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54 **Magnesium-calcium alloys for debismuthizing lead.**

57 A novel alloy for use in lead refining is disclosed which comprises magnesium and calcium. The preferred ratio on a weight basis of magnesium to calcium is between 1.2 and 5.2. A method of adding this alloy to a lead bath is described which brings calcium into solution with the lead and provides a high recovery ratio.

Description

MAGNESIUM-CALCIUM ALLOYS FOR DEBISMUTHIZING LEAD

The present invention relates to calcium-magnesium alloys for use in the removal of bismuth from lead by the Kroll-Betterton process, or for similar lead refining processes which require alkaline-earth metals.

In the Kroll-Betterton process, alkaline earth metals are added to the lead melt in order to react with the bismuth therein. One or more alkaline earth metals, usually magnesium and calcium, are added in either a continuous or batch fashion to the unrefined lead. The preferred temperature range for making the addition is between 380°C to 500°C. Below this temperature range, the reaction is sluggish while above the range excessive oxidation of reactive alkaline earth metals, particularly calcium, occurs. Oxidation gives rise to bright flaring, excessive fume generation and an overall loss of reagent leading to lower reagent recoveries, excessive processing costs, unpredictable final bismuth levels and environmental concerns. Furthermore, the addition of calcium metal to the lead bath is often accompanied by an increase in the bulk temperature of the lead either due to an exothermic release of heat during the reaction and/or the heat generated by the oxidation of calcium metal. This increase in bath temperature may result in additional calcium oxidation as well as lengthening the overall processing time since the melt must be cooled to just above its solidification point prior to removing the bismuth rich dross.

Another disadvantage of calcium metal is that it is highly reactive with atmospheric oxygen and humidity. Hence, calcium metal must be packaged, shipped and stored in such a way as to eliminate contact with air and moisture. Excessive contact with water will result in heat and hydrogen evolution which can cause fire and explosion. Mild contamination of the calcium prior to the lead treatment will result in lower than expected reagent recoveries and unpredictable final bismuth levels.

After the lead has been treated with the alkaline metals, the melt is then cooled to a temperature near its solidification point which causes the alkaline-earth bismuth compounds to float up as a solid dross which may be skimmed from the surface of the melt.

Most commercial debismuthizing processes utilize a heterogeneous mixture of magnesