VACLITE™ Al-Li ALLOY PRODUCTS - A NEW APPROACH TO Al-Li ALLOY PRODUCTION

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Abstract

Vacuum refining technology developed and patented by Comalco Aluminium Limited, Melbourne, Australia has enabled the production of Al-Li alloys with very low alkali metal impurities (AMI) and hydrogen contents, ie <1ppm each of Na, K, Cs, Rb and <0.2ppm H_2. The resulting products, manufactured in the United States and marketed as VACLITE™ Al-Li alloy products, exhibit significant improvements in fracture toughness, stress corrosion crack resistance and ease of fabrication by welding.

A further feature of the Comalco vacuum process technology is its suitability for the recycling of Al-Li alloy scrap to saleable products and for the production of alloys with lithium contents in excess of 3 Wt%.

Introduction

The low density and high modulus advantages of Al-Li alloys have been well documented but their impact on the aerospace market has, so far, fallen short of initial expectations. Part of the reason is the low ductility, low toughness and stress corrosion cracking resistance of Al-Li alloys compared to conventional aerospace grade aluminium alloys. A further reason is the loss in toughness in commercially available Al-Li alloys during long-term exposure at room temperature or short-term exposure at elevated temperatures below the initial ageing temperature. These property limitations suggest an inherent characteristic of the alloys that results in embrittlement at or near grain boundaries.

While various researchers [1, 2, 3, 4, 5] have considered the possible influence of alkali metal impurities and hydrogen on the mechanical properties of Al-Li alloys, Comalco has focused on liquid metal embrittlement caused by the presence of alkali metal impurities (AMI), ie Na, K, Cs and Rb and hydrogen [6,7]. These impurities are introduced into the alloys via the lithium, (typically containing ≥ 100ppm AMI), the aluminum pig, (typically containing 3-8ppm AMI), the alloying elements and master alloys, (typically containing 3-3000ppm AMI). Additional AMI can be introduced by the refractories in the melting and casting facility. Commercially available Al-Li alloys produced via non-vacuum routes generally contain 3-10ppm (Na + K) with lesser amounts of the other alkali metal impurities.

The addition of lithium as an alloying component in aluminum alloys significantly increases the solubility of hydrogen in alloys in both the liquid and solid state. Standard degassing procedures which are effective in reducing the hydrogen content of non-lithium containing aluminum alloys to <0.1ppm are incapable of reducing the hydrogen content of Al-Li alloys below approx 0.35ppm (8, 9). Until recently the Aluminum Industry has made no real attempt to reduce the AMI and hydrogen levels below those found in commercially available Al-Li alloys. Industry thinking has been that the levels of AMI and hydrogen in commercially available products were sufficiently low that further purification would have no appreciable effect on toughness and other material properties.

The role and distribution of AMI and hydrogen in Al-Li alloys has been determined by Webster (7) and Lynch (10, 11) and summarised in a recent review paper by Webster (12). An embrittlement mechanism involving the presence of liquid AMI phases at grain boundaries has recently been proposed (13). It is suggested that the presence of such impurities significantly influences the fracture toughness properties at levels as low as 3-5ppm (Na + K).

The Process

Having determined in 1988 that the removal of AMI and hydrogen below the levels found in commercially available Al-Li alloys may improve the toughness and other material properties, Comalco was faced with the dilemma of a lack of an enabling process technology to effect such removal. A vacuum refining process was designed and evaluated on a pilot scale by the company.

Initial trails were associated with the remelting of purchased Al-Li alloy scrap and it was found that the vacuum-refined products produced from scrap billet and rolling slab exhibited superior mechanical properties to those determined for saleable product of the same composition. Subsequent trails in which Al-Li alloys were produced from virgin raw materials confirmed the effectiveness of vacuum refining.

It should be noted that a sharp distinction is drawn between **vacuum melting**, ie melting in vacuum followed by casting where vacuum is used solely as an inert environment and **vacuum refining** where the liquid metal bath is maintained under an extremely low chamber pressure (typically 10 um of Hg) for a specific period of time until the total AMI has been reduced to the required level.

The refining process depends on the fact that AMI have higher vapour pressures than both aluminum and lithium so that under the optimum process conditions of vacuum chamber pressure, melt temperature and refining time, the AMI total content can consistently be reduced to <1ppm without any appreciable loss of lithium from the liquid melt. The refining process for Al-Li, Al-Mg and Mg-Li alloys is proprietary to Comalco Aluminium Limited and has been granted patent coverage (14).

