



ALUMINIUM DIVISION

ENHANCED TITANIUM-ALUMINIUM GRAIN REFINERS

George T. Campbell and Stephen A. Danilak
Shieldalloy Metallurgical Corporation, U.S.A.

and

Stuart R. Thistlethwaite and Peter Fisher
London & Scandinavian Metallurgical Co Limited, U.K.

**TVMIS LIGHT METALS
CAST SHOP TECHNOLOGY 1992**

March 1-5

SAN DIEGO CA

www.metallurgical.com

ABSTRACT

In the vast majority of grain refining applications, Titanium-Boron-Aluminium alloys ranging from 3% Ti to 10% Ti and 0.2% B to 1% B are used. These alloys are widely accepted due to the presence of controlled size and quantities of TiB₂ particles which

allow for low cost consistent grain refining. Some applications still require the use of grain refiners substantially free of insoluble third phase particles. Typically a 6% Ti-Al alloy is used in such applications. Recently, industry has demanded a product which grain

refines better and more consistently than the standard 6% Ti-Al alloy. The capabilities/characteristics of "enhanced" titanium-aluminium alloys containing low levels of insoluble particles are reviewed.

INTRODUCTION

Grain refining in the aluminium cast shop is normally accomplished by the use of Ti-B-Al and/or Ti-Al master alloys. An overwhelming portion of grain refining is accomplished by the use of the Ti-B-Al family of grain refiners. Ti-B-Al grain refiners are used in such diverse applications as can stock, foil, extrusion billet, and hard alloys for the Aerospace Industry. In the U.S., the largest quantity of aluminium alloys are grain refined with 3% Ti-1% B master alloy; whereas in Europe, 5% Ti-1% B is predominant along with 3% Ti-1% B. Other alloys commonly used are 3% Ti-0.2% B, 5% Ti-0.6% B, 5% Ti-0.2% B, and 10% Ti-0.4% B depending on application and market area.

In some applications, cast shops use grain refiners with low levels of insoluble particles. For such applications, the preferred grain refiner is 6% Ti. Inherently, the 6% Ti alloy is a poor, inconsistent grain refiner compared with the Ti-B-Al alloys. In the past, the use of 6% Ti has resulted in intermittent occurrences of twin columnar grains

(feather grains). Enhanced 6% Ti products have been developed and marketed which have improved/more consistent grain refining properties. The enhanced performance is achieved by the presence of low levels of insoluble particles such as titanium carbides or titanium borides. The current Aluminium Association specification for 6% Ti alloys for other elements allows .03% maximum. Hence this specification permits carbon additions up to .03%. The Aluminium Association specification for 6% Ti has a .004% boron maximum. Hence, boron cannot be added to 6% Ti at the same level as carbon to enhance grain refining performance without a specification variance.

The effectiveness of a grain refiner in an alloy system will be determined by the number of potential nuclei, their potency, the alloy cooling rate, and alloy constituents¹.

Knowledge of the number of insoluble particles which must be added to an aluminium alloy to obtain a given grain refined state or to avoid columnar/twin columnar grains is important. Optimum usage of grain refiners in the most restrictive applications will be determined by a trade-off between the number (weight of) insoluble particles, the weight addition of the master alloy to obtain a given grain refined state, and size distribution of the insoluble particles in the master alloy. Weight addition is important both from a cost viewpoint and because of the presence of small amounts of oxides in the grain refiner which cannot be totally avoided.

This work (1) compares the grain refining response on 1070 and 5657 alloys of a "pure" 6% Ti alloy (minimum insoluble particles), and enhanced 6% Ti with 0.02% carbon, an enhanced 6% Ti with a 0.02% boron and a 3% Ti-0.2% B alloy; (2) compares the boron/carbon addition efficiency of 6% Ti-0.02% B, 6% Ti-0.02% C and 3% Ti-0.2% B alloys; and (3) compares the microstructure of the different alloys.

EXPERIMENTAL PROGRAM

Materials

Table I lists the analysis of the master alloys studied, while Table II gives the chemistry of the aluminium alloys used for the grain refining test.

The master alloys listed in Table I were produced in production size heats or experimental heats at London & Scandinavian Metallurgical Co Limited (LSM) or at Shieldalloy Metallurgical Corporation (SMC).

Table I—Chemical Analysis of Master Alloys Studied

MASTER ALLOY	% Ti	% B	% C	% Fe	% Si	% V	% Mg	Others
3% Ti-0.2% B	2.99	0.20	—	0.09	0.03	0.08	0.02	<0.01
6% Ti-0.02% B	6.06	0.019	—	0.16	0.04	0.22	<0.01	<0.01
6% Ti-0.02% C	5.93	0.003	0.021	0.22	0.03	0.26	<0.01	<0.01
Pure 6% Ti	6.03	0.001	0.002	0.15	0.03	0.23	<0.01	<0.01

Table II — Chemical Analysis of Aluminium Alloys Used for Grain Refining Test

ALLOY	% Fe	% Si	% Mg	% Zn	Others
1070	0.2	0.05	<0.01	0.015	<0.01
5657	0.08	0.02	0.9	0.01	<0.01

Grain Refining Tests

Grain refining tests were carried out by the ALCOA Cold Finger Test (CFT)².

Grain size was determined by the linear intercept method employing a three coloured light system³. The grain size was measured horizontally and vertically along a 1/2" line, the centre point being 1" below the bottom of the chill.

Metallography

Samples for light microscopy were prepared by the technique described in Appendix A.

RESULTS

Grain Refining Tests

Figure 1a and 1b shows the five minute Cold Finger Test grain size in 1070 and 5657 alloy as a function of weight addition, while Figure 2a and 2b shows the grain size as a function of boron or carbon addition rate for the master alloys investigated.

Figure 1a — 5 minute CFT Grain Size

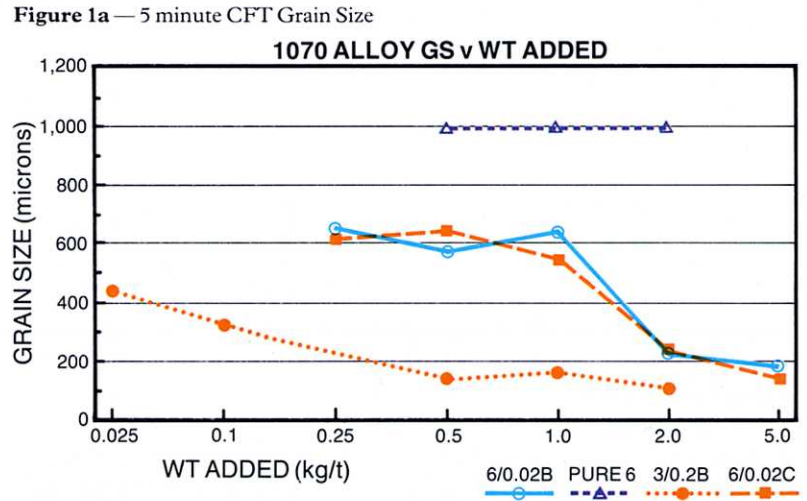


Figure 1b — 5 minute CFT Grain Size

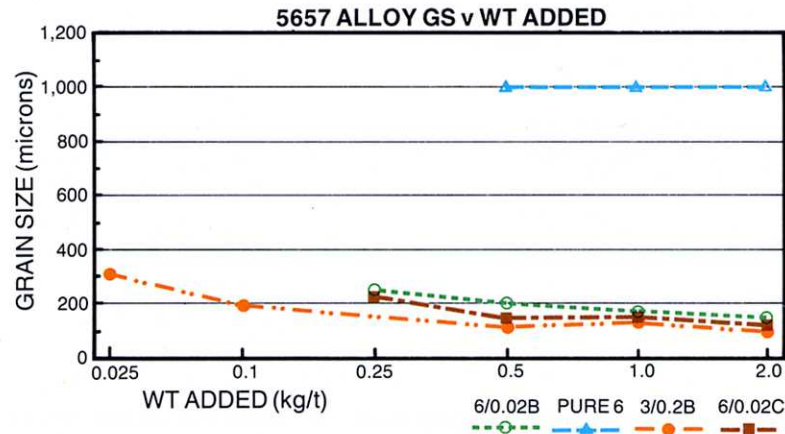


Figure 2a — Grain size as a function of boron or carbon addition rate.

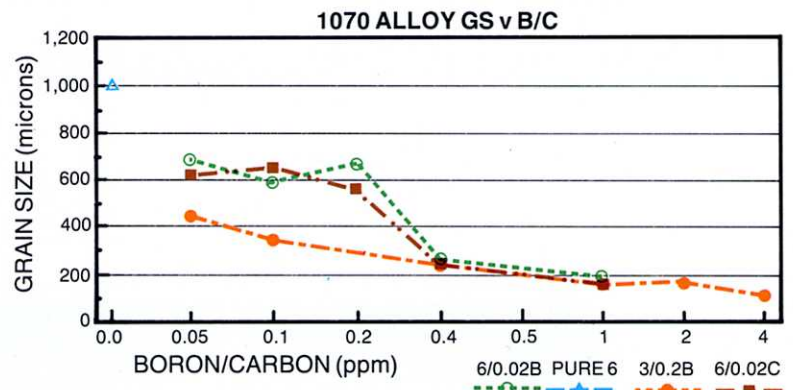


Figure 2b — Grain size as a function of boron or carbon addition rate.

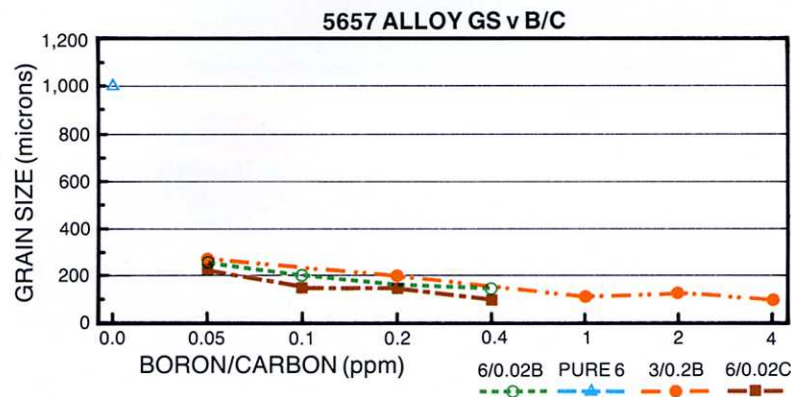


Table III and IV shows the weight addition and the corresponding carbon or boron addition of the master alloys investigated required to avoid formation of columnar/twin columnar grains for both 1070 and 5657 alloys in the Cold Finger Test, respectively.

Table III — Grain Refiner Addition to Avoid Columnar/Twin Columnar Grains in 1070 Alloy

Grain Refiner	Wt. % Addition (kg/t, lbs./1000lb)	Third Element Addition (ppm)
3% Ti-0.2% B	0.5	1
6% Ti-0.02% B	5	1
6% Ti-0.02% C	5	1
6% Ti (pure)	>5	N/A

Table IV — Grain Refiner Addition to Avoid Columnar/Twin Columnar Grains in 5657 Alloy

Grain Refiner	Wt. % Addition (kg/t, lbs./1000lb)	Third Element Addition (ppm)
3% Ti-0.2% B	0.05	0.1
6% Ti-0.02% B	1	0.2
6% Ti-0.02% C	0.5	0.1
6% Ti (pure)	>2	N/A

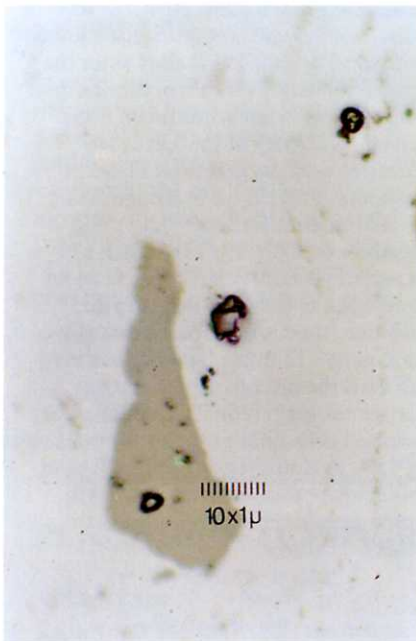


Figure 3a — Largest insoluble particle (excluding oxide) in 6% Ti-0.02% C (1000X)



Figure 3b — Largest insoluble particles (excluding oxides) in 6% Ti-0.02% B (1000X)



Figure 3c — Largest insoluble particles (excluding oxides) in 3% Ti-0.2% B (1000X)

Microstructure

Figure 3 shows the largest insoluble particle (excluding any oxides present) found in the alloys investigated.

