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ALUMINIUM℠

Compacted Product Additives for the Aluminium Casthouse

Technical Reference Guide

Compacted Product Additives for the Aluminium Casthouse

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1. Introduction

The properties of aluminium alloys are largely dependent on the correct addition of the alloying elements before the casting process. There are a number of ways of making these alloying additions such as pure metal, master alloys, powder injection and a variety of tablets and briquettes.

The choice of which alloying addition to use for each element is complex[1]. A number of competing factors have to be taken into account and their relative importance may vary from plant to plant and product to product. Some of the key criteria include metal temperature available, virgin:scrap ratio, furnace type and layout, alloy change frequency and end product quality.

The cost of alloying is not always easily defined. It is not only raw materials costs, but also processing, yield, quality and overhead considerations, which need to be taken into account when selecting the most appropriate alloying technique.

This booklet is designed to give an insight into compacted products (tablets, mini-tablets and briquettes) for alloying. These have found increasing usage throughout the world's aluminium industry for a whole range of end applications, including rolling ingot for foilstock and canstock, billet for precision extrusions and high quality foundry casting alloys. They are used for both bulk element addition and for precise compositional adjustments of alloy melts.

Metallurg Aluminium offers a unique supply capability with plants in England – London & Scandinavian Metallurgical Co Limited (LSM), the United States – Shieldalloy Metallurgical Corporation (SMC), Brazil – Companhia Industrial Fluminense (CIF), Norway – Hydelko AS and Spain – Bostlan, S.A.

Each plant within the group is registered to one or more of the following quality standards: QS 9000, ISO 9001 and ISO 9002.

2. Review of Alloying Techniques

2.1 Alloying methods

Several methods of alloying are practiced in the industry. The choice of method is largely dependent on performance, economics, health and safety and environmental considerations.

Elements such as Si and Mg, which melt or dissolve readily in aluminium, are added as the pure metal. The natural drive is towards 100% element additions for other alloying additives, as realized in some casthouses by the practice of powder injection. In recognizing this, Metallurg Aluminium has looked to develop and promote 100% element-contained compacted products where possible in elements such as Ti, Fe and Zr. Powder injection has not been widely adopted across the world due to equipment cost, small element addition levels or powder handling concerns.

The alloying additive type which is most readily dissolved is the master alloy, typically in the form of waffle plates. A more recent development is to add some of these dilute master alloys in a cast bar form called Castcut™ nugget. These have an advantage over waffle in terms of weight consistency and cleanliness. They generally contain a mixture of aluminium and the aluminide of the alloying element. The rapid dissolution of the aluminide at normal melting or holding furnace temperatures makes it relatively simple to use (or difficult to misuse!!) and ensures high and rapid recoveries. However, their relatively high cost means that many casthouses consider a switch to a more concentrated additive.

Concentrated additives, for example ALTAB™, which has continued to show significant growth since introduction in the early 1980s, are a mixture of alloying element (75%, 80%, 85% and in some cases 100%) in powder, sponge or needle form, aluminium powder, and/or a sodium-free, non-hygroscopic flux.

An overview of common alloying elements, including their addition methods and their effects in aluminium, is given in Table 1.

Alloying Methods and Effects

ELEMENT	
Bi	Principally used to enhance machinability. Bi is added both as the pure metal and as a dilute master alloy.
Cr	Cr has a number of uses including inhibiting grain growth in Al-Mg alloys, inhibiting recrystallization in Al-Mg-Si and Al-Mg-Zn alloys and as a corrector for Fe to produce a golden color in anodizing. The main addition technique is as a concentrated tablet or briquette, although a significant quantity is also added as dilute master alloys. A less common addition method is powder injection.
Cu	Cu is mainly added to increase strength. It is added in many forms, the main ones being as pure metal or master alloys, but concentrated tablets and powder injection are also used.
Fe	Fe improves high temperature strength. All possible addition methods described are practical. A 100% Fe flake (Ferrosol™100) product has recently found increasing use.
Mg	Mg provides high strength with good ductility, together with excellent corrosion resistance and weldability. It is mostly added as the pure metal, although master alloys are also widely used.
Mn	Mn improves strength and also plays a role in preventing recrystallization. The main addition techniques are concentrated tablets or briquettes, powder injection and to a lesser extent master alloys.
Pb	Principally used to enhance machinability. The main addition method is the pure metal, although concentrated tablets and master alloys are also used.
Si	Si is used in 'foundry alloys' as it gives excellent fluidity in casting. It is also used in extrusion alloys to which it contributes to high mechanical properties. The main addition method is pure metal, but significant amounts are added as master alloys and through powder injection
Ti	Ti provides an important contribution to grain refinement. The main addition methods are tablets (including 100% Ti) and master alloys.
Zn	Zn is used to improve strength. It is almost exclusively added as the pure metal.
Zr	Zr is added to inhibit recrystallization. It is mainly added as a master alloy (up to 15% Zr), but also as a concentrated tablet.

