

# CHEMICAL TREATMENT OF MOLTEN NON-FERROUS METALS

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## Abstract

The use of different fluxes for the removal of undesirable impurities from various non-ferrous metals and alloys has been stated. Oxidizing conditions for the removal of hydrogen and deoxidation of some alloys by phosphorus, copper, magnesium magnesium-boron, etc., have been described. The fluxes for elimination of lead oxide and the effect of nickel on lead bronzes have been mentioned. Elimination of  $Al_2O_3$  by different fluxing techniques is described. The use of  $MgCl_2$  flux for Al-Mg alloy sand degassing by chlorine through the introduction of hexachloroethane have been outlined. Grain refinement by boron and titanium has been described.

## Introduction

EVERY alloy has its individual characteristics, and for every type of metal there are numerous methods of melting and casting, and the chemical treatment of molten metals can vary accordingly.

Why is it necessary to treat metal with chemicals at all? To remove impurities, to improve castability, to adjust or control alloy composition, to improve physical properties.

New and modern developments in this field have arisen out of old time, long established practices; and fluxing as such is as old probably as the actual casting of molten metal.

Bell founders in the Middle Ages are known to have used potash as a covering and cleansing flux for their copper-tin alloys. Very often a great deal of superstition was attached to the fluxing of metals, and many odd secret formulae existed until quite recently.

This paper sets out to consider some of the new methods of fluxing and refining with some brief explanation of the usefulness of the chemical reactions which are deliberately set up.

*Let us take in the first instance the copper alloys.*

These can be divided into four broad groups:

(a) The high-zinc alloys or brasses for which during melting a reducing atmosphere, or at any rate an inert atmosphere, is considered desirable. Also under this heading can be classed pure copper.

(b) The bronzes or red brasses for which it is now accepted that an oxidizing atmosphere is, during melting, advisable.

(c) Some of the specialities, such as phosphor bronze, high-nickel copper alloys, leaded bronzes, etc.

(d) The high tensile brasses — aluminium bronze, manganese bronze and silicon bronze.

Taken one at a time — first the yellow brasses and pure copper. What do we set out to achieve?

Protection from outside influences, i.e. prevention of losses by oxidation or burning in the atmosphere, prevention of pick up of gases, in the furnace, such as hydrogen. A slag cover will effect this, either wet or dry, whichever is most suitable, dependent upon the type of furnace employed and the type of the charge melted. Remember, in most cases wet flux has the advantage of dousing effectively the finely divided charges, such as swarf, turnings, etc., and is probably more economical and effective in the wide surface area melting units.

Removal of impurities either inherent in the metal charge itself or developed during the melting process, the main undesirables being sulphur, silicon and the oxides of all the metals present. Silicon and sulphur present in the form of silica and sulphides give rise to hot-shortness, hot tearing, leakers, drossy and dirty fractures, and the oxides also tend to impair the fluidity of the metal.

The removal of these impurities can be achieved by using fluxes which have the ability to dissolve or inspissate them. For example, sodium-calcium carbonates combine with silica and copper oxide to form sodium and calcium silicates and give off carbon dioxide. The former pass into the slag and the latter acts as an inert mechanical degassing agent. In addition, borax will combine with almost all metallic oxides to form borates, which also pass into the slag. Sodium carbonate reacts with the metallic sulphides to form complex sodium and sulphur salts, which are also either taken into the slag or released in gaseous form.

Thus, it is clear that a variety of chemical reagents will effectively deal with most of the common impurities and so clean and purify the melt. However, on selecting the proportion in which these chemicals are mixed to form an efficient flux, great care must be taken to control the fusion or melting point of the mixtures as otherwise little or no reaction might be promoted at the normal temperature of the molten metal.

Aluminium is often present in brass as an impurity, and a very undesirable one too. Its presence is most frequently characterized by the appearance of a whitish skin on the casting. Its removal is most effectively carried out by the use of an oxidizing agent combined with a double fluoride, which in turn oxidizes the aluminium and then dissolves or inspissates the aluminium oxide so produced. Here again, the flux mixture is composed to produce either a wet or dry slag by controlling the fusion or melting point.

