THE DEVELOPMENT OF A COMMERCIAL
Al-3%Ti-0.15%C
GRAIN REFINING MASTER ALLOY

A. J. Whitehead and S. A. Danilak
Shieldalloy Metallurgical Corporation
P. O. Box 768, Newfield, New Jersey 08344 U.S.A.

D. A. Granger
Aluminum Company of America
Alcoa Technical Center
Alcoa Center, Pennsylvania 15069 U.S.A.

The 126th TMS Annual Meeting & Exhibition
February 9-13th, 1997, Orlando, Florida, U.S.A.

ABSTRACT

An Al-3%Ti-0.15%C master alloy has been developed and is now being used for ingot grain refinement in Alcoa. A description is given for the development of a high ratio Ti:C Al-6%Ti-0.02%C master alloy and the progression from this to the more acceptable, lower ratio, Al-3%Ti-0.15%C. Acceptance for commercial use came only after extensive metallurgical characterization and evaluation of the grain refining performance, including the impact of alloy type and the presence of tramp elements. Details of the production, testing and characterization of this new grain refining master alloy are discussed.

BACKGROUND

The Al-Ti-B grain refiners have been the preferred choice for controlling the as-cast grain structure of aluminum alloys since the 1960's. While there is still no universal agreement as to what is the active nucleant in these master alloys, practical results indicate that in most circumstances it is the insoluble diboride particle. Unfortunately, large clusters of diboride particles are implicated in many quality problems ranging from linear streaks in brightened and anodized sheet to crack initiation in high strength aluminum alloy plate and forgings. As a consequence, there has been a long-standing desire on the part of the primary Aluminum Industry to have an acceptable replacement for Al-Ti-B master alloys.

In the early 1980's Alcoa initiated a program with its master alloy suppliers to develop a boron-free grain refiner that would provide consistent as-cast grain size control in a variety of alloys, particularly those used for surface sensitive products. It appeared that the Al-Ti-C system would be worthwhile investigating, since the seminal work of Cibula in the late 1940's(1) identified TiC, in addition to TiB_2, as an inoculant particle for aluminum alloys.

As a consequence of this program with master alloy suppliers, a commercial master alloy based on the Al-Ti-C system was introduced by Anglo-Blackwells in 1986. The alloy had a nominal composition of Al-6%Ti-0.02%C and was used successfully to control the as-cast grain structure in Properzi cast 1350 alloy(2), continuously cast plate and ingot used to produce sheet for a brightened and anodized application. The principal drawback to this alloy composition was the high ratio of Ti:C, which results in high titanium additions to provide enough TiC nuclei to control grain structure. This gave impetus to request further developmental work which was undertaken by Shieldalloy Metallurgical Corporation (SMC) starting in 1993. The goal of this activity was to manufacture an Al-Ti-C grain refining alloy that would have a substantially reduced Ti:C ratio in addition to the other desirable characteristics such as a small TiC particle size, low level of nonmetallic inclusions, absence of unreacted titanium, no aluminum carbides, and would provide consistent grain refining performance in a wide selection of aluminum alloys produced under a range of casting conditions.

DEVELOPMENT OF Al-3%Ti-0.15%C ALLOY

In order to understand how the commercial application of the low ratio Ti:C alloy (Al-3%Ti-0.15%C) evolved, it would be beneficial to review the development of the higher ratio Ti:C alloys first. The effects of carbon in titanium aluminum master alloys have been known to producers for many years. Typically, Ti-6%Al-4%V alloy scrap was the raw material of choice for the Al-6%Ti master alloy. The scrap was added to a molten aluminum bath in an induction furnace and after completely melting the alloy was cast. The castings were usually in the form of waffle castings which had a metallurgical structure comprising of an aluminum matrix and Al_3Ti intermetallics. While SMC was developing a production process in the 1970's, evaluation of the microstructural quality of Al-6%Ti revealed the presence of oxides in addition to many small titanium carbides. Efforts were made to improve the microstructural cleanliness of the Al-6%Ti master alloy by switching from an oily titanium scrap charge to one that was degreased and dry. The change in the charge material had the desired effect of eliminating the carbides and oxides but it also resulted in a decrease in grain refining performance due to the lack of insoluble TiC particles. Furthermore, the heats were less fluid and considerably more difficult to cast. Through further development it was discovered that the casting difficulties could be resolved with a small addition of oil to a clean scrap charge which resulted in a chemical reaction as the titanium went into solution. It was assumed that the oil was breaking down. The hydrogen and carbonaceous gases which evolved generated additional turbulence and helped the bath fluidity by keeping the Al_3Ti intermetallic particles in suspension. Although there was a noted improvement in the microstructural cleanliness, grain refinement varied due to the inconsistent level of insoluble TiC particles. As previously stated, an Al-6%Ti-0.02%C alloy was developed which performed more consistently and reliably than the earlier binary Al-Ti master alloys. It was demonstrated that high processing temperatures led to the level of grain refining needed for aluminum alloys(3). As a result of this processing, the carbon enhanced alloys had a fine dispersion of TiC particles about 2-microns in size which acted as effective nuclei in some commercial aluminum alloy systems(4). The Ti:C ratio in Al-6%Ti-0.02%C was considered high and a lower ratio was desired as such an alloy would provide more nuclei for a given titanium addition.

