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MICROSTRUCTURE AND MECHANICAL PROPERTIES OF HOT ROLLED HIGH LI CONTENT ALUMINIUM ALLOYS PRODUCED BY SPRAY-CASTING

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Abstract

Al-Li-Zr alloys have been produced by spray-casting with compositions based on the solubility limit of Li in Al in order to maximise their specific properties. Anticipated problems with increasing the Li level to 4 wt% have been addressed at a microstructural level by TEM, with reference to the need for hot working to different product section thicknesses. These include; the distribution of Zr, the quench sensitivity of thick sections, the surface oxidation behaviour, and the tendency for discontinuous precipitation of δ' . The mechanical properties have also been measured as a function of hot rolling reduction.

Introduction

There is considerable interest in maximising the specific stiffness of aluminium lithium alloys for use in various product forms, such as forging stock, and thin sheet. Alloys based on the ternary Al-Li-Zr system with densities approaching 2.4 g cm^{-3} have been developed for this purpose; for example the Alcan designated UL40 (4% Li, 0.2 % Zr). Because of the brittle nature of the δ phase the practical Li content is limited to the maximum solubility of Li in Al ($\sim 4.2 \text{ wt\%}$). The Zr is added to form β' dispersoids to provide grain refinement. However, alloys with Li contents greater than 3 wt% can not be easily made by conventional casting. Rapid solidification (RS) methods, such as gas atomisation [1], have been used to produce higher lithium content alloys. Unfortunately powder processing leads to the incorporation of significant quantities of oxide and carbonate debris [2] which are detrimental to ductility and fracture toughness. Spray-casting offers a compromise solution. While cooling rates are not as high ($\sim 10^2 - 10^4 \text{ K s}^{-1}$) the process still achieves substantial microstructural refinement relative to conventional casting and has the major advantage in that it is possible to achieve low H and Na contents, and very little oxide contamination [3].

Generally, spray-casting is carried out under conditions whereby a partially liquid-partially solid layer is maintained on the billet surface. Whilst large drops arrive at the surface fully liquid and small drops are deposited already solidified, the majority of drops arrive semi-solid containing partially developed dendrites[4]. There is, therefore, potential for trapping elements which form peritectic reactions with aluminium in solid solution during the droplet flight, when cooling rates would be expected to be comparable to those for producing RS powders and Al-Li Alloys have been successfully sprayed with Zr contents of up to 0.4 wt% without forming primary particles [3,5]. However, little is known about the distribution of Zr in spray cast materials.

With high Li content alloys certain difficulties might be anticipated. For example, the larger driving force for precipitation from solid solution, combined with a lower thermal conductivity, would be expected to give rise to a greater quench sensitivity and a stronger tendency to form the undesirable equilibrium δ phase. Because of the higher amount of Li supersaturation that is possible the alloys are also potentially more prone to the discontinuous precipitation of δ' than lower lithium content materials [6]. Furthermore, due to the high Li content and the elevated heat treatment temperature required in order to maximise the amount of Li in solid solution, the alloys are more susceptible to oxidation during solution treatment. The aim of this paper is to present recent work aimed at investigating these anticipated problems and the mechanical properties of these high Li content spray cast alloys as a function of hot rolling to a range of section thicknesses from the sprayed billet.

Experimental

The compositions of the alloys produced by the spray-casting process at Alcan Int. Ltd. are given in table 1. The Na and H levels were less than 4 and 0.5 ppm respectively. The alloys were all examined optically and by TEM in the spray-cast condition and AL4.1 and AL4.2 were further investigated after hot rolling at 450-500°C from an 85 mm thick rolling block to 28 and 2mm thick sections. Through thickness hardness profiles were measured on the AL4.1 28 mm sections after solution treatment and water quenching and on subsequent ageing. Solution treatments were carried out in air at 575°C for 30 min followed by water quenching. Edge on TEM specimens were prepared to investigate the near surface structure after solution treatment from specimens heat treated as 2mm thick slices, with a pre-polished surface, and quenched onto a copper block to retain the oxide coating. The specimens were subsequently aged (24hrs at 150°C) so that the depth of local Li loss could be identified from the δ' distribution, after the method of Newcomb et al. [7]. Tensile tests were conducted on AL4.1 and AL4.2 28mm hot rolled plate in 3 orientations (L, T, and S) and on material further rolled to 12 and 2 mm thick sections in the longitudinal (L) and transverse (T) directions only. For the 28 and 12 mm plate standard round section tensile specimens were used, however, the 2mm thick material necessitated the use of flat sheet tensile specimens.

TABLE 1.	Alloy Designation	Li wt%	Zr wt%	Cu wt%	Mg wt%
	AL4.1	4.33	0.11	-	-
	AL4.2	3.89	0.25	-	-
	AL3.3	2.9	0.34	1.01	0.78

Results and Discussion

Microstructure of the Spray-castings

The typical microstructure of a spray-cast billet is shown in fig.1a. The billet has a fine grain size of ~ 40 μ m and has solidified with a divorced eutectic of δ on the grain boundaries. No coarse primary Zr particles were seen in any of the sprayed materials. The distribution of Zr in solid solution in the spray-casting can best be seen from the highest Zr material (AL3.3) following solution treatment, the solution treatment precipitating the L₁₂ β' phase in regions richest in Zr (fig.1b). From fig.1b it can be seen that, though far better than in conventional castings, the distribution of β' is still inhomogeneous being largely restricted to the cores of the original dendrites as would be expected for the solidification of a peritectic system. This original inhomogeneity of the β' distribution in the casting is reflected in the banded distribution of β' often found in the rolled plate (fig.1c).

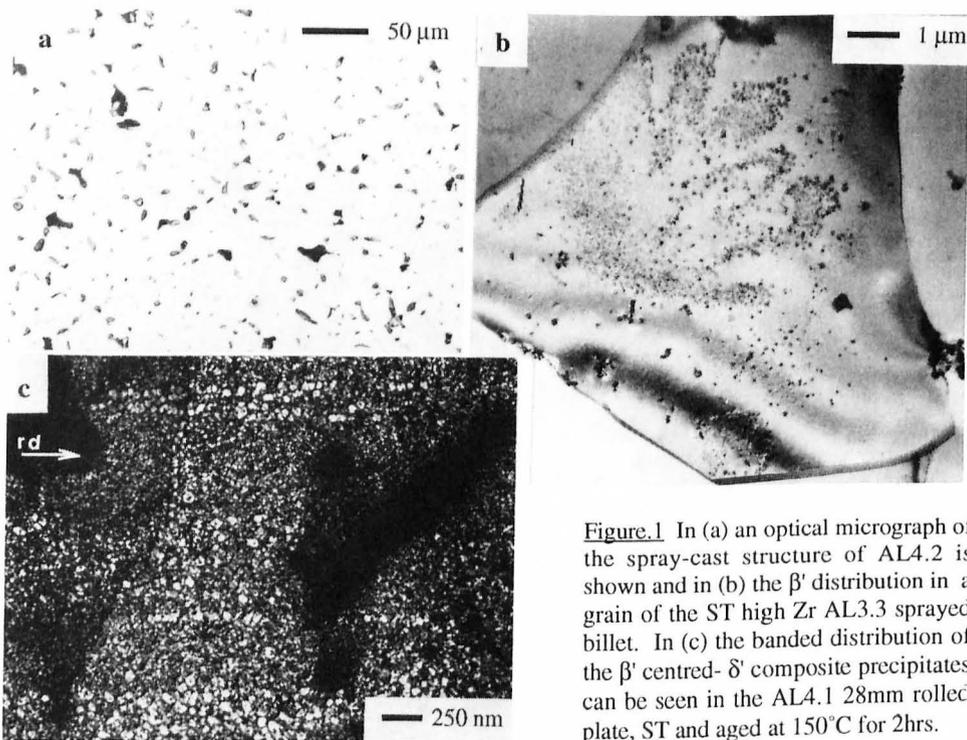


Figure.1 In (a) an optical micrograph of the spray-cast structure of AL4.2 is shown and in (b) the β' distribution in a grain of the ST high Zr AL3.3 sprayed billet. In (c) the banded distribution of the β' centred- δ' composite precipitates can be seen in the AL4.1 28mm rolled plate, ST and aged at 150°C for 2hrs.

Microstructures of the Hot Rolled Materials

Near surface structure The edge on TEM study of the solution treated material (fig.2) revealed severe surface oxidation with a thick Li_2CO_3 surface coating. Damage to the subsurface region was concentrated in pits "burned" into the surface (fig.2a) and a very high subsurface dislocation density was observed. The remnants of LiH precipitates, damaged by specimen preparation, were seen to a depth of $\sim 150\mu\text{m}$ (fig2d), however, these were found to be larger than the LiH precipitates reported by Newcomb et al. [8] in a 3 wt% Al-Li alloy (solution treated at 530°C for 25 min.) and this probably reflects the higher solution treatment temperature used. The depth to which Li had been lost to such an extent that no δ' could be found, corresponding to a Li content of $\sim 6\%$ [9] was $60\mu\text{m}$, as opposed to $40\mu\text{m}$ reported by Newcomb et al. at the lower temperature.

The 28mm Hot Rolled Plate: Hardness measurements revealed a considerable variation with depth in the solution treated AL4.1 28 mm thick plate associated with the degree to which δ' had precipitated on water quenching (fig.3), being $\sim 100\text{ H}_v$ for the first 5mm below the surface and then increasing to a plateau of $\sim 120\text{ H}_v$ for the central 10mm. The inhomogeneity in initial hardness through the section was progressively removed on artificial ageing, becoming virtually constant after 32 hrs. at 150°C, due to the surface regions catching up with the centre. This behaviour suggests that there was insufficient variation in the precipitation of δ through the section during quenching to affect the peak aged local hardness values. Dark field super lattice images for typical regions from AL4.1, in the as-solution treated and water quenched condition, are shown of the centre and 2mm below the surface of the 28 mm plate in fig.4 and confirm this supposition. δ precipitation can be inferred from the patches of δ' free regions seen in these images. While it can be seen that the incidence of,

in particular, intergranular δ precipitation is more pronounced in the centre than at the edge of the plate the overall volume fraction is low. Grain boundary precipitation of δ had not been suppressed in either region and narrow precipitate free zones were already observed at grain boundaries in the quenched condition, both at the centre and edge of the plate (e.g. fig.5).

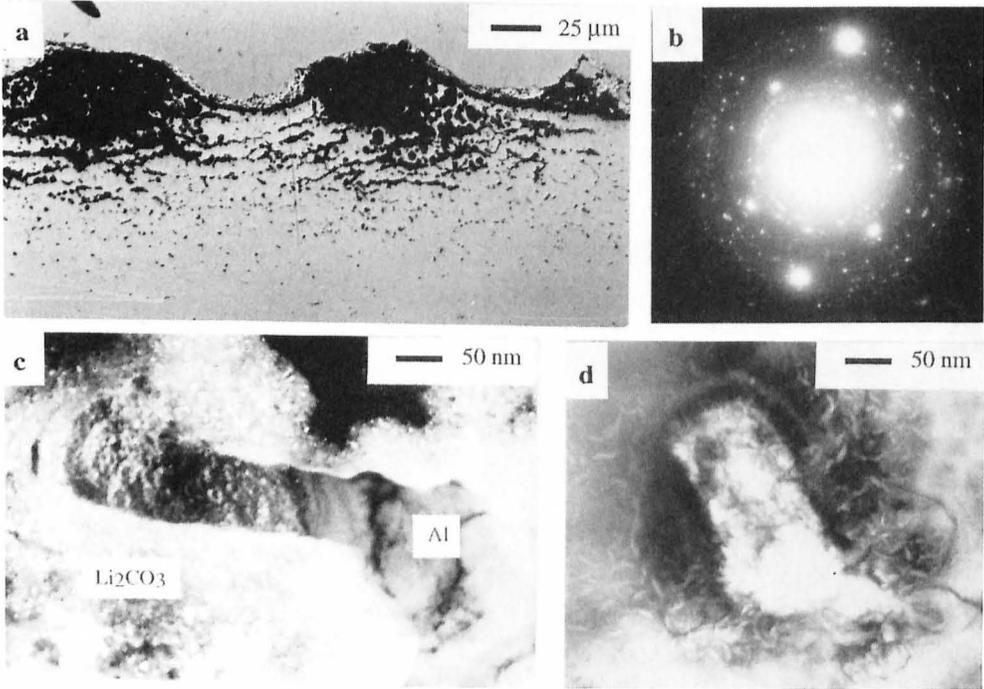
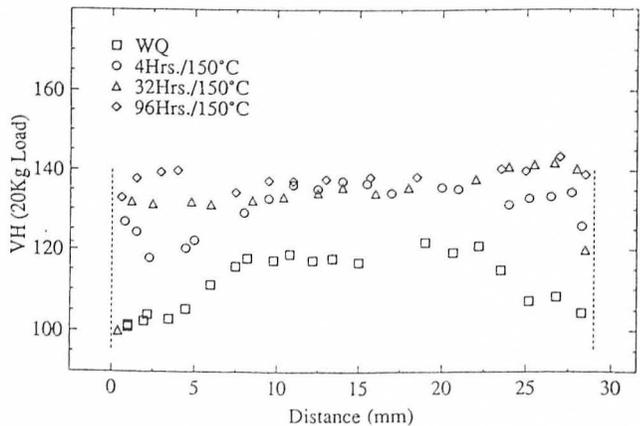


Figure 2. The subsurface structure of AL4.1 after solution treatment in air shown in cross section, optically in (a) and by TEM in (b), (c) and (d). In (c) the carbonate/Al interface is shown with a diffraction pattern from the Li_2CO_3 (b) and in (d) the remnants of a LiH particle damaged during ion beam milling.

Figure 3. Vickers hardness profiles measured through the 28 mm AL4.1 plate after solution treatment and water quenching, and as a function of ageing time at 150°C.



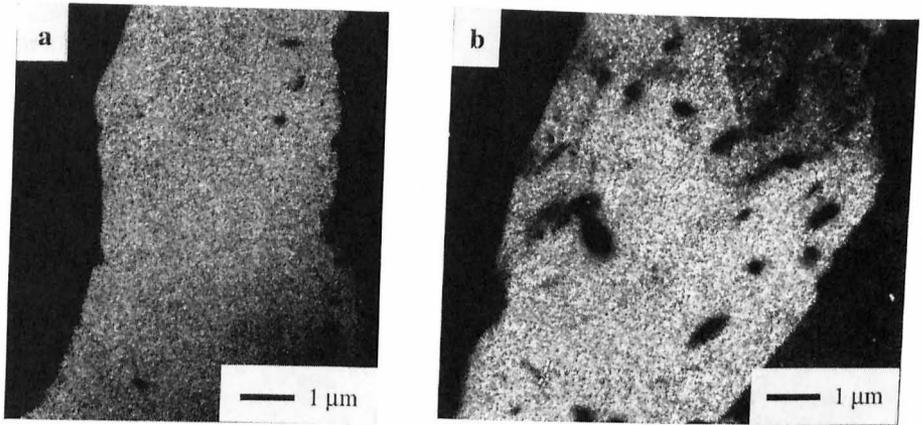
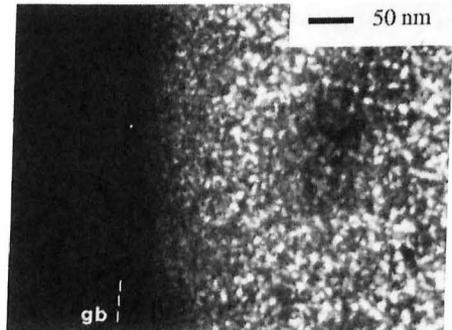


Figure 4. The δ' distribution found in the ST and WQ AL4.1 28 mm plate from 2 mm below the surface a) and from the centre b). The incidence of δ precipitation on quenching can be seen from the local areas where δ' has not formed.

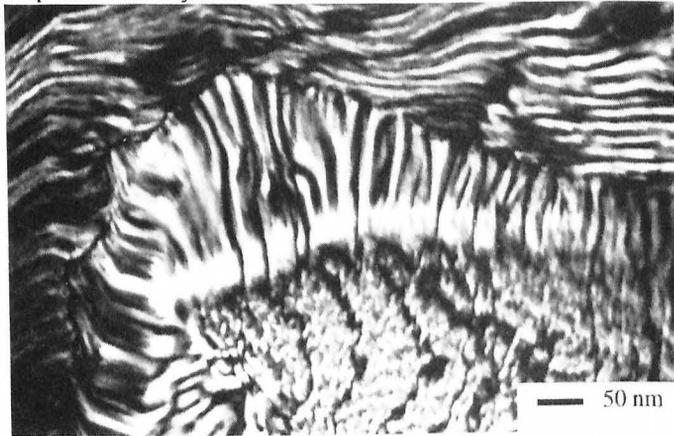
Figure 5. δ' precipitate free zone at a typical grain boundary from the centre of the ST, WQ AL4.1 28 mm plate.



The 2mm Hot Rolled Sheet In both of the 2 mm thick rolled materials discontinuous precipitation of δ' (fig.6) was commonly found at grain boundaries in the solution treated and water quenched condition, whereas, this form of precipitation was not seen in the 28 mm thick plate. This observation is in contradiction with earlier investigations into discontinuous precipitation in Al-Li alloys where it was suggested that this morphology of δ' only develops on artificial ageing and is not seen in the ST water quenched condition [10]. In light of their observations Williams and Butler [11] have described the reaction as "discontinuous coarsening", being driven in their view primarily by the far smaller surface area of the lamella form of δ' relative to that of the normally seen homogeneously nucleated spherical precipitates. More recently Prangnell et al. [6, 12] have demonstrated that discontinuous δ' formation initiates on quenching from solution treatment under conditions where a high Li concentration is present in solid solution at grain boundaries and is not just a discontinuous coarsening reaction, nucleation probably occurring directly from solid solution and involving a phase change. Prangnell et al. [6] have also shown that the reaction is sensitive to the quench rate and does not take place when there is sufficient time for δ precipitation at grain boundaries to lower the local lithium supersaturation, as is the case in the 28mm plate specimens where PFZs were already observed at grain boundaries in the quenched condition. The extent of grain boundary migration, driven by the discontinuous reaction, is reduced in higher Zr content

alloys due to the increased drag on the grain boundaries imposed by the closer average inter-particle spacing of the β' particles [6]. That the discontinuous reaction occurs despite the presence of the β' particles reducing grain boundary mobility, reflects the larger driving force for precipitation of δ' in 4 wt% Li alloys compared to conventional lower lithium Al-Li-Zr alloys, such as 8090 (2.5 wt% Li), in which discontinuous precipitation is rarely seen.

Figure 6. Discontinuous precipitation of δ' observed in the 2 mm thick ST and water quenched AL4.1 sheet.



Substructure. None of the alloys had recrystallised on solution treatment, due to the pinning effect of the β' precipitates and the relatively high rolling temperature employed, and showed well developed subgrains. Despite the observed inhomogeneous distribution of β' particles, increasing the Zr content from 0.11 to 0.25 wt% still gave rise to a substantial refinement of the subgrain size in AL4.2 relative to AL4.1 due to their larger average volume fraction. Subgrain sizes were also reduced with increasing rolling reduction and were measured as approximately 8 μm and 5 μm in the 28 mm plate compared to 4.7 μm and 2.9 μm in the 2 mm sheet for the AL4.1 and AL4.2 alloys respectively.

Mechanical testing. Tensile test data for the two alloys AL4.1 and AL4.2 as a function of hot rolling reduction for the peak aged condition of 96 hrs. at 150°C are shown below in table 2 .