Now a word as to deoxidation of these in copper-zinc alloys. The higher the zinc

content, the less is the need for deoxidation, as the zinc itself usually acts as a deoxidant. However, with pure or commercially pure copper, it is a somewhat different matter. Calcium introduced in the form of calcium copper will successfully deoxidize commercial copper, while for high conductivity copper it is generally accepted that either lithium or calcium boride is more efficient as a degassing and deoxidizing agent. In either case, it is purely a matter of reducing the copper oxide to the pure copper state and either the calcium or lithium takes up the oxide through a reaction which is both chemical and mechanical. The mechanical action gives a 'scavenging' effect, which helps release entrapped impurities out of the melt into the slag.

When dealing with the recovery or refining of brass from swarf and residues, the important thing is to use a flux based on the same principles as applied to casting processes and with the emphasis on a strongly basic slagging mixture.

Very often brass swarf contains considerable quantities of silica and siliceous material, such as emery dust, etc. The strongly basic flux must act with these impurities to form silicates with them. Obviously, it must have a low melting point and be capable of separating cleanly from the melt so as to provide the maximum yield. Naturally, the furnaces used for refining brass have much wider surface areas than is the case in melting for casting, thus a great deal more flux is needed to provide an efficient cover and to this extent economy is a major factor.

So far we have only dealt with yellow brass and pure copper; *so now a word about the red brasses, tin bronzes or gunmetals, as they are sometimes called.*

The first and main consideration is probably that these alloys are very sensitive to gas and will not only pick up hydrogen during melting, but often already contain hydrogen in the ingot, which has to be eliminated from the outset to ensure a gas-free and a dense-grained casting.

To this end, it is now generally accepted that not only is an oxidizing atmosphere desirable, but that an oxidizing condition should be induced and maintained throughout the melting cycle. Possibly the best method of achieving this is to use a flux based on manganese dioxide, which will have started to decompose ( $700^{\circ}\text{C}.$ ) by the time the metal starts to melt and give off a constant stream of oxygen during the melting period. This oxygen combines with whatever hydrogen is present in the melt to form water vapour and as this will again break down into hydrogen and oxygen in order to maintain the persistent removal of hydrogen, it is obvious that one must always ensure an excess of oxygen. Moreover, this excess of oxygen creates a very effective barrier at the surface of the melt against the pick up of hydrogen from the furnace atmosphere.

During the last seven or eight years, a great deal of research work has been carried out in support of this now widely accepted theory, mainly by British research associations such as the British Non-ferrous Metals Research Association, and numerous publications have been issued on the subject of oxidizing melting, notably by Baker and Child. Similar work has also been done by Pell-Walpole at the Tin Research Institute and previously by Dr. Henri Lepp of France.

The bubbling through of the oxygen has also a mechanical scavenging effect which is very advantageous. Of course, the residue from the breakdown of the  $\text{MnO}_2$  is taken off into the slag and it is interesting to note that it forms a slag with calcium carbonate and silica which in itself is still oxidizing. For example, manganese silicate will oxidize hydrogen without any difficulty. These slagging compounds will also determine the melting point of the slag and will vary according to the alloy composition. The removal of aluminium from these bronzes is just as important as mentioned earlier in the case of brasses and can be effected by the same means.

Deoxidation of the red brasses or bronzes is usually much more important than is the

case with yellow brass, owing to the lower zinc content, especially when, as described, the melting has been carried out under an oxidizing atmosphere. Phosphor copper is generally used for this purpose either in the form of shot or compressed powder, in which the phosphorus reduces the metallic oxides and creates the well-known and easily recognized increased fluidity of the metal on pouring. Sometimes, a little zinc powder is added with the phosphorus to act as a compensation against melting loss. Care must always be taken not to overdo the phosphorus which, if used in any greater quantity than about 0.25 per cent, as a residue may harm the physical properties of the cast alloy, will bring in the possibility of metal mould reaction.

