



Recent Studies of Compacted Additives Including Industrial Scale Tests

Dr. Gregorio Borge¹,
Dr. Paul Cooper²

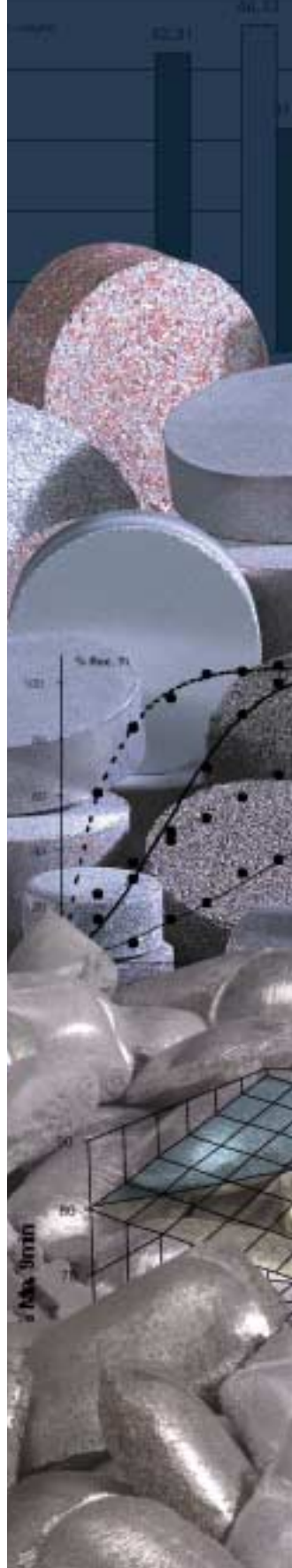
¹ Bostlan, S.A.
Mungia (Spain)

² London & Scandinavian Metallurgical Co Limited, (LSM)
Rotherham, South Yorkshire, UK

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Abstract

There have been several studies in recent years aimed at improving the understanding of how compacted additives behave when added to molten aluminium in a furnace. Most of these have been on a laboratory scale, where it is impossible to reproduce some of the situations encountered in the casthouse. They have also mostly concentrated on casthouse practice.

This paper reviews the previous studies and how they have helped generate a model of dissolution mechanisms. Results from new studies based on more realistic conditions are presented. An emphasis of the studies is on the characteristics of the compacts themselves. Conclusions are drawn on how good and poor performances are achieved with compacted additives.

Introduction

For the past 20 years, the use of compacted alloying additives has been the most common method to increase the Mn, Fe, Ti, Cr and/or Cu content in the aluminium casthouse. Different scientific groups have carried out studies on the mechanism and performance of these materials. It is the

intention of this paper to review the understanding of the mechanisms involved in the dissolution of compacted alloying additives, and also to explore the effects of the processing parameters of the compacts themselves, as well as the processing parameters in the casthouse.

Model of dissolution from the literature

A number of authors have contributed to the development of a model of the dissolution mechanisms involved. The summary presented by Guthrie^[1] gives a useful outline, and forms part of the basis of the following description:

Solid shell formation

On addition to the melt, a solid shell is formed around the compact. Its thickness is dependent on melt superheat and thermal conductivity of the compact.

Temperature rise in compact

In a short period of time, the compact reaches the melting point of aluminium. Below this temperature there is little reaction between the aluminium and the alloying element^[2]. A distinction needs to be made at this stage between compacts containing a flux and those without. The flux used in some compacts typically has a melting point below that of aluminium, such that this component of the compact will start to melt before the aluminium powder component.

Chemical reactions within the compact

Several workers have shown^[1,3] that for Mn-based compacts there is an exothermic reaction between the Mn and Al components of the compact. This can be witnessed as a glowing of the compacts at the melt surface^[2]. This has been shown to occur after the Al powder component of the compact has melted. Before a chemical reaction can occur, particle wetting and nucleation events need to occur. It has been suggested^[4] that one of the reasons flux-containing compacts dissolve more readily is that they help in the wetting stage by breaking down the inherent surface oxide layer on the alloying element particle. This is particularly relevant for Mn, as it has been shown^[5] that the reaction between Mn and oxygen can affect dissolution rates

adversely. Fisher^[4] indicated that the flux is significant to compact dissolution rate for the Mn-Al system.

It is suggested that the liquid Al transports to the solid Mn sites by a capillary action. For the Mn-Al and Fe-Al systems, Guthrie^[1] showed that although several layers of intermetallics are formed, there is only one dominant phase present in the compacts as these reactions occur. These are MnAl₄ and Fe₂Al₅ respectively. These are dominant because, although other intermetallic phases are possible, diffusion of the alloying element and Al within these particular phases is more rapid. In the Mn-Al system, growth of MnAl₄ has been shown^[1] to occur at both the MnAl₄-Al and Al-MnAl₄ interfaces. For the Mn-Al system, the intermetallic phase grows inside the liquid aluminium, and for the Fe-Al system it grows within the solid Fe phase.

Further chemical reactions occur following both swelling and dispersion of the compact. One issue associated with the use of compacts is the recovery to be expected from the aluminium powder content. This arises due to the known poor recoveries from the direct use of fine aluminium powder or chips. Perry^[2] showed that high (above 90%) recoveries can be expected due to the nature of the dissolution mechanism.

Swelling of the compact

Researchers^[1,2,6] have shown that compact swelling occurs and can be significant. The specific volume of the intermetallics is greater than the volume of the pure metals, which causes the expansion of the compact. Borge^[6] showed that for a Mn-Al compact after 30 seconds in the melt, the expansion was just under 50%. He also showed that at this time there had been no penetration from the melt into the tablet.

The swelling of the compact creates a porous structure, which can encourage capillary forces within, and so allow penetration of liquid aluminium from the melt. This allows the reactions to continue. The necessity of this penetration mechanism may provide another reason for the more rapid dissolution of the flux-containing compacts.

Compact disintegration

Some people^[1,2] have assessed compact disintegration by indirect methods, such as visual examination after immersion in wire cages or on the end of load cells. Bristow^[7] used a variant of the industry standard grain refining test^[8] to observe compact break-up more directly. Borge^[6] described a technique of direct observation, based on x-ray monitoring of a compact dropped into an aluminium melt. Most of the literature indicates compact disintegration within one minute of immersion. However, Lee^[3] claimed longer times occurred if there is no aluminium in the compact (but did not indicate what the compact compositions were).

Dissolution of discrete particles

From the description so far, it is clear that some dissolution and some intermetallic formation has occurred before compact disintegration. However, immediately following compact disintegration, there are still likely to be some metallic alloying element particles partially undissolved. Guthrie^[1] compared dissolution rates of compacts with that of the original classified particles. He concluded that

dissolution rates are higher when compacted for the reasons outlined in the previous description. Fisher^[4] noted that the industry standard test for dissolution was not appropriate in terms of being able to identify the processing time required in the casthouse to dissolve compacted additives.

The role of melt stirring in the successful use of compacts cannot be over emphasized. The need for good mixing to achieve rapid dissolution has been well documented^[5,9 to 11]. Fisher^[4] showed that stirring is essential or full recovery may not be achieved, and indeed that full recoveries are significantly more rapidly achievable with good stirring practice. The requirement for melt stirring can be related to both the spreading out of compacts in the bulk of the melt, and the re-suspension of settling alloying element particles once the compacts have disintegrated.

Summary of literature

It is possible from the literature to summarize a reasonable model of the dissolution mechanisms involved with the use of compacted alloying additives. However, most of the work done has been on small-scale laboratory testing such as the Aluminum Association standard test procedure^[12], with some notable exceptions^[4,6]. The current work is concerned primarily with the effects of processing parameters of both the compacts themselves as well as in the casthouse. Apart from stirring considerations, performance of the compacted alloying additives (dissolution speed, alloying metal recovery and reactivity) has not previously been related to the production parameters and/or to casthouse working practices and conditions.

Parameters and experimental methodology

The behaviour of compacted alloying additives when added into aluminium furnaces depends on different factors which can be divided into two groups. Firstly, those factors which are controlled directly by the compacted alloying additives production: these include size/weight of the compact, raw materials chemistry (including oxidation), the use of aluminium and/or flux powders as the binder, and the grain size of the raw materials powders.