Table V lists the size of the largest insoluble particle (TiB_2 or TiC) found in each of the master alloys investigated.

Table V — Largest Insoluble Particles (TiB_2 or TiC)

Master Alloy	Largest Insoluble Particle
6% Ti-0.02% C	6 μ m
Pure 6% Ti	—
3% Ti-0.2% B	3 μ m
6% Ti-0.02% B	2 μ m

DISCUSSIONS

Grain Refining

The results in Figures 1 and 2 show significant variations in grain refining efficiency. The "pure" 6% Ti-Al master alloy, with few insoluble intermetallic particles to act as nuclei is an extremely poor grain refiner in both 1070 and 5657 alloys. The presence of small amounts of boron or carbon, in the form of TiB₂ or TiC, gives a significantly improved grain refining response compared to the "pure" 6% Ti-Al alloy. This is in agreement with previous work⁴, which concluded that the enhanced performance of certain Ti-Al alloys is due to the presence of effective, insoluble nuclei rather than TiAl₃ morphology. The TiAl₃ morphology is similar in all the alloys examined. The 3% Ti-0.2% B alloy on a weight addition basis performed significantly better than the enhanced 6% Ti-Al master alloys on both 1070 and 5657 alloys.

As stated earlier, the final as-cast grain size is determined by a number of factors¹ i.e., the number of potential nuclei, their potency, casting rates and alloy constitution. Since the latter two are controlled in this work, the differences in grain size and freedom from twinned columnar growth are determined by the number and potency of the nuclei. At high addition levels, the grain size of boron and carbon containing alloys are similar since there are excess potential nuclei available for nucleation. The final grain size is controlled by the cooling rate and the alloy constitution. Lower grain sizes are found in 5657, as expected, due to the higher solute levels in this alloy. As the addition rates are reduced, coarser grains and twinned columnar growth are observed. In both alloys this appears to be closely linked to boron or carbon level (see Figures 2a and 2b, and Table IV). This implies that the number and potency of nuclei are approximately equal in each master alloy. This, however, is not known in practice, since it has not been possible to establish accurate size distributions for each alloy. Small differences in particle size can give large differences in particle numbers⁵.

The 3% Ti-0.2% B alloy appears to give somewhat lower final grain size but not freedom of twin columnar grains in 1070 alloy at very low boron addition levels compared to the 6% Ti-0.02% B/C alloys. This is believed to be due to different processing techniques being used to produce the alloys resulting in more potent TiB₂ particles in the 3% Ti-0.2% B master alloy. Significant improvements have been made during recent years on both the efficiency and cleanliness of the 0.2% B containing alloys.

Microstructure

As explained previously, binary Ti-Al alloys are mainly used in applications where hard, insoluble particles can cause down-stream quality problems such as pin-hole defects in foil or razor streaks in bright trim/anodized applications. Borides are often found in these defects, especially in conjunction with oxides. There is some evidence that borides can agglomerate after Ti-B-Al addition, especially in filters, to be released as "showers" by metal surges in misused filter systems.

Ideally, the metal cleanliness of the various master alloys needs to be measured after addition to the metal stream by methods such as LIMCA or PODFA. Unfortunately these techniques are not fully developed or commercially available to master alloy producers and therefore the more traditional method of measuring defects, metallography, has to be used. This has two problems: firstly, large numbers of samples have to be examined to obtain statistically significant results; and secondly, there is no account of any agglomeration or de-agglomeration of particles after addition to the melt. However, metallographic techniques do give indications of what can be expected.

The "pure" 6% Ti-Al alloy is almost totally devoid of any insoluble intermetallic particles. The 6% Ti-0.02% C shows a fine dispersion of small carbides, generally less than 2 microns but with an occasional larger particle up to 6 micron. This is due to the relative high processing temperatures required to produce this alloy⁶. Some TiC particles are associated with the TiAl₃ intermetallics, others adhere to oxides, which makes observation more difficult.