Sometimes it is found that these metals, in spite of all the melting precautions taken, will still show gas porosity, especially where there is a wide variation in casting section and as this sort of porosity is generally associated with a coarse interdendritic structure of grain, it generally only shows up after machining. If the section is very heavy, the outer skin of close grain may be thick enough to take machining without disclosing the pin-hole porosity, but if it is there, it will certainly develop into a leaker sooner or later. For pressure-tight castings, therefore, it is advisable to degas the melt in the ladle just before deoxidation, and here again a manganese dioxide-based degasser is usually very effective. The plunging action creates a very effective and beneficial scavenging effect, so as to clean up and degas the melt at one and the same time.

*Although phosphor bronze* is not very widely used in India for casting, it is often employed in England for bearings, and needs quite different treatment from most of the other bronzes. Obviously, the presence of phosphorus precludes the use of an oxidizing flux and by the same token the alloy is itself deoxidizing.

The main considerations are to remove suspended impurities without chemically

affecting the alloy constituents and to provide a slag cover to prevent excess oxidation of the melt from the furnace atmosphere. The first part is carried out purely mechanically by a neutral gas (carbon dioxide produced from calcium carbonate) and the second by additions of neutral fluorides which promote the fluid slag cover.

The high-nickel copper alloys also deserve special mention especially in relation to their super-sensitivity to hydrogen gas and the need to take extreme precautions against the unfortunate gas condition so often encountered in this type of casting. A strongly oxidizing flux must be used during the melt to achieve the elimination of hydrogen as described for the tin bronzes. Degassing in the ladle with a powerful oxidizing regenerator on the basis of manganese dioxide, as earlier mentioned, is also sometimes desirable in order to remove the last traces of hydrogen, but this ladle treatment has to be carefully handled to avoid a serious loss in temperature.

Deoxidation of nickel-copper alloys is usually best carried out with magnesium or a combination of magnesium-boron and manganese. Pure magnesium successfully reduces the metallic oxides, and the alloying properties of a balanced mixture of both boron and manganese will have the effect of coalescing the melt, closing the grain and squeezing out as it were into the slag a variety of suspended impurities, which often persist in this type of alloy.

Lead bronzes also deserve special mention because the main consideration in the melting technique is the elimination of lead oxide.

Borax and phosphates will both dissolve and carry off the lead oxides into the slag. Calcium carbonate decomposes in the melt and evolves carbon dioxide which acts as a scavenger. Actually, of course, when metal oxides come into contact with fused phosphate, they are dissolved and form the corresponding metal phosphates. Thus, not only lead bronzes, but similarly the chrome bronzes can be treated in the same way.

As before, fluorides in the flux aid slagging properties.

Lead, which is not soluble in copper alloys, tends to segregate and 'lakes' must be avoided. Distribution of lead should be wide and although the simple flux medium already described cannot rightly claim to have a direct influence on proper lead distribution, it is true to say that the cleaner the alloy, the less tendency there will be for lead to segregate. Sulphur and nickel have been mentioned in various literature as having the direct effect of facilitating fine distribution of lead.

Finally, on the copper alloys, *we have the manganese bronze, aluminium bronze and silicon bronze* — these sometimes being referred to as high tensile brasses. The melting technique for these alloys embodies one major consideration above all others, namely the prevention and elimination of the oxide of aluminium in the case of the first two, and oxide of silicon in the case of the third.

Aluminium oxide cannot be eliminated by normal deoxidizing processes because it does not react with any of the more commonly used deoxidants. Therefore, it must be dissolved and carried into the slag. The amount of aluminium oxide present in these alloys is never very great, but as little as 0.2 per cent can make the metal so sluggish that it will not pour. An efficient flux for these alloys must, therefore, contain carefully balanced fluorides which will absorb or dissolve these oxides and protect the metal with a slag which must form at a temperature lower than that of the melting point of the alloy. Liquid fluoride-bearing fluxes are usually more efficient because they form a more effective cover, but powder drosses in small melts are quite successful.

These fluorides actually take the metallic oxides into solution in the slag and their preventive action reduces the crucible build-up and dross formation which is often a serious handicap in this type of alloy.

For example, and in addition, sodium fluoride combines with aluminium oxide to

form aluminium fluoride and sodium aluminium fluoride (cryolite) can actually dissolve up to 20 per cent of its own weight of aluminium oxide. The same fluorides react with silica to form silica fluoride, which is a gas. A mixture of these fluorides is, therefore, generally quite sufficient to ensure a good casting, but in some cases, especially where it is difficult to ensure a quiet and non-turbulent flow into the mould cavity, it is a good idea to treat the melt just before pouring to a dose of boron and manganese so as to achieve the coalescing effect of squeezing out impurities and suspended dross.

For instance, it is generally realized that these alloys will form dross very easily during a pour, and inside the mould cavity, and it is very desirable, therefore, to ensure that the metal introduced into the mould is, from the outset, as clean and dross-free as it is physically possible to make it. This coalescing action has its counterpart in the old-fashioned method of hammering wrought iron to remove slag.

This is all for now on the subject of copper alloys, and as detailed consideration of any one of these ideas could take several hours, the foregoing is merely intended as a bare outline of first principles. It will, however, show how highly specialized the subject of fluxing and purifying can be and what a very essential part it plays in the successful casting of the non-ferrous alloys.

*Now on the subject of the aluminium alloys.*

For simplicity we will divide these up into various headings thus:

- (a) The commonplace everyday alloys such as D.T.D. 424.
- (b) The high-silicon aluminium alloys containing up to 13 per cent silicon such as L. 33.
- (c) Alloys having a magnesium content of from 3 to 10 per cent, including those sometimes referred to as the wrought alloys.

Then for the purpose of differentiation of treatment, we should subdivide these again under the headings of: (i) sand casting; (ii) die casting; (iii) permanent mould casting;

and also (iv) billet or slab production for forging and finally the refining and recovery processes for secondary ingot production.

What are the main considerations in the need to treat molten aluminium whatever the alloy?

There are two main bogies, the first is aluminium oxide and the second is hydrogen gas, and either separately, or in combination, they are a very serious handicap, whatever the casting methods. Aluminium oxide forms a fine film at the grain boundaries, which impairs physical properties. It also tends to settle in fine feeding channels, thus preventing sufficient feed metal from reaching the casting.

In sand casting or die casting aluminium alloys it is necessary to use a flux which will fuse at a lower melting point than that of the alloy, so as to set up a chemical reaction in which whatever aluminium oxide as may be present in the melt is eliminated, either chemically by decomposition or physically by absorption into the slag. For this purpose we generally employ a combination of fluorides, in combination with sodium and potassium salts.

The fluorides reduce the oxides of aluminium very effectively and the salts provide a cleansing and protective cover into which the processes of reduction are dissolved.

In sand casting and die casting with comparatively small melts, it is usually more practical to use a flux mixture on this basis which will form a dry dross. This is to simplify skimming, and in these days, when metal is so scarce and expensive, it is sound economics to produce a metal-free dross, to avoid skimmings wastage.

This can be achieved by incorporating in the flux mixture some silico-fluorides which in contact with the surface heat of the metal will break down producing exothermic heat. This in turn prevents the metal globules in the dross from solidifying and, in their renewed molten state, they run back into the main melt and a metal-free powdery dross results. This reaction is of considerable

significance in the remelting of skimmings and scrap and residues in refineries and can provide an effective short-cut to good, clean, secondary ingot without tedious repetitive ball-milling, etc.

In making up flux mixtures for the aluminium alloys, we have to very carefully consider the question of melting points, because the most efficient chemicals from the cleansing aspect are often the high melting point constituents. Consequently, we add salts of various descriptions in varying quantities so as to depress the fusion point of the flux, dependent upon the melting point of the alloy.

