ALUMINUM MASTER ALLOYS AND ADDITIVES "THE MAGIC INGREDIENTS"
by W. G. Lidman

The U.S. Aluminum Industry is the world's largest, producing about 20 billion pounds of metal annually. The industry employed 141,000 people with an annual payroll of $5.2 billion and shipped $38.8 billion in products in 2000. The high quality of these products and the profitability of the industry are due, in large part, to the contributions of a niche industry made up of the Master Alloys and Additives companies. These companies have dedicated their efforts to providing the Aluminum Industry with special alloys and additives that reduce manufacturing cycle time and enhance product quality. Some of their contributions to the aluminum industry are presented below.

<u>Grain Refiners</u>
Grain refinement of aluminum provides a number of technical and economic advantages, including reduced ingot cracking, better ingot homogeneity, better mechanical deformation characteristics and improved mechanical properties (See Figures 1 and 2 for visual comparison of microstructure before and after the addition of grain refiner.). Grain refining elements, titanium and boron, were originally introduced into molten metal as refractory titanium alloy and as corrosive complex potassium metal fluoride salts. Use of these materials resulted in inconsistent performance and detrimental side effects, such as, corrosion of furnace refractories, risk of inclusions and unpredictable grain refining response. These side effects and uncertainties were eliminated when master alloy companies together with aluminum producing companies developed a master alloy, which included aluminum, titanium and boron in precise quantities. Because the alloys were originally provided in ingot form, the product was added to the melting furnace 30 to 60 minutes before casting. The next improvement in grain refiners was the development in 1972 by the master alloy companies of a rod feeder and a fast acting aluminum alloy grain refiner that could be produced in 3/8 inch diameter rod form. This improved product could then be added to the molten metal stream enroute to the casting station. With the introduction of each new product (ingot then rod) the required quantity of grain refiner was reduced because of the improved recovery of the grain refining ingredients and better furnace utilization was achieved, which translates to lower costs for the industry.

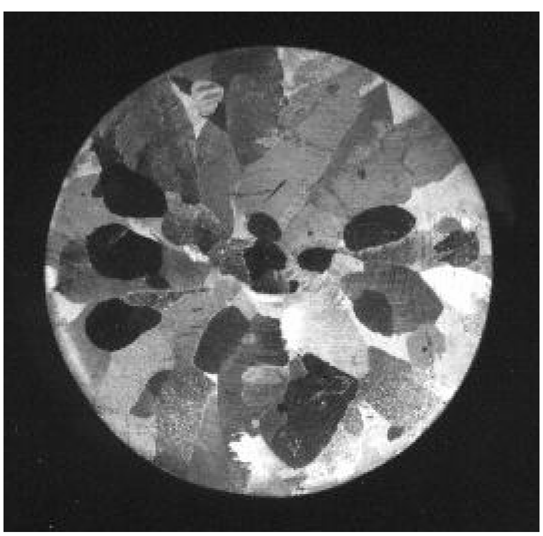

Figure 1; 1.5x; 99.9% aluminum ungrain-refined; frozen in the TP-1[1] method, sectioned, faced with a lathe and etched with Poulton's etch. The nominal grain size is 4500μ.

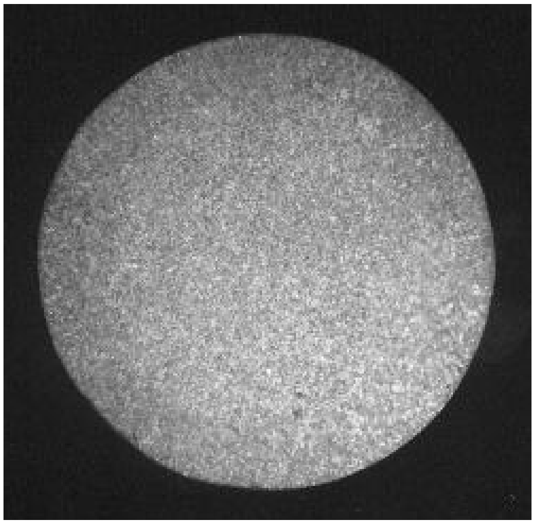

Figure 2; 1.5x; 99.9% aluminum grain-refined with 0.008% Titanium added as 5%Ti-1%B-Al H2252 rod; frozen in the TP-1 method, sectioned, faced with a lathe and etched with Poulton's etch. The nominal grain size is 120μ.