Table 1: Addition methods and effects of common alloying elements

No single addition method has achieved dominance, and all methods consume significant tonnages. There is, however, a tendency towards using higher concentration products such as tablets/briquettes since these generally give fast and consistent dissolution rates and have lower overall costs. Master alloys are used extensively throughout the world. In Europe and Japan there is a higher proportion of dilute master alloys compared to North America where high-concentration alloys or briquettes have been preferred.

Injection techniques made rapid progress in the 1980s but seem to be limited to a few large plants in Europe and North America due to concerns on handling powders, reduced plant flexibility, the need for high alloying temperatures, high capital costs and control of raw material/process conditions to obtain consistent yields.

2.2 Alloying cost

The total cost of alloying is made up of a number of factors as shown in Figure 1. Some of these are relatively simple to measure (such as product cost) and generally form the basis of the purchasing decision.

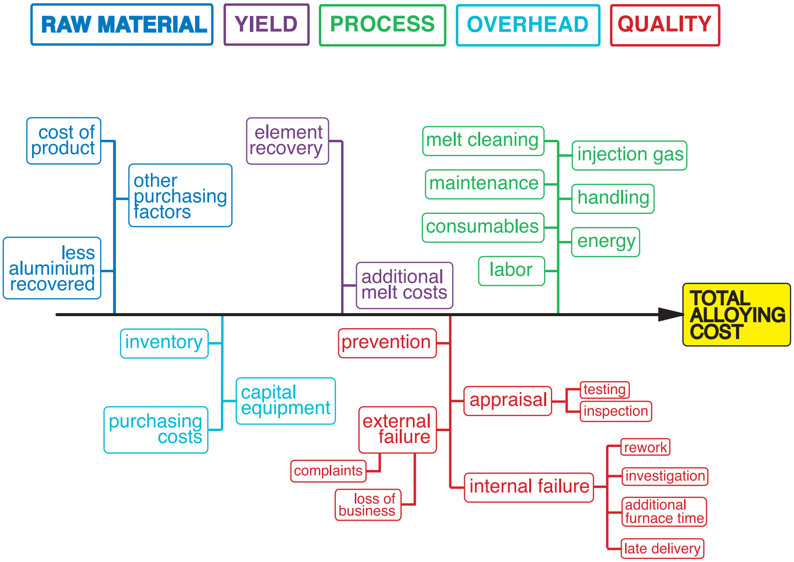


Figure 1: Factors affecting the total cost of alloying

Other costs (such as yields, additional processing costs and overhead costs) are less easy to measure, but possible. However, the cost of quality is difficult to quantify and is probably not measured by most companies.

2.3 Choice of alloying method

The main driving forces when choosing alloying process are:

- Performance
- Economics
- Health and Safety
- Environmental Issues

Performance includes such aspects as dissolution rate, reactivity of the additive, generation of drosses, and consistency of recovery. Economics is clearly a function not only of price but also of elemental yield, metal loss and overall productivity. Health and safety issues concentrate on manual handling limitations, fume emissions and in the case of powders, precautions against explosions and the exposure of operatives to fine particles. The environmental issues in question are essentially the use and subsequent disposal of packaging along with the desire to ever-reduce fume emissions.

