

## **Industrial Development of Non-Heat Treatable Aluminum Alloys**

R. E. Sanders Jr., P. A. Hollinshead, E. A. Simielli

Alcoa Technical Center, 100 Technical Drive, Alcoa Center, PA 15069

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### **Abstract**

The last 25 years have seen the continued improvement of many aluminum products developed for packaging, automotive and other industrial customers. Higher performance non-heat treatable alloys have been developed for new and existing applications ranging from foil to structural plate. These developments were driven largely by a clear definition and understanding of customer needs. The ability to control microstructure as it evolves through solidification, thermal and deformation processing have enabled these products to be manufactured with the quality, consistency, and low cost demanded by the marketplace. Alloy and process improvements will be reviewed for a number of important aluminum wrought products. Products sourced from continuous casters as well as DC ingot will be examined. The importance of understanding the end customer's needs and microstructure evolution will be highlighted in specific examples from rigid container, foil, and automotive sheet applications.

### **1. Introduction**

Non-heat treatable aluminum (NHT) alloys are utilized in all of the major industrial markets for aluminum flat-rolled products. Transportation, packaging and the building/construction sectors have represented the largest usage of NHT sheet during the last part of the 20<sup>th</sup> century. Higher performance non-heat treatable alloys have been developed for new and existing applications ranging from foil to high strength structural products. The development of new or improved alloys has been based on the need for structural performance or appearance in the end product and productivity during the customer's manufacturing process. The availability of competitive materials has driven the need to keep the cost of the aluminum product as low as possible. The ability to control microstructure as it evolves through solidification, thermal and deformation processing have enabled these products to be manufactured with the quality, consistency, and low cost demanded by the marketplace.

NHT alloys can provide an extremely wide range of properties to meet many needs in the marketplace. Figure 1 shows that yield strengths of 20 MPa to 500 MPa are attainable from the 1xxx, 3xxx, and 5xxx alloy families in the range of work hardened tempers from "O" to "H19" [1]. The highest strength alloys are capable of strengths similar to many of the heat treatable alloys while the low strength alloys can provide high levels of formability when needed.

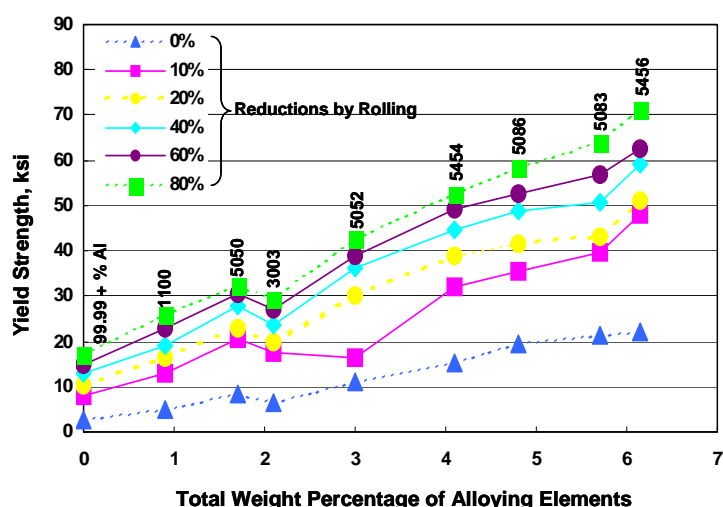


Figure 1: Data from Reference 1 illustrating the attainable strength levels of NHT alloys with different levels of cold work.

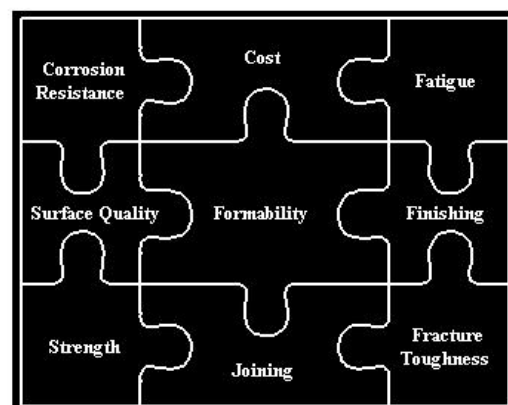


Figure 2: Schematic diagram illustrating the various characteristics required for NHT sheet.

The basic metallurgy of NHT alloys has been covered extensively in other publications [2-6]. This review will focus on alloy and process improvements for a number of important aluminum wrought products. Products sourced from continuous casters as well as DC ingot will be examined.