The 6% Ti-0.02% B alloy shows a fine, uniform dispersion of TiB₂ particles, generally less than 2 microns, the largest measured particle observed was 2 micron. The 3% Ti-0.2% B shows many more TiB₂ particles, less evenly distributed than in the more dilute alloys. However, the maximum observed particle sizes are similar (see Table V).

Since the 3% Ti-0.2% B alloy can be added at much lower addition levels to achieve effective grain refining, the total amount of added borides or carbides is similar with each alloy. Also, the level of added oxides will be significantly lower with the 3% Ti-0.2% B alloy since the alloy is relatively clean and the addition rates so low. What is unknown is the relative tendency of the borides or carbides to agglomerate on filters of launders. There have been significant improvements in the efficiency and cleanliness of the 3% Ti-0.2% B alloys in recent years. If suitable tests can be developed to measure defects after addition, then it is probable that alloys such as 3% Ti-0.2% B could be added AFTER the filter to achieve more consistent grain refining/freedom from twinned columnar growth without danger of TiB₂ agglomeration. This will be at much lower total costs compared to present grain refining methods with 6% Ti-Al alloys.

CONCLUSIONS

1. 6% Ti-Al, or any Ti-Al alloy, produced in the "pure" state without the presence of insoluble particles such as TiB₂ or TiC, is a poor, ineffective grain refiner.
2. The addition of 0.02% boron or 0.02% carbon to a 6% Ti-Al alloy significantly improves the grain refining response of 6% Ti-Al alloys but is still a factor of approximately 10 worse than 0.2% B containing alloys by weight.
3. In alloys with high solute content, such as 5657 alloy, effective grain refining and freedom from twinned columnar growth can be achieved with very low levels of boride or carbide nuclei and is dependent on actual carbon/boron addition rather than master alloy type.
4. In pure alloys, such as 1070, higher levels of grain refiner are necessary to produce fine grain sizes and freedom from twin columnar growth.
5. With the recent improvements in TiB₂ particle size control (Table V) and grain refining efficiency, 3% Ti-0.2% B alloys should be acceptable for use in more critical applications at much lower addition levels and hence less cost than enhanced 6% Ti-Al alloy.

APPENDICES

Appendix A

Metallographic Preparation Technique

All the samples were prepared using a Struers Prepamatic machine. This machine employs a fully automatic program over four stages after the sample has been cut and mounted in bakelite.

Stage 1 — Polish on fixed diamond pad (200m μ) for major stock removal.

Stage 2/3 — Polish with diamond suspensions of 15m μ then 3m μ .

Stage 4 — Final polish is with 0.4m μ colloidal silica.

The samples were then examined at the following magnifications; $\times 100$, $\times 500$, $\times 1000$; on an Olympus Light Microscope.

REFERENCES

1. I. Maxwell and A. Hellawell, *Acta Metall* (1975), 23:229-237.
2. D.A. Granger (Int. Seminar) "Refining and Alloying of Liquid Aluminium and Ferroalloys", Trondheim, Norway (1985), 231-244.
3. Aluminium Association Standard Test Procedure for Aluminium Grain Refiners (1987), TP-1.
4. D. Hadlet, D.G. McCartney, and S.R. Thistlethwaite in *Aluminium Technology '86*, Institute of Metals Book No. 391, London 1986, pp 125-132.
5. G.T. Campbell, and S.A. Sutker, "The Effect of Titanium and Boron Concentrations on Aluminium Grain Refiners" (Paper presented at the 115th AIME Annual Meeting, New Orleans, Louisiana, 2-6 March 1986), 741.
6. A. Banerji, W. Reif, and London & Scandinavian Metallurgical Co Limited, U.K., Patent Application GB 8505904 (March 1985).



LONDON & SCANDINAVIAN METALLURGICAL CO LIMITED

HEAD OFFICE AND EXPORT SALES: 45 Wimbledon Hill Road, London SW19 7LZ, England. Tel: 081-947 1221 Telex: 929830 Fax: 081-947 2966

UK SALES OFFICE AND MANUFACTURING PLANT: Fullerton Road, Rotherham, South Yorkshire S60 1DL, England. Tel: 0709 828500 Telex: 54581 Fax: 0709 828367