

METAL CONTAMINATION ASSOCIATED WITH DROSS PROCESSING

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Abstract

Processing dross to recover the contained metal units has been practiced almost as long as there has been an aluminum industry. While the primary goal is to maximize metal recovery from the dross, other factors are important as well. It is normally desirable to produce metal with a composition similar to the starting alloy. This may not be possible in many instances. This paper will look at the sources and mechanisms for metal contamination. It will also offer suggestions on how the contamination can be minimized.

Introduction

Processing of white dross from Primary and Remelt cast shops for the recovery of the contained metal is a common practice in the aluminum industry [1, 2]. First pass metal loss is usually the largest single cost in a cast shop. Consequently it is critical to recover any remaining metal from the dross. As stewards of our resources it is incumbent on us to maximize the recovery of metal from our cast shop by-products. This practice fits nicely with most company's Sustainability programs. It also makes strong economic sense. Finally energy usage and Greenhouse Gases are reduced by recovering the aluminum metal from the dross.

Most cast houses have their dross and other aluminum-containing by-products processed by an outside contractor although this practice seems to swing in and out of fashion approximately once per generation. The outside processor typically processes the material for a fee on a best effort basis and then returns the recovered metal to the customer. The processor never owns the metal, but is responsible for it while it is on their premises; this is called toll processing. The argument in favor of outside tolling is that the processor will do a better job since that function is the core focus of their business. The counter argument for in-house processing is the desire of the producer to control the cost and recovery of his dross processing. In most areas white dross is processed with a tilting rotary furnace (TRF) although other processing paths are practiced as well. Historically most tilting rotary furnaces were operated with a salt flux mixture to maximize metal recovery. More recently in some countries the disposal of the by-product, salt cake to landfills has been prohibited. In these areas the additional step of Closed Loop Processing of the salt cake must be practiced or the TRF is operated in a flux-free mode.

From a customer's view point the biggest concern in dross processing is always the metal recovery rate. Small changes in recovery can have a large impact on a cast shop's profitability. In actuality, the more important parameter for the customer is net melt loss [2, 3]. Net melt loss reports the actual fraction of metal that is lost from a melting operation after all processing is complete.

$$\text{Net Melt Loss} = \frac{\text{Metal In} - (\text{Metal Out} + \text{Metal from Secondary Recovery})}{\text{Metal In}} \quad (1)$$

$$\text{Net Melt Loss} = \frac{\text{Metal In} - (\text{Metal Out} + \% \text{ Recovery} * \text{Dross})}{\text{Metal In}} \quad (2)$$

Net Melt Loss factors in the generation rate of the dross in the producing furnace and multiplies that by the dross recovery rate in the second step. This recovered metal is counted towards the metal out since it can be used again. Net melt loss is the best indicator of a Cast Shop's ability to avoid oxidizing the metal.

White dross recovery is impacted by a number of variables:

1. *The feed materials to the producing furnace* – Melting heavy solids like T-bar or RSI in a dry hearth furnace will produce less dross than melting lighter gauge scraps like cold mill side trim or swarf. The presence of more surface area allows more aluminum metal to be exposed to products of combustion which creates surface oxidation and leads to the generation of more dross. Another example of feed material impact is the alloy composition. Magnesium containing alloys will generate more dross than non-magnesium-containing alloys.
2. *Furnace practice* – Furnace temperature and exposure time has a large impact on how much oxidation can occur [4]. Like most chemical reactions, higher temperatures increase the kinetics of oxidation. As Theile showed, longer holding times for molten aluminum allow more oxidation to occur and allow different forms of aluminum oxide to form. Other furnace practices that can impact dross recovery are the manner in which material is loaded into the furnace; the best practice is to load light gauge scrap in the bottom of the furnace followed by the heavier materials on top to act as protection from combustion gases and direct flame impingement. Furnace operational parameters such as Air-Fuel Ratio, Furnace Pressure, and Fire Rate can all have an impact on oxidation. Timing of the dross removal step can impact the degree to which the dross has oxidized. In very extreme cases, the dross will begin to thermite in the furnace because it has gotten too hot from prolonged exposure to the burners.
3. *Dross handling after furnace removal* – Once dross is removed from the furnace it is very easy for the contained aluminum to continue to oxidize. This is

especially true if a thermite is allowed to occur. A thermite is the uncontrolled oxidation of the aluminum with the gas components in air. Extreme heat is generated by the thermite and metal content is quickly decreased leading to lower recovery. To avoid continued oxidation after the dross has been removed from the furnace, a whole host of inventions have been developed. Examples of these devices include dross presses, rotary coolers, and inert gas coolers, to name a few.

