The Effect of Misch Metal Additions on the Structure and Workability of Al-Mg (7-10°/.) Alloys

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• N the alloying elements used in aluminium alloys, copper was one of the earliest employed commercially and for many years it has been the principal one. Aluminium-copper alloys to which manganese, magnesium or silicon has been added, belong to the important group generally known as "Duralumin".

The binary alloys of aluminium with magnesium attracted the interest of investigators as early as 1900. There have been numerous attempts to utilise for general purposes alloys containing as much as 10% magnesium; alloys containing up to 30% magnesium have been used for special purposes.

Cast and wrought alloys of aluminium with magnesium are characterised by their high resistance to corrosion in certain media, high room and elevated temperature tensile strength and good machineability, together with their inherent light weight. These alloys are extensively used in applications requiring these properties, such as in structural members in marine vessels and aircraft, in brake-shoes, etc. Table I shows some of the commonly used aluminium-magnesium alloys, their specific characteristics and typical uses. However, aluminium-magnesium alloys with magnesium contents higher than about 6% are used only in the cast form because they are not normally hotworkable. Thus, the advantages of high strength, excellent machineability, and corrosion resistance cannot be utilised in the wrought condition.

The beneficial effects of the addition of rare earth metals, including cerium, on aluminium and magnesium have been studied by several authors. There are conflicting reports about the effects of addition of cerium or cerium misch metal to aluminium and its alloys. Schofield and Wyatt¹ and Dennison and Tull² have observed grain refinement of the metal, while Bowen and Bernstein³ found little or no refining or coarsening effect, especially in aluminium-copper alloys. Similarly Hodge et. al.⁴ did not find any effect of cerium addition on the elevated temperature properties of cast aluminium alloys. On the other hand, Lorig and co-workers⁵ have developed an aluminium misch metal alloy (called SAM) which contains 11% misch metal and has superior high temperature stressrupture properties in the range 700°-800°F. Russel⁶ has patented an aluminium alloy, containing 10-12% misch metal (50% Ce). 1-3% Si and up to 5% Cu, which is claimed to have high temperature strength in the cast condition.

Addition of cerium or misch metal to magnesium extrusion alloys has been shown by Grube and co-workers⁷⁻⁹ to impart to them better high temperature properties such as high creep and fatigue resistance at 600°-700°F. They also observed that the tensile properties of these alloys varied directly with the cerium content, and that the optimum range of misch metal addition was 1.4% to 2.4%. Danks¹⁰ studied the effect of adding rare earth metals to magnesium-zirconium alloys; an addition of 3% misch metal was observed to confer high fatigue and creep resistance on these alloys. McDonald11, 12 observed that the addition of rare earth metals to magnesium produced cast alloys having elevated temperature properties markedly superior to those obtainable with the older alloys. By suitable heat treatment, creep resistance of 8,000 psi at 400°F could be developed compared with 1,500 psi for magnesium-aluminium-zinc type alloys. Here again the optimum concentration of misch metal was 3%. Mellor and Ridley¹³, and McDonald¹⁴ have attributed the improvement in the high temperature properties to the formation of fine precipitates in the grain boundaries. Leontis15 has found that addition of cerium to magnesium-thorium alloys introduces a magnesiumcerium compound into the structure, which forms a coarse eutectic with the magnesium solid solution. Mellor and Ridley13 have further observed that the presence of manganese in magnesium alloys restrains such coarsening effect of the Mg9 Ce in the eutectic.

No work has, however, been reported so far on the influence of the addition of rare earth metals on either cast or wrought alloys of aluminium with

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magnesium. A systematic study has been initiated at this Laboratory with the object of developing aluminium-magnesium alloys to replace aluminium-copper alloys (duralumin type), in view of the fact that at the present rate of consumption, the known reserves of copper in India would not last for long. On the other hand, India has plenty of rare earth metals available from the monazite residues left after the extraction of the atomic energy metals : uranium, thorium, etc. The present paper deals with the observed effects of the addition of misch metal (up to 5%) to binary Al-Mg (7-10%) alloys (at present used only in the cast state), on their structure, workability, tensile strength and hardness.

Experimental procedure

Preparation of the alloys: The alloys were obtained by melting together calculated quantities of aluminium, magnesium (both of commercially pure quality) and misch metal (51% Ce), in an oil-fired furnace, using "Salamander" graphite crucibles. In the initial stages, degassing of the melt was done with dry nitrogen gas but this did not materially help in reducing the porosity in the castings; the resulting ingots were rather brittle and showed very low tensile strength. Degassing with chlorine, although somewhat better than that with nitrogen, was also not found to be completely satisfactory. Recourse was then taken to degassing with proprietory degassers, specially recommended by the manufacturers for high magnesium content aluminium-magnesium alloys. The melt was cast into cylindrical $(1\frac{1}{8}^{"}$ dia.) and square $(2^{"} \times 2^{"})$ section cast iron moulds for tensile test specimens and hot working respectively. Care was taken to avoid the undesirable introduction of gases into the melt during melting, degassing and pouring processes.

Microstructure

For a study of microstructure the specimens were polished on emery paper down to 000 grade, followed by hand polishing on "selvyt" cloth. In the case of cast alloys, discs of about 1" dia were used for the study, while for wrought alloys specimens were mounted in bakelite moulds from both the rolled surface and transverse section perpendicular to both the surface and the rolling direction.

Working

During preliminary work carried out at various temperatures in the solid solution range, e.g. at 380°C, 400°C, 425°C and 450°C, on the workability of untreated Al-7% Mg alloy, it was established that a suitable temperature for working these alloys would be around 450°C. If the temperature was allowed to rise above 500°C, even for a short period, precipitation of a finely dispersed phase (Mg₂Si) occurred both in the grain boundaries and within the grains (Fig. 1) resulting in a failure of the ingot during working. The square section (2" × 2") ingots were, therefore,

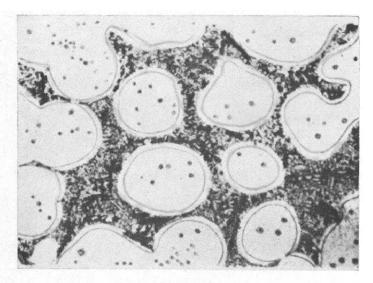


Fig. 1. Showing precipitation of Mg ₂Si in the grain boundaries on heating beyond 500°C. ×240

soaked at about 460° C for 4 hours to homogenize the mass, before being worked. Forging and rolling were carried out in the range $460-400^{\circ}$ C. The material was kept in the furnace again for a minimum period of about 20 minutes before working was continued. The ingots were first reduced to a thickness of 0.5" to 0.8" by hot forging, and were then further reduced to about 0.125" thick sheet by hot-rolling. Stages at which the alloys showed signs of failure were noted, sound portions separated and worked further. Ease of reduction in forging, and rolling determined by reduction in size in each pass, was taken as a criterion of the workability of the particular alloy.

Tensile strength and hardness

Tensile test specimens were made to BSS 18:1950 by machining from the cylindrical ingots, from which discs about 1" dia. and 1/8" thick were also cut for study of cast structure, and as cast hardness. Tensile strength of these specimens was measured in an "Avery" tensile strength testing machine. Flat tensile test specimens were made (also to BSS 18:1950) from the rolled sheets and tested in an "Amsler" tensile testing machine.

For hardness measurements, the specimens were mounted and polished as for study of microstructure, except that the finishing was not done to fineness.

Results

The actual chemical analyses, particularly showing the magnesium and cerium contents of the alloys are given in Table II which also gives the order of the impurities present.

TABLE I									
Common	casting	and	wrought	aluminium-magnesium	alloys.				

	A.S.T.M.	DCC		Mechanical properties					
SI. No.	or Al. Assocn. designa- tion	B.S.S. desig- nation	Nominal composition	U.T.S. p.s.i.	Elonga- tion in 2″g.l.	Fatigue strength p.s.i.	Brinnel hardness	Outstanding charac- teristics	Typical uses
A-	Casting	alloys							
1.	G4A	LM5	4% Mg	25,000 (C)	9.0	5,500	50	Excellent resist- ance to corrosion and tarnish.	Dairy and food handl- ing equipment, cook- ing utensils, chemical fittings, hardware, etc.
2.	G8A	_	8% Mg	45,000 (C)	8.0	23,000		Excellent resist- ance to corrosion and tarnish, excel- lent strength and ductility.	Aircraft fittings, wheel- flanges and brake- shoes, marine fittings, hardware, outboard motor brackets.
3.	G10A	LM10	10% Mg	46,00 (W)	0 14.0	7,000	75	Highest strength of aluminium sand casting alloys, ex-	Refrigerator fittings carburator b o d i e s, thin section general
								cellent machine- ability and corro- sion resistance.	purpose castings.
4.	GS42A		4% Mg, 1.8% Si	20,00 (C)			50	Good corrosion resistance.	Pipe fittings for marine and general use, cook- ing utensils.
5.	GZ42A		4% Mg, 1.8% Zn	27,000 (C)			60	Good resistance to corrosion and tarnish.	Cooking utensils.
B-	-Wrough	t alloys	S.						
6.	5,250	H10 H20 H30	0.4-1.5% Mg, 0.1-0.4% Cu, 0.4-0.8% Si, 0.7% Fe	24,600 (O) 40,300 (WP)		 17,900	90-100	High work-harden- ing capacity, high strength, better formability and excellent corro- sion resistance.	Trim mouldings, in- side and outside panels for refrigerat- ors, window frames, auto-trailors, kitchen cabinets, machinery parts, etc.
7.	5,086 5,083	N5/6	3·5–5·5% Mg, 0·6% Si, 0·7% Fe	38,000	12-18	23,000	70	High strength, and corrosion resis- tance, excellent weldability.	In sheet form and as structural members for marine vessels, truck and trailor bodies, chemical stor- age tanks.
8.	5,052		2.5% Mg, 0.25% Cr	29,000 (O)	30	18,000	45	High strength.	Pressure tubes and ves- sels, fan blades, tanks, fittings, aircraft engine, cylinder baffles.
9,	5,056	N6	4·5-5·5% Mg, 1·0% Mn, 0·7% Fe, 0·6% Si	31,500 (O)	18	18,700	55	High strength at elevated tempera- tures, good weld- ability.	Fuel tanks, structural uses, welded dump truck bodies.
10.	5,454		2 [.] 4-3 [.] 0% Mg, 0 [.] 5-1 [.] 0% Mn, 0 [.] 4% max Si + Fe	36,000 to 48,000	8-22		62-81	Maximum high temperature stren- gth in Al-Mg al- loys, resistant to high temperature corrosion and stress corrosion, welding grade alloys.	cal and process

TABLE II

Chemical	composition	of different	alloys
	(Base-Alu	minium).	

	1		
Heat No.	Magnesium per cent	Cerium per cent	Other impurities per cent
CE 1	7:43	0.00	Si 0.2-0.3, Fe
		0.50	0 [.] 2-0 [.] 3, Mn, La.
CE 2	7.08	0.68	do
CE 3	7.21	1.30	do
CE 4	7.87	1.71	do
CE 5	7.54	2.39	do
CE 6	7.54	2.87	do
CE 7	10.22	0.00	do
CE 8	10.92	0.89	do
CE 9	10.27	1.09	do
CE 10	10.49	1.78	do
CE 11	10.27	2.32	do
CE 12	11.14	2.05	do
CE 13	8.31	0.00	do
CE 14	8.52	0.23	do
CE 15	8.08	1.02	do
CE 16	8.08	1.44	do
CE 17	8.52	2.20	do
CE 18	8.31	2.79	do
CE 19	9.45	0.00	do
CE 20	9.23	0.73	do
CE 21	9.13	1.20	do
CE 22	9.40	1.86	do
CE 23	9.07	2.93	do
CE 24	9.25	2.93	do

Microstructure

The as-cast microstructure of the untreated Al-Mg (7-10%) alloys was similar in all cases (Fig. 2). The

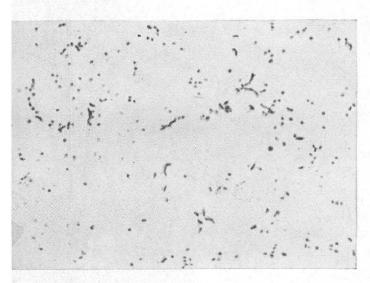
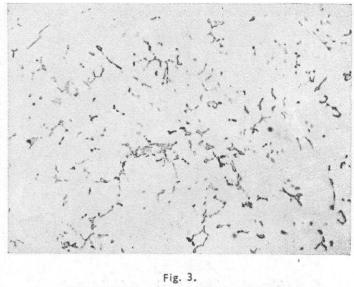


