"I Have Inclusions! Get Me the Cheapest and Best Flux for Cleaning My Melt!"—Is This the Best Driven, Cost-Saving Approach by a Foundry?

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ABSTRACT

Elimination of inclusion defects requires proper collection and analysis of data. Attempting a corrective action without knowing exactly what the inclusion is may prove very expensive. Unfortunately, it is not uncommon practice that despite the magnitude of the cost of quality due to inclusion defects in castings, a large number of aluminum foundries continues to: 1) inaccurately identifying an inclusion based on an educated guess, 2) erroneously avoiding paying for the cost of properly diagnosing the inclusion, 3) inaccurately correlating the effects of all the molten metal and casting process contributing factors, and 4) incorrectly blaming the melting department for producing and delivering "bad metal".

To make matters worse, in many instances foundries limit defect analysis to a single or a couple of defects despite having inclusion issues in a number of different castings. In many instances, foundries overlook the fact that in most other part numbers there are no inclusion issues. Thus, why to blame the melting department for the inclusions instead of analyzing why other castings do not have inclusion defects if the starting molten metal cleanliness is the same?

Molten metal cleanliness is determined by the amount of hydrogen gas, dissolved chemical impurities and inclusions present in the molten bath before it is cast. The use of a solid flux is the first step for eliminating dissolved impurities, and for ensuring molten cleanliness by preventing excessive oxide formation, removing nonmetallic inclusions from the melt, and preventing and/or removing oxide build up from furnace walls. Furthermore, some fluxes could also help in maximizing metal recovery from the dross.

Foundries need to understand, recognize, and accept that a commercial flux recipe is created for a specific metallurgical need, and that none of all the commercially available fluxes could provide all the optimum benefits in just one recipe -since some of the benefits are conflicting in nature. In addition, foundries must understand that the cost of flux is influenced by the quality of the compounds, as well as by the type and complexity of the formulation. In general, as the cost of the flux decreases, so does the effectiveness and efficiency of the flux.

This article will provide a guideline to better understand the interrelated aspects between oxides, inclusions, dross, fluxes and molten metal quality.

Keywords: molten metal quality, inclusions, oxides, dross fluxes

INTRODUCTION

Many foundries have experienced costly outbreaks of high reject rates due to inclusions in castings. An inclusion defect may arise from a single clearly defined cause or may be a result of a combination of factors, so that the necessary preventive measures are initially unclear. However, to prevent recurrence it is necessary to correctly identify the inclusion before troubleshooting the process to find the root cause of the defect.

The root cause of the inclusion defects may present great difficulty because of the wide range of interdependent molten metal and casting process contributing factors.

The elimination of inclusion defects in castings require the proper collection and analysis of data. There are many statistical techniques to help us control process variables, correlate the effects of variables, and establish priorities for problem solving. Perhaps the Pareto chart is the most common tool used to pinpoint major causes of scrap in a foundry. Still, these techniques are of little use if the defect is improperly diagnosed.

To correctly diagnose inclusion casting defects, it is imperative to: A) fully examine the general characteristics and occurrence of the inclusions and to describe in detail their size, distribution, and appearance, B) document the defects location with photographs, and C) understand the casting process. Attempting a corrective action without knowing exactly the type of the inclusion may prove very expensive. Once a corrective action is found, it must be not just implemented but also monitored and re-evaluated. Even though quantitative metallography is essential to effectively obtain data on the inclusions, foundries are not always willing to invest time, effort, and money for proper inclusion assessment either in the molten bath or the castings.

Typically, 4 techniques are being used in foundries to evaluate casting inclusion defects:

- In the majority of the cases, when inclusion defects are considered a minor nuisance, a simple visual evaluation ("educated guess") of the inclusion is conducted.
- An optical microscope and/or stereomicroscope.
- Optical microscope coupled with computer and image analysis.
- A SEM analysis. Unfortunately, many foundries would limit the usage of this technique to a few samples that in many instances are not enough to properly identify the different inclusion casting defects that they are facing.

Nearly everyone who casts aluminum alloys, regardless of sophistication, has at some time experienced an issue with inclusions from molten aluminum. Even the molten aluminum being used for sheet ingot and beverage cans, which is considered the cleanest molten aluminum, will have inclusions to some extent (smaller sizes and lower concentrations of them). Thus, various types of inclusions such as oxides, nitrides, carbides, fluorides, borides, chlorides and salts may be present in molten aluminum alloys.

While the existing types of inclusions that would be present in the melting furnaces will vary from foundry to foundry, their removal is essential for proper molten metal cleanliness. A number of commercially accepted melt treatment techniques is being used by aluminum foundries to remove and separate inclusions from the molten aluminum alloy prior to casting. These include various methods of fluxing, degassing, and filtration in the furnaces and in the gating system. Any of these techniques will have an impact on the melt cleanliness of the molten aluminum alloy. However, the effectiveness to evaluate their removal would rely on the melt cleanliness measurement technique being used. Ideally, the optimum technique would provide assessment of three inclusions parameters: size, distribution, and composition.

During the last 50 years, several techniques have been developed and used for assessing the cleanliness of molten aluminum casting alloys. These include qualitative, quantitative, and analytical laboratory procedures, as well as on-line and off-line techniques.

Better understanding of the cleanliness level of the molten metal being delivered by the melting department and the additional influence that other casting process factors may have on the molten metal quality level would help aluminum foundries to implement feasible, practical and robust controls during the molten metal treatment and handling operations to minimize inclusion defects. However, implementation alone would not be sufficient to guarantee success if melting and/or casting operational changes are made intentional or unintentional.

A robust system will work for specific restraints. However, if such restrictions change, the system that was originally implemented would become inefficient. Typical and very common process changes and deviations, noticed in a vast number of foundries, related to the treatment and handling of liquid aluminum that would negatively impact the quality of the molten metal are:

- Accepting raw materials of lower quality.
- Charging dirtier returns/scrap (i.e., contaminated with oil, and grease due to poor foundry equipment maintenance).
- Operating equipment which has inoperative and malfunctioning flow meters, pressure regulators, and RPM counters.
- Failing to replace worn off degassing consumables.
- Reusing poor quality residual pieces of ceramics and/or graphite materials (that have already exceeded their life expectancy) to make other components to be used in molten aluminum.
- Lack of preventive maintenance in both: equipment, and refractory in furnaces and transport ladles.
- Failing to follow process procedures during the casting (molding) process. For example, not placing the filter in the gating system and/or not blowing air before closing the mold.