The second group includes those factors related to the casthouse practice such as: the final alloy composition, the working temperature in the furnace, and the addition practice (this includes the skimming and stirring operations).

In terms of use of compacted alloying additives, issues of importance in the casthouse include high recovery in a short time, the production of skims and/or dross due to the operation, and the reactivity (flames, fumes, bubbles) of the material added to the furnace.

The experimental work in the present study has been performed in a rotary oxycombustion 400 kg capacity furnace, which is shown in Figure 1.

The furnace size is well-suited to studying the performance

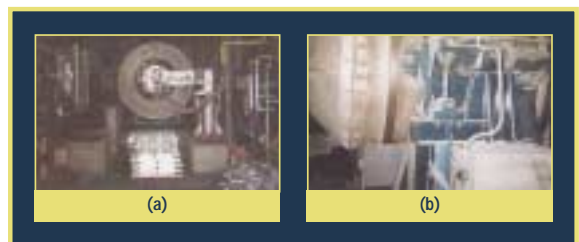


Figure 1 – A rotary 400 kg furnace for aluminium dissolution tests.

of compacted alloying additives: it is not a small laboratory furnace with possible scaling problems, and it is not a big industrial furnace in which operation parameters are more difficult to control.

The furnace was fed for each experiment with preweighed 99.7% chemical purity aluminium ingot (400 ± 10 kg). After the melting process drosses were removed, temperature was adjusted, a blank sample was taken, and the compacted alloying additives were added. Homogenization of the melting bath is necessary for maintaining the temperature and for adequate and repetitive sampling. Stirring was performed before every sampling process, using a ceramic

rake (avoiding hitting the compacted alloying additives). Samples were usually taken every five minutes for 40 minutes (for Mn, Fe or Cr tests, for example) or even for 90 minutes (for Ti) experiments. Materials were added using a ladle and without any packaging. Temperature control was performed with a thermocouple sunk in the bath;

Results

This work presents results for different parameters, and is mainly focused on dissolution rate and final recovery of the alloying metals added as compacts. Each alloying element yields different results and even different trends for each parameter to be studied. The trends are not always straight forward and sometimes complex mathematical treatments are necessary. Examples are described in the following section:

Effect of powder grain size on Ti sponge dissolution

General experience on dissolution processes indicates that smaller particles (i.e., lower grain sizes) give better dissolution rates since the contact surface between the material to be dissolved and the solvent is larger. This is not so clear when working with metal powders, since higher specific surfaces mean increased contact with atmosphere and higher oxidation of the material.

Pure titanium sponge materials are adequate for addition as compacted alloying additives into aluminium baths due to their good compaction characteristics. Titanium sponge is available in very different grain sizes. In order to assess the influence of this factor, two different 97% titanium sponges were used for producing 80% Ti tablets, aluminium being the balance of the compact. Figure 2 shows the different grain sizes of the materials used.

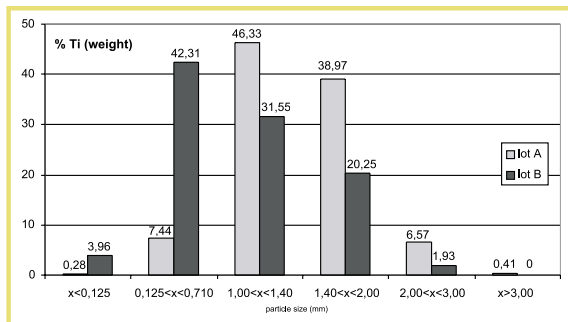


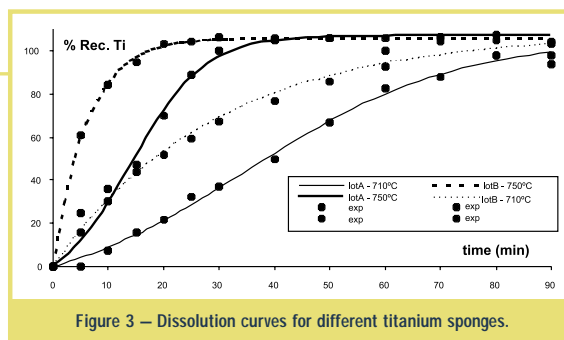
Figure 2 – Grain sizes of two different titanium sponge materials.