Various efforts are being made throughout the world to develop an effective, commercial Al-Ti-C master alloy. M.A Hadia et.al.(5) experienced some success developing a series of Al-Ti-C master alloys with lower Ti:C ratios on a laboratory scale. There has been no report that these alloys have been successfully used in commercial aluminum alloys under production conditions. An Al-3%Ti-0.15%C has been successfully developed by SMC and is being used in production in one and evaluated at several other ingot plants within the Alcoa system.

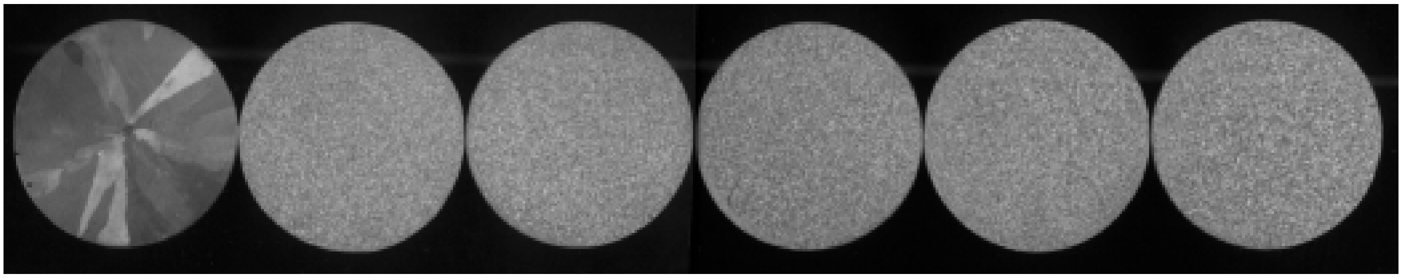

Figure 1 - Modified TP-1 test samples using a 0.01%Ti addition of the Al-3%Ti-0.15%C grain refining master alloy in 99.7% aluminum.

EVALUATION

Grain Refining Tests

In the course of developing a new commercial grain refining master alloy, it is desirable that both the producer and consumer have small scale methods of gauging the performance and consistency of the product. For the producer, the critical capability of the test is that of being able to assess heat to heat variation and performance while the consumer needs to have a test procedure that provides a good correlation with grain structure control in commercially produced aluminum alloys. For the purpose of evaluating Al-3%Ti-0.15%C master alloy, SMC used a modified version of the Aluminum Association's Standard Test Procedure of Aluminum Alloy Grain Refiners 1990 (TP-1) while Alcoa used an in-house developed method.

Aluminum Association Test Procedure (TP-1)

The Aluminum Association developed and published a standardized test for evaluating grain refining master alloys, TP-1, in 1987 and revised the standard in 1990(6). TP-1 includes a grain refining performance test procedure. This standard test was established as a relative method for producers and consumers of grain refining master alloys to compare different types of grain refining master alloys and/or different addition levels.

For the Al-3%Ti 0.15%C alloy, SMC used TP-1 grain refining test procedure with minor modifications. The modified test procedure is as follows:

Ten kilograms of 99.7% aluminum to be grain refined is melted in a small resistance furnace to a temperature of 1350°F ±15°F. The Al-3%Ti-0.15%C grain refining master alloy is added at a 0.01% Ti level. After the addition of the grain refiner, the bath is stirred for 30-seconds and the melt is sampled by means of a coated steel ladle. Prior to sampling, the ladle is held submerged in the bath for 30-seconds. Samples are taken at 2, 5, 10, 15, and 30 minutes after the grain refiner addition. Each sample is quenched and then sectioned horizontally 1-1/4″ from the base for grain size determination. The sectioned sample is polished, etched in Poulton's reagent and then viewed on a binocular scope at 25x magnification. The number of grains is counted in an area of a 1/2-inch diameter at the center of the etched surface using a linear intercept technique.

The differences between the modified and the standard TP-1 test are that in the former the temperature of the bath was 25°F higher: the bath is stirred only before the 2-minute sample and further samples are taken at 15 and 30 minutes after the grain refiner addition.