Following vacuum refining, the melt is filtered and cast to product while still under the high vacuum conditions. With the sequence of melting-alloying-refining-casting all being performed under a high vacuum, dross formation is minimised. The only dross present throughout the production sequence is that derived from the surfaces of the aluminum pig, alloy additions and master alloys that make up the charge. No 'new' dross is generated.

In addition to its effectiveness in removing AMI and hydrogen, the vacuum processing route provides further capabilities.

- An economic and safe means of treating Al-Li alloy scrap. Solid scrap can be remelted, refined and cast into high quality product with less than 5% loss of its lithium content.

- Al-Li alloys with lithium contents in excess of 3.0 wt% can be produced via this liquid metallurgy route. Alloys of 3.3-3.5 wt% Li have been produced and there is no reason to limit the lithium content until the 4.0 wt% maximum solubility is reached.

- Being a batch process, the vacuum metallurgy route offers business opportunities for production of 'tailored' or 'customised' alloys in volumes appropriate to the small (but growing) market demands.

In association with Teledyne Allvac, a US- super-alloy producer, Comalco has up-scaled the vacuum refining process technology to a capability for production of commercial-size Al-Li alloy billets for extrusion and forging. Current capability is for billet or forging stock cast to a maximum 305mm diameter and scalped to 290mm maximum diameter, 2.5 metre maximum length and marketed as VACLITE™ Al-Li alloy products. Production capability will be further up-scaled as the market dictates. The vacuum refining technology is not specific to one Al-Li alloy system but is generic to any lithium containing alloy.

Property Improvements

In Al-Li alloys with AMI levels in the range 3-10ppm (Na + K), impurity elements diffuse to grain boundary locations during ageing where they precipitate as lenticular liquid phases that remain liquid at and below ambient temperatures. Further, during ageing, hydrogen that has been locked in solid solution diffuses to grain boundary locations where the liquid AMI acts as a 'sink' for hydrogen collection[7]. It is these grain boundary phases that provide the sites for embrittlement ahead of an advancing crack tip.

The removal of AMI to <1ppm each and hydrogen to <0.2ppm from Al-Li alloys results in the virtual elimination of those impurities that are the cause of liquid metal embrittlement.

Fracture Toughness/Yield Strength

Variations in toughness and strength properties are possible in Al-Li alloy systems by manipulation of such variables as alloy composition (Li, Cu, Mg), degree of cold work (eg percentage of stretch between solution heat treatment and age) and the ageing practice (temperature and time). By necessity, there is usually a trade-off between toughness and strength, ie an increase in toughness can be achieved at the expense of yield strength. These manipulations do nothing to change the inherent toughness/strength relationship of a particular alloy composition.

VACLITE Al-Li alloy products demonstrate inherent toughness/yield strength relationships that are superior to those obtained by identical alloys with total AMI and hydrogen levels above those achieved by the vacuum refining process.