The choice of alloying method is therefore a complex issue, and raw material cost is by no means the only thing to consider. Some of the other factors are reviewed here:

a) Hot/Cold Metal Plant

This is one of the key factors since many of the lower-cost alloying methods rely on temperatures above 750°C (1380°F) to give adequate dissolution rates. In order to control energy, yields and production rates, cold metal plants need to operate below these temperatures.

b) Virgin: Scrap Ratio

Where high scrap contents are used, the purity of the additives may need to be higher in order to not exceed trace element specification limits. Dissolution rates are generally slower when scrap contents in the bath are high.

c) Furnace Types

The furnace type can affect the mixing ability and rate of dissolution. For example, induction furnaces will generally give better mixing and faster dissolution rates. Reverberatory furnaces require either manual stirring or preferably additional mechanical or electro pneumatic stirring, as demonstrated by the Alcan Jet Stirrer[2].

d) Furnace Layouts

In plants which do not have separate melting and casting furnaces, the melting and alloying process will tend to be the rate-controlling stage. As such, speed of alloying is a very significant factor. Rapid and accurate dissolution is essential. In a two-stage furnace set up, longer times can be spent in the melting/alloy furnace, since this is generally not the rate-determining stage.

e) Alloy Change Frequency

In large plants concentrating on a small number of alloys, there is greater potential for using the more capital-intensive processes such as powder injection. For smaller plants, or those requiring a wide range of alloying elements, the more flexible master alloys or tablets/briquettes are preferred.

f) End-Product Quality

The two main effects alloying techniques will have on end-product quality are chemical analysis and metal cleanliness. Chemical purity will depend on the choice of raw material. For example Cr, Mn or Fe metals can all be produced by different processes, which give different trace element contents. Thus, care has to be taken in trace element specifications. There are also likely to be differences in metal cleanliness. Inclusions can be oxides, high melting point intermetallics, non-metallic inclusions, or undissolved elements.

g) Chemical Purity

Master alloys are normally supplied to the approved National or International standards such as the Aluminum Association or the European standard CEN/TC 132. For the raw materials available for master alloy production, the AA specifications are considered too prescriptive. In general, all the alternative alloying products are able to meet the industry's requirements.

h) Dissolution Rates

Rates of dissolution are dependent on metal temperature, turbulence, particle size and physical characteristics (whether intermetallics or pure metals) and melt composition (see section 4.2).

i) Element Yield

The main yield losses are due to element entrapment in the surface drosses. This is more prevalent in low-density master alloys or powders, which tend to float or be trapped in the surface oxide layer. Additions to clean bath surfaces are also important to give high, consistent yields. Other potential areas for element losses are:

- Surface oxidation of reactive elements such as Mg, Sr.
- Absorption into furnace refractories of elements such as Pb.
- Settling of low-solubility elements/intermetallics onto the furnace floor.

Typical element yields for most addition processes are between 95 and 99%. If they are less than 95%, the process should be evaluated for improvement. Furnace yields are also of considerable importance. Small changes in furnace yields, due to longer holding times, dross formed by gas injection, etc., can have major cost implications. However, variations of a fraction of a percent are very difficult to measure except over a long period.

j) Metal Cleanliness

Even though most products will be cleaned subsequently, either by fluxing in the furnace or in-line treatment, there is a cost to cleaning. A cleaner input will give increased filter life and allow higher productivity in the furnace by reduced settling times, etc.

k) Process Capability Consistency

To achieve optimum quality at lowest cost, target analysis must be met with minimum variation. For example, over-addition against a target value will incur extra raw material costs and potential inferior end quality. Low recoveries against target will mean a further addition is necessary, which will normally have a high cost penalty on productivity.

The factors which affect process capability will depend on the process employed. In addition, the process capability will also be very dependent on weighing-in variations and estimates of bath weights.

l) Health, Safety and Environment

Providing correct procedures are adopted, all products can be safely used. Special areas of attention are: explosions with powders, wet products or foreign materials; ingestion of powders, fluxes or oxides formed during the alloying process; fume emissions; physical injuries such as lacerations or back damage through material handling.

3. Production of Tablets

3.1 Tablet manufacture

Tablets are produced by the following process:

- Weigh required quantity of high-purity alloying element, aluminium powder and/or flux.
- Mix ingredients.
- Press in a cold die to produce tablets with precise quantity of element contained, for example 1kg (2.2 lbs) contained.
- For standard-size tablets, collate into a pack.
- Package.