More progressive foundries have made continuous efforts to better understand and disseminate, within their organization, concepts and knowledge such as:

- Molten metal quality and molten cleanliness.
- Difference between impurities, inclusions, and dross.
- Influence of the raw material charge on oxides.
- Importance of minimizing skim generation.
- How fluxes work.
- Importance of identification, and quantification of the inclusion defects.
- Benefits of using analytical commercial instrument to evaluate metal cleanliness, and seeking assistance in identifying and solving defects due to inclusions.

MOLTEN METAL QUALITY AND MOLTEN CLEANLINESS

It is very important to understand that molten aluminum quality encompasses molten metal cleanliness.

The level of quality of a molten aluminum bath is based on the degree to which the chemical properties (chemical element composition) and physical properties (hydrogen content, dissolved chemical impurities, and inclusions) are controlled within a specific foundry's internal specification, which is established to meet casting requirements. In general, the goal of the melting department is to produce and deliver quality metal, while minimizing dross generation.

It is well accepted in the foundry community that the concept of molten metal cleanliness considers the amount of "impurities" present in the molten bath before it is cast. In that regard, the term "impurities" imply hydrogen gas,

dissolved chemical impurities and inclusions. To avoid misinterpretations and misunderstandings, the word "impurities" must not be confused with inclusions only.

The highest molten metal quality is obtained by: A) holding chemical elements within relatively narrow ranges to optimize effects on castability, and mechanical properties, B) degassing, fluxing and filtering the molten metal, and C) properly skimming the dross off.

CHEMICAL ELEMENT COMPOSITION

The chemistry of the alloy affects the surface tension, the viscosity of the molten metal, and the solidification characteristics of the alloy. In some occasions the molten alloy can be within specification and still cause unsatisfactory casting performance, especially by the presence of many other unmeasured tramp elements that may significantly affect the properties of the melt. Consequently, it offers advantages that a foundry be equipped with an optical emission spectroscopy unit capable of measuring alloy's chemical composition at the level of alloy's element additions as well as at the ppm level of secondary and/or trace elements. Important metallic tramp elements to monitor depending of the alloy being used may be: Bi, Cd, Ni, P, Pb, Sb, Sn, Zn, and P.

HYDROGEN CONTENT

Hydrogen absorption is common to all casting aluminum alloys. The hydrogen, which is absorbed, is made available at the surface of molten aluminum alloys through the reaction of the molten bath with water vapor (moisture) present in the melting environment.

The reaction between water vapor and molten aluminum yields not only hydrogen gas but also the formation (within milliseconds) of amorphous aluminum oxide films (Al₂O₃) on the surface bath. The thickness of these films is less than 1 µm. By the time the melting has been completed, the skin layer is a mass of randomly oriented oxide skins with metal and gas trapped in between, floating on top of the melt. During that time, the amorphous Al₂O₃ films crystallize first into gamma alumina (γ -Al₂O₃) films (10 μ m thick), and then they will transform to a much denser alpha alumina (α-Al₂O₃) films, given sufficient time and temperature. The alpha alumina films favor more oxidation at a faster rate. Since virtually all molten aluminum contains some level of hydrogen in solution, hydrogen removal is often necessary. The optimum hydrogen content that can be tolerated in the melt may vary widely based on several factors such as alloy type, casting process being used, casting solidification rate and the final casting product.

The most effective method to degas molten aluminum is by injecting an inert gas, such as nitrogen or argon, or by a combination of an inert gas with a small amount of a halogen gas (i.e., Cl). The most effective method to inject the purging gas is by using rotary impeller technology. Furthermore, rotary degassing also assists in floating solid particles which are swept to the melt surface by flotation, where they accumulate in the dross.

The amount of hydrogen gas allowable in a molten bath at the time of pouring is established on "engineered critical hydrogen concentration ranges" that take into consideration specific casting quality requirements.

DISSOLVED CHEMICAL IMPURITIES

These impurities fall into two sub-categories: alkali hearth metals and alkali metals that are tramp elements and in excess of the alloy compositional limits. Alkali earth elements relevant to molten aluminum are: Be, Mg, Ca, and Sr. Alkali metals are: Li, Na, and K.

Although alkali metals are part of the chemical composition, usually they are referred as impurities. Because of the deleterious effects that they could cause, they must be controlled to very low levels. Due to the difficulty in separating these impurities, they are best handled by a policy of avoidance (i.e., foundry having and adhering to a well –defined incoming material specification sheet with respect to elements and levels accepted). Nevertheless, there are generic treatments that can be employed to deal effectively with potential contamination by each element.

Foundries must realize that while alkali elements usually derive from two distinctly different aluminum making sources: reduction of alumina in the Hall-Heroult process (virgin or primary metal) and recycled aluminum, their respective concentration levels vary among them.

Typically, impurity levels in prime metal (from single electrolysis) are: Na (30-50 ppm), Ca (2-5 ppm), and Li (0-20 ppm). Impurity levels in recycled metal are: Na \leq 10 ppm, Ca \leq 10 ppm, and Li \leq 1 ppm. However, impurity levels in prime metal could be reduced to \leq 1 ppm by using three-layer electrolysis in the process.

Based on the potential impurities that may be present in the incoming material, foundries must be aware of them and should either have robust molten metal practices to remove and control the alkali elements to the desired operating range, or to pay upfront for reducing and tightening control limits in the specification. Thus, foundries must pay attention to lower scrap grades because of the greater probability of poorly defined composition and content of deleterious contaminants.

Alkali elements can be removed during the degassing process if the treatment contains a reactive gas such as chlorine. The presence of chlorine also assists the removal of non-metallic solid particles, which are swept to the melt surface by flotation, where they accumulate in the dross.

INCLUSIONS

It is well established that a variety of inclusions exists in molten aluminum alloys. Their source derives from the type of metal charge, alloying additions, melting practices, and liquid metal treatments and handling practices. Inclusions can be broadly classified as intermetallic and non-metallic.