Experiments were performed in the 400 kg furnace at different working temperatures. Final alloying level was intended to be 0.12% Ti. Final recovery curves are shown in Figure 3.

It is observed that the grain size has a significant influence on dissolution for this kind of titanium material. Differences are also enhanced in this metal since the grain size interval is

it is usually accepted to have a range of $\pm 10^{\circ}\text{C}$ for each experiment, but usually a $\pm 4^{\circ}\text{C}$ interval after material addition can be achieved.

Samples obtained were roughly polished using a laboratory lathe and analysed for metal content with an ARL spark spectrophotometer.



quite wide if compared to typical grain sizes of other metallic materials used in compacted alloying additives. For titanium, a great dependency on temperature can be also observed. The differences between the experiments are so clear that no mathematical treatment is needed in order to draw conclusions.

Study of Fe compacts

A study of 6 factors on the dissolution performance of atomized Fe was carried out following a two-level 2^{6-2} fractional experimental design of 16 experiments. The 6 factors studied were:

- compact size
- nature of binder used to produce compact
- % Fe in compact
- % Fe to be alloyed
- level of oxidation of Fe
- melt temperature

The experimental factors and levels studied are presented in Table 1. Alloying level and iron oxidation level were taken as the confused factors for the fractional design. Experiments were randomly performed in order to avoid any possible block effect. All studied factors are qualitative except for the binder, whose value corresponds to presence of aluminium or flux (the flux was a non-hygroscopic sodium-free inorganic salt). Because of this, two different centre points were taken into account in order to study the influence of the aluminium, or the flux, in the reproducibility of the casting experiments.

Figure 4 shows the curves for the 16 cast experiments of the fractional design. Experimental points are not shown to avoid confusion. It is clear that it is not possible to obtain direct conclusions from a visual examination of the results.

Fe recovery at 5 and 10 minutes, and the final recovery, were used as the responses for a mathematical treatment of the results. A multiple regression analysis allows the empirical equations governing the system to be obtained. Calculations were performed considering a 95% confidence level for accepting a factor as significant. Equations 1 to 5 are the empirical expressions obtained.

Table 1 – Experimental design for Fe studies

Experiment (random order)	Fe weight in the compact (g)	Binder	%Fe in compact	Furnace temperature (°C)	Alloying level (% Fe)	Iron oxidation level (%)
1 (16)	155	Al	75	710	0.25	0.16
2 (18)	1000	Al	75	710	0.75	0.16
3 (17)	155	Flux	75	710	0.75	0.80
4 (6)	1000	Flux	75	710	0.25	0.80
5 (14)	155	Al	80	710	0.75	0.80
6 (10)	1000	Al	80	710	0.25	0.80
7 (20)	155	Flux	80	710	0.25	0.16
8 (15)	1000	Flux	80	710	0.75	0.16
9 (21)	155	Al	75	750	0.25	0.80
10 (13)	1000	Al	75	750	0.75	0.80
11 (4)	155	Flux	75	750	0.75	0.16
12 (3)	1000	Flux	75	750	0.25	0.16
13 (22)	155	Al	80	750	0.75	0.16
14 (24)	1000	Al	80	750	0.25	0.16
15 (12)	155	Flux	80	750	0.25	0.80
16 (19)	1000	Flux	80	750	0.75	0.80
17 (1)	500	Al	77.5	730	0.5	0.32
18 (7)	500	Al	77.5	730	0.5	0.32
19 (5)	500	Al	77.5	730	0.5	0.32
20 (8)	500	Al	77.5	730	0.5	0.32
21 (9)	500	Flux	77.5	730	0.5	0.32
22 (11)	500	Flux	77.5	730	0.5	0.32
23 (23)	500	Flux	77.5	730	0.5	0.32
24 (2)	500	Flux	77.5	730	0.5	0.32

$$\text{Rec, 5 min (Al binder)} = 113.5 - 140.6 * \text{Fe ox. level} + \varepsilon \quad (1)$$

$$\text{Rec, 5 min (flux binder)} = 83.5 - 28.1 * \text{Fe ox. level} + \varepsilon \quad (2)$$

$$\text{Rec, 10 min (Al binder)} = 104 - 69 * \text{Fe ox. level} + \varepsilon \quad (3)$$

$$\text{Rec, 10 min (flux binder)} = 101 - 25 * \text{Fe ox. level} + \varepsilon \quad (4)$$

$$\text{Tot Rec} = 50.7 + 390.3 * \text{Fe ox. level} + 0.64 * \% \text{Fe in compact} - 5.25 * \% \text{Fe in compact} * \text{Fe ox. level} + \varepsilon \quad (5)$$