A comparable product is a briquette. The pressure produced between two compacting rolls with 'pillow-shaped' indentations in the rolls forms the tablet shape.

3.2 Product description

Each tablet contains a precise weight of high-purity alloying element, the balance being aluminium, or a mixture of aluminium plus selected sodium-free, non-hygroscopic fluxes to accelerate dissolution and recovery. Tablets are plastic shrink-wrapped or Aluminium foil-wrapped to reduce dust and wastage – distinct colour coding ensures clear identification of the element contained.

Standard ALTAB™ tablets, with a nominal diameter of 90mm (3.5 in), contain 1kg (2.2 lbs) of the alloying element, except for Ti which contains 0.5kgs (1.1 lbs). Tablets are also available as mini-ALTAB™ with a nominal diameter of 45mm (1.8 in), typically weighing 100 to 200 grams (0.22 to 0.44 lbs). Compacted products are also available in briquetted form.

3.3 ALTAB™ Product Range

%	Element	Nominal Tablet Weight (g)	Tablets per Pack	Weight of Element per Pack (g)	Pallet Net Weight (g)
75	Cr, Cu, Fe, Mn, Ni, Zn Ti	1,333	3	3.0	1,440
75	Ti	667	3	1.5	720
80	Cr, Cu, Fe, Mn, Ni, Zn Ti	1,250	3	3.0	1,350
80	Ti	625	3	1.5	675
85	Mn	1,176	3	3.0	1,270
100	Ti	500	4	2.0	720

Element	European Colour Code	AA Color Code	Symbol	ALTAB™ 75%	ALTAB™ 80%	Typical Density (g/cm^3)
Chromium	Light Blue	Orange	Cr	74.0 – 76.0	79.0 – 81.0	4.0
Copper	Orange	Yellow*	Cu	74.0 – 76.0	79.0 – 81.0	4.5
Iron	Green	Black	Fe	73.5 – 76.5	78.5 – 81.5	4.0
Manganese	Silver Grey	Purple	Mn	74.0 – 76.0	79.0 – 81.0	4.0
Nickel	Yellow	Grey*	Ni	74.0 – 76.0	79.0 – 81.0	4.5
Titanum	Red	Red*	Ti	73.5 – 76.5	78.5 – 81.5	2.8
Zinc	White	-	Zn	74.0 – 76.0	79.0 – 81.0	4.0

* *These color codes are not registered by the Aluminum Association but are supplied by our North American plant.*

Manganese is also available as 85%. Titanium is also available as 100%.

ALTAB™ is protected and robustly packaged to ensure arrival of a damage-free, dry product. Standard tablets are wrapped (plastic or Al foil) into packs, which are contained in cardboard boxes and are securely packed on wooden pallets. For mini-ALTAB™, the tablets are supplied in easy-to-handle paper sacks, or large bulk bags. In North America, briquettes are available in 11.3kg (25 lbs) or 22.7kg (50 lbs) paper bags, packed on pallets, or in large bulk bags.

All packaging maintains the element identification, element weight contained and color coding.

Note: ALTAB™ and Quick-Sol™ briquettes should be stored in a dry area, preferably under cover. Do not add any wet product to molten metal.

4. In-House Research

4.1 Test methods

Various test methods are used to assess the quality and fitness for use of compacted additives.

The key raw material characteristics are cleanliness and chemical purity (assessed by traditional chemical analysis techniques such as optical emission spectrometry) and physical size (assessed by mesh tests for particle size distribution).

Tablet integrity is also a key feature, and this can be assessed by a drop test (how many times the tablet can be dropped from a height of one metre before break-up) or a sieve shaker test (in which breakdown of the tablet when subjected to vibration is tested). Solubility testing can be carried out using the Aluminum Association TP-2 test, in which a small furnace of molten aluminium has an addition made to it. The TP-2 test stipulates stirring to be carried out at distinct times after addition. The test is generally recognized to have poor reproducibility and not to be representative of real practice. This has led to several variations of the test, as well as other completely different tests being developed.

Work has been done by Metallurg Aluminium using a 400kg (880 lbs) gas-fired furnace – the traditional tests are in 10kg (22 lbs) furnaces – to better simulate furnaces in the casthouse. A rake is used to stir for such tests. The rake does not come into contact with the added tablets.