All of the Al-3%Ti-0.15%C master alloy heats produced by SMC have been assessed using this method. Figure 1 shows a typical series of modified TP-1 test cones in 99.7% aluminum at a 0.01% Ti grain refiner addition level.

Alcoa Grain Refining Test Procedure

In the early 1970's a method for evaluating grain refining master alloys was developed in the Alcoa laboratories. The need for a more discriminating test was recognized because the methods in use at the time, which took the form of either a simple permanent mold or sand casting, did not predict the occurrence of twin columnar growth (TCG). Since TCG is the most undesirable grain structure found in aluminum alloy ingots, this was a serious shortcoming of the incumbent methods. The Alcoa method has been outlined elsewhere(7) but a more complete description is given here.

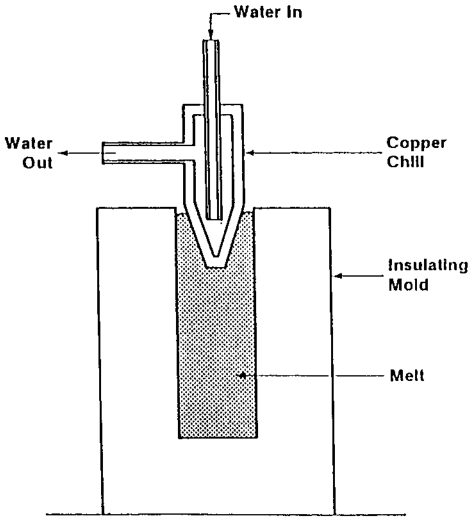

Figure 2 - Alcoa Grain Refining Test Mold-Chill Configuration During Solidification.

The test method comprises a plaster mold, preheated to approximately 1400°F, into which the molten alloy is introduced before being solidified with a water-cooled copper cone (Figure 2). Solidification proceeds vertically downwards from the copper chill to the bottom of the mold. This provides a very exacting test for any grain refiner since the nuclei, such as TiB_2, are more dense than molten aluminum and tend to fall away from the solidifying interface. Most other test procedures, such as TP-1 have the nuclei settling onto the interface. Experience has shown that the Alcoa method is a very good predictor of grain refining master alloy performance in commercial ingot casting processes.

In order to assess the performance of a grain refining master alloy, the following procedure is adopted. A 25-kg melt of the alloy is prepared. This melt is fluxed with an Argon-10%Cl_2 gas mixture and the temperature is stabilized at 1300° ±15°F. A sample is taken from the melt for chemical analysis and the first grain refining test casting is poured. The melt is then inoculated with the desired grain refining addition which is well stirred for 40-seconds. At one minute, a sample is taken for chemical analysis and a test casting is poured. No further stirring of the melt takes place but sampling continues at about 5-minute intervals for up to 30-minutes.

The chemical analysis samples are subjected to quantometer analysis and the grain refining test castings are sectioned longitudinally and the sawed face of one half is surface-machined. The machined face is macro etched in Tucker's reagent, or a similar etching solution, to reveal the as-cast grain structure. A typical series of 5657 alloy castings before and after grain refining with Al-6%Ti-0.02%C at the 0.015%Ti addition level is shown in Figure 3. In order to obtain a quantitative grain size a small sample is cut from a location 1-inch below the copper chill. This sample is prepared using standard metallographic polishing procedures, electro-etched in Barker' s solution and viewed under polarized light to reveal the grains. Grain size is determined using the linear intercept method as described in ASTM 112.

To date, all the Al-3%Ti-0.15%C master alloy heats produced by SMC have been assessed using this method. Although the grain refiner has been evaluated in many aluminum alloys, the bulk of the testing has been conducted in 5657 alloy. Figure 4 illustrates the range of performance observed in the many heats that have been manufactured to date.

Application of Al-3%Ti 0.15%C

A successful application of Al-3%Ti-0.15%C grain refiner rod has been for the control of grain structure in Alcoa continuously cast plate, which is produced from a 7xxx alloy of nominal composition:

Si	0.75	Zn	4.06
Fe	0.75	Ti	0.069
Cu	0.91	B	0.0007
Mn	0.11	Be	0.0004
Mg	1.79	Ca	0.0084
Cr	0.12	Zr	0.006
Ni	0.06		

Al-6%Ti-0.02%C was used for a number of years, but was not entirely satisfactory. The high level of titanium addition, typically 0.015%, could result in coarse intermetallic particles when the other alloying elements were on the high side of the specification range. Also, there was the occasional occurrence of TCG or columnar grain growth. For over a year, Al-3%Ti-0.15%C has been used at about one third the titanium addition rate of Al-6%Ti-0.02%C to provide superior control of the grain structure at a reduced risk of coarse intermetallic particle formation. Comparative grain structures with the two master alloys are illustrated in Figures 5 and 6.