## 2. Applications of NHT Alloys

The three major criteria for selecting or developing new NHT aluminum alloy products are:

- structural – based on strength and durability,
- forming – based on complexity or productivity in making the final part,
- surface – based on finishing characteristics, reflectivity or surface appearance.

Every product application will have a unique balance of requirements. The diagram in Figure 2 suggests that other characteristics will inevitably come into play when developing or specifying an alloy for a given application. Typically, applications with high structural strength requirements will not require high formability or surface attributes. Extra steps in the fabrication flow path or more stringent process control may be required to meet more exacting combinations of the product attributes in Figure 2. The requirement of any successful industrial alloy development is to meet the needs of the customer by manipulating the alloy composition and process (i.e., controlling the microstructure) of the final product. The sizes of the various “puzzle pieces” in Figure 2 will vary with the final application and customer.

**Trends in Applications:** The packaging industry (dominated by rigid container sheet) remains the largest market for NHT flat rolled products. Table 1 shows a comparison of the distribution of rolled product usage in North America [7].

Table 1: Production Volumes of Major Flat-rolled Products

	1992 Metric tonnes x 1000 (Lbsx10 <sup>6</sup> )	2002 Metric tonnes x 1000 (Lbsx10 <sup>6</sup> )
Packaging (foil, can stock)	2,266 (4,995)	2,258 (4,978)
Building & Construction	561 (1,237)	751 (1,656)
Transportation (sheet and foil -excluding plate)	336 (741)	~611 (~1,348)

Notes: data from Reference 7, 2002 data is US & Canada, 1992 data is US only.

In packaging, the leveling off of can growth and continued lightweighting have reduced the amount of rigid container sheet (RCS) needed to supply the 100 billion cans used in North America each year. During the last 10 years, the growth of NHT alloys has been most dramatic in the transportation sector, with the volume of sheet and foil nearly doubling to more than 600,000 tonnes. This is primarily due to the growth of sheet for automotive applications. While some of the growth is undoubtedly in the area of 6xxx heat treated sheet for closure panels (automotive hoods and deck lids), growth in demand for brazing sheet and fin stock for aluminum radiators, heat shields and other applications has greatly increased the demand for NHT sheet products.

**Building Products:** Table 1 indicates that building products represent a substantial market for aluminum sheet in North America. From a customer standpoint, the product requirements are typically a surface that can be painted, and adequate formability and corrosion resistance. In the highly cost sensitive building products market, the alloy of choice is typically 3105, a composition that can be successfully produced from high recycled scrap content. The alloy can be easily partially annealed to an H2x temper to provide the required bending characteristics. Furthermore, much of North American building sheet production has moved to continuous casters to lower conversion costs compared to traditional ingot-based processes.

**Foil:** The foil market in North America has grown steadily and represents nearly 500,000 tonnes per year of production. Due to its capability of being cold rolled to very thin gauges (6.3µm), aluminum foil has been used as an effective barrier to light, water vapor, and gases. In laminated structures, with plastic or paper films, aluminum foil is an ideal packaging structure for applications such as pharmaceuticals, aseptic food containers, cigarettes, confectionary, lids, etc. Some other characteristics that are required of aluminum foil are appearance, formability and dead fold capability.

Historically, 1xxx aluminum alloys such as 1145, 1050, 1100, 1200 and 1235 had widespread use for foil applications. However, as the need for alloys with higher levels of strength and ductility increased over the years, aluminum producers developed new alloys with better performance characteristics. Typical examples of those developments are the alloys containing up to 1.5% Fe (8079) or a combination of Fe and Mn (8006, 8014, 8150) with or without some other minor elements such as copper (8023). Figure 3 shows the composition limits for various 1xxx and 8xxx alloys used for foil products.