Another test developed by Metallurg Aluminium involves a piece of tablet being placed in a preheated mould cone which is then lowered into a bath of molten aluminium, allowing the cone to be filled. By holding for various times before quenching and sectioning, the dissolution procedure can be monitored. Figure 2 shows cast cones sectioned vertically, bisecting the circular face of the mini-tablet. The cut faces of the samples are ground flat to reveal the structure, and any undissolved remnants of the tablet.

A further technique to observe the dissolution procedure in real time involves dropping a tablet into a super-heated bath of molten aluminium in a rectangular mould. An x-ray source allows real-time video monitoring.

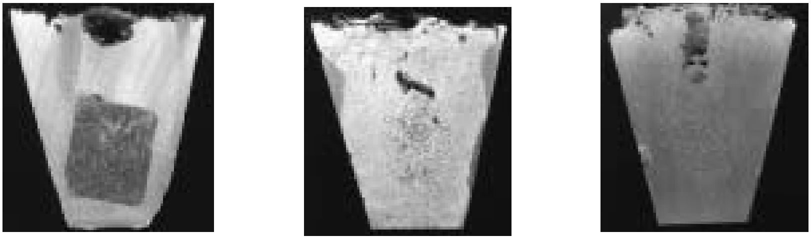


Figure 2: Some scanned images of the cast samples for 85% Mn-containing 200 gram mini-tablets. The tablets were extracted after 60 seconds, 120 seconds and 240 seconds after addition.

4.2 Dissolution mechanisms

An intense program has been carried out by Metallurg Aluminium in recent years[4,5]. Some of the key features identified include:

4.2.1 An incubation period is required, during which any oxide film present on the metallic powder particle is broken down (the use of fluxes improves speed of dissolution by removing such oxides).

4.2.2 An intermetallic layer (between element and Al) forms and builds up, and acts to slow down dissolution, as diffusion must occur through it. For this reason, the effect of melt stirring is critical for high level (95%+) recovery at rapid rate.

Figure 3: At left – dissolution of a Cr particle (surrounded by $CrAl_7$ with a thin layer of Cr_2Al_{11} between) in Al. At right – dissolution of an Mn particle which forms several aluminides during the dissolution process.

4.2.3 On addition to the molten bath, tablets break apart within one minute of addition. It is the creation of aluminides within the tablet which cause the forces which break the tablet apart. A high compaction pressure can help, as thermal conduction within the tablet is easier if more highly compressed.

4.2.4. Aluminide phases are formed during dissolution as follows:

Mn: $MnAl_4$ ($MnAl_3$, MnAl)
Ti: $TiAl_3$
Cr: $CrAl_7$, Cr_2Al_{11}
Fe: $FeAl_3$

4.2.5 The metallic content in the tablet is generally not critical to recovery or speed of dissolution.

4.2.6 Recovery of Mn from ALTAB™ (particularly the flux-containing grades) can be adversely affected if the melt already contains high levels of Mg (e.g. 5XXX series alloys). High Mn recoveries are achieved by adding and allowing to dissolve, prior to Mg addition.

4.2.7 The data presented in Figure 3 is all from TP-2 tests carried out at LSM, and should only be taken to give an indication of solubility. The repeatability of the recovery value at the end of the TP-2 test is typically of the order of ± 5%.