Carbon Analysis

The analytical method used for evaluating the total carbon present in Al-3%Ti-0.15%C and Al-6%Ti-0.02%C was a Combustion Instrumental Measurement Method (CIMM), specifically the LECO® CS 244 Carbon/Sulfur Determinator. The measurement process consists of carbon combustion in oxygen, conversion of CO to CO$_2$, and measurement by infrared absorption of CO$_2$. A sample 0.5 to 1 gram of grain refining master alloy was put into a crucible with a combustion accelerator, in this application LECOCEL® II, a tungsten and tin accelerator. The crucible was placed in the combustion tube which utilized an induction furnace to heat the crucible in a purified oxygen atmosphere for combustion of carbon in the grain refiner master alloy sample. CO gas product was converted to CO$_2$ gas. The CO$_2$ detection method was solid state infrared absorption. A microprocessor was used to process the results and set the calibration(8). The calibration standards used were LECO® Certified Carbon and Sulfur in Steel. The standards were analyzed prior to the grain refining master alloy sample using the same combustion method and accelerator.

CHARACTERIZATION

The microstructure of the Al-3% Ti-0.15%C rod was compared with the Al-6%Ti-0.02%C rod. Both grain refiners were manufactured on a production scale by casting bar and extruding to a 3/8˝ diameter rod by means of a Conform™(9). The samples were obtained by cutting longitudinal sections of the rod and prepared using standard metallographic techniques. The samples were evaluated in an unetched condition. The methods of characterization used were optical microscopy and quantitative image analysis (QIA) by scanning electron microscopy (SEM).

Figure 7 shows the microstructure of each rod alloy, Al-3%Ti-0.15%C and Al-6%Ti-0.02%C, as examined by optical microscopy at 100x and 500x magnifications. The volume of TiC particles is greatly increased in the Al-3%Ti-0.15%C but the particles remain largely submicron in size similar to those in Al-6%Ti-0.02%C. The size and quantity of the Al$_3$Ti phase are significantly reduced in the Al-3%Ti-0.15%C.

Backscattered electron images (BEI) produced by SEM were analyzed at 2000x for TiC particle size and distribution using the TRACOR 5500 analyzer (Figure 8). The TiC particle statistics are listed in Table I. The average diameter measured in Al-3%Ti-0.15%C is 0.59 microns as compared to 0.26 microns in Al-6%Ti-0.02%C. The number of TiC particles

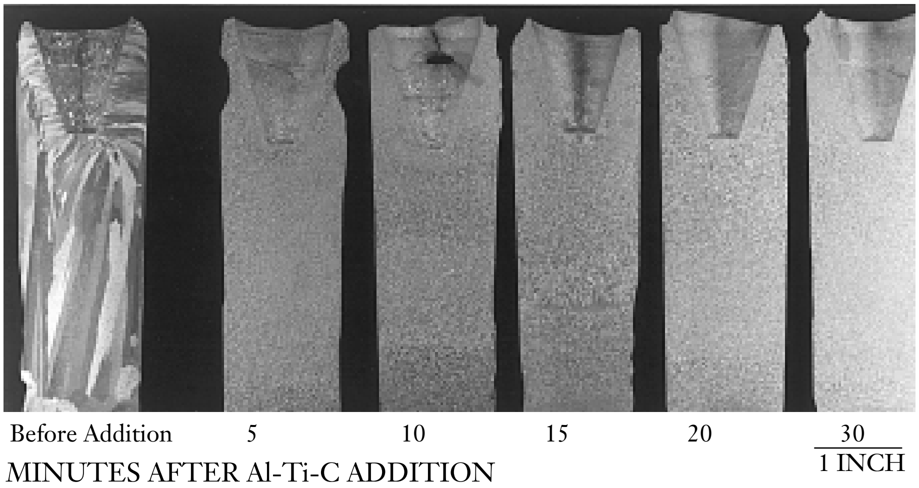

Figure 3 - Typical series of 5657 alloy Alcoa grain refining test castings inoculated with Al-6%Ti-0.02%C at a 0.015% Ti addition level. Tucker's reagent.