As can be seen, the factors showing some influence on dissolution rate (5 and 10 minutes) and total recovery are the Fe oxidation level, the concentration of Fe in the compact, and the nature of the binder. Since the binder is a qualitative factor, different relationships with the iron oxidation level were obtained for aluminum powder and for flux for 5 and 10 minutes recovery.

The empirical models explain approximately 80% of the experimental information.

Figures 5 and 6 show the corresponding plots of the equations. As can be seen, the most important factor influencing the Fe recovery in molten aluminum baths is the oxidation level of the Fe raw material used in the compacted alloying additive. A high Fe oxidation level yields lower dissolution rate and final recovery. The presence of flux enhances the Fe recovery just after the addition, especially if the iron oxidation level is higher than 0.4%, but no effect of the flux has been found on the Fe final recovery. Fe powder percentage in the compact is a significant factor for final

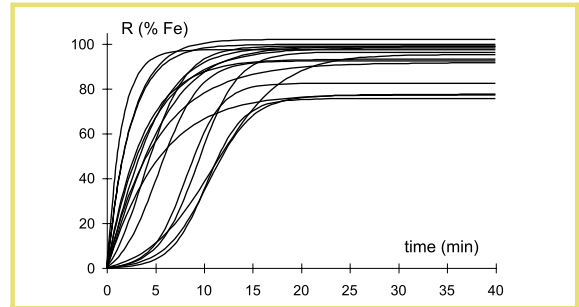


Figure 4 – Recovery curves for the cast experiments of the fractional experimental design.

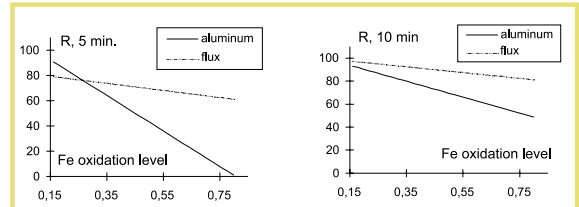


Figure 5 – Fe recovery vs. Fe oxidation for 5 and 10 minutes recovery time.

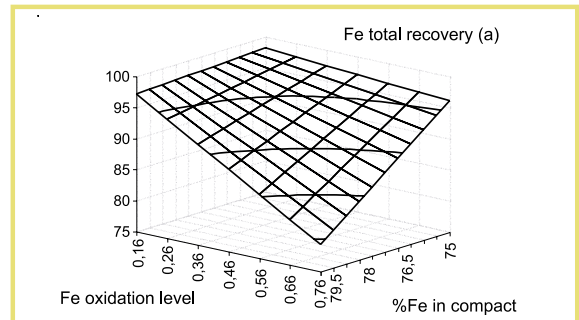


Figure 6 – Fe recovery vs. Fe oxidation and Fe percentage in compact for Fe total recovery.

recovery if very oxidized Fe is used (final recovery can be reduced up to 15%, this effect being more clear in compacts with high iron percentages).

It can be concluded that Fe recovery in molten aluminum baths from compacted alloying additives can be strongly influenced by factors related to the compacts themselves (the nature of the binder, the Fe percentage in the compact, and the Fe oxidation level). The furnace temperature and the required Fe alloying level have not been found as significant factors in the intervals studied in this work. However, it is emphasized that these experiments have been performed under controlled conditions (dross removal before addition, periodic stirring, temperature control), which can undoubtedly affect the results in a negative way if not considered.