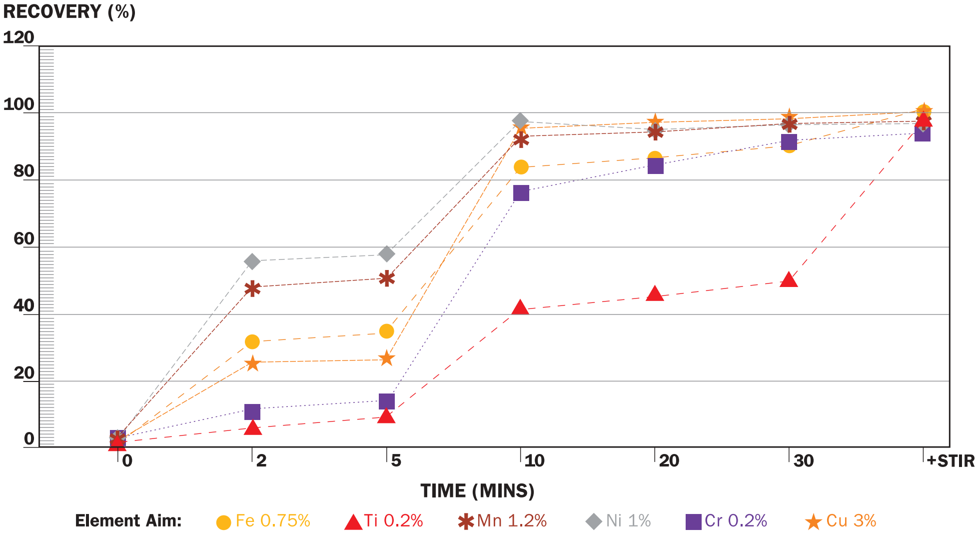


Figure 3: TP-2 tests for ALTAB™ additives

4.2.8 The data presented in Figure 4 is from tests carried out in a 400kg (880 lbs) gas-fired furnace, with raking of the surface but no scraping of the furnace floor. It is seen that faster recoveries are obtained than found in Figure 3, because of the continuous stir in this case. If stirring also included disturbing the material which has settled to the furnace floor, then even faster dissolution rates can be shown. This highlights the differences which can be apparent between laboratory-reported dissolution rates, and those found in practice using larger-scale furnaces.

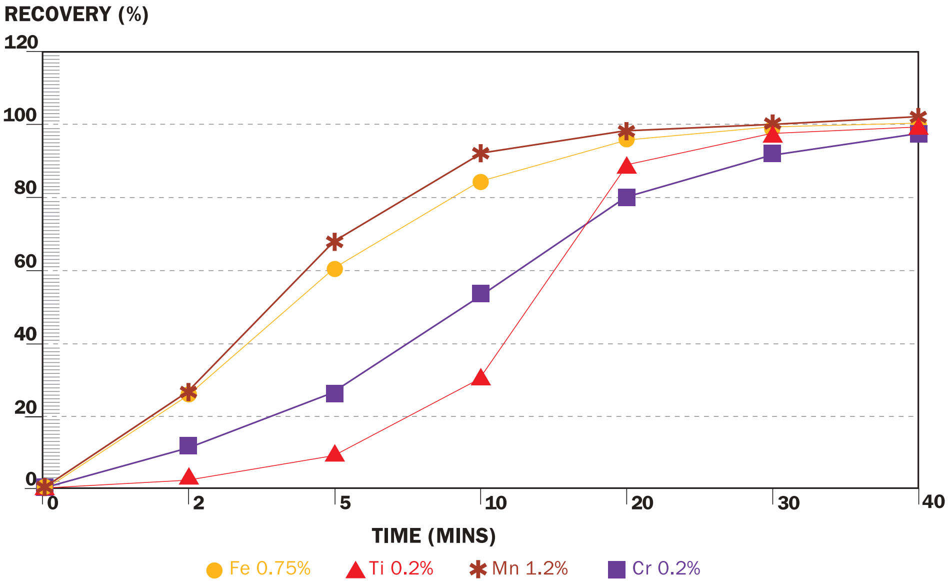


Figure 4: Large-Scale Solubility Tests for ALTAB™ Additives

The key steps to achieve rapid and high recoveries are therefore:

- molten metal temperature
- time
- type of stir
- time of stir
- alloying level
- removal of surface drosses before addition
- even tablet distribution in furnace

5. Advice for Users

5.1 Choice of tablet

The highest % element contained is the most cost effective and preferred choice, with no detrimental effect observed on speed of dissolution.

Flux-containing grades dissolve quicker but do produce slight fuming. This is discussed further in the next section.

Tablet size (standard or mini) has no major effect on dissolution, but mini-ALTAB™ are essential in bulk handling applications.

5.2 Casthouse practice

The following is a guide to the efficient use of ALTAB™ tablets for alloy additions in aluminium casthouses.

