zn-Mg alloys, as concluded by all earlier workers. The presence of a microspic grain boundary precipitate in the solution heat-treated condition has not been indicated by earlier investigators, and may be due to the impurities in Indian aluminium in the present studies.

(*h*) Although there is every possibility of developing satisfactory high-strength alloys from Indian aluminium, even without copper, further X-ray and electron-optical studies leading to a clear picture of the ageing process in Al-Zn-Mg alloys with or without other elements seems to be necessary for a successful development in India of a series of light alloys with desired properties.

REFERENCES

1. Polmear, I. J. .. .. *J. Inst. Metals*, 1957, **86**, 113, 1960, **89**, 51 *and* 1961, **89**, 193.
2. Varley, P. C., Day, M. K. B. and Sendorek, A. .. *Ibid.*, 1958, **86**, 337.
3. Polmear, I. J. and Scott-Young, P. .. *Ibid.*, 1958, **87**, 65.
4. Chadwick, B., Muir, N. B. and Grainger, H. B. .. *Ibid.*, 1957, **85**, 161.

5. Graf, R. .. .. *Compt. rend.*, 1956, **242**, 1311 and 1957, **244**, 337.

6. Mondolfo, L. F., Gjostein, N. A. and Levinson, D. M. *Trans. Amer. Inst. Min. Met. Eng.*, 1956, **206**, 1378.

7. Thomas, G. and Nutting, J. .. *J. Inst. Metals*, 1959, **87**, 429.

8. Strawbridge, D. J., Hume-Rothery, W. and Little, A. T. *Ibid.*, 1947, **74**, 191.