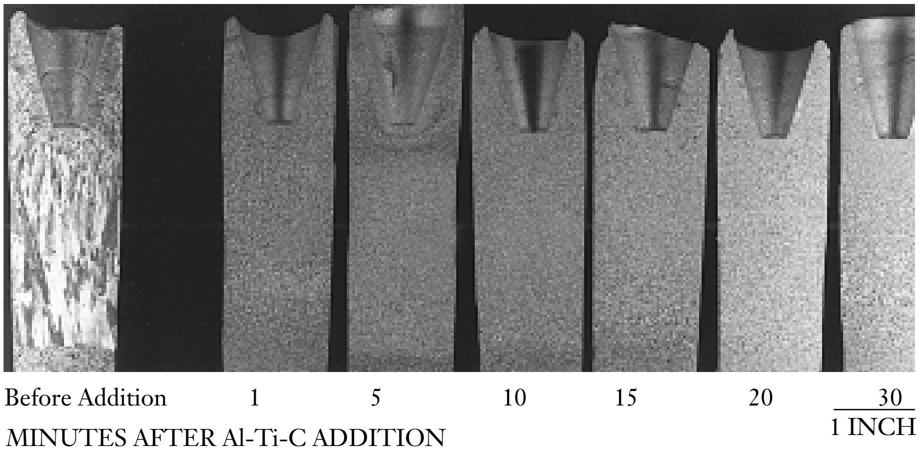

Figure 4 - Typical series of 5657 alloy Alcoa grain refining test castings inoculated with Al-3%Ti-0.15%C at a 0.005% Ti addition level. Tucker's reagent.

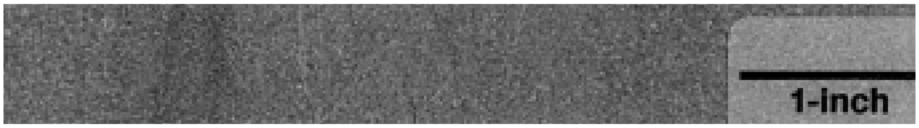

Figure 5a - A longitudinal section of a 7xxx continuously cast plate with Al-6%Ti-0.02%C addition showing TCG. Etch: Fennell's reagent.

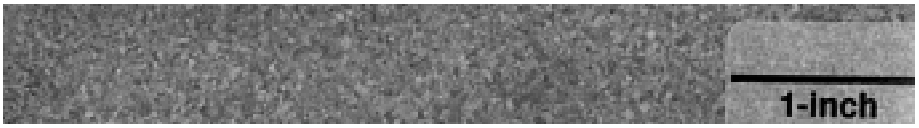

Figure 5b - A transverse section of a 7xxx continuously cast plate with Al-6%Ti-0.02%C addition. Etch: Fennell's reagent.

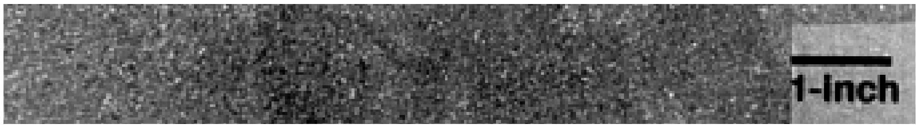

Figure 6a - A longitudinal section of a 7xxx alloy with Al-3%Ti-0.15%C at 30% of the normal Ti addition level showing no TCG. Etch: Fennell's reagent.

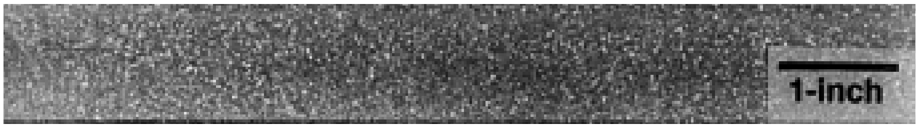

Figure 6b - A transverse section of a 7xxx alloy with Al-3%Ti-0.15%C at 30% of the normal Ti addition level showing no TCG. Etch: Fennell's reagent.

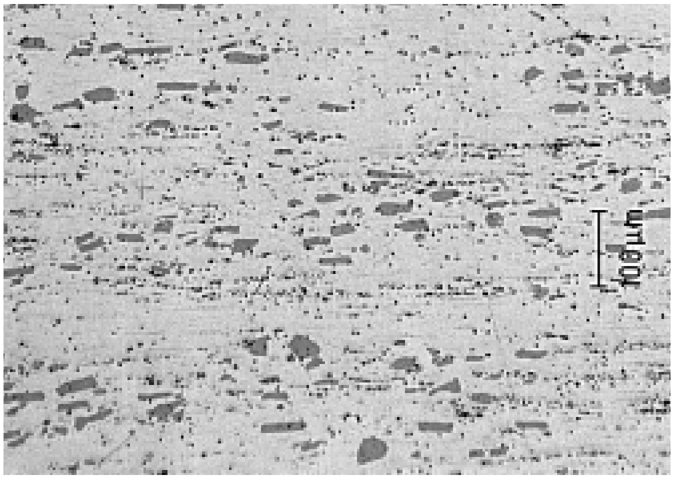

Figure 7a - A longitudinal section of Al-3%Ti-0.15%C rod showing relatively large Al_3Ti particles and smaller TiC particles. Unetched.