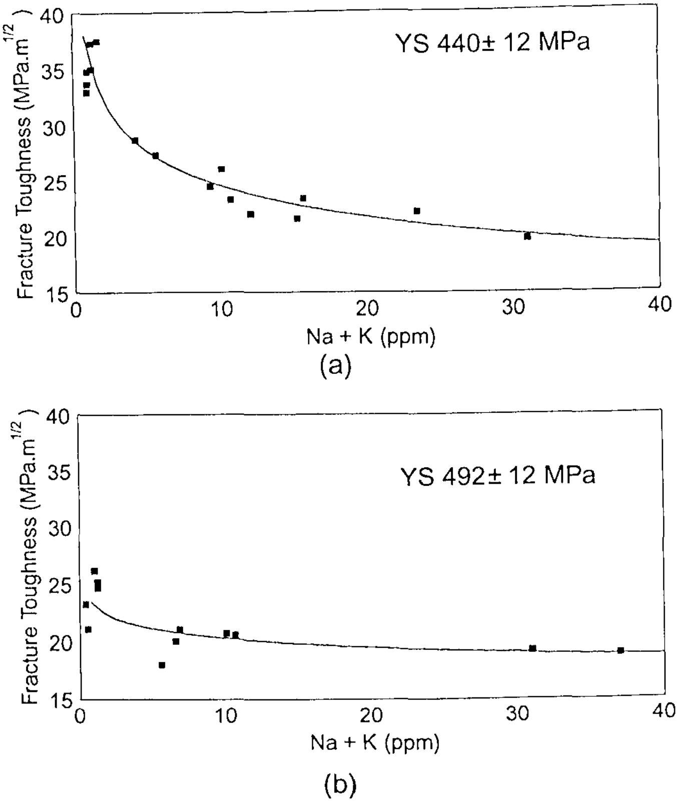

Figure 1: S-L Fracture Toughness versus AMI content for yield strengths of (a) 440 ± 12 MPa (b) 492 ± 12 MPa. Alloy composition 2.0 wt% Li, 2.4 wt% Cu, 0.1 wt% Zr

In Figures 1(a) - (b), S-L fracture toughness data are presented for samples of 2090 alloy extrusions (2.0Li, 2.4Cu, 0.1Zr) with AMI contents over the range 1-40ppm (Na + K). All mechanical testing was performed on specimens in the T8 condition that were machined from the center location of 60mm x 14mm rectangular section extrusions. Short transverse (S-L) fracture toughness was determined at 20°C using chevron-notch short bar testing (ASTM E1304) and yield strength was determined for the longitudinal direction. At each level of yield strength, the fracture toughness for samples with 1-2ppm (Na + K) is significantly higher than the toughness of samples with >5ppm (Na + K).

<u>Time and Temperature Stability</u>

Commercially available Al-Li alloys suffer a rapid loss of toughness during exposure at elevated temperatures (150°F and above) and a more gradual embrittlement over several years exposure at room temperature [15].

In Table 1, S-L fracture toughness and yield strength data are presented for center samples of alloy extrusions (2.0Li, 2.4Cu, 0.1Zr) that have been tested after exposure following ageing for approx 100 hours at room temperature, 1900 hours at room temperature and 800 hours at room temperature followed by 1100 hours at 66°C (150°F).

Table 1 Exposure Data for 2.0 wt%Li, 2.4 wt%Cu, 0.1 wt%Zr extrusions in the T8 condition. S-L fracture toughness and longitudinal yield strength of center samples.

IMPURITIES			Aged Condition	Exposure	100 hrs @ RT	Exposure	1900 hrs @ RT	Exposure	800 hrs @ RT plus 1100 hrs @ 66°C
* Na (ppm)	* K (ppm)	** H (ppm)	°C/hrs	YS (MPa)	K_{IV} (MPa m½)	YS (MPa)	K_{IV} (MPa m½)	YS (MPa)	K_{IV} (MPa m½)
0.41	0.42	0.23	150/24	429	33.6	433	32.0	458	31.9
0.95	0.24	0.21	150/24	414	36.1	441	28.2		
7.2	1.5	0.42	150/24	409	20.2	423	19.0	433	15.7
0.41	0.42	0.23	150/48	480	21.4	476	22.5	505	21.3
0.95	0.24	0.21	150/48	473	23.3	496	22.9	492	23.4
7.2	1.5	0.42	150/48	442	14.8	457	13.4	510	13.6

* Glow Discharge Mass Spectrometry ** Inert Gas Fusion Technique

Al-Li alloy products with <1ppm of Na and K and 0.2ppm hydrogen demonstrate greater stability of fracture toughness with exposure at both room temperature and elevated temperature than the identical alloy with higher levels of AMI and hydrogen. In both cases, exposure has resulted in an increase in yield strength (5-10%) and some loss of toughness could be expected due to additional ageing which can occur even at room temperature. For alloys with 1ppm AMI and 0.2ppm hydrogen this increase in yield strength has not led to a loss of toughness. There is, in fact, an improvement in the fracture toughness/yield strength relationship.

Stress Corrosion Cracking Resistance

Typically, commercially available Al-Li alloys exhibit threshold stress levels for stress corrosion cracking in the short transverse direction of less than 200 MPa in the peak-aged to over-aged condition. Threshold stress levels have been determined using 'tuning fork' specimens where the legs of the fork are deflected to pre-determined stress levels between 100 MPa and 380 MPa and then subjected to alternate caustic immersion in accordance with ASTM G44.