4. *Rotary furnace recovery processing* – The recovery of the dross can be impacted by the type of equipment used in the rotary furnace and the manner in which it is used. The type of burner (conventional air-fuel versus oxy-fuel) can impact the environment the dross is exposed to during the recovery process. Similarly the type of flux, the amount of flux used, and the timing of the flux additions for a salt processing TRF can impact recovery. From a processor’s standpoint it can be difficult to assess their performance due to the high variability associated with the incoming feed. Creating a standardized process for a variable feed material can be challenging.

Another concern for a customer of a dross processor is the turnaround time or the time from the delivery of the dross until the recovered metal is returned either in molten form or as Recycled Secondary Ingot (RSI). This is critical for two reasons: The metal can change in value due to changes in the world aluminum market. Secondly the longer the material is held, the greater the opportunity of continued oxidation of the dross leading to a loss in metal recovery.

The final concern of the customer is the chemistry of recovered metal. Typically customers want to return this metal to the process from which it came. It is not uncommon for a customer to ask, “Why does my recovered metal from the dross have a different chemistry than the alloy from which it came?” Both the customer and the processor should have a mutual goal of minimizing the degradation of the alloy. The remainder of this paper will examine the causes and cures for changes in recovered metal chemistry.

Contamination

One of the most common reasons for degradation of metal from dross is contamination. Contamination can occur at many points in the process. These points can be grouped into three major categories:

1. In the Melting Furnace
2. Post Melting Furnace, and
3. In the Rotary Furnace

Each area will be discussed in more detail.

In the Melting Furnace

Very few remelt furnaces melt and process pure prime metal. Instead most furnaces have scrap additions made to the charge or have alloying additions made to molten metal. In-house

manufacturing scrap is typically a very clean metal source, but it is possible for mixed alloy contamination to occur in the scrap tubs. If post-consumer scrap is used, the potential for contamination is increased significantly. As an example, extrusion scrap is often wrapped with steel bands or wires to facilitate transport and storage. At some cast shop operations a portion of the bands will be left in place prior to furnace charging for safety and handling reasons. These steel bands and wires end up in the furnace. Typically some of the steel dissolves into the molten hearth metal, but a significant amount reports to the dross and is removed when the furnace is skimmed. An example is shown in Figure 1. It is also possible to find alloying materials in the dross skimmed out of furnaces. This would indicate poor furnace practices. Not only does this impact metal composition in the metal recovered from the dross, it is also a waste of expensive alloying elements. Another source of dross contamination in the furnace can be from contaminated scraps that may be charged to the hearth. If these scraps have undesired contaminants like copper wire or stainless steel, it is possible that a portion of the contaminants will dissolve into the molten hearth metal and a portion will report to the dross. Once in the dross, these contaminants will usually report to the recovered metal during dross processing.

These contamination problems are solved by proper charging practices and furnace alloying practices. Examples would include more attention to removing banding before charging scrap and exercising more care in alloying practices.



Figure 1. Steel wire embedded in white dross.

Post Furnace Contamination

The most common source of contamination in dross processing is in the interval after the dross has been removed from the furnace to the time it is delivered to the dross processor. What is often observed is that some individuals treat dross with a “garbage mentality.” It is not uncommon to see foreign objects in the dross that are associated with the disposal of used items. Examples and the issues they create are listed in Table 1 on the next page.

Not only is there a huge potential to cause off chemistry issues and process upsets for the dross processor when contamination is present, the dross producer will have to pay the toll for the additional material in the dross that will not yield any benefit to recovery. In other words the customer is wasting money by having the contaminants in the dross.