Fig. 2. Untreated Al-Mg alloy, showing presence of Al₃Mg₂ and Mg₂Si. ×240



Al-Mg cast alloy with 1% misch metal shows presence of cerium-phase. ×240

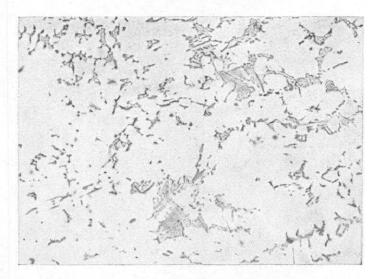


Fig. 4. Cast-AI-Mg alloy with 3% misch metal shows increase in cerium containing phases. ×240

only phases present were the β -Al-Mg and Mg₂Si (from the Si present as impurity in aluminium). When misch metal was added, a new phase appeared (Fig. 3) along with the two previously observed phases. With increase in the misch metal content, from 1% to 5% the amount of the Al-Mg phase gradually decreased and there was a gradual increase in the new phase (Figs. 4, 5) until practically no Al-Mg phase was observed (Fig. 5). The new phases which could be due to the formation of Mg₉Ce or Al₄Ce or both or to a ternary Al-Mg-Ce compound have a typical skeleton type structure. Identification of these new phases was not possible by metallographic examination and it is

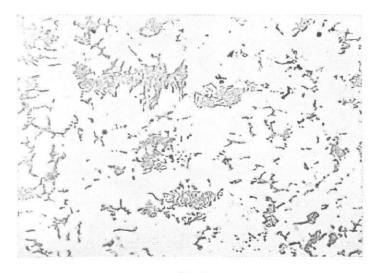


Fig. 5. Cast Al-Mg alloy with 5% misch metal (Al, Mg, absent, more of cerium containing phases). ×240



Fig. 6. Untreated AI Mg alloy—rolled sheet—presence of Al Mg. and Mg. Si. ×240

proposed to study their structure by either the X-ray diffraction or the electron diffraction technique.

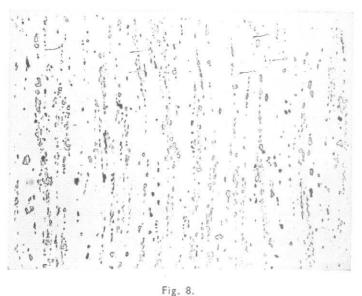
The microstructure of the rolled sheets also followed the same pattern as in the case of the cast specimens, except that the grain size was much smaller in this case possibly due to the homogenisation treatment followed by mechanical working. The untreated alloy showed the presence of the β -Al-Mg and Mg₂Si phases (Fig. 6) and as the misch metal was added and its content increased, the quantity of the cerium containing phases showed a gradual increase, with the content of Al-Mg phase getting correspondingly reduced (Figs. 7, 8, 9). In the wrought condition, the cerium containing phases could be seen separately (c.f. Fig. 9). It was, however, not possible to identify the phases by microscopic examination alone.

Workability

Workability of the various alloys was studied by actually hot forging and rolling ingots to a predetermined size of 0.125" thickness. The ease of reduction and the amount of reduction per pass in rolling were taken as a qualitative criterion of workability. The effect of adding varying quantities of misch metal to



Fig. 7. Rolled Al-7% Mg alloy with 3% misch metal. $$\times 240$$



Rolled AI-9% Mg alloy with 4% misch metal. ×240

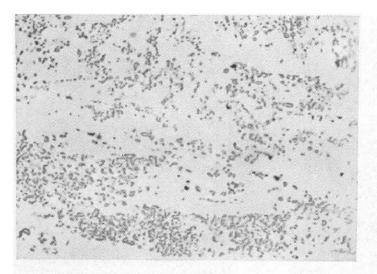


Fig. 9. Rolled AI-8% Mg alloy with 5% misch metal. $\times 240$

the various Al-Mg alloys (normally unworkable) is summarised below :

- (i) Al-7% Mg alloy: The untreated as well as the misch metal treated ingots could be forged and finally rolled down to thickness of about 0.125". It was observed that the workability of the alloy improved with increase in the misch metal (or cerium) content.
- (ii) Al-8% Mg alloy: The untreated Al-8% Mg alloy ingots could be hot forged to slabs of about 0.68" thickness, but further forging resulted in the appearance of longitudinal cracks along the entire length of the slab. Further forging was therefore discontinued.

The alloy containing 1% misch metal could be hot forged to a thickness of 0.5'', after which rolling of the slab was attempted. The slab failed resulting in a crocodile type of crack (Fig. 10*a*). This effect was noticed in several slabs of this composition.

Ingots of Al-8% Mg alloy with additions of 2-5% misch metal could be successfully hot forged and rolled down to about 0.125" thick sheet. The amount of reduction per pass was found to increase with increase in the misch metal content.

(*iii*) Al-9% Mg alloy: The untreated ingots of this composition could be forged to a thickness of about 1", but attempts at further reduction in size resulted in development of cracks in the slab.

The ingots containing 1% added misch metal could be forged to 0.67'' but it failed in the first pass in rolling, showing a crocodile crack (Fig. 10b).

With misch metal content at 2 and 3%, the ingots could be hot forged to about 0.6'' thickness, and could also be further rolled to

about 0.4'' thickness. In the next pass in rolling, however, the slabs in both cases crumbled to pieces, The cause of this failure is being separately examined. In the case of the alloy containing 4% misch metal, although the ingot could be ultimately hot worked

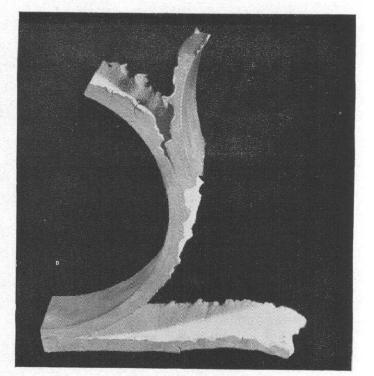


Fig. 10a.

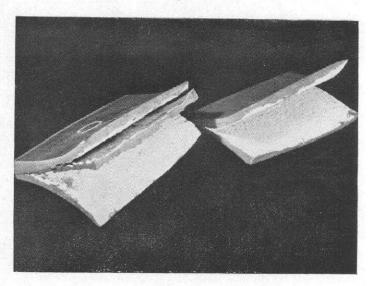


Fig. 10b. Failure of high magnesium content Al-Mg alloy during rolling—showing crocodile cracks. (10a). Al-8% Mg alloy. (10b). Al-9% Mg alloy.

down to about 0.125" thickness, edge-cracks developed in the slab during rolling, and the cracked portions had to be discarded before rolling was continued. With misch metal content at 5%, the ingot could be successfully forged and rolled without any visible failures.

(iv) Al-10% Mg alloy: The untreated alloy could be hot worked to about 0.75", when the forging was done very cautiously. Further rolling caused appearance of cracks on the edges. Continued rolling, after discarding the cracked portions resulted in a crocodile failure in the slab (similar to Fig 10).

Ingots with 1% added misch metal did not stand hot forging at all, as cracks developed at several places during forging without any reduction in the section of the ingot. When the misch metal content was raised to 2 and 3%, the ingots could be hot forged to about 0.8% thickness and further hot rolled to about 0.2" thick sheet with considerable difficulty. Extensive edge cracks appeared in the 2% alloy after rolling to 0.5" thickness and further rolling was done only on the small uncracked portion. In the case of the 3% alloy, cracks appeared in the very first pass in hot rolling from 0.8'' thickness, but an unaffected portion could be rolled down to 0.2'' when handled very carefully. At this stage, a part failed showing a fracture somewhat similar to alligatoring. When the misch metal content was raised to 4 and 5%, the ingot could be reduced from the initial $2'' \times 2''$ section to only about 1" thickness, but the slabs showed severe edge cracks, rendering further working impossible.

Tensile strength

The effect of addition of up to 5% misch metal on the as-cast tensile strengths of different Al-Mg alloys with magnesium contents of 7, 8, 9 and 10% is shown graphically in Fig. 11. It will be seen that in all cases the tensile strength of the alloys initially shows a fall with addition of misch metal. The reduction in tensile strength continued till a misch metal addition of 2-3% is reached, after which the tensile strength again showed a rise.