Thus, it stands to reason that the efficient treatment of aluminium alloys demands a fairly wide variation of fluxing techniques. In refineries where sometimes very dirty scrap is melted and where loss from oxidation by burning is a very serious consideration, a heavy liquid layer of flux is essential in order to douse the charge before it has a chance to ignite. This liquid flux must, however, be of such a composition that it does not thicken up as impurities are absorbed, which is the case with ordinary salts, and that is why we consider the addition of certain combined fluorides to be essential. Sometimes a proportion of calcium chloride is incorporated, but as this chemical is hygroscopic, it is not generally used in ordinary foundry practice where the risk of the introduction of gas may be serious.

This, then, covers the general fluxing procedure for the normal and more widely used aluminium alloys, but in the case of the *high-silicon aluminium alloys*, although we can use the same general methods of cleansing and protection, we also have to consider the so-called modification of these specific alloys. Sodium is generally accepted as the means of achieving modification, but there are definite and obvious hazards in its application. We, therefore, prescribe the easier and safer method of introducing sodium by the means of sodium salts which are included in the flux mixture. For example, sodium fluoride com-

bines with aluminium to form sodium and aluminium fluoride (a vapour). It is worth mentioning that as iron and manganese are usually present in these aluminium-silicon alloys, the actual quantity of these ingredients has a profound effect upon modification and we have found that a combination of iron and manganese in excess of about 1 per cent will actually prevent modification altogether.

*And now a word about aluminium magnesium alloys.*

A great deal of research has now been carried out in the technique of fluxing the aluminium magnesium alloys and while we are about it, we may as well try and cover the latest developments in this, and also the magnesium-base alloys themselves.

In the fluxing treatment of aluminium alloys with 2 per cent or more of magnesium, it is essential to use a proportion of anhydrous magnesium chloride, the quantity being dependent upon the magnesium content of the alloy. This has the effect of reducing the magnesium oxide which is formed in preference to aluminium oxide. The reaction produces magnesium oxychloride which is absorbed into the slag. Magnesium chloride is, however, hygroscopic and we prefer the magnesium chloride-base flux to be pre-fused where possible. This pre-fusing ensures the flux melting immediately, it is placed on the surface of the metal and, incidentally, reduces the risk of water absorption during storage and usage.

Whether magnesium chloride forms magnesium oxychloride by reacting with magnesium oxide or whether magnesium chloride actually holds magnesium oxide in a sort of non-reactive suspension is not altogether certain, but the cleansing results are, at least, quite conclusive.

A great variety of additional ingredients, besides magnesium chloride, are to be found in these fluxes according to the alloy to be treated, to the type of metal melted (scrap or virgin) and to the specific gravity desired

for the spent flux. According to the choice of these additions, melting points between 400° and 750°C. can be achieved. Cheap compounds of alkali chlorides are the most common. For example, a mixture of one-third of each of sodium, potassium and magnesium chloride will melt slightly above 400°C. and is, therefore, most successful for melting dirty magnesium swarf.

Addition of calcium chloride produces flux of very low viscosity where needed. Fluorides are added when the slag is required to be of a more viscous nature, and by choosing the right proportion of chlorides and fluorides any degree of viscosity can be achieved, and the tendency for the flux in cover to sink into the melt can thus be controlled. Although these fluxes are employed for both magnesium-base alloys and aluminium alloys containing magnesium (so as to prevent the formation of magnesium oxide, which gives rise to discolouration and porosity), there are certain alloys, especially D.T.D. 300 (90 per cent aluminium, 10 per cent magnesium), which need to have all sodium salts eliminated.

This is due to the fact that it has been found that small quantities of sodium in this alloy can cause excessive brittleness, especially after heat treatment. These principles, when applied to the wrought alloys, need to be taken a stage further, owing to the need for the very great care which has to be exercised in the prevention of such things as blisters, cracks and adhering, which show up in rolled and drawn sheet or extrusion.

It is now fairly firmly established that these typical and unwelcome conditions are caused by either or both a combination of gas and oxide. Thus, the fluxing technique applied has to be very assiduously followed. Simple rabbling is not usually enough to ensure the removal of the last trace of oxide and a complete 'washing' effect has to be practised, so as to promote the most intimate mixing possible between flux and metal and combined with a very complete degassing action.

Before leaving the question of fluxing these light alloys, we ought to consider the occasion where magnesium is present in the form of an impurity in an aluminium alloy and how it is best removed.

As magnesium even as an impurity is the most reactive element in the alloy, it can be attacked either by oxidizing or by treatment with reactive gases. The latter is preferred because metal losses are less than in the case of oxidizing treatment. Chlorine, hydrochloric acid gas, silico-fluoride gas and boro-fluoride gas, all have a tendency to combine with magnesium in the molten form in preference to the other metals, and compounds are formed with the magnesium which are taken up into the slag. These reactions require high temperatures so that magnesium removal is carried out above 800°C. In the treatment of gaseous chlorine, for example, the chlorine reacts with the magnesium to form magnesium chloride. It also reacts to some extent with aluminium forming aluminium chloride which, however, is volatile and escapes into the atmosphere, while magnesium chloride, which is molten above 700°C., is removed into the slag.

Another type of treatment suggests itself whereby the magnesium is replaced by other elements such as aluminium. If, for example, aluminium fluoride is brought into contact with metallic magnesium, magnesium fluoride and metallic aluminium are formed.

We should now turn to the functions of degassing and grain-refining the light alloys. Nowadays, the degassing of aluminium is considered an essential part of the melting process for almost every method of successful casting. Chlorine, because of its affinity for hydrogen, is accepted as being the most efficient degassing agent and is often bubbled through the molten aluminium from cylinders for quite lengthy periods dependent, of course, upon the size of the melt and the type of alloy. Naturally the combination of chlorine and hydrogen produces hydrochloric acid, which escapes into the atmosphere in vapour form. Owing to the toxicity

and hazards of using pure chlorine gas, to say nothing of the complications of plant involved, dry nitrogen is sometimes employed as an alternative, but never, I believe, so successfully. The latest development in degassing aluminium is quite an ingenious discovery, by which chlorine is produced in its nascent and, therefore, more reactive form through the decomposition of hexachloroethane.

This hexachloroethane introduced into the melt in a completely harmless and very easily handled tablet form is plunged to the bottom of the melt where a very interesting chemical breakdown takes place.

It is decomposed by the heat of the metal, but only partially. The extent of decomposition depends upon the temperature of the metal and its composition. Part of the hexachloroethane passes through the melt undecomposed and simply as hexachloroethane vapour, part is decomposed into carbon, carbon tetrachloride ( $\text{CCl}_4$ ) and tetrachloroethylene ( $\text{CCl}_2$ ) which either pass through the melt in gaseous form or are further decomposed into carbon and chlorine. It is not easy to determine exactly how far decomposition does take place, but with D.T.D. 424 at about  $740^\circ\text{C}$ . ( $1364^\circ\text{F}$ .), approximately 40-50 per cent of the available chlorine in hexachloroethane (which contains approximately 94 per cent of chlorine) is present as chlorine gas. The important thing is, of course, that apart from the actual and obvious advantages derived from the production of pure chlorine gas, all the other products of the reaction create additional mechanical degassing effects and produce further combinations for the removal of the undesirable hydrogen present with any other impurity.

Simply as a theory and without any very definite supporting proof, I believe that sometimes the most troublesome traces of hydrogen in aluminium alloys are only present in an inert or atomic form, which is very difficult to remove. However, the nascent atomic chlorine produced as des-

cribed, which is released through the decomposition of hexachloroethane, should have a much closer affinity for the hydrogen in this condition, but whatever the established superior efficiency of hexachloroethane, it is quite obviously very acceptable as an alternative to straight chlorination by virtue of its complete safety and ease of handling.

Having degassed the aluminium alloy, it is sometimes found necessary to refine the grain structure. This is particularly applicable to aluminium which has been degassed with chlorine from a cylinder which apparently has the effect of coarsening the grain of the as-cast metal. On the other hand, it is found that when using hexachloroethane as previously described, no such coarsening of the grain takes place. The coarse grain of cast aluminium is generally and most commonly typified by a large columnar structure, particularly at the outside edges of the casting and can, of course, adversely affect the physical properties.

It is also believed that this coarse-grained structure can seriously impair the results of rolling and drawing aluminium alloy. The refinement of this coarse grain is, therefore, an extremely vital and interesting study.

Several theories and ideas have been tried out and small quantities of either boron or titanium have been found to be effective. The latest development, however, which shows remarkable success is by the use of a combination of both boron and titanium. I think the reason for this is as follows:

The introduction of either or both these elements is designed to create a series of additional centres of nucleation, around which the grains of the solidifying metal will grow and build up. Obviously, the more centres of nucleation there are, the finer the eventual grain will be, but it is not quite so easy as that, because there comes a stage when either the boron or titanium complex separates out and segregates, forming carbides and other compounds, which then become harmful impurities.



It takes very little of either element to reach this so-called saturation point. However, a carefully balanced mixture of both boron and titanium seems to have the effect of forming, after the saturation point has been reached, a titanium boride compound which in itself provides additional centre of nucleation without any improper separation. The result is in practice a beautifully close-grained, clean and evenly distributed structure.

For many general purpose applications, a new and very useful tablet has been evolved which contains partly hexachloroethane to achieve the degassing effect through the emanation of chlorine, plus the salts of a balanced mixture of boron and titanium, thus, while the degassing action is being carried out, the grain-refining action is taking place simultaneously.

Most of the work on the theory of grain refining aluminium alloys has been carried out by the British Non-ferrous Metals Research Association who developed the theory that whereas titanium by itself had the effect of producing a fine grain around the formation of a titanium carbide, a mixture of both titanium and boron provided the function already described through the formation of titanium boride and it now seems fairly certain that the latter is the most effective.

When it comes to the degassing and grain refining of the magnesium-base alloys, we come to a happy combination of facts, for not only does hexachloroethane successfully degas the magnesium alloys by the emanation of chlorine in the same way as with the aluminium alloys, but the nascent carbon, which is also produced during the decomposition cycle, has the fortunate effect of acting as a grain refiner of considerable effectiveness. In this case, therefore, it is the carbon itself which forms the additional centres of nucleation around which the grain is more closely built up.

It is, of course, possible to refine the grain of magnesium by the introduction of lamp black into the melt, but it seems obvious

that the carbon particle size, which is very much bigger than that produced from the decomposition of hexachloroethane, cannot achieve nearly so fine a distribution.

### Discussions

**MR. M. C. DUBE ( Aluminium Corpn. of India Ltd., Jaykaynagar )**

Would the author please give further information on the part played by nitrogen in degassing aluminium and its alloys ?

*Author's Reply*

Nitrogen being an inert gas, its action is purely mechanical, whereas chlorine, whether introduced in a gaseous form or produced in its nascent state through the disintegration of carbon hexachloride, acts both chemically and mechanically by forming hydrochloric acid.

**MR. PARVEZ MEHTA ( Tata Iron & Steel Co. Ltd., Jamshedpur )**

I would like to know the most desirable flux that can be used in the melting of chromium bronzes.

*Author's Reply*

Chromium bronze is not a common alloy and I have not had much experience of it. I should imagine the necessary chemical treatment would be to have a reducing atmosphere during melting, and the flux should have strong oxide absorption properties. Bearing this in mind, I would suggest trials with crushed dolomitic limestone with about 10 per cent cryolite.

**MR. A. T. PAL ( Metallurgist, Annapurna Metal Works )**

We made two melts by gunmetal (85.5.5.5) — one with a proprietary flux and another without any flux at all; from the latter we made a few test pieces with 'shell moulding' and from the former a few pieces with 'green sand moulding'. Mechanical and hydraulic tests were carried out in both the cases and were found not to differ at all excepting that in case of melt without any flux, metal loss was about 0.50-0.75 per cent higher. So we find that the fluxes can only prevent metal loss to some extent and were found not to have any effect on degassing, cleaning and refining operations. Of course, in green sand moulding fluxes have shown very good results. Would the author offer some clarifications on this matter ?

*Author's Reply*

A mixture of  $MnO_2$  and sodium fluoride will probably give much superior results.