Intermetallic inclusions are primary compounds that result because of the precipitation, and growth phenomena from the liquid state. However, not all of them are necessarily detrimental to the quality of the molten bath. While TiB_2 , AlB_2 for grain refining, and AlP for grain refinement in hypoeutectic and hypereutectic alloys respectively are not detrimental, sludge formation (Cr-Fe-Mn) is detrimental. Nevertheless, Al_3Ti particles in excess of $10~\mu m$ can cause inclusion related defects.

Non-metallic inclusions can be present in the form of films, fragments, particles, and clusters. The inclusions can have different composition, texture, morphology, and appearance. Common types of non-metallic inclusions are: borides, carbides, nitrides, oxides, and salts. Throughout the years, different researchers have characterized the sizes of inclusions by thickness, length and diameter or cross section. Table #1 summarizes some of the results from various sources. 1,2,3,4 The size of the inclusions may vary from less than one micron to a hundred microns, and larger.

Non-metallic inclusions are typically grouped as exogenous, or as in-situ. Inclusions that are imported to the molten metal from external sources are referred to as exogenous while inclusions that arise from either chemical reactions within the melt itself, or as a result of a melt treatment are considered indigenous.

Sources for exogenous inclusions include refractory particles, usually from degradation of furnace walls, transfer ladles, launders, riser tubes, filling funnels, and in some instances from pieces of the sand mold. In addition, inclusions derived from charging materials are also considered exogenous. Sources for in-situ inclusions are oxides, fluxing products, alloying elements, and intermetallic compounds. Figure 1 depicts the sources of non-metallic inclusions.

Oxides are the most prevalent type of inclusions, from either direct melt oxidation or the oxidation of certain elements during alloying. Because of the nature of molten aluminum to readily oxidize, different oxides can form during different stages of the melting and liquid metal handling processes. Typical examples are: Alumina (Al₂O₃), calcium silicate (CaSiO), magnesia (MgO), magnetite (Fe₃O₄), silica (SiO₂), spinel (Al₂MgO₄).

Sedimentation, flotation, filtration, and fluxing are common techniques being used to remove and separate inclusions from aluminum alloy melts. Any of these techniques will have an impact on metal cleanliness. However, fluxing is the first step for ensuring molten cleanliness, by preventing excessive oxide formation, removing non-metallic inclusion from the melt, and preventing and/or removing oxide build up from furnace walls.

IMPURITIES, OXIDES, AND DROSS

To successfully eliminate inclusion related defects in castings and to properly define the required flux to be used in the melting operation requires a clear understanding of metallurgical terms and concepts with respect to chemical impurity, inclusion, and dross when discussing the cleanliness of the molten aluminum bath. However, it can not be forgotten that the cleanliness of the molten bath is also greatly affected by the degassing operation which in turn significantly impacts removal of inclusions and method of flux addition. The steps taken to prevent hydrogen pickup and dross formation will minimize inclusions in molten aluminum alloys.

Chemical impurity means an unwanted chemical element which has been dissolved in the molten bath. Inclusion refers to a foreign particle present in the molten metal prior to casting. Dross denotes crumpled aluminum oxide films which encapsulate a significant amount of unoxidized aluminum, floating on the surface of the molten bath.

With the exception of sludging associated with high levels of Cr, Mn, and Fe that could be considered chemical impurities, the other typical chemical impurities (previously discussed) do not cause inclusion related scrap defects in castings. Scrap related defects due to chemical impurities are associated with:

- a) the adverse effect that excessive levels of Fe has on tensile properties,
- b) the poisoning effects that several ppm of P or Sb have on Na or Sr, during modification of hypoeutectic al-Si alloys.
- c) the high levels of Ca, and Na that cause edge cracking during hot rolling,
- d) the high levels of Li that produce the "blue" corrosion in aluminum foil, and
- e) the high levels of Na that cause embrittlement in 5XX alloys.

Potential methods for removing unwanted elements from molten aluminum alloys include selective oxidation, chlorination, fluorination, and intermetallic compound formation.

Table 1. Classification of Inclusions in Molten Aluminum

Туре	Phase	Shape	Density lb/in³	Size range thickness, cross section µ	Melting Point °F
Oxides	γ-Al ₂ O ₃	Films		≤ 1, 10-500	
	α -Al ₂ O ₃	Particles, films		1-5, 10-1000	
	Al ₂ O ₃ (Corundum)	Particles, skins	3.97	0.2-30, 10-5000	3717
	MgO	Particles, skins	3.58	0.1-5, 10-5000	3839
	Al ₂ MgO ₄ (Spinel)	Particles, films, lumps	3.6	0.1-100, 10-5000	5117
	AIMgO ₄				
	SiO ₂	Particles	2.66	0.5-30	3002
	CaO	Particles	3.37	≤5,	4766
	CaSiO	Lumps, particles		, 10-100	
	Fe ₃ O ₄	Clusters, films		50-1000, 0.1-1	
Borides	TiB ₂	Particles, clusters	4.5	, 1-50	5054
	AlB ₂	Particles	3.19	0.1-3, 20-50	3920
Carbides	Al ₄ C ₃	Particles, clusters	2.36	0.5-25	3812
	SiC	Particles	3.22	0.5-5	4604
Nitrides	AIN	Particles, films	3.26	0.1-3, 10-50	
Salts	NaCl, KCl, CaCl ₂ , MgCl ₂	Liquid droplets	1.9-2.2	0.5-1	1300-1472
	Na ₂ SiF ₆	·	3	2-60	1832
	Na2SIF6	Spheres	3	2-00	1032
Sludge	(Cr-Fe-Mn)Si	Particles	≥ 4.0		
Inter metallics	TiAl, TiAl₃, NiAl	Particles, clusters		10-100	

Based on the type, origin, and storage of the raw material, returns, and scrap type and charging methods, the molten bath can contain considerable amounts of inclusions.

Oxide films and particles are introduced and/or generated during the charging and melting practices, as well as during the molten metal treatment, and handling operations. Different alloys under similar charging practices can have significantly different oxide skins, and identical alloys from different "heats" will enter the molten metal with different oxide contents. Even primary ingot can introduce oxides. Entrained oxides particles and other inclusions can be floated out with the assistance of inert and/or chlorine gas purging. The non- metallic particles attach to the surface of the rising gas bubbles, collect on the surface and therefore can be skimmed off.