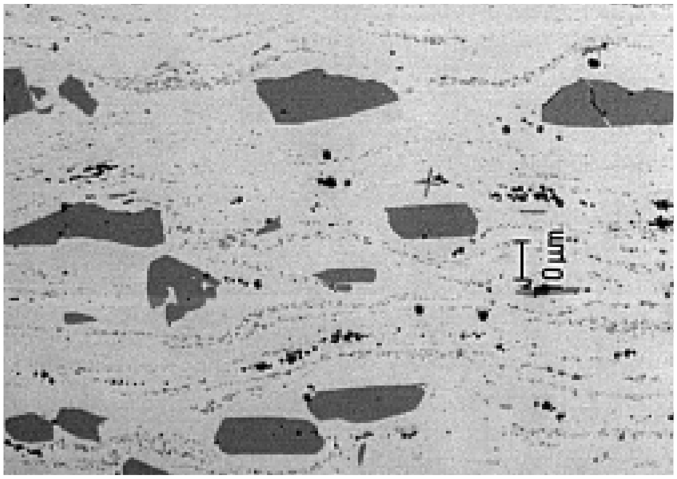

Figure 7b - Same as 7a above but at a higher magnification.

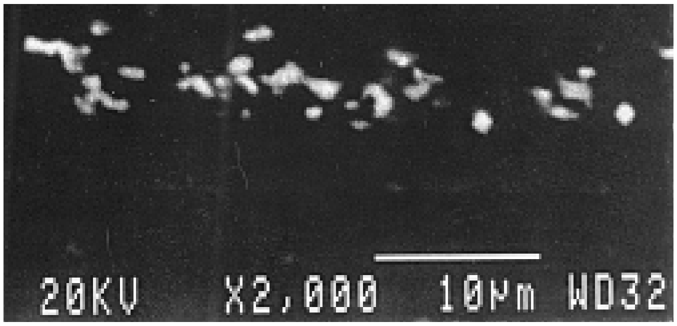

Figure 8a - Quantitative image analysis area illustrating the size and distribution of TiC particles in Al-3%Ti-0.15%C, 2000x.

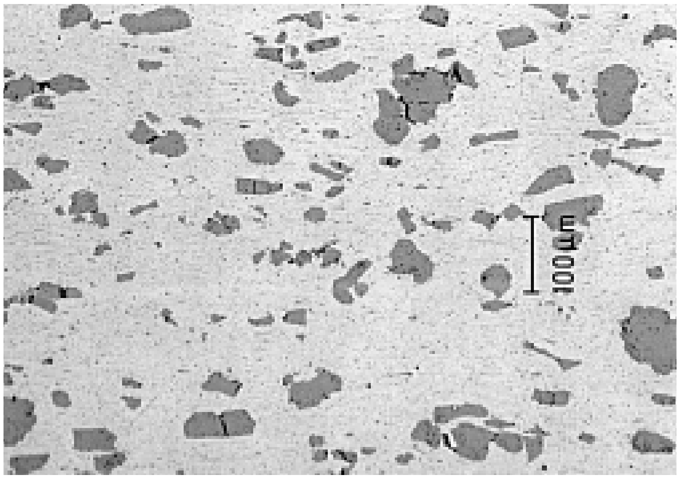

Figure 7c - A longitudinal section of Al-6%Ti-0.02%C rod showing relatively large Al_3Ti particles and smaller TiC particles. Unetched.

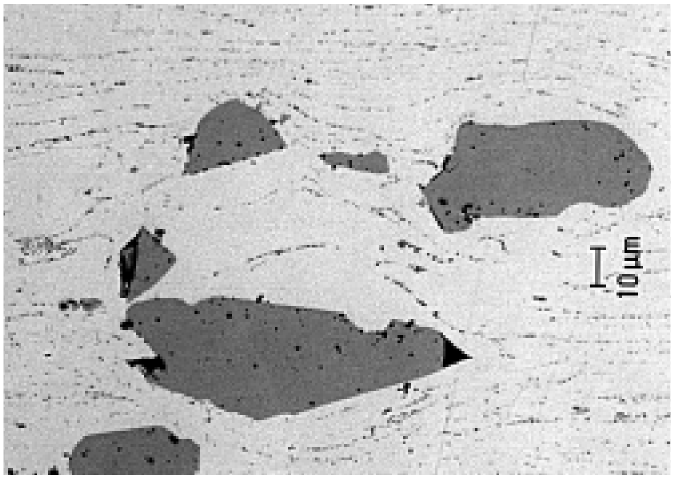

Figure 7d - Same as 7c above but at a higher magnification.