Tuning fork specimens of three VACLITE Al-Li alloys were tested in duplicate at five levels of pre-stress. Specimens were machined from the central sections of 60 mm x 14 mm extrusions in the T8 condition. None of the specimens failed during the 28 day test period regardless of the pre-stress level although one alloy, XT110 (ie 2090 alloy composition) pre-stressed to 380 MPa, showed evidence of one stress corrosion crack that had propagated through approximately 80% of the section and was therefore deemed to have a threshold stress of >310Mpa, <380Mpa, refer Table 2.

Table 2 Stress Corrosion Testing* of VACLITE Al-Li alloys pre-stressed to levels within the range 100-380 MPa

ALLOY	COMPOSITION (wt%)	YIELD STRENGTH (MPa)	RESULT AFTER 28 DAYS	REMARKS
XT110	1.96Li, 2.4Cu, 0.13Zr	540	No specimens failed. Only one SC crack observed on one specimen at 380 MPa pre-stress	General corrosion with numerous pits
XT130	2.0Li, 1.8Mg, 0.08Zr	345	No specimens failed, no SC cracks observed even at 380 MPa pre-stress	No evidence of corrosion
XT140	2.4Li, 0.32Cu, 0.9Mg, 0.18Cr	480	No specimens failed, no SC cracks observed even at 380 MPa pre-stress	Only slightly stained, no appreciable corrosion

* Tuning fork specimens. ASTM G44 test procedure

Weld-crack Susceptibility

Commercially available Al-Li alloys often demonstrate poor weldability performance due to their susceptibility to hot tearing/hot cracking in the weld pool zone and a susceptibility to the formation of weld metal porosity.

Alloy weldability, as defined by crack susceptibility, was evaluated on a range of VACLITE alloys using the varestraint test in which the weld pool is subjected to controlled amounts of strain while autogenous welding is in progress. Post weld, the specimens are machined and polished to reveal the number, maximum crack length and total accumulative crack length of any hot tears/hot cracks so formed. Details of the evaluation are presented in Table 3(a).

Table 3(a) Varestraint Test* data for VACLITE Al-Li alloys. Maximum crack length and total crack length in millimeters for 0.5%, 1.0% and 4.0% augmented strain.

ALLOY	COMPOSITION (wt%)	0.5% STRAIN		1.0% STRAIN		4.0% STRAIN	
		Max (mm)	Total (mm)	Max (mm)	Total (mm)	Max (mm)	Total (mm)
XT110	1.96Li, 2.4Cu, 0.13Zr	0.06	0.06	1.05	5.47	2.47	22.5
XT120	1.8Li, 1.14Cu, 0.76Mg, 0.08Zr	-	-	-	-	4.55	28.9
XT130	2.02Li, 1.8Mg, 0.08Zr	0.00	0.00	0.82	2.48	1.95	8.5
XT140	2.4Li, 0.32Cu, 0.9Mg, 0.18Cr	1.82	7.10	1.95	7.15	2.84	18.7
XT150	3.3Li, 1.1Mg, 0.08Zr	0.00	0.00	1.83	6.13	3.36	19.2
2090	Commercial Extrusion	1.5	5.0	3.0	17.9	3.7	60.2

* Sample thickness 12.5mm, welding conditions: GTA-DCEN 180 amps, 20 volts, 250mm/min, 1.42m^{3}h He

VACLITE alloys XT110 thru XT150, with low AMI and hydrogen levels demonstrate superior resistance to weld-crack formation than the commercially available sample of 2090 alloy. Alloy XT110 is of 2090 alloy composition (1.96%Li, 2.4%Cu, 0.13% Zr) and can be compared directly with the commercial 2090 alloy. Even for alloys of high lithium content (XT150 with 3.3% Li), superior performance is achieved.

On a comparative basis, varestraint data is presented in Table 3(b) from the literature [16] for the commercially available 2090 alloy, the Weldalite™ Al-Li alloys and the typically used conventional weldable aluminum alloys 2014 and 2219.

Table 3(b) Varestraint Test* data from Reference [16] Total crack length in millimeters for 0.5% and 1.0% augmented strain.