Study of Mn compacts

Following experimental design techniques similar to those explained above, 24 experiments were performed for studying the influence of the size/weight of the compact (from 100 g to 1250 g), the furnace temperature (from 710°C to 750°C),

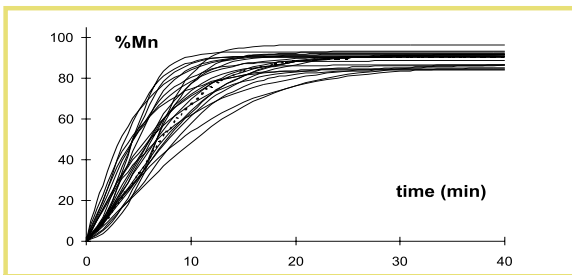


Figure 7 – Recovery curves of Mn.

the final alloying level in the aluminium bath (from 0.25% to 1.25% Mn), and the oxidation level of the manganese powder (from 0.22% to 0.56%) on the dissolution rate and the recovery. Figure 7 shows the dissolution curves obtained.

It is clear that no conclusions can be obtained from a visual inspection of the plot. However, it is observed that differences of up to 50% in the Mn recovery can appear in the first minutes of dissolution. On the contrary, not very significant differences are observed for the final recovery, making it difficult to obtain conclusions. Because of this, a mathematical treatment was performed with the Mn recoveries at 9 minutes (for dissolution rate) and 40 minutes (for final recovery). The results of this treatment can be summarized in the following empirical equations:

$$\text{Rec, 9 min} = -6.5 - 60.6 (\text{all lev}) + 28 (\text{all lev})^2 - 26.4 (\text{Mn ox lev}) + 0.15 * \text{Temp} + \varepsilon \quad (6)$$

$$\text{Rec, 40 min} = 91.88 + 6.40 (\text{all lev}) - 7.60 (\text{all lev})^2 + \varepsilon \quad (7)$$

The main factor ruling the system is the alloying level (which decreases the recovery at higher levels). The oxidation of the manganese powder and the temperature present negative and positive influences, respectively. Figure 8 shows some surface responses for the recovery at 9 minutes.

The empirical equation proposed for the recovery at 9 minutes explains over 80% of the experimental information given by the system, whereas the one proposed for the recovery at 40 minutes explains only 60% of the information, which is not a statistically satisfactory quantity. This is not unusual for final recovery studies, especially when there are small differences between the experiments.

Mn dissolution rate and recovery are highly dependent on casthouse conditions. Higher alloying levels will require longer dissolution times (or more vigorous or frequent stirring practices), and temperature also helps for a faster dissolution. Oxidation, on the other hand, yields lower dissolution velocities. Mn oxidation can arise from many factors coming from the compacted alloying additive production, the addition practice, and the chemical quality of the raw materials. It is important to avoid the presence of very fine manganese particles, since these make the additives weaker and increase

Summary

From the literature and the work presented here, it is possible to summarize the key influences of compacted additives. Three main points are related in the following items:

Raw materials for compacts

- Alloying element powder size. If size is too fine, there will

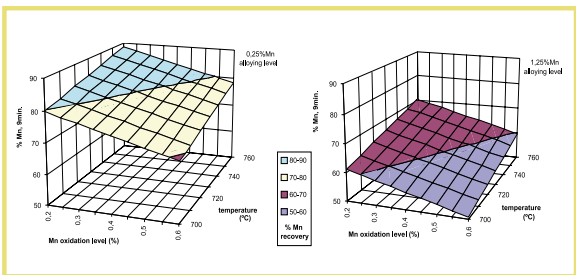


Figure 8 – Recovery of Mn for 9 minutes time at different alloying levels.

the presence of fines (which are more easily retained on the aluminium bath surface). Finer particles present a higher surface contact with the atmosphere and are therefore more oxidized.

Effect of compact size and compaction pressure on Mn dissolution

The usual methodology was followed for the experimental tests with the variables shown in Table 2. Temperature was kept at $710 \pm 5^\circ\text{C}$, with a final 1% Mn alloying level. Figure 9 shows the corresponding recoveries obtained at 5, 10, 15, 20, 30 and 40 minutes for all the experiments. The differences among the experiments are not highly significant except for one case: those compacts of 200 grams produced at 100 bars (the lowest pressures used), which showed a high recovery for the first minutes of the experiment. These differences disappear in the final recovery of the experiments. Such behaviour suggests that a different dissolution mechanism takes place. It is suggested that a breakage occurs for the 200-grams, 100-bars additives when they are added into the aluminium bath due to the poor mechanical strength of the additives.