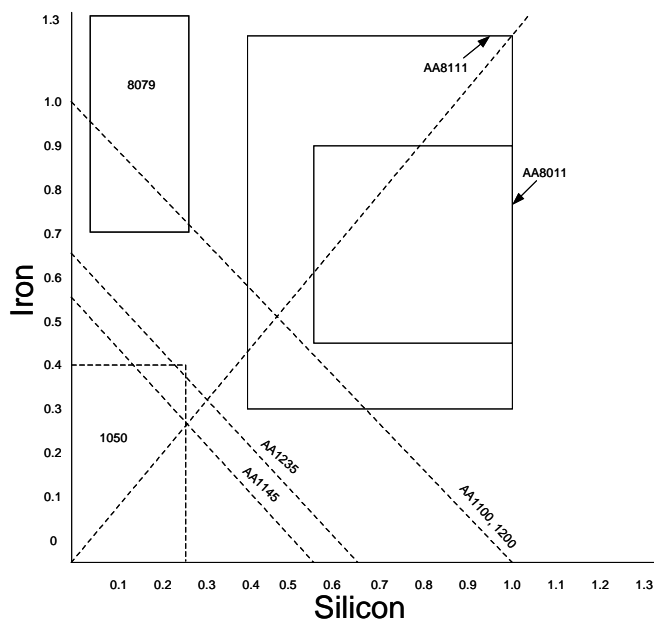


Figure 3: Composition Limits for some 1xxx and 8xxx alloys used in foil applications.

The development of alloys containing Fe and Mn can produce foils with higher strength and ductility due to the intermetallic particle size and volume fraction [8]. In the presence of manganese on the order of 0.5%, the  $(\text{Fe}, \text{Mn})\text{Al}_6$  intermetallic phase is formed in the as cast structure as rods with an average diameter of  $0.1\text{--}1.5\mu\text{m}$  and volume fraction in the range of 5-20%. By suitable cold working, these rods break down into a very fine dispersion of particles, which can be used in combination with the annealing temperature to control strength and ductility to the desired levels. These particles can control the microstructure during recovery and recrystallization resulting in an attractive combination of properties in the H1x and H2x tempers.

In the industrial world, burst tests are commonly used as an assessment of foil strength and biaxial ductility. The values can be directly related to the microstructure of the foil as determined by the chemical composition and processing path. As an example, Figure 4 shows typical values for several alloys produced by conventional DC-route and continuous casting means [9].

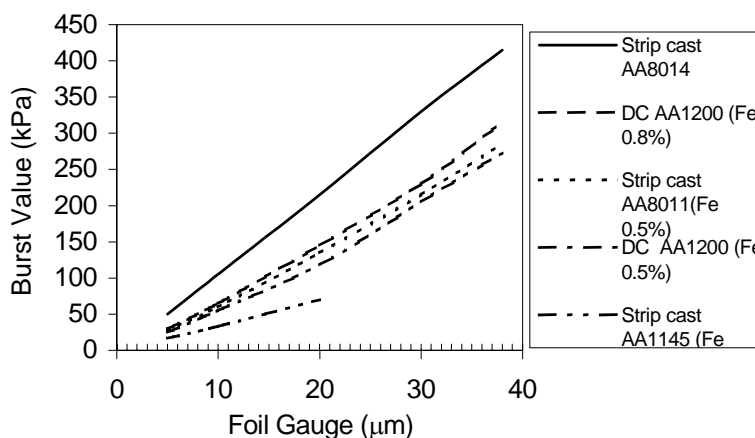


Figure 4: Typical burst strength of soft annealed aluminum foils [9].

In Europe, most aluminum foil is still produced by a DC-casting and hot rolling process, but strip casting or twin roll casting has been growing in use, especially in North America. Basically, the use of roll casters provides a lower capital cost and shorter production route compared to the traditional DC-route since ingot casting, scalping, preheating and hot rolling can be eliminated. The higher solidification rate associated with the roll caster process can also be translated to smaller particles and higher levels of elements in solid solution.

One common problem associated with foil produced from roll cast strip is the segregation of alloying elements in the as cast condition at approximately the center of the strip thickness (centerline segregation). It is formed due to the shearing action of the rolls on the formed dendrites, squeezing the interdendritic liquid towards the center and enriching its concentration as can be seen in Figure 5a. The result is a region that contains higher amounts of Al-Fe-Si intermetallic phases, Figure 5b. These particles are harder than the matrix, and if not reduced by further thermal treatments and cold working, will produce a foil containing an unacceptable level of pinholes [10, 11]. It can also be noted from Figure 5(a) that the concentration of alloying elements along the centerline is more pronounced with the higher solute alloy 8011.