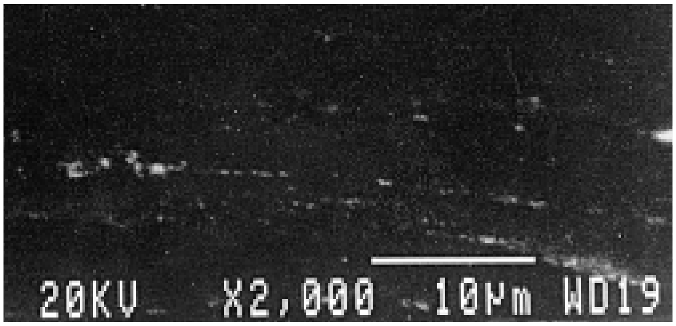

Figure 8b - Quantitative image analysis area illustrating the size and distribution of TiC particles in Al-6%Ti-0.02%C, 2000x.

TABLE I : Quantitative Image Analysis TiC Particle Summary for two Al-Ti-C Master Alloys

	Al- 3%Ti- 0.15%C	Al- 6%Ti- 0.02%C
Magnification	2000x	2000x
Number of Particles	199	67
Analysis Area	1764 micron^2	1764 micron^2
Average TiC Area	0.38 micron^2	0.08 micron^2
Percentage TiC in Analysis Area	1.00	0.07
Average TiC Diameter	0.59 micron	0.26 micron
Average TiC Length	0.77 micron	0.31 micron
Average TiC Width	0.49 micron	0.23 micron
Shape Factor	1.02	0.53
Aspect Ratio	1.44	1.25

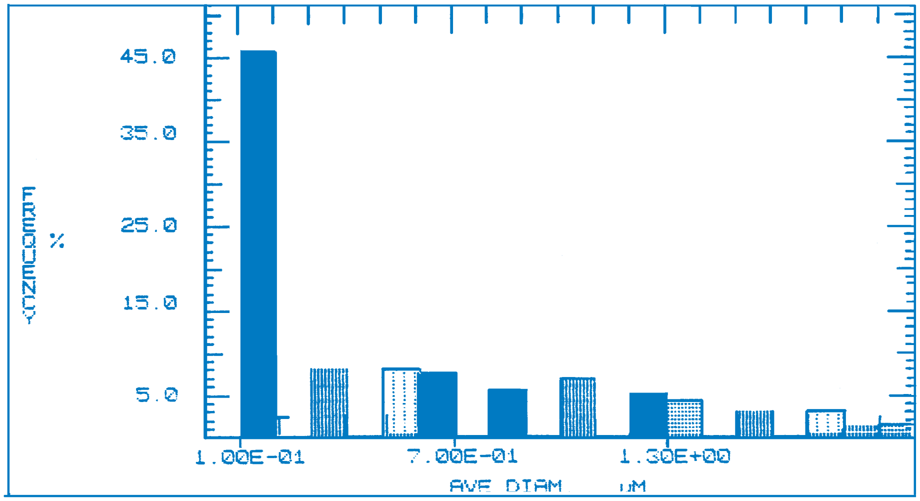

Figure 9a - Quantitative image analysis TiC histogram of an Al-3%Ti-0.15%C master alloy for 1764-micron² area, 2000x.

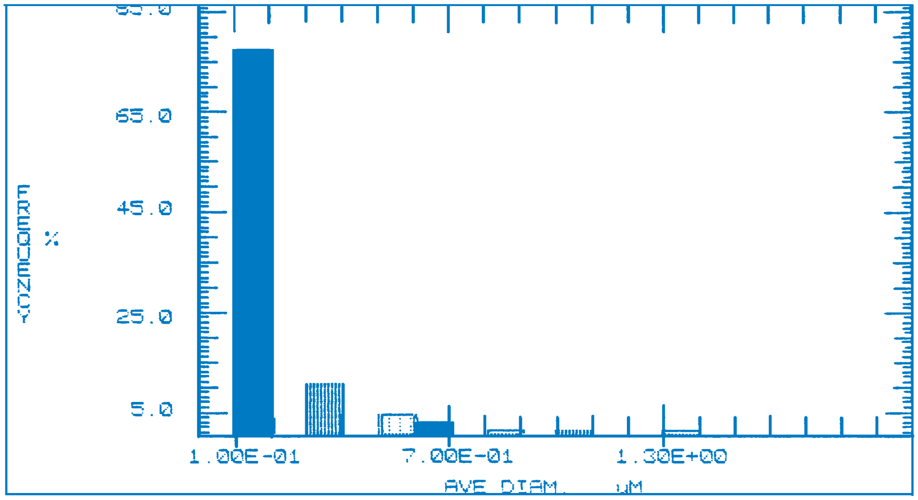

Figure 9b - Quantitative image analysis TiC histogram of an Al-6%Ti-0.0%C master alloy for 1764-micron² area, 2000x.