After a meltdown, any molten aluminum alloy will have a large variety of finely divided small quantities of particles suspended in the body of the melt and a layer of wet dross on the surface of the aluminum alloy. The initial thin oxide film that develops on the surface of the melt offers protection from further oxidation. However, the constant movement of the surface of the molten bath due to the different melting practices (charging, skimming, cleaning, degassing, transferring, and ladling) causes the thin alumina films to break, to crumble, to thicken and to encapsulate unoxidized molten aluminum, generating what is known as wet dross. The presence of alkali and alkali earth elements, even in small amounts, could increase the permeability of the film which in turn increases both melt oxidation and dross formation.

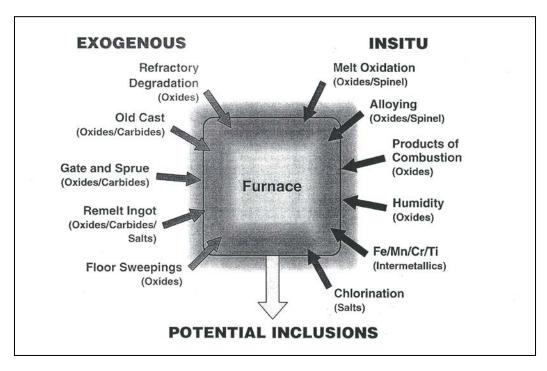


Figure 1. Sources of non-metallic inclusions in molten aluminum alloys⁵.

The aluminum content of wet drosses is typically reported to be in the order of 60% to 80% while the remaining 40% to 20% is aluminum oxide. The amount of trapped liquid metal in the dross varies according to the melting practice. The aluminum oxide is a very stable compound that cannot be reduced to aluminum under ordinary melting conditions. However, the amount of suspended liquid metal could be reduced from the 60%-80% range to 30% by proper fluxing and drossing techniques. The dross is considered to be the main contributor in influencing the total metal loss during melting. Depending upon the efficiency of the melting furnace, and melting practices, the amount of dross generated may be from 5% to 10% of the total metal melted. However, the total melt loss throughout the operation can also be influenced by other process steps that are insensitive to the charged material.

FLUXES FOR MOLTEN ALUMINUM

Fluxing is the best means of obtaining clean metal by preventing excessive oxide formation, removing non-metallic inclusions from the aluminum melt, and preventing and removing oxide build up from furnace walls. In general, fluxes may be grouped in two classes: gaseous or solids. Gaseous fluxes may be a blend of an inert and a chemically active gas that is injected into the molten bath. Solid fluxes are blends of salts.

Solid fluxes can broadly be categorized as passive or active fluxes. Passive fluxes protect the surface of the molten aluminum from oxidation and prevent hydrogen pick up by the melt. Active fluxes strip away the aluminum oxide layer from molten metal promoting coalescence of metallic drops, and help in reducing unwanted chemical impurities.

The removal of aluminum oxide by halides has its foundations in basic research and development on the systems NaF--AlF₃--Al₂O₃ and NaF—AlF₃. Studies on these systems have shown that the solubility of aluminum oxide increases with the sodium fluoride content. The reaction between cryolite and aluminum oxide in the presence of a surplus of NaF takes place according to the following reactions:

$$4\text{NaF} + 2\text{Al}_2\text{O}_3 \rightarrow 3\text{NaAlO}_2 + \text{NaAlF}_4$$
 Eqn. 1

$$2\text{NaF} + \text{Al}_2\text{O}_3 \rightarrow \text{NaAlO}_2 + \text{NaAlOF}_2$$
 Eqn. 2

Halide and fluoride salts have been thoroughly used by secondary (recycled) aluminum producers. The aluminum recovered results from the effectiveness with which non-metallic and metallic impurities are removed or reduced to acceptable levels. In these operations, low-melting-point fluxes are typically used. They are basically sodium and potassium chloride with additions of fluorides and some other chlorides, such as calcium chloride and magnesium chloride.

Solid fluxes are basically blends of sodium chloride and potassium chloride salts, with or without addition of fluorides. In addition, small quantities of oxidizing compounds, such as carbonates, sulphates, and nitrates,

are added to promote exothermic chemical reactions.⁶ Such reactions are important because they prompt the coalescence of the trapped liquid aluminum particles in the dross.

The mechanism of how salt fluxes work has been attributed to thermodynamic chemical reactions and surface tension effects between A) the aluminum oxide and the flux, B) the aluminum oxide and the molten metal, and C) the molten metal and the flux. This interaction between aluminum oxides, flux, and molten metal has been documented in earlier papers. ^{6,7,8}

In addition, the effect of the flux on the liquid metal will depend on the chemistry of the flux used, morphology of the flux, total amount of flux added, molten metal temperature, flux contact time, rabbling (stirring) technique, etc. Nevertheless, from the point of view of flux chemistry, it is important to understand that different combinations and proportions of ingredients will impart different flux properties, such as flux density, flux fluidity, flux wettability, and flux reactivity. These four different flux properties are responsible for the characterization of any particular flux.

To understand better how these flux properties are accomplished, it is necessary to recognize that essentially each different ingredient provides different effects that directly influence the final property of a flux. Generally, ingredients can be classified in four major groups based on their primary influence over the mixture. The following paragraphs that describe the basic flux ingredients and the typical classification of commercially available fluxes is just a brief summary of an earlier published article.⁹

CHLORIDES

Examples are: aluminum chloride (AlCl₃), barium chloride (BaCl₂), calcium chloride (CaCL₂), lithium chloride (LiCl), magnesium chloride (MgCl₂), potassium chloride (KCl), and sodium chloride (NaCl).

The melting point of these compounds, in their pure state, may range from 375 to 1765F (190 to 963C). However, they form low temperature eutectics in combinations. In addition, it is very typical to have at least three compounds in a given flux so that none of these compounds would be used as a single compound in a flux recipe.

Chlorides are mainly used because of their fluidizing effects, and because they are used as fillers. Fluxes based only on chloride salts should not react with molten aluminum, or at least the reaction should be negligible. In addition, these salts provide negligible effects on surface tension as compared to fluorides.

FLUORIDES

Examples are: simple fluorides such as aluminum fluoride (AlF₃), barium fluoride (BaF₂), calcium fluoride (CaF₂), lithium fluoride (LiF), magnesium fluoride (MgF₂), potassium fluoride (KF), sodium fluoride (NaF), and double fluoride compounds such as sodium silicofluoride (Na₂SiF₆), and potassium silicofluoride (K₂SiF₆).

The melting point of these compounds, in their pure state, may range from 1553 to 2600F (845 to 1426C). The high melting point of these compounds provides thickening effects on a flux.

Fluorides salts act as surfactants affecting surface tension forces between flux, liquid metal, and aluminum oxides. As the flux wets the interface between the aluminum oxide particles and the liquid metal, the adhesion force between the liquid aluminum and the oxides decreases, promoting oxide separation and metal coalescence. Fluorides are still the most effective compounds being used in fluxes to improve aluminum recovery from wet dross.

Although fluoride-containing salts are being subjected to stricter environmental regulations and constraints, it is still prudent to mention that emissions from powder fluxes are within standard environmental limits. It is important to realize that fluoride-free fluxes will never perform as efficiently as fluxes containing fluorides.

OXIDIZING COMPOUNDS

Examples are:

- Nitrates such as potassium nitrate (KNO₃), sodium nitrate (NaNO₃).
- Carbonates such as calcium carbonate (CaCO₃), potassium carbonate (K₂CO₃), sodium carbonate (Na₂CO₃).
- Sulphates such as potassium sulphate (K₂SO₄), and sodium sulphate (Na₂SO₄).

The melting point of the nitrates range from 585F (307C) and 642F (339C); the melting point of the carbonates range from 1564 to 2442F (851 to 1339C); and the melting point of the sulphates range from 1578 to 2642F (859 to 1450C).

Oxidizing compounds are used to promote exothermic chemical reactions. They react with the smallest molten aluminum particles that are present in the dross, yielding aluminum oxides as well as considerable heat. The purpose of the exothermic reaction is twofold: 1) allows larger pockets of entrapped aluminum to coalesce and fall back into the molten bath, and 2) facilitates reactions between aluminum and fluorides. The exothermic reaction continues until all the fine aluminum particles are burned.

SOLVENTS OF ALUMINUM OXIDES

Examples are: borax $(Na_2B_4O_7)$, potassium borate $(K_2B_2O_4)$, and sodium cryolite (Na_3AlF_6) .

The Hall and Heroult patents both covered the electrolysis of aluminum oxide in a bath of molten halide salts. Since then, dissolution of aluminum oxides (Al₂O₃) by cryolite has been documented.

CLASSIFICATION OF FLUXES

Historically, solid fluxes have been classified in four categories depending on their use and function at the foundry operation. These categories are: cover fluxes, drossing fluxes, melt cleaning fluxes, and furnace wall cleaner fluxes.

Cover, drossing, and melt cleaning fluxes can be either manually spread, shoveled, or thrown onto the melt surface. Drossing and melt cleaning fluxes can also be injected under the molten bath. Furnace wall cleaner fluxes are typically blown (with a gunning device) onto the furnace walls at the melt line.

To ensure that melt-cleaning and drossing fluxes will do their job effectively, it is essential that, after addition, the flux be stirred into the melt to achieve as much as possible contact with the molten metal and dross layer. It is also important to emphasize that the flux reaction efficiency depends on three factors that are interrelated to each other: molten metal temperature, stirring, and activation time.

COVER FLUXES

Cover fluxes are designed to be liquid at operating metal temperatures in such a way that the flux will form a molten barrier "blanket" on the surface of the metal to protect it against oxidation and hydrogen gas absorption. The basis of any cover flux is mainly a blend of NaCl and KCl salts with small quantities of fluorides. Fluxes having these three compounds are suitable for almost all types of aluminum alloys, excluding hypereutectic aluminum alloys and aluminum magnesium alloys with over 7% Mg.

Over the years, a considerable number of different commercial cover fluxes have been developed with preferred additions and proportions of NaF, KF, Ca₂F, and other compounds such as CaCl₂ for lowering the melting point of the flux, as well as for providing cleaning effects.

Cover fluxes are used in foundries and smelting operations. Foundries use these types of fluxes during the melting of heavily oxidized foundry returns and machining chips, as well as when metal holding temperatures exceed the 1420 to 1450F (771 to 787C) range.

In smelting operations, cover fluxes are mixed in the rotary furnace during the melting of fine scrap, turnings, sawings, fines, etc. Typically, cover fluxes for smelting applications have lower melting points than those used for foundry applications; e.g., 795F (424C) versus 1229F (665C).

DROSSING FLUXES

Drossing fluxes may be based on salt blends of chlorides, simple and or double fluorides, and oxidizing compounds. Therefore, drossing fluxes are able to react exothermically, generating heat and improving flux wettability. The wetting action of the flux promotes coalescence, which brings the fine aluminum drops tighter to form larger drops that are much easier to recover. The work of drossing fluxes is considered to be due to both the surface tension effects and dissolution of aluminum oxides.

There are wide commercial ranges of different flux compositions. Even though a drossing flux will always be considered as "hot or reactive flux" in furnace tender terms, it is important to realize that the reactivity in a drossing flux is due to a combination of the oxidizers and the double fluoride compounds. This is an important concept to understand, because even without double fluorides, the flux may look too reactive due to an excess of oxygen-bearing compounds that may be burning excessive amounts of good metallic aluminum without actually dissolving aluminum oxides in the melt.

Some manufacturers may decrease the use of double fluorides, since they are more expensive as compared to other compounds. At the same time, it is important to notice that a lower grade compound, which is cheap, may also decrease the effectiveness of the flux. The same concept will be true for any other type of flux because the quality of the chemical compounds will influence the price of the flux.

A good drossing flux must be designed to reduce the rich metallic aluminum content of the dross. As the dross is treated with the drossing flux, it changes from a wet dross appearance (bright, shiny metallic color) to a dry dross appearance (dark, powdery). Proper flux treatment could reduce the amount of metallic aluminum content of the dross to 30%.

CLEANING FLUXES

Melt cleaning fluxes are designed to remove aluminum oxides from the melt, and/or to reduce unwanted chemical alkali impurities from the molten bath. Melt cleaning fluxes usually are higher in chloride salt compound content. They may use similar chlorides and oxidizing compounds as the ones used in the drossing fluxes, but in different proportions. In addition, the composition of a melt cleaning flux will typically include only simple fluorides as compared to the simple and double fluorides that are present in drossing fluxes. Since a melt cleaning

flux is less reactive than a drossing flux, it will yield less dry dross than a drossing flux. The main purpose of the cleaning flux is to facilitate wetting of the oxide inclusions for easier separation of the melt.