Wait until the aluminium bath (ALTAB™ can also be added in the transfer ladle) has reached a holding temperature of approximately 720 to 750°C (1330 to 1380°F). Dissolution will be slower at lower temperatures. For Ti, higher temperatures – around 760°C (1400°F) – allow significantly better performance. ALTAB™ additions can be made as follows:

1. Move any dross which has built-up on the surface of the melt to the sides of the furnace. This will allow the ALTAB™ tablets to sink quickly under the surface of the molten metal.
2. Add the ALTAB™ at different points around the furnace to ensure an even distribution. If necessary, the ALTAB™ packs can be cut open and the individual tablets scattered into the melt.
3. Once the ALTAB™ has dissolved, stir the furnace thoroughly, preferably from the bottom of the bath to the top. This will ensure maximum recovery and homogenous composition.

Both temperature and composition can be checked before casting begins.

Flux-containing ALTAB™ grades will dissolve quicker than zero-flux grades. The exact reason for this is not known. However, it is believed that one or both of the following factors plays a part:

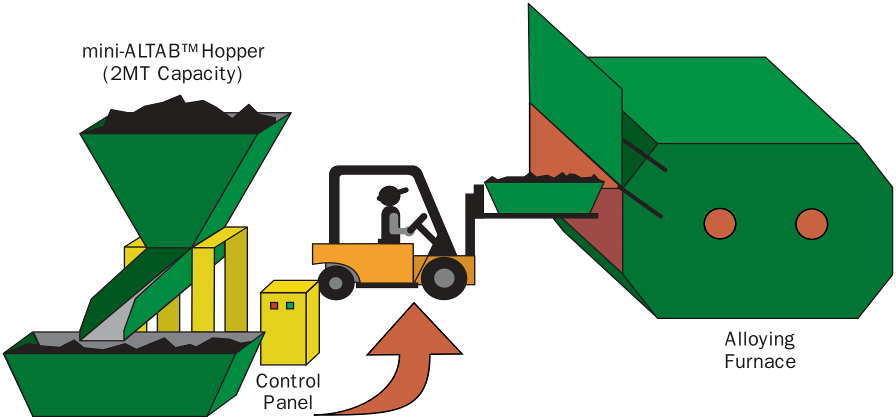
1. The low-melting-point flux 560°C (1040°F) brings about a rapid dispersion of the metal particles. This good dispersion then allows rapid dissolution due to the large surface area exposed.
2. The sodium-free, non-hygroscopic flux removes any surface oxide films from the metal particles to allow fast dissolution.

In certain critical applications, some users prefer to have no flux (as it produces a slight fuming) and accept longer dissolution times, although some users produce high-quality products with flux grades.

The longer dissolution time on flux-free grades can be shortened by extra stirring.

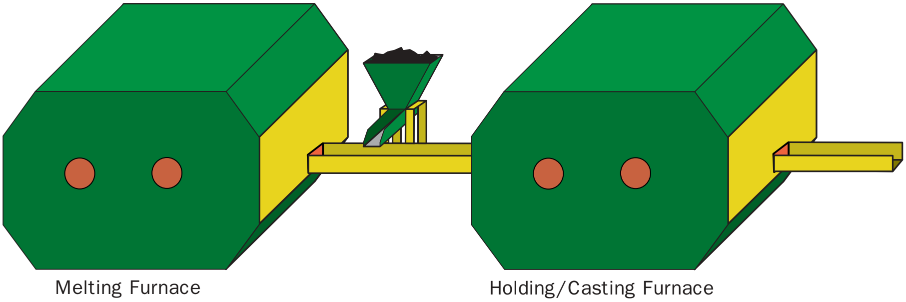
Recovery of Mn from ALTAB™ (particularly the flux-containing grades) can be adversely affected if the melt already contains high levels of Mg (e.g. 5XXX series alloys). High Mn recoveries are achieved by adding and allowing to dissolve, prior to Mg addition.

For the aluminium casthouse, small tablets such as mini-ALTAB™ represent an opportunity to implement improved alloying by bulk handling. One method of addition is shown in the schematic below:



mini-ALTAB™ can be delivered in bulk bags for putting in a hopper, from which they can then be accurately discharged to a central weigh station.

Multiple hoppers give the opportunity for one-shot additions to be made to the furnace. An alternative layout is shown below:



In this case, the tablets are slowly charged into the transfer launder between the melting and holding furnaces. This takes typically 15 to 20 minutes. The turbulence on entering the holding furnace allows rapid dissolution to occur.

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Notes:

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