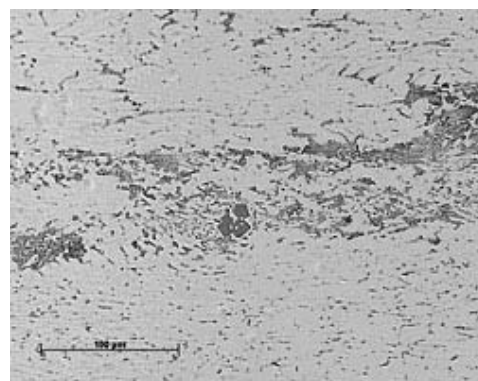
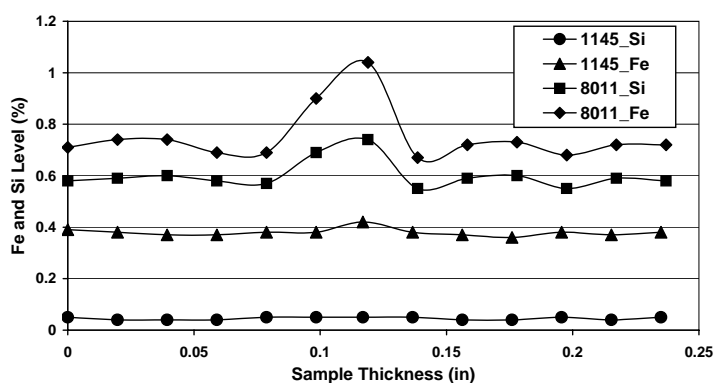


Figure 5(a): Centerline segregation of alloying elements in roll caster material.

Figure 5 (b): Centerline segregation of 8011 alloy, produced by twin roll caster.

Control of the number of pinholes is an essential requirement for thin foil that will be used as a barrier layer against light, moisture and air. Most foil production calls for a pinhole limit of less than 500/m<sup>2</sup> and sizes below 20μm. Besides its deleterious effect on pinholes, coarse centerline segregation can also lead to other problems such as broken matte, higher foil breakage at the mill and reduced foil final strength.

As an example, Figure 6a shows a pinhole with its counterpart after the foil separation stage. One side shows a foil with a pinhole void and the other a “bump” that caused the problem. In Figure 6b, the remnants of centerline segregation are seen as the source of pinholes in pack-rolled foil.

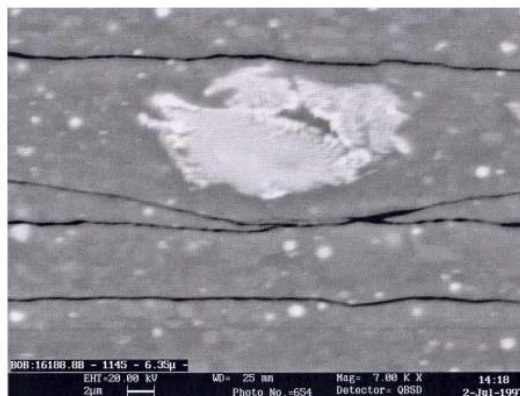
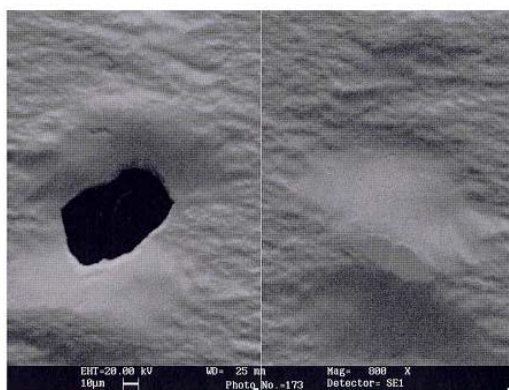


Figure 6(a): Pinhole in pack-rolled 6.35 $\mu$ m gauge foil. Figure 6(b): Centerline segregation on doubled foils at 6.35 $\mu$ m gauge foil.

**Rigid Container Sheet: Can Body Stock** – Development of 3x04-H19 can body stock, including high strength products with “heat-treatable” compositions, was pursued during the 1980’s to increase dome reversal pressures and support can lightweighting. After-bake strength levels of 275-280 MPa were typical for these high strength products. The reduction in metal thickness of the can body has continued incrementally over the past 20 years, at times facilitated by alloy development but mostly through optimization of can design. Thickness reduction as shown in Figure 7 continues in many parts of the world.