The work of melt cleaning fluxes is considered to be only due to the surface tension effects as previously stated. It is very important not to confuse a melt cleaning flux with a furnace wall cleaning flux.

FURNACE WALL CLEANING FLUXES

Wall cleaning fluxes are specifically designed for the softening and removal of excessive aluminum oxide build up that occurs on melting furnaces walls, especially along the melt line. This type of flux helps keep crucible and furnace walls above and below the melt line free of oxide build up.

Wall cleaning fluxes contain the highest amounts of double fluoride compounds such as Na₂SiF₆ and Na₃AlF₆. The exothermic reactions that occur because of the oxidizing compounds and the double fluorides enhance more penetration of the flux into the oxide build-up, facilitating the removal of the oxide build-up at the furnace wall.

Fluoride free fluxes cannot be used effectively as a wall cleaning flux.

THERMODYNAMICS OF FLUXES

Salt fluxes contain reactive elements that could chemically interact (positively or negatively) with element additions and/or the chemical elements from the molten metal. Knowledge of the Gibbs free energy of formation of several compounds with respect to the main different flux ingredients would help in understanding the behavior of the chemical elements of an alloy. Figure 2 shows the standard Gibbs free energy of formation for several fluorides, chlorides, oxides and sulphides. As shown, the stability of the compounds increase with increasing the negative value of the Gibbs energy of formation, with a few exceptions, the stability increases from the sulphides down to the fluorides.

From Figure 2 it is obvious that chemical elements will react first with fluorides and then with chlorides. Figure 2 also depicts the order in which the chemical elements will react: Ca before Ba, Ba before Li, and so on.

QUANTIFICATION OF INCLUSIONS IN MOLTEN ALUMINUM

Over the last 50 years, several techniques have been developed and used for assessing the cleanliness of molten aluminum casting alloys. These include qualitative, quantitative, and analytical laboratory procedures, as well as on-line and off-line techniques such as: MetalVision, Reynolds 4MTM (The Mansfield

Molten Metal Monitor), Porous Disc Filtration Analysis (PODFA), Liquid Aluminum Inclusions Sampler (LAIS), Liquid Metal Cleanliness Analyzer (LIMCA), Pressure Filtration Technique (Prefil-Footprinter), Qualiflash, Reduced Pressure Test (RPT), and the K Fracture Mold. The strengths and weakness of these methods with regards to equipment requirements, sampling, sensitivity, timing, and practical means of assessing molten metal cleanliness and/or inclusion levels in the foundry floor have been fully discussed and published in the literature. 10,11,12,13,14,15,16,17,18,19,20,21,21,22,23,24,25

The level of inclusions in molten aluminum alloys can be substantial. The inclusion concentration may be in the range of parts per million (ppm) to fractional percentage (by volume). For example, a "low" inclusion concentration of 1 ppm per pound of molten metal would contain around 5.155 inclusions if all the inclusions were considered to be spheres of 40 um (0.04 mm or 0.0016 in.) diameter. The assessment of the level of inclusion present in the melt has been a very important parameter that needs to be controlled by proper inclusion removal and detection techniques. In addition to inclusion particle size, a significant attribute of molten metal cleanliness is inclusion size distribution. Furthermore, while some inclusions particles may have the same dimensions, they could have significant differences in their chemical properties. Thus, it is of primary importance that inclusions evaluations distinguish differences in chemical and physical properties among them. In general, the larger the inclusions are, the greater are their deleterious effects to casting quality.

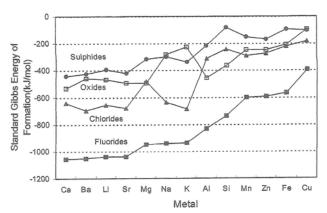


Figure 2. Standard Gibbs energy of formation for a number of compounds.8

With present technology commercially available for removing inclusions, a wide range of levels are achievable (0.10 to 10 ppm). Common techniques for the removal of inclusions involve settling during holding of the melt, flotation during the injection of gases, filtration, and fluxing. The question to ask is to what level of treatment a foundry should commit for a given casting/process. It appears that most crisis due to inclusion casting defects are caused by unforeseen generation of inclusions.

Sedimentation processes are effective for particles whose density is significantly greater than aluminum. Particles greater than about 90 μm (0.09 mm or 0.0036 in.) settle at the bottom of the bath within 30 minutes. Due to the typical purging bubble sizes: ≤ 5 mm (5,000 μm) encountered during rotary degassing, inclusions greater than 30 to 40 μm may be reliably separated from the melt by flotation.

Furthermore, inclusion particles larger than 80 μm (0.08 mm or 0.0031 in.) can be removed with rising degas bubbles of 10 mm (10,000 μm) diameter. Filtration methods can further remove inclusions smaller than 30 μm (0.03 mm or 0.0012 in.). However, filtration efficiency depends on the type of the filter used, filter size, pore structure, initial molten cleanliness and metal velocity.

INCLUSION DEFECTS IN CASTINGS

Although foundries still have difficulty for accurately assessing aluminum melt cleanliness prior to pouring, most foundries understand that molten metal handling and treatment techniques would have an impact on the melt cleanliness prior to pouring. Having a notion of the level of molten cleanliness is just a third of the solution to eliminate inclusion related scrap in castings. The second third of the solution is to establish a correlation between the inclusion defect (s) in the casting (s) and the inclusions present in the molten metal (molten cleanliness level). The last third of the solution is the implementation of the proper corrective action to eliminate the root cause and the continuous monitoring of the solution.

There appear to be two different schools of philosophy with respect to defining inclusion limits in molten metal for foundry applications:

- That the inclusion content in molten aluminum alloys has to be several volume parts per billion and that the average particle size in the population can be no more than 50 μm (0.05 mm or 0.002 in.) to produce quality castings.
- The extent in which inclusions render a molten alloy "unfit for use" is considered a function of the casting application and therefore of suitable molten metal practice. This notion is a very practical outlook from a foundry perspective.