Characterization continued

present is 199 for Al-3%Ti-0.15%C and 67 for Al-6%Ti-0.02%C in the 1764-micron^2 area. The particle size distribution for each alloy is presented by the histograms in Figure 9.

The number of TiC particles in Al-3% Ti-0.15%C is approximately three times greater than Al-6%Ti-0.02%C for a similar area of analysis. If Al-3% Ti-0.15%C was substituted for Al-6% Ti-0.02%C at the same Ti addition level, the number of TiC particles would increase by a factor of six.

FURTHER DEVELOPMENTS

With the great improvement in grain refining performance achieved by lowering the Ti:C ratio in Al-Ti-C, there should be further evaluation of Al-Ti-C master alloy as a substitute for Al-Ti-B in applications where TiB$_2$ nuclei are a potential source of problems or may lose their effectiveness through poisoning by other elements in the melt stream.

Development of Al-Ti-C alloys should be continued to determine if the grain refining performance can be further improved by variations in the Ti:C ratio and processing condition. Further studies are recommended to determine the comparative effectiveness of TiC nuclei in Al-Ti-C versus those found in Al-Ti-B grain refiners.

CONCLUSIONS

1. The Al-3%Ti-0.15%C grain refining master alloy has been developed, tested and can be used in commercial ingot production as a substitute for Al-6%Ti- 0.02%C.

2. A higher concentration of effective nuclei are present in Al–3%Ti-0.15%C as compared with Al-6%Ti-0.02%C at similar Ti addition levels.

3. The TiC particle size, range and distribution in Al-3%Ti-0.15%C are acceptable for use in critical applications such as brightened and anodized sheet, micron foil, and litho sheet.

4. The Al-3%Ti-0.15%C grain refiner is effective in the presence of B, Cr, and Zr at the levels found in the 7xxx continuously cast plate alloy.

ACKNOWLEDGMENTS

The authors wish to thank Dr. G. T. Campbell, previously of SMC, for his initial role in the development of a commercial Al-3%Ti-0.15%C grain refining master alloy; I. N. Rossi of Alcoa who prepared the evaluation castings using Alcoa test procedure; and J. B. Heck of SMC for preparing this paper for publication.

REFERENCES

1. A. Cibula, “The Mechanism of Grain Refinement of Sand Castings in Aluminum Alloys,” J Inst. Met., 1949-50, 76, 321-360.

2. D. A. Granger and L. D. Hammar, “Grain Size Control in EC Aluminium ,” Proceedings of 3rd International Conference on Aluminium Alloys, Vol. 1, Trondheim, Norway, 22-26 June 1992, 9-14, Publ. SINTEF .

3. A. Banerji and W. Reif, Metallurgical Transactions., Vol., 17A , 1986, 2127-37.

4. G. T. Campbell and S. A. Danilak, “Enhanced Titanium Aluminum Grain Refiners,” Light Metals 1992, ed.: Euel R. Cutshall (Warrendale, PA: The Minerals, Metals & Materials Society, 1991) 831- 836.

5. M. A. Hadia, A. A. Ghaneya and A. Niazy, “Development and Evaluation of Al-Ti-C Master Alloys as Grain Refiners for Aluminum,” Light Metals 1996, ed. Wayne Hale (Warrendale, PA:The Minerals, Metals & Materials Society, 1996) 729-736.

6. Aluminum Association Standard Test Procedure for Aluminum Grain Refiners 1990, TP-1, The Aluminum Association, Washington, D.C. 20006.

7. D. A. Granger, Proc. Int. Seminar, “Refining and Alloying of Liquid Aluminium and Ferroalloys,” Trondheim, Norway 1985, 231-244.

8. LECO® CS-244 Simultaneous Carbon/Sulfur Determinator, Brochure Form No. 200-926, 1988, LECO Corporation, St. Joseph, Missouri, USA.

9. G. T. Campbell, D. G. Kenyon, D. T. Leavers, and S. A. Sutker, “Castform ™/ Castcut™, The Latest Technology for Master Alloy Production,” Light Metals 1991, ed.: Elwin Rooy (Warrendale,PA:The Minerals, Metals & Materials Society, 1990) 1095-1103.

Printed in USA