Boron

For Boron additions, products were developed by the master alloy companies, which parallel the grain refiner improvements. Originally borax ($Na_2B_4O_7$), or B_2O_3 was added to the electrolytic cell, or KBF_4 was added to the melting furnace to tie up transition metal impurities such as vanadium and titanium which adversely affect electrical conductivity of aluminum. These procedures resulted in cell contamination, or generation of toxic fumes and residual spent salt ($KAlF_4$) in the melting furnace. An aluminum-boron alloy was developed by the master alloy companies that eliminated the fumes, contamination, spent salt and the uncertainty of boron addition using the boron compounds. Then following the development of aluminum-boron in rod form which is used to introduce boron into the molten metal stream, thus reducing furnace time and avoiding furnace contamination.

Hardeners

The mechanical and physical properties of pure aluminum can be enhanced with the use of alloying elements. Additions of these alloying elements can be made using elemental metals. Density differences between the alloying elements and aluminum frequently results in segregation, with high density elements sinking to the bottom of the furnace unless the melt is actively stirred until the element is completely in solution. Low-density active elements like lithium or calcium require special handling in storage and in use to minimize hazards. High melting temperature elements will only go into solution when the liquid aluminum temperature is increased substantially. These high temperatures effect furnace life, require more energy and cause excessive dross.

Producers of aluminum additives discovered a novel method of harnessing the exothermic energy of intermetallic reactions by employing mixtures of pure metal powers and aluminum powder to create a briquette additive. The briquette additive reduces the time required to dissolve elements such as manganese and chromium from hours to minutes. The compacted briquette is manufactured at room temperature to circumvent the historic problems associated with oxidation and liquid metal segregation. The briquette addition technology eliminated the headache of cell contamination from the potroom and eliminated the energy intensive costs associated with producing master alloys in an aluminum reduction cell. The production of briquette additives requires the use of substantial amounts of atomized aluminum powder.

Master alloy producers have developed high concentration of hardener elements alloyed with aluminum in ingot form. These hardener ingots may require more time to dissolve in liquid aluminum than the briquettes; however, their use still provides shorter furnace cycles and better furnace utilization than does the use of elemental alloying metals. Health hazards associated with handling of some alloying elements are minimized using master alloy ingots.

Aluminum Castings

The silicon content in most aluminum castings is in the range of 5 to 12%. When castings of melts of these alloys are not modified, coarse platelet crystals of the aluminum silicon eutectic phase form in the casting during solidification (Figure 3.). These particles are brittle and tend to reduce the strength and ductility of the casting. Modification of the silicon phase produces a silicon phase that is fibrous and finely dispersed (Figure 4.). Ductility of the castings improves markedly and the tendency for cracking or brittle fracture is less.

For many years, sodium was the only means available for modification of aluminum silicon alloys. However, sodium is a very reactive metal. It can react when exposed to air and can burn violently during addition to molten aluminum silicon alloy. Therefore, close control of the addition level is difficult. Some foundrymen have been known to use antimony as a modifier, however, antimony is toxic and not recommended. The search by master alloy producers for alternative elements for modifying aluminum silicon castings revealed that strontium could be used in place of sodium. Fortunately, none of the special precautions required in the use and handling of sodium apply to strontium. Strontium alloyed with aluminum is produced and supplied by the master alloy companies. The alloy is available in several forms for furnace addition, or in rod form for addition to the liquid aluminum stream which eliminates furnace contamination.