Foundries may scrap castings due to inclusions after radiographic and/or fluorescent penetrant inspection. Quality casting requirements on inclusions could usually be met if foreign particles (inclusions) sizes, in the casting are smaller than 60 μm (0.06 mm or 0.0024 in.). However, particles larger than 60 μm would not necessarily damage the quality of the castings. An important evidence to take into consideration is the fact that the acceptable foreign material discontinuity sizes (width and length) established by the ASTM E155

standard for radiographic inspection for plate 1 varies from 762 μ m (0.762 mm or 0.030 in.) and 1524 μ m (1524 mm or 0.060 in.).

Castings having internal inclusions not exceeding such limits are considered to be acceptable castings while meeting such quality standard. Larger inclusions sizes established for plates 2 and 3 are also used to define lower acceptable quality castings.

It is not uncommon to find out that more than 50% of the inclusion scrap defects that a foundry experiences, occur after the machining operation. Such castings would be rejected because of poor machinability due to hard spots and/or because of failure to meet stringent cosmetic requirements on machined surfaces. Cosmetic requirements may cause a casting to be scrapped if inclusions are larger than 400 μm (0.400 mm or 0.0157 in.). Such size is considered to be about the smallest size defect that could be seen by the naked eye on a machined surface. Thus, many inclusions are only discovered when the inside and/or the outside customer complains.

The negative effect of inclusions in mechanical property evaluations is first most commonly noticed during the tensile testing of separate cast test bars and then from test bars designated from specific casting locations. However, the negative effects of inclusion occurrence in the test bars are almost never related to castings being scrapped due to inclusion defects. Flaws in test bars due to inclusions in the fracture surface do not necessarily cause rejection of the castings because the test bar can be replaced with another one and retested per ASTM B 557.

Regarding potential harmful discontinuities sizes, past studies have revealed that porosity defects of $100~\mu m$ (0.1 mm or 0.004 in.) start affecting mechanical strength and fatigue life.

Standard foundry melting and handling procedures, which are considered to be "good and sound practices", include proper melting, degassing, fluxing, and refinement practices. Molten cleanliness evaluations 11,25,26 show that molten A356, C355, A357, A206, and 319 aluminum alloys subjected to such practices will have inclusions (particles) sizes from 20 μm (0.02 mm or 0.0008 in.) to 60 μm (0.060 mm or 0.0024 in.) suspended in the molten bath prior to casting. These particles sizes can be regarded not as making the melt "unfit for use" but rather as inherent, and characteristic of the alloy and melting practice. Such particles would be normally dispersed throughout the casting.

Foundry melting and handling processes, in particular without the best degassing, fluxing, and refinement practices, which are typically considered as "minimum enough practices", will make these previously mentioned alloys to have inclusions (particles) sizes over 60 µm.

Yet the question remains as to what is the effect of the different inclusion sizes present in the molten bath on the final composition, morphology and size of the inclusion(s) defect found in the casting(s).

MOLTEN METAL INCLUSION ASSESSMENTS AND INCLUSION CASTING DEFECTS

Molten metal cleanliness assessments with Prefil (referred to as Analyzer 1 from this point on) and/or MetalVision (referred to as an Analyzer 2 from this point on) could provide the foundry with practical information about their melting process. If properly done, in conjunction with optical microscopy and SEM analysis a foundry would be able to correlate inclusions defects in castings with molten metal quality and/or to better understand from where the inclusions in the castings are coming from. Any foundry that at least from time to time audits the melting process and/or uses such technology during inclusion casting issues (after properly identifying the inclusions in the castings) would have a strong knowledge that would facilitate finding the root cause of the inclusion defect.

In this last section of the article, some minimum information and concepts obtained during recent Analyzer 2 and Analyzer 1 trials will be shared but without deep discussion of the results since such information will be the basis of a future article that is under development.

The objective of showing just the type of information that could be obtained by these two techniques is to disseminate the advantages of using them to eliminate inclusion defects and/or to establish best high quality molten metal practices. Therefore, since molten metal quality could be related to inclusion casting defects, it is also important not to lose track of the importance of casting defects analysis. Thus, some of the typical defects that foundries commonly and inaccurately identify as inclusions will be discussed. The intention of the concluding section is to provide "food for thought" so that before blaming the molten metal and the flux used, a better and proper inclusion casting analysis be done. Nevertheless, getting the casting defect analysis without any further correlation with the molten metal bath and/or the casting process to eliminate the defect in question is a waste of time and effort.

Figure 3 shows the MetalVision oxide analyzer and an Analyzer 1 unit in operation at the same time.

As it is known, the advantage of the MetalVision analyzer is that it can provide continuous cleanliness level measurements (every twelve seconds) while particle size measurements are continuously measured over a ten second period followed by a two second pause. The instrument displays a graphical representation of the molten cleanliness as a function of time and a histogram of the various quantities, and the relative number of particles in each of 10 size ranges (from less than 20 µm

to over $160~\mu m$), as shown in Figure 4. By looking at the screen, one could monitor any change in the melting process and/or disturbance in the molten bath.



Figure 3. The Analyzer 2 and Analyzer 1 units operating at the same time in a foundry.

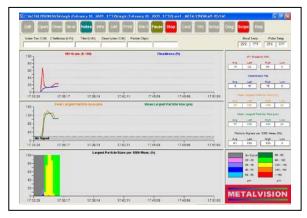


Figure 4. The Analyzer 2 screen display showing cleanliness curve, and particle sizes distribution.

As it is commonly known, the use of the Analyzer 1 unit offers other benefits. It is a batch evaluation, obtained at one particular point in time. Figure 5 is a typical representation of the Analyzer 1 curves (filtration weight versus time). The slope and the overall shape of the weight (gr) filtered versus time (sec) indicates the level of inclusions present in the molten bath.

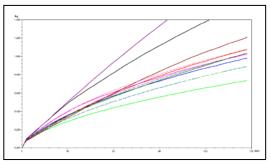


Figure 5. Analyzer 1 curves depicting different melting processes evaluated.

A detailed metallographic examination of the corresponding Analyzer 1 filter cross-section provides

information on the overall metal cleanliness by inclusion content given in mm²/kg, oxide films (number/Kg) and inclusion type given by mm²/kg and in percentage of the respective total content. Typical total inclusion counts have been found to vary from 0.037 to 8.10 mm²/kg and over 1,500 films/Kg depending on individual foundry's melting practices. However, the higher inclusion count does not necessary makes the molten metal unfit for the casting process. Figure 6 represents a typical micrograph obtained during the laboratory assessment. In this case, the microstructure is used to reveal aluminum oxides.

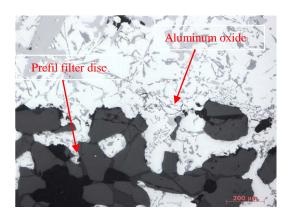


Figure 6. Microphotograph showing aluminum oxide films.

As a closing argument to emphasize the importance of properly identifying inclusion defects in castings before blaming the molten metal right away after visually assessing scrap rejects, 3 different castings sections are being presented. Each section is from a different foundry (Figures, 7, 8, and 9). Each of these sections is a representative sample of specific castings defects that foundry personnel visually identified as inclusions due to bad metal. Two of the defects were detected in the as-cast condition, and one after machining. To keep the article within given directives, only 3 samples are presented out of a several dozen different encountered cases of initially erroneously casting inclusion defects identification.

After the casting defects, corresponding microphotographs from the SEM results for each of the defects will be given. Such information is enough to properly identify what type of defect the castings had and if one knows the process, the solution is obvious.

Since a picture is worth a thousand words, and since the purpose of this last paragraph in the article is to close the loop between why we may fail to eliminate casting inclusions despite the fact of what we know or not know on molten metal cleanliness, impurities, oxides, inclusions, dross, and fluxes, no further discussion of the metallographic analysis will be presented.

It is up to the foundry to decide what approach to use to solve inclusion defects in the casting. Sporadic outbreaks of high casting scrap rates due to inclusions indicate lack of understanding and/or constantly monitoring not just the melting process but also the casting process.



Figure 7. Casting made by using the dry sand process. Defects detected in the as-cast condition.

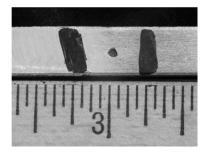


Figure 8. Section of top flange, of a green sand casting, in contact with a sand core. Defect detected after machining.



Figure 9. Casting made in permanent mold. Defect detected in the as-cast condition.

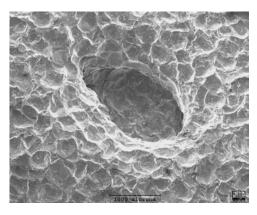


Figure 10. SEM image of the defects (voids) shown in Figure 7. Proper identification reveals that surface voids are due to texture of dry sand grains molds.

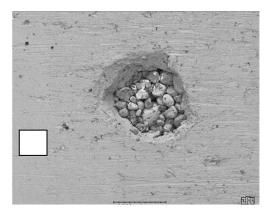


Figure 11. SEM image of the casting defect shown in figure 8. Proper identification reveals that inclusion is due to green sand molding.





Figure 12. Higher magnification (left) and SEM image (right) of the casting defect shown in figure 9. Proper identification reveals that defect is embedded wire from the paint brush.

CONCLUSIONS

Finding the root cause of inclusion defects in castings represents a challenge because of the wide range of interdependent molten aluminum and casting process contributing factors.

Molten metal factors are linked to the level of molten aluminum cleanliness which in turn depends on the

degree to which the chemical properties (chemical element composition) and physical properties (hydrogen content, dissolved chemical impurities, and inclusions) are controlled within the foundry operation.

Inclusions can be broadly classified as intermetallic and non-metallic. Non-metallic inclusions are typically grouped as exogenous, or as in-situ.

Intermetallic inclusions are primary compounds that result due to the precipitation and growth phenomena from the liquid state.

Non-metallic inclusions can be present in the form of films, fragments, particles, and clusters. The inclusions can have different composition, texture, morphology, and appearance. Common types of non-metallic inclusions are: borides, carbides, nitrides, oxides, and salts.

Sedimentation, flotation, filtration, and fluxing are common techniques being used to remove and separate inclusions from aluminum alloy melts. However, fluxing is the first step for ensuring molten cleanliness, by preventing excessive oxide formation, removing nonmetallic inclusion from the melt, and preventing and/or removing oxide build up from furnace walls.

Solid fluxes can broadly be categorized as passive or active fluxes. Passive fluxes protect the surface of the molten aluminum from oxidation and prevent hydrogen pick up by the melt. Active fluxes strip away the aluminum oxide layer from molten metal promoting coalescence of metallic drops, and help in reducing unwanted chemical impurities.

Solid fluxes are basically blends of sodium chloride and potassium chloride salts, with or without addition of fluorides. Additional oxidizing compounds that may also be present are: carbonates, sulphates, and nitrates.

To obtain the correct benefit of a flux, it is necessary to recognize that not only each different ingredient provides different effect but also that the combination and proportion of them directly influence the final property of a flux.

Knowledge of the Gibbs free energy of formation of compounds with respect to the different flux ingredients would help in understanding the behavior of the chemical elements of a molten aluminum alloy after fluxing.

Different levels of quantification (qualitative, and quantitative) of inclusions in molten aluminum alloys is possible throughout the different on-line and/or off-line commercially available techniques.

The level of inclusions in molten aluminum alloys can be substantial. The inclusion concentration may be in the range of parts per million (ppm) to fractional percentage

(by volume). The boundary in which inclusions (sizes, types, and concentration) render a molten alloy "unfit for use" is settled based on the casting process.

Having a notion of the level of molten cleanliness is just a third of the solution to eliminate inclusion related scrap in castings.

The second third of the solution is to establish a correlation between the inclusion defect (s) in the casting (s) and the type of inclusions present in the molten metal (molten cleanliness level).

The last third of the solution is the implementation of the proper corrective action to eliminate the root cause, and the continuous monitoring of the solution.

When dealing with inclusion defects or casting scrap issues rule of thumb's solutions must be avoided and replaced by careful and detailed analysis.

Molten metal cleanliness assessments with Analyzer 1 and/or an Analyzer 2 could provide a foundry with practical information about its melting process. If properly done, in conjunction with optical microscopy and SEM analysis (from both samples: the molten bath and the casting defect) a foundry would be able to correlate inclusions defects in castings with molten metal quality.

Molten metal cleanliness assessments with an Analyzer 2 were still being conducted, in different foundries during the writing of this article. Thus, such data would be presented in a future article.

A foundry request of "give me the cheapest and best flux for cleaning my melt" will not be the best driven cost saving solution to eliminate inclusion defects in castings if neither the inclusions in the castings nor in the molten metal are not properly identified, nor if the selection and application of the flux are not properly understood.

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