Table 2 – Mn compacted alloying additives for different weights and pressures

Weight (g)	Pressure (bars)*	Density $\pm \sigma_{n-1}$ (Kg/dm ³)	Height $\pm \sigma_{n-1}$ (mm)
100	100	4.62 \pm 0.05	34.4 \pm 0.1
100	150	4.73 \pm 0.04	32.9 \pm 0.4
100	220	4.81 \pm 0.08	31.4 \pm 0.2
200	100	4.49 \pm 0.08	17.0 \pm 0.4
200	150	4.66 \pm 0.04	17.4 \pm 0.6
200	220	4.89 \pm 0.04	16.7 \pm 0.2

* relative values depending on pressing machine design

The mechanical resistance of compacted alloying additives is usually measured by means of a 1m drop test. Results for this test are shown in Figure 10. The results also depend on raw materials (powder morphology and size of both Mn and binder products used for compaction).

be too much oxidation, leading to poor performance. If size is too coarse, time to reach final recovery may be too high. The size also affects ease of tableting.

Alloying element powder oxidation. Oxidation reduces rate of dissolution and final recovery.

Al powder. Exerts a positive influence, as it is responsible for the initiation of chemical reactions within the compact, leading to compact swelling and disintegration.

Flux. Usually of lower melting temperature than aluminium, and so helps provide a porous structure after addition to the melt, and also positive influence on breakdown of oxides.

Production of compacts

Compaction pressure. If pressure is too low, a sound tablet is not achieved, this can cause problems of tablet break-up in transportation and generation of fines. Even if the tablet survives to the casthouse, it may break up prematurely in the melt, reducing dissolution rate. Some elements tablet more readily (e.g. Fe) than others (e.g. Mn). Percentage element adversely affects ease of producing a sound tablet.

Compact size. The current work and industrial experience suggest that this is not a major influence. This can be explained by the mechanism of tablet swelling and disintegration.

Casthouse practice

Melt temperature. Charging compacted additives to a cold furnace is discouraged as the effective dissolution mechanisms described would not be allowed to occur.

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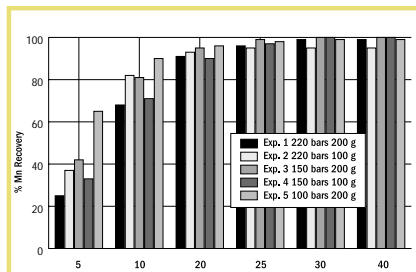


Figure 9— Mn recoveries for experiments considering different production pressures and compacted sites.

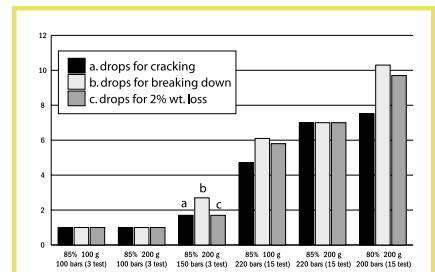


Figure 10 —Mechanical resistance of Mn-compacted alloying additives.

In the range of melt temperatures typically used, temperature has a more significant effect for some elements (in particular Ti, but also Mn) than others (e.g. Fe).

Melt dross. Removal of surface drosses before addition of compacts is essential to high recoveries, otherwise there will be losses, particularly of any fines.

Spread addition. For large additions, spreading them out in the furnace will help avoid local concentrations of element. If these occur, solid masses may be found in the bottom of the furnace, and high-melting-point intermetallics formed.

Melt stirring. Stirring of the melt is essential to rapid recoveries. Stirring encourages dispersion of the aluminides being formed, spreads out the additions and resuspends any dissolving particles.

Effect of alloy. The higher the alloying addition to be made, then the longer the time to be expected for full dissolution.

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For further information please contact:

Canada: +1.888.625.5678

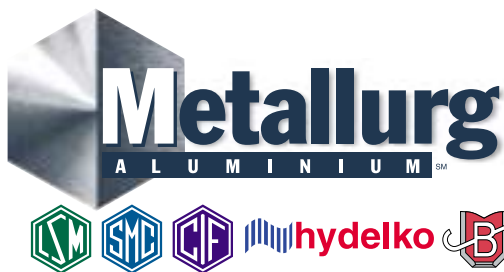
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