ALLOY	COMPOSITION (wt%)	0.5% STRAIN Max (mm)	0.5% STRAIN Total (mm)	1.0% STRAIN Max (mm)	1.0% STRAIN Total (mm)	4.0% STRAIN Max (mm)	4.0% STRAIN Total (mm)
2090	2.08Li, 2.52Cu, 0.12Zr	-	47	-	48	-	-
2219	6.27Cu, 0.13Zr	-	18	-	20	-	-
2014	4.6Cu, 0.52Mg	-	53	-	57	-	-
Weldalite™	1.19Li, 4.83Cu, 0.39Mg, 0.36Ag, 0.16Zr	-	39	-	46	-	-
Weldalite™	1.23Li, 5.22Cu, 0.38Mg, 0.40Ag, 0.15Zr	-	39	-	46	-	-
Weldalite™	1.16Li, 6.07Cu, 0.40Mg, 0.40Ag, 0.17Zr	-	28	-	39	-	-

* Sample thickness 6.4mm,. welding conditions: GTA-DCEN 102-125Amps, 14-16 volts, 150mm/min, 1.42m^3h He

The VACLITE Al-Li alloys have been shown by varestraint testing to have a susceptibility to hot tearing during welding lower than the commercially available Al-Li alloys and comparable at least, to the best conventional aluminum alloy, 2219.

Summary

The removal of alkali metal impurities (AMI) to <1ppm in Al-Li alloys can be achieved by vacuum refining the melt prior to casting.

The removal of AMI results in the virtual elimination of grain boundary phases that can remain liquid at and below ambient temperatures, leading to liquid metal embrittlement and providing sites for high hydrogen concentration.

The resulting low impurity Al-Li alloy products, marketed as VACLITE Al-Li alloy extrusion billet and forging stock, exhibit significant improvement in those properties where grain boundaries have an important role, namely:

- Fracture toughness/yield strength relationship
- Time and temperature stability of the toughness/strength relationship
- Stress corrosion cracking resistance
- Weld-crack susceptibility

References

1. A.K. Vasudévan, A.C. Miller and M.M. Kersker, Aluminium-Lithium Alloys II, ed. E.A. Starke, Jnr., T.H. Sanders, Jnr., Met. Soc. AIME, U.S.A., 1984, pp 181-199.

2. D.N. Fager, M.V. Hyatt and H.T. Diep, Scr. Metall., Vol. 20, 1986, pp 1159-1164.

3. W.S. Miller, M.P. Thomas and J. White, Scr. Mettal., Vol. 21, 1987, pp 663-668.

4. C.D. Buscemi and E.S.C. Chin, Micr. Sci. ed. H.J. Cialoni, M.E. Blum, G.W.E. Johnson, G.F. Vandervoort, Vol. 16, 1988, pp 221-230.

5. J.J. Lewandowski and N.J.H. Holroyd, Mater. Sci. Engng. A123, 1990, pp 219-227.

6. D. Webster, Aluminium-Lithium Alloys III, ed. C. Baker, P.J. Gregson, S.J. Harris, C.J. Peel, Inst. Mets., 1986, pp 602-609.

7. D. Webster, Metall. Trans., Vol. 18A, Dec 1987, pp 2181-2193.
8. P.N. Anyalebechi, D.A. Granger and D.E.J. Talbot, Metall. Trans., Vol. 19B, April 1988, pp 227-232.

9. P.N. Anyalebechi, D.A. Granger and D.E.J. Talbot, Lightweight Alloys For Aerospace Applications, Ed. E.W. Lee, E.H. Chia and N.J. Kim. Min. Met. & Mat. Soc., 1989, pp 249-270.

10. S.P. Lynch, Mat. Sci. Engng., A136, 1991, pp 45-57.

11. S.P. Lynch, Mat. Sci. Tech., Vol. 8, Jan 1992, pp 34-42.

12. D. Webster, Adv. Mats. & Proc., May 1994, pp 18-24.

13. C.G. Bennett, E.D. Sweet, J. Kotsios and I. Musulin, Metallic Materials for Lightweight Applications, Proc. 40th Sagamore Army Materials Research Conf., 1993, (to be published).

14. US Patent 5 085 830.

15. P.D. Pitcher, D.S. McDarmaid and C.J. Peel, Aluminium-Lithium, ed. M. Peters, P.J. Winkler, DGM Informationgesellschaftmbtt, Germany, 1992, pp 235-240.

16. L.S. Kramer, F.H. Heubaum and J.R. Pickens, Aluminium-Lithium Alloys, ed. T.H. Sanders Jnr., E.A. Starke Jnr., Materials and Components Engineering Publications Ltd, UK, 1989, pp 1415-1424.