TABLE 2		0.2 % Proof Stress ($\sigma_{0.2}$) MPa		Tensile strength (σ_{TS}) MPa		% Elongation ϵ_T	
		AL4.1	AL4.2	AL4.1	AL4.2	AL4.1	AL4.2
28 mm [†] Plate	L	336	323	425	440	5.1	6.9
	T	333	322	409	420	4.2	5.3
	S	327	319	360	357	1.3	1.4
12 mm [†]	L	340	348	438	452	5.9	5.5
	T	346	349	425	470	5.2	7.1
2 mm* Sheet	L	337	360	372	382	1.9	1.7
	T	361	385	406	424	2.9	2.4
† Tested as round tensiles. * Tested as flat sheet							

The elongation to failure and tensile strength data for the 2mm thick sheet was artificially low and should not be compared directly with that of the round tensile bars because of the tendency of the flat sheet specimens to fail prematurely by shear, giving rise to poor ductilities. This behaviour is responsible for the lower tensile strengths in the sheet, though the proof stress data should be less sensitive to specimen geometry. Unfortunately, it has not yet been possible to determine whether the effect of the grain boundary discontinuous precipitation, or the surface oxidation damage, is in any way responsible for the low ductility of the sheet specimens. Where it could be measured (i.e. in the 28mm plate) the ductility perpendicular to the plane of the plate (i.e. S direction) was also found to be relatively low.

In unrecrystallised plate, rolled to different thicknesses, the yield stress would be expected to be affected by; the change of grain shape, giving rise to a reduced slip line length (which would be different in different orientations), increasing levels of texture, and the development of substructure. For example, Trowsdale et al. estimate a ~ 24 % increase in longitudinal yield stress in an Al-Li-Zr unrecrystallised rolled plate relative to that for the recrystallised material due to differences in texture [13]. Thus the proof strength and anisotropy in the mechanical properties might be expected to increase with rolling reduction. The yield stress is also sensitive to composition. The still small volume fraction of β' precipitates after an increase in Zr content from 0.11-0.25 wt%, and the inhomogeneous particle distribution, suggests that this increase is unlikely to have a large direct effect on the yield strength through Orowan strengthening (this is probably of the order of 10-20 MPa [14]). The slightly reduced yield stress of AL4.2 in the 28 mm thickness, relative to AL4.1, can be attributed to the lower Li content of AL4.2. In both materials the anisotropy in proof stress is very small in the 28 mm plate, but increases to a similar magnitude in the 2mm gauge, the proof stress being higher in the transverse direction by ~ 25 MPa. This suggests that the effect of texture and grain shape change is similar in both materials with rolling reduction. The longitudinal yield stress remains surprisingly unaffected by rolling reduction. In AL4.2 it increases only by 37 MPa from the 28 mm to the 2mm thick material and remains constant with rolling reduction for the lower Zr content alloy AL4.1. This differential increase can be partially explained in terms of the refinement in substructure in the higher Zr content alloy. For example, it can be roughly estimated using typical values for aluminium alloys [15] that the increase in yield stress on rolling from 28-2mm would be ~ 13 MPa in AL4.1 compared to ~ 20 MPa AL4.2 due to refinement of the subgrain size. The incremental increase in strength from proof stress to failure is higher for AL4.2 than AL4.1 in all conditions, which is a reflection of the generally higher strain to failure and slightly faster work hardening rate of the higher Zr content alloy.

Conclusions

1/ Spray-casting allows the successful fabrication of Al alloys with high Li concentrations and low levels of contamination. The solidification conditions give rise to extended solid solutions particularly for elements forming peritectic reactions with Al, though the distribution of such elements is inhomogeneous, being concentrated in the dendrite cores.

2/ High Li content alloys are prone to severe oxidation during solution treatment in air, rapidly forming a surface layer of Li_2CO_3 and giving rise to; Li loss to a considerable depth, surface damage, and hydrogen penetration. However, this can be avoided by prudent use of salt baths or inert furnace gasses.

3/ High Li content alloys are quench sensitive, giving rise to δ precipitation and the formation of grain boundary PFZs in solution treated water quenched sections greater than ~ 1 cm thick. On quenching thin sections, under conditions where high supersaturations of Li are maintained locally at

grain boundaries, the alloys are prone to discontinuous precipitation of δ' . This occurs despite the presence of grain boundary pinning phases such as Al_3Zr β' .

4) Increasing the Zr content reduces the subgrain size and increases the response of the alloy to improvement of the mechanical properties through hot deformation, the strength in the transverse direction increasing most with rolling reduction.

Acknowledgements

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