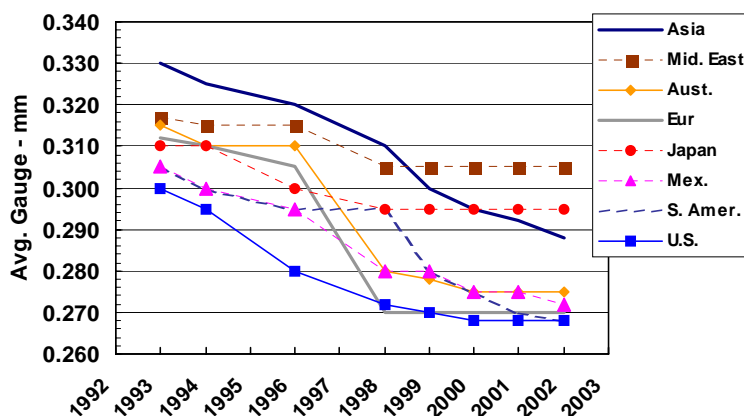


Figure 7: Reduction in can body stock thickness over time in various parts of the world.

Body stock alloy development has been described in previous publications [4, 12, 13]. More recently, the use of stronger can bottom dome designs has reduced the need to use high strength alloys. In fact, the trend has been to avoid higher strength products in order to increase productivity in the can-making process. Even in Japan where high strength heat treatable compositions were in wide use in the 1990’s, more standard strength levels are currently used in the drawing and ironing of can bodies. Typical can body stock strength levels after baking are currently 255-265 MPa.

Recently, the focus of can body stock research has changed from higher strength to improved consistency in microstructure and preferred orientation.

Academic research in Europe and North America has been directed to understand recrystallization and the effects of particles and deformation process on 3xxx alloy texture

development and earing [4, 5, 14-18]. Application of this understanding has resulted in more consistent hot rolling and annealing practices to achieve higher levels of earing consistency.

Recent research has not been limited completely to the metallurgical aspects of aluminum can materials. The mechanical aspects of the can as a pressure vessel have been studied to provide further understanding of the limits to can lightweighting. To quantify the impact of sidewall thickness reduction on can integrity, one unique study was done at the University of Tulsa to investigate the “fracture toughness” of ironed 3xxx can body sheet [19]. The results of this study, Figure 8, quantified the importance of internal pressure and sidewall thickness in the leak vs. rupture characteristics of aluminum cans.

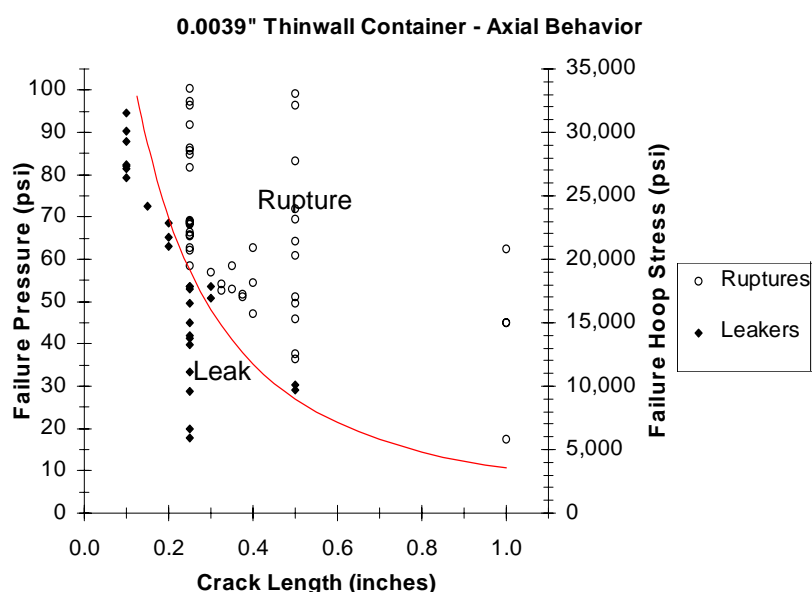


Figure 8: Relationship of failure pressure and flaw size to rupture of aluminum beverage can side walls[19].

**Rigid Container Sheet: Coated End Stock** – Beverage can lid stock is almost universally supplied in coated coil form and the trend has been persistently toward higher strength products in order to allow lightweighting. Typical lid stock thicknesses in the late 70's were around 0.335 mm, but some current lid designs call for metal thickness approaching 0.208 mm, and thicknesses below 0.200 mm are possible in the not too distant future. Although a proportion of these lightweighting achievements can be attributed to alloy design, lid design also has been a major contributor. A “quantum leap” in the amount of material required to make a lid became commercial in 2000 when Crown, Cork and Seal Co. introduced SuperEnd<sup>TM</sup>, achieving about a 10% decrease in weight while increasing the buckle failure strength of the lid. Figure 9 shows a comparison of profiles of the new SuperEnd<sup>TM</sup> and the older designs.

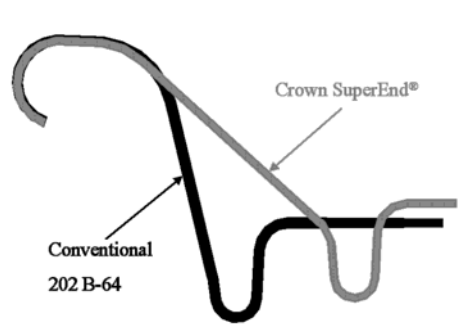


Figure 9: Cross-section of end profiles showing a conventional end and a new SuperEnd™ design.

The alloy of choice for most of the history of the aluminum beverage can lid was 5182, used in the extra hard temper (H19) condition. When 5182 was registered with the Aluminum Association in 1967, a typical lid stock composition contained about 4.5 % by weight Mg, and 0.3 % by weight Mn. In the mid 80's, typical coated lid stock yield strengths were around 320 MPa. Recognizing the valuable contribution of Mg and Mn to the strain hardened strength of lid stock, these elements were gradually increased with time. Eventually, Mg contents exceeded the maximum limit of 5.0 wt.% specified for 5182 and alloy 5019A was registered with the Aluminum Association in 1999 with an allowed Mg range of 4.4 to 5.4 wt.%. Small increases to some other minor alloying elements, such as Cu, also occurred in this progression to higher lid stock strengths. Coated sheet yield strengths in excess of 370 MPa presently are not uncommon.

**5xxx Structural Alloys:** The major 5xxx structural alloys were developed in the 1950's and have been used for shipbuilding, armor plate, railroad cars, and tankage for almost 50 years. In most of these applications, strength after welding is a major consideration and higher Mg, Mn and Cr contents are important in maintaining as-welded mechanical properties. The most common alloys used historically in high-strength applications are 5083, 5454, 5086 and 5456. However, as automotive applications have grown over the last 25 years, alloys such as 5182 and 5754 have seen increasing use where formability requirements come into play. Figure 10 shows a time line for the development of 5xxx structural alloys.

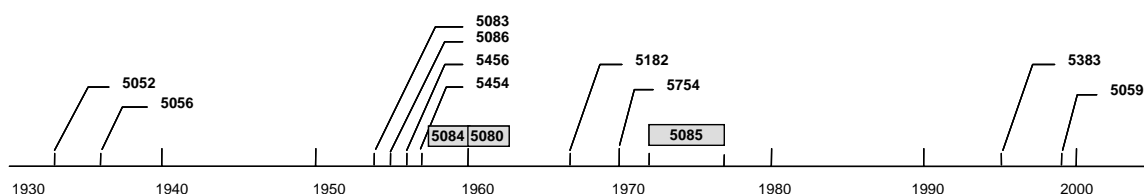


Figure 10: Time line for development of important 5xxx structural alloys.

**High Strength Weldable Alloys:** Research has continued with the goal of increasing the useful strength ranges of Al-Mg alloys. The benefits of higher Mg levels for increasing strength levels of 5xxx alloys are counterbalanced by its tendency to promote corrosion if the product is not fabricated appropriately [20]. Mg in solid solution is essentially benign regarding corrosion, but with Mg contents greater than about 3.5 wt.%, the propensity exists for precipitation of the  $\beta$ -phase ( $\text{Mg}_2\text{Al}_3$  or  $\text{Mg}_5\text{Al}_8$ ) at low to moderate temperatures.  $\beta$ -phase precipitation is generally heterogeneous and grain boundaries are favored nucleation sites.



At room temperature the precipitation rate is so low that “sensitization” of grain boundaries by precipitation of the anodic  $\beta$ -phase practically does not occur. At temperatures greater than about 80°C, however, grain boundary precipitation of  $\beta$ -phase can be of concern. Countermeasures are available, however, that can allow high Mg contents, and provide a highly corrosion resistant alloy. Such countermeasures usually involve either providing alternative nucleation sites for the  $\beta$ -phase (or the metastable  $\beta'$ -phase) such as dislocations within grains, or preventing precipitation along the grain boundaries in the form of continuous films. Precipitation of  $\beta$ -phase along grain boundaries is relatively benign as long as it occurs discontinuously. Most manufacturers of high Mg alloys for structural applications understand the general principles of encouraging discontinuous  $\beta$ -phase precipitation along grain boundaries.

Years of research at both Alcoa and Reynolds [20, 21] have shown that improvements in performance in these alloys are more related to control of microstructure through processing than on the variation in composition. The amount of work hardening, degree of recrystallization, and  $\beta$ -phase precipitate distribution in the final product have long been known to control the strength and corrosion resistance of 5xxx alloys. Navy-sponsored work in the 1970's resulted in trials of an 8.2% Mg alloy with extremely high post-welded properties and acceptable but not exceptional corrosion resistance. More recent alloy registrations have occurred in the area of 5xxx alloys for marine plate. Alloy 5383, a modification of 5083 (AA reg.), was introduced in 1995 to provide higher welded strength compared to 5083. However, its registered composition limits overlap considerably with existing alloys 5083 and 5456 as shown in Figure 11. A Russian alloy, Al 1561, has been approved by DNV for use as a clad structural product.

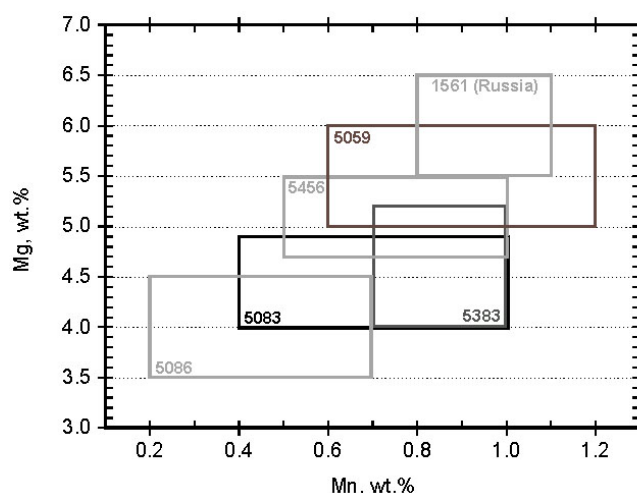


Figure 11: Chemical composition limits for high strength Al-Mg-Mn 5xxx alloys.

Another recent development, alloy 5059, utilizes a Zn addition to a 5.5% Mg alloy to increase the strength and corrosion resistance. While alloy 5059 has not been thoroughly tested in service at this writing, previous Zn-containing alloys (5080 and 5084) were registered in the 1960's and then withdrawn from use due to severe localized corrosion in the heat affected zones adjacent to welds. Recent research on welded Al-Mg-Mn(Zr) alloys at Alcoa showed higher localized corrosion of welded samples as Zn levels increased from 0.4 to 1.5%, Figure 12. Other published work has also pointed to the detrimental effects of Zn on corrosion behavior of 5xxx alloys [22].

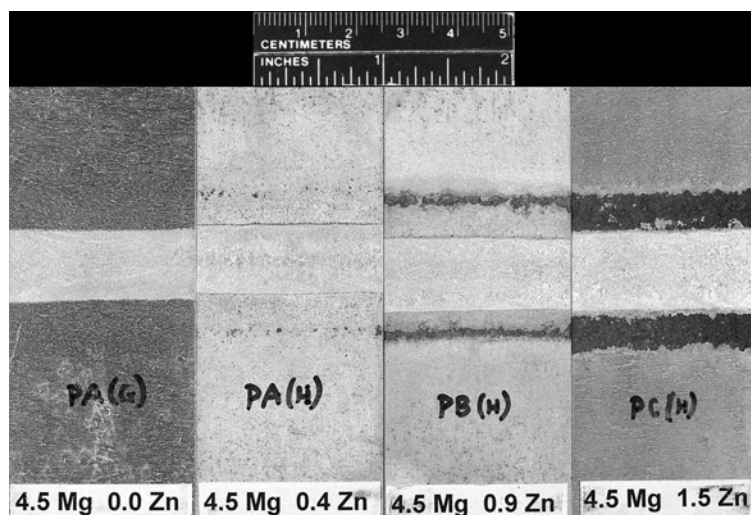


Figure 12: Results of asset corrosion tests on 4.5%-0.7% Mn alloy with various levels of zinc.

Mg containing alloys are prone to a surface cosmetic defect known as Lüdering. Stretching, either as a final stage of sheet fabrication, or in forming the part, causes the appearance of objectionable highly elongated “feathery” surface marks. The phenomenon occurs as a result of the complex interaction of dislocations and Mg atoms during plastic deformation. In certain thicknesses and tempers, the means often can be found to reduce or eliminate Lüdering, but in many cases it has to be tolerated, or the material is not applied where surface appearance is of paramount importance.

**5xxx Automotive Alloys:** The high O-temper strengths have made higher Mg alloys popular candidates in the rapidly growing automotive structural sheet area. In these applications, strength and corrosion resistance are needed but formability is also an important requirement. Alloy 5182, with 4.5Mg and 0.3Mn, develops an O-temper yield strength of approximately 124 MPa and is common for deep drawn parts. Alloy 5754, with approximately 3% Mg, is favored in areas where concerns about long term exposure to temperatures above 100°C are expected. Alloys with higher strength have been extensively studied and, in some cases, commercialized. Alcoa introduced alloy 5085 in 1972 for automotive sheet applications. This 6.2% Mg alloy had a yield strength of approximately 165 Mpa and excellent ductility in the O-temper. However, questions regarding its manufacturability and long term corrosion resistance caused it to be removed from service in favor of alloy 5182. More recently Japanese developments of alloys such as 5030 have offered improved formability/strength combinations. However, to the writers’ knowledge, these products are not in common use outside of Japan [23].

**Surface Critical Products:** Surface quality has become a key attribute for many types of NHT alloy sheet products. Structural products with bright rolled finishes are in common use for tanks and tread sheet, Figure 13. These products are fabricated from corrosion-resistant 3xxx or 5xxx alloys and provide an attractive aluminum finish without the need for hand polishing or other customer finishing operations. These finishes may be attained by either hot or cold rolling to final thickness.



Figure 13(a): Typical tread sheet application.



Figure 13(b): Tanks produced from bright rolled 5xxx alloy sheet.

Other products may require special controls to insure that a uniform surface is obtained after chemical surface treatments such as bright dipping, etching, or anodizing. Chemically brightened products are usually fabricated from high purity alloys such as 1085, 5657, or 3002. The low volume fraction of constituent phases reduces surface pitting and enhances the brightness of the sheet after chemical treatment [3]. Common uses for these alloys are cosmetic containers, reflectors, and bright trim of various types.

Lithographic and anodizing quality (AQ) sheet are other common products that require a high degree of surface quality and consistency. High quality litho sheet is typically produced from alloys such as 1050 or 3103 in work hardened tempers. Anodizing quality (AQ) sheet is typically produced from alloy 5005 or its derivatives. The need for non-directional, non-streaky, matte finishes after electrochemical finishing requires careful control of the grain structure of the work hardened sheet. Anodizing or litho “graining” processes serve to highlight any surface irregularities including the grain structure prior to cold rolling. The control of recrystallization and grain size are critical in the manufacturing process for these surface sensitive products.

### 3. Summary

The industrial development of NHT alloys has been described for foil, rigid container sheet, and structural 5xxx alloy sheet that comprise the largest usage of flat rolled products in the transportation, building and construction, and packaging markets. All developments are based on a tradeoff and balance of various customer requirements and the cost of the final product. Understanding the sometimes conflicting customer needs and selecting the right alloy components and fabrication process to meet them is the ultimate responsibility of the metallurgist.

Al-Fe-Si alloys have been optimized for use with continuous casters and large scale production of both 1xxx and 8xxx alloys is common for a wide range of foil products. Higher strength alloys are a key component to further lightweighting of the can end, but new designs for the can body have removed the need for higher strength. The performance of structural alloys such as 5xxx marine products depends much less on the actual alloy composition than on the control of fabrication parameters to produce a corrosion-resistant microstructure. Control of recrystallization and near-surface grain structure is key to controlling the appearance of anodized and other surface-critical products. Future improvements for all of these products will feature the need for consistency and high performance in the customer's process.

For example, higher strength thin foil will require high solute 8xxx alloys but the continuous casting process must produce segregation-free strip to successfully roll these products. Modifications to rigid container alloys may be required as new products are developed. Cans which are shaped after forming or aerosol containers may present structural and forming requirements that are different from those of traditional beverage cans. Opportunities for improvements in 5xxx structural alloys for marine and other applications include higher ductility, strength and corrosion resistance. In the fast-growing automotive sector, different alloys may be used in different parts of the structure in a manner similar to aircraft construction. However, it is likely that formability will be a key requirement in producing high volume parts. In any of these applications, “new” or modifications of existing alloys will be used where the benefit can justify any added cost.

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