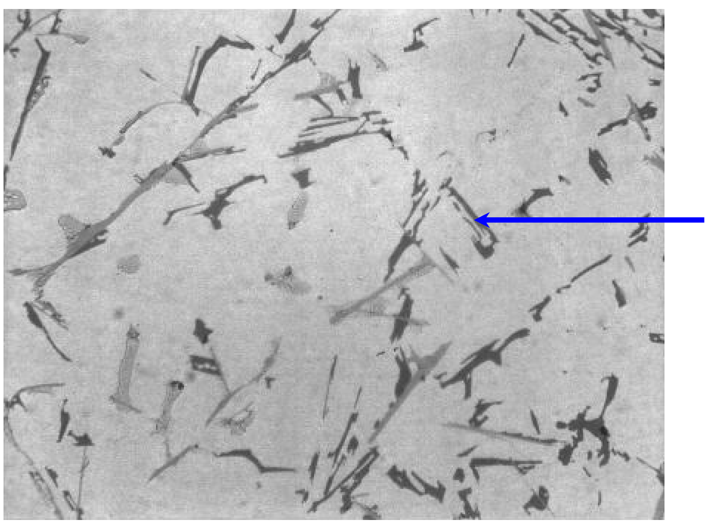

Figure 3; 400x; etched with dilute Keller's etch; 319.0. Unmodified silicon particles are very dark gray. The idiomorphic form of eutectic silicon diminishes the ductility of the alloy.

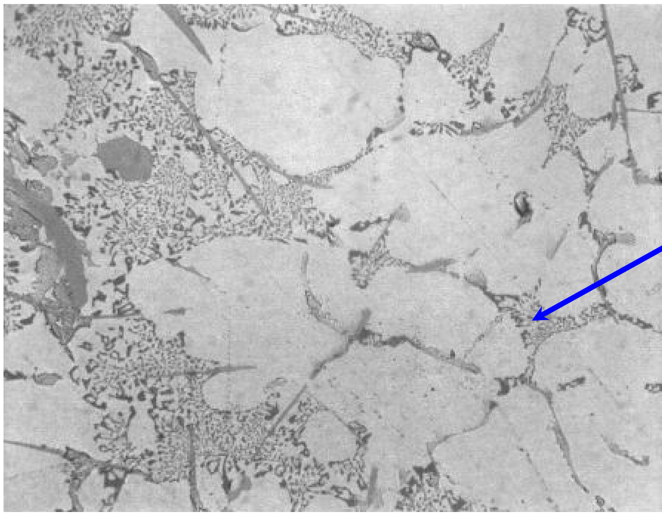

Figure 4; 400x ; etched with dilute Keller's etch; 319.0 with 0.018%Sr. Fully modified silicon particles are very dark gray. The fibrous form of eutectic silicon enhances the ductility of the alloy.

<u>Standards</u>

One of the first contributions of the Master Alloys and Additives Division came in 1973 with the much needed designation system and listing of chemical composition limits for the aluminum hardeners and grain refiners. This formal designation system was later approved by the American National Standards Institute as an American National Standard[2] in 1975. The list[3] is maintained by the Association's Technical Committee on Product Standards. The listing gives the aluminum industry a recognized referenced conformance for the master alloys and hardeners. The standard is the foundation for most members' raw material product specification.

As recently as 1987, there were no standard procedures in the Aluminum Industry for evaluating the performance of grain refiners or the dissolution rate of aluminum hardeners. The master alloy producers developed standards for both the grain refiners (TP-1) and the hardeners (TP-2)[4]. These standards were reviewed by technical people at the aluminum companies, accepted, and then published by the Aluminum Association during 1987. These procedures were reissued during 1990.

<u>Conclusion</u>

The Master Alloys and Additives Division members are proud of the many worthwhile contributions it has made to the aluminum industry. Member companies are in the unique position of producing aluminum alloys and products from aluminum that are returned to the aluminum industry. The Association provides to the Division Members the opportunity to gain knowledge about working with aluminum while being close to their customers needs, a partnership that has proven over time to be mutually beneficial.

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[1] TP-1 - Standard Test Procedure for Aluminum Alloy Grain Refiners.

[2] ANSI H35.3 - American National Standard Designation System for Aluminum Hardeners.

[3] Registration Record of Designations and Chemical Composition Limits for Aluminum Hardeners.

[4] TP-2 - Standard Test Procedure for Measurement of Dissolution of Aluminum Hardeners.

The above standards are published by The Aluminum Association and can be ordered from the electronic bookstore available on the Association's web site at www.aluminum.org.