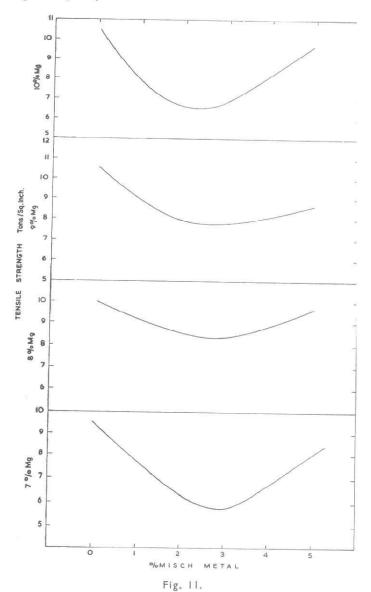
The curve for fall and rise in tensile strength was very steep in the case of the Al-10% Mg alloy, with the minimum of the curve at a little above 2% misch metal. This fall in tensile strength at 2-3% misch metal content may have some correlation with the workability of the alloy.

Fig. 12 shows a comparison between the tensile strengths of the as-cast and wrought Al-7% Mg alloy, as affected by the addition of varying amounts of misch metal. Whereas the curve for as-cast tensile strength showed a depression in the region of 2-3% misch metal, the tensile strength of the wrought alloys showed a continuous increase.

Hardness

Hardness of the as-cast and rolled specimens was determined in a Vickers Hardness testing machine. Hardness in the case of the rolled specimens was measured both on the surface and on transverse section perpendicular both to the surface and the rolling direction. The results are shown in Table III which gives comparative values of hardness of as-cast and rolled specimens from the same heat. (Average values are mean of not less than five measurements).

In general, the hardness increased with an increase in the misch metal content in both cast and wrought conditions, the values in the as-cast condition being very much lower than those of wrought form. The variation between the minimum and maximum values was also greater in the as-cast than in the corresponding wrought specimens.

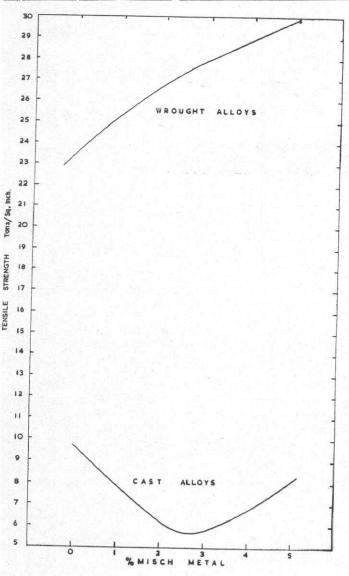


Effect of misch metal on tensile strength of Al-(7-10%) Mg alloys.

 TABLE III

 Hardness of cast and wrought specimens (V.P.N.).

					Wrought specimens							
		Cast specimens		Surface			Transverse section					
Heat	No.	Average	Minimum	Maximum	Average	Minimum	Maximum	Average	Minimum	Maximum		
CE	1	77.4	59.1	82.9	103.0	100.0	107.0	111.0	108.0	114.0		
CE	2	74.4	67.0	80.5	111.6	110.5	114.0	114.6	112.0	117.0		
CE	3	74.4	72.4	81.8	119.3	116.0	122.5	117.0	116.5	118.5		
CE	4	88.8	83.5	96.2	117.0	114.0	124.0	117.0	114.0	126.0		
CE	5	96.2	93.6	101.5	121.4	118.0	123.6	125.5	121.0	128.0		
CE	6	97.8	93.5	101.0	127.0	126.0	128.5	125.0	124.0	126.0		
CE	15	90.2	85.7	94.3	106.3	104.0	107.8	102.3	99.5	107.0		
CE	16	91.8	89.4	94.3	106.8	106.0	109.5	108.8	108.5	113.0		
CE	17	95.4	87.1	99.5	114.5	110 0	119.0	123.5	122.0	126.0		
CE	18	99.2	97.1	102.0	123.6	120.0	122.0	132.0	127.0	140.0		
CE		102.6	101.0	106.0	102.2	115.0	126.0	139.0	135.5	146.0		
CE		105.2	104.0	106.0	120.8	118.0	122.0	124.0	123.5	126.0		



Discussion

The preceding results show that addition of misch metal to aluminium-magnesium alloys, with magnesium content between 7 and 10% imparts improved properties to the alloys. The as-cast microstructure changes considerably inasmuch as the Al₃Mg₂ (or β —Al-Mg) content decreases, and a new cerium containing phase or phases is present in increasing quantities.

The workability of these alloys is improved progressively with an increase in the misch metal content, possibly because of the elimination or reduction below a critical value of the Al_3Mg_2 phase, which is perhaps responsible for its unworkability particularly when present in larger quantities.

The tensile strength of all the cast alloys shows an initial decrease with misch metal additions up to 2-3%, beyond which it again rises. The lowering of the tensile strength in this region may be due to the balancing of the Al₃Mg₂ and the cerium containing phases, and may be, in some way, responsible for the improved workability of the alloys. This is particularly brought out in the case of the Al-10% Mg alloys, which is only somewhat workable when misch metal is added in the range 2-3% (where the as-cast tensile strength is at a minimum value) (c.f. Fig. 11) but is again unworkable with higher additions of misch metal. The tensile strength of the wrought alloy shows generally an increase with higher misch metal additions (Fig. 12).

Hardness of the cast as well as wrought alloys generally shows an increase with the increase in the amount of misch metal added. This may be due to the higher hardness of the cerium containing phase. The reduction in variation between the maximum and the minimum values of hardness may have been caused by

Fig. 12.

Influence of misch metal additions on the tensile strength of cast and wrought AI-7% Mg alloy.

the reduction in grain size and more even distribution of the harder phases, during working.

The cause of failure of the various ingots with edge cracks or crocodile effect during hot forging and rolling has not so far been definitely established. Ransley and Talbot¹⁶ have attributed such failures to embrittlement of the high magnesium content Al-Mg alloys by "free" sodium. However, analyses of the various samples that cracked, did not show the presence of estimatable quantities of sodium. There may, therefore, be some other reason for these failures. It is proposed to investigate this aspect in greater detail, and report the results separately.

Conclusions

1. Addition of misch metal to Al-Mg $(7-10^{\circ})$ alloys changes their as-cast microstructure, inasmuch as the β -Al-Mg phase is progressively eliminated and new phases, essentially containing cerium are formed.

2. The addition of misch metal to Al-Mg (7-10%) alloys imparts to them improved hot-workability and increases their hardness.

3. Addition of 2-3% misch metal to Al-Mg (7-10%) alloys has been found to be optimum for their hot workability, particularly in the case of the Al-10% Mg alloy.

4. The tensile strength of the cast Al-Mg (7-10%)alloys is reduced by the addition of misch metal up to about 2-3%, above which it again shows a rise. The tensile strength of the wrought specimens, on the other hand, continuously rises with an increase in the quantity of misch metal added, and reaches values comparable to those for steel or duralumin (\sim 30 tons per sq in.)

Proposed work

In the light of the above work, it is proposed to study the new phases formed by the addition of misch metal to the high magnesium content Al-Mg alloys, by X-ray or electron-diffraction technique. The ageing characteristics, high temperature mechanical properties and corrosion resistance of these alloys will be examined. Development of new compositions based on aluminium-magnesium alloys, to replace "Duralumin" type of Al-Cu alloys for certain specific purposes, will also be taken up.

Acknowledgments

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testing, and to Sarvashri S. P. Bhadra and S. K. Mukherjee, of the General Metallurgy Division, for technical assistance during the course of the investigation.

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DISCUSSIONS

Mr. H. P. S. Murthy, NML: I would like to compliment the authors on the rather detailed work conducted and also the fact that the authors have found some proof against the earlier work reviewed concerning the case of crocodile cracking.

Mr. M. S. Chopra, NML: From the photomicrographs projected, I think after 3% misch metal addition and rolling only two or possibly three phases are discernible. Could Dr. Trehan please let me know the basis of distinguishing the four phases ? 1 think it may be due to the effects of pits left over after polishing. What was the basis on which the phases were distinguished? Was it colour or something else?

Dr. Trehan (Author): In my opinion, it is not due to pits left after polishing. Four phases can be distinctly seen in the alloy to which only 1% misch-metal had been added (Fig. 3). The quantity of the fourth phase, i.e. the Al-Mg phase got reduced as the misch-metal content went up. That was also just what we actually observed under the microscope. The phases were distinguished from the colour in the unetched specimens.