Table I List of Dross Contaminants

Type	Examples	Issue
Tramp Iron and Steel	Wire and banding, welding rod, bolts, small tools	Raises Fe levels
Stainless Steel	Tools and equipment	Raises Ni and Cr levels
Grain Refiner	Refining rod	Raises Ti level
Organics	Wood, cardboard, paper, rags, plastic, oil, grease, and other hydrocarbons	Recovery impact - Counts as weight to the furnace. Also causes problems with the combustion system.
Wire and Electronics	Copper wire, printed circuit boards	Raises Cu levels and organic compounds that could form dioxin / furans.
Furnace Temperature Sensing Hardware	Thermocouples and thermo-wells	Raises Fe, Ni, and Cr levels
Graphite	Gas injectors, spinning nozzles, etc.	Recovery impact - Counts as weight to the furnace.
Slab Ingot Casting Materials	CFFs, distribution bags, bone ash or whiting	Source of calcium impurities [5]
Closed Containers	Beverage bottles and cans, spray paint cans	Explosion risk
Moisture	Water & rain	Recovery impact

A few examples of dross contamination are presented below. In Figure 3, general trash such as rags, paper, plastic and cardboard are intermingled with the dross. Obviously someone was mixing trash with the dross. In Figure 4, grain refiner rod was thrown into the dross. This is both a waste of an expensive alloying agent and will cause chemistry issues in the recovered metal.



Figure 3. Garbage mixed in with dross.



Figure 4. Grain refiner rod mixed in with dross.

In Figure 5 below, the background levels of chromium and nickel in most batches of the recovered metal from a 6061 dross are approximately 0.04% and 0.01% respectively. Yet several pairs of spikes with Cr and Ni content can be observed where stainless steel contamination occurred. From the chart we cannot determine how the contamination occurred – only that stainless steel was the culprit.

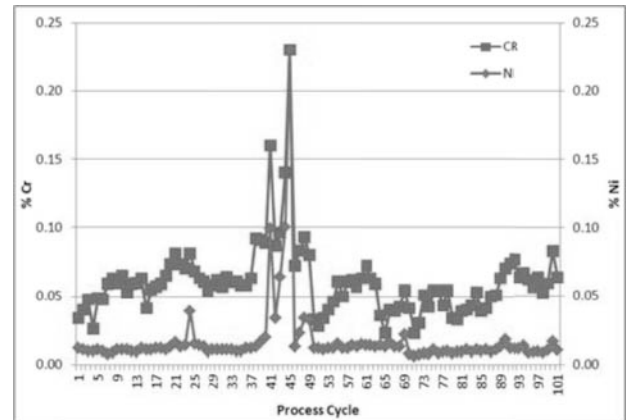


Figure 5. Example of Stainless Steel contamination of dross.

Most of the issues with the contamination in the table above are self-evident with the possible exception of the impact of water on dross. Obviously it is not possible to get aluminum metal from the weight associated with water; a loss in recovery would be expected. But more importantly the presence of water will cause a rapid drop in recovery due the accelerated oxidation of the aluminum in the dross. Drosses often have aluminum nitride, AlN, present. When in the presence of water, AlN will react to form ammonia gas, NH₃ (see Equation 3 below) which is soluble in water and creates a weak base.



The aluminum metal reacts with the base to generate hydrogen and aluminum hydroxide. The aluminum metal is lost to the conversion reaction and the recovery drops.

Another form of contamination that may be less obvious is the comingling of drosses from different alloys. The recovered metal may not be compatible with either parent system. An example of this is mixing 3XXX and 5XXX alloys. The recovered metal is usually sold at a significant discount if it cannot be used back into the original product.

The solutions to these types of contamination are employee training and to provide alternative disposal bins for non-aluminum materials. Additionally the dross processor can provide photographic evidence as feedback to the customer.

Rotary Furnace Contamination

The third area that contamination of the dross can occur is by the dross processor. This can occur in the raw materials storage area or in the rotary furnace during the processing step. The rotary furnace is a batch operation so in theory contamination should not be an issue, but the reality can be different if care is not taken. At the end of a campaign with a customer's material, all products must be removed from the furnace, but if the furnace is not operated correctly, buildup of salt cake on the furnace walls can occur. This buildup can include entrapped metal from earlier cycles. When the furnace finally gets hot enough, the build-up on the wall will melt out and the entrapped metal will be released. The entrapped material has the potential to change both the recovery and chemistry of the batch that is being processed. This undesired event can be avoided by several methods. First the operators must strive to keep the barrel clean and free from buildup. In extreme cases this can even include barrel flux washes to remove buildup. Secondly the rotary furnace loads should be staged in a manner of progressing from "clean" or lightly alloyed materials to "dirtier" or more heavily alloyed materials within an alloy family. In some cases it is possible to move from one alloy family to another depending upon the alloys involved. One example of a staging scenario is shown in Figure 6 below.

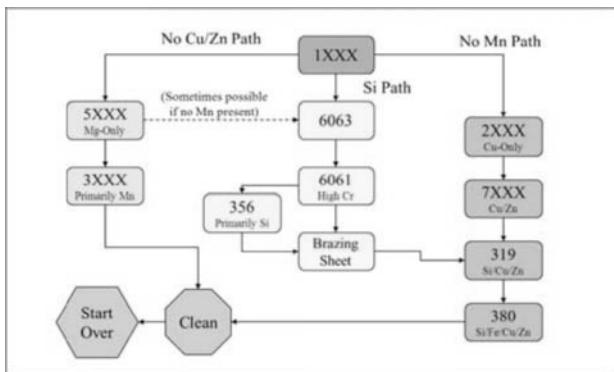
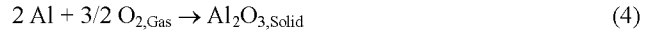


Figure 6. Processing path for multiple alloys to avoid contamination.

Generally it is a straightforward process to determine if contamination has occurred within a rotary furnace. The culprit element (or elements) is identified and then previous furnace batches are examined for an alloy that would have that element at a level higher than the batch in question. Avoidance of this form of contamination is up to the dross processor.

Impact of Oxidation on Contamination

There is one other mechanism that can account for higher concentrations of alloying elements than in the starting aluminum alloy. Aluminum metal is highly reactive and is more thermodynamically stable with respect to oxide formation than most other metals. For the reaction:



$$\Delta G = -1055 \text{ Units kJoules / mole O}_2 \text{ at } 298\text{K.}$$

The negative Free Energy in Equation 4 indicates the reaction will proceed to the right. The fact that the Free Energy is very negative indicates the reaction will essentially go to completion.

An easy graphical way to compare the oxide stability of various metals is through the use of an Ellingham Diagram (see Figure 7 below). All oxidation reactions are written in terms of one mole of oxygen reactant. This allows comparison of exchange reactions between different metals and metal oxides. With only a few exceptions most metal oxidation reactions are less negative than aluminum's oxidation reaction. This implies that if metallic aluminum comes in contact with one of these metallic oxides, the aluminum will reduce the oxide and leave behind the other oxide as a metal. Additionally, the reaction will generate heat. This oxide exchange reaction is the basis of the classic "Thermite reaction" used to weld steel rails by igniting a mixture of aluminum metal with iron oxide. Only magnesium and the alkalis and alkaline earth elements are more reactive than aluminum.

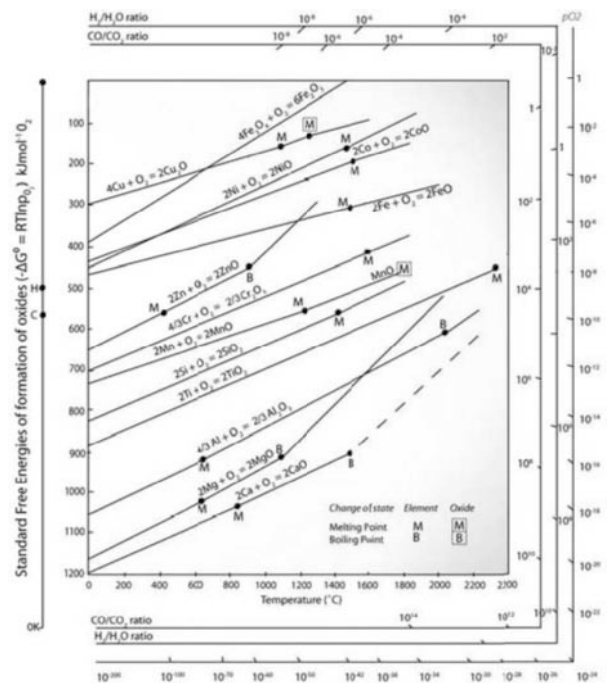


Figure 7. Ellingham Diagram for metal oxides (courtesy of University of Cambridge website)

For dross processing this exchange reaction is important because any metal oxides present in the dross that are more noble than aluminum during the remelting operation will be reduced by the

aluminum. This decreases aluminum recovery and increases the pickup of contamination. Once any alloying element is in the molten aluminum (with the exception of Mg) it is not possible to remove the metal by further chemical processing as is so common in other non-ferrous systems. Unfortunately virtually all metals are soluble in molten aluminum.

This phenomenon can cause the dross to produce a recovered metal product that will have a higher alloy content than the original alloy. The degree of concentration for the alloying element is dependent upon the degree of oxidation that has occurred. This enriching behavior is especially pronounced when dross is allowed to thermite in the melting furnace or at the cast house after removal from the furnace.

Let's look at an example of oxidation starting with a hypothetical aluminum alloy containing 9% Si and 0.5% Fe. Consider a thin layer of metal at the metal / air interface that contains 100 kg of alloy. We will assume that this thin layer will eventually form the skimmed layer of mixed dross removed from the furnace. If 15% of the 100 kg of the alloy on the surface of the load oxidizes, the metallic content of the layer now containing the remaining metal and the newly formed dross will decrease to 85 kg. The aluminum oxidation will create an oxide that weighs 28.2 kg and which creates a total dross layer weighing 113.2 kg. This newly created dross layer now contains 75% metal content. The remaining 85 kg of metallic content now contains all of the alloying elements. The Si concentration will rise to $9 / 0.85$ or 10.6%. The Fe concentration will rise to $0.5 / 0.85$ or 0.59%. The Concentration Factor (the ratio of the final concentration divided by the starting concentration) for this case is 1.18. This change in metal content and Concentration Factor in the recovered metal can be expressed by the equation:

$$\% \text{ Metal Content} = (100 - X) / (100 + 0.88X) \quad (5)$$

And

$$CF = 100 / (100 - X) \quad (6)$$

Where X = % of aluminum oxidized in fixed volume of metal.

Figure 8 below shows the relationship between metal oxidation to metal content of the dross (the maximum theoretical recovery) and the Concentration Factor of alloying elements. As you can clearly see, if the oxidation is greater, less metal will remain in the dross and the concentration of the remaining alloying elements will increase dramatically. Or stated another way, "Lower recovery dross will have a higher concentration factor and higher levels of the more noble metals in the recovered metal."

Now let's look at actual data from processing a 6061 dross. Since Fe contamination can come from so many potential sources, it will not make a good candidate for this evaluation. Typically it is best to select an element that is present in the alloy, but not likely to be a contaminant. In this case zinc will be examined for concentration due to oxidation since it is much more unlikely for zinc to show up as a contaminant in the dross. Due to rotary furnace practices, it is difficult to get paired results of metal recovery (a function of metal content) and zinc content to test the previously mentioned relationship. Additionally, percent oxidation of the starting dross is difficult to measure, but the magnesium content of the recovered metal is straight forward to

determine. Since Mg is more reactive than Al, the magnesium content can be used to indicate how much oxidation has occurred in the dross since the time of its formation. If the Mg content is high, very little oxidation has occurred. If the Mg content is low, the dross has oxidized; the lower the Mg value, the more oxidation has occurred.

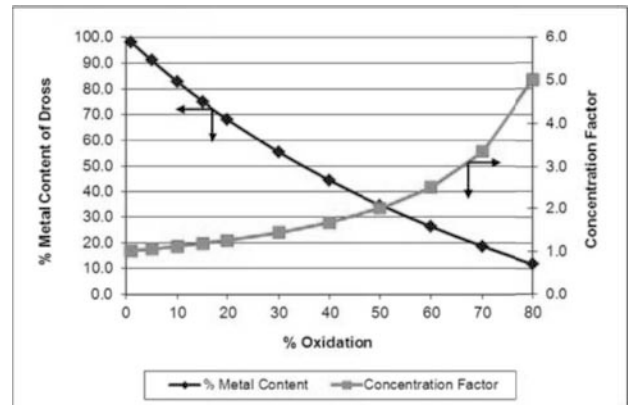


Figure 8. Relationship of Concentration Factor versus % Oxidation.

A data set for the processing of 1063 loads of 6061 dross from a single cast house source was examined for Zn content in relation to Mg depletion. The raw results are presented in Figure 9. While there does seem to be a trend of increasing Zn content in more heavily oxidized metal (lower % retained Mg), the amount of scatter in the data makes it difficult to see the trend clearly.

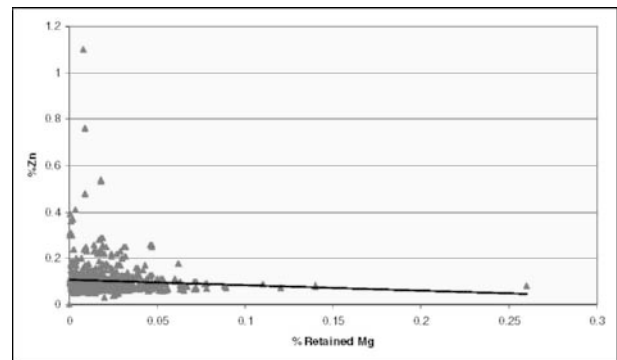


Figure 9. Relationship of Zn enrichment versus Mg depletion – Full data set.

In order to clarify the situation, the data set was divided into a number of smaller Mg content ranges. The average Zn content for each range was determined. This analysis is presented in Figure 10. While still possessing a significant degree of scatter, the trend of increasing Zn content when the dross has been oxidized (as measured by Mg depletion) can be clearly observed.

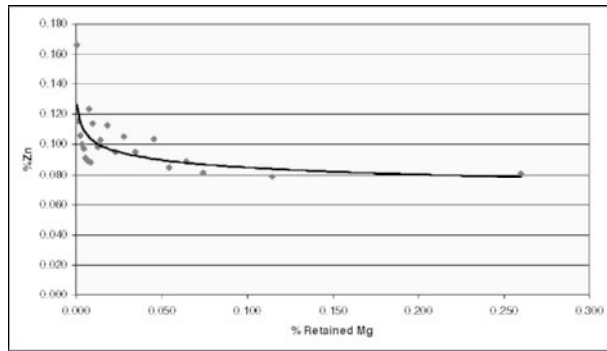


Figure 10. Relationship of Zn enrichment versus Mg depletion – Ranged data set.

The best way to avoid this form of contamination is to generate high recovery drosses through avoidance of oxidation, either in the primary melting furnace, outside of the furnace after removal, or in the rotary furnace in subsequent processing.

Conclusions

There are many paths for contamination of the recovered metal from dross to occur. These paths have been outlined in the paper. While conventional contamination may be the most common reason for contamination (and usually the easiest to solve), a new mechanism was presented based on the selective oxidation of aluminum and the enrichment of more noble metals. This mechanism explains higher levels of impurities observed in recovered metal when metal recovery drops. A portion of the higher contamination levels observed in the recovered metal from dross can be attributed to the degree of oxidation of the dross. Lower recovery drosses will have higher levels of impurities.

Every effort should be made to minimize oxidation of dross either in the furnace or after skimming to ensure the best level of metal quality possible. This effort also coincides with the positive economic impact on recovered metal value by minimizing oxidation. Working closely with dross processors can lead to identification of dross contaminants. Most dross processors will be happy to provide feedback to the customer on contaminants and help them with programs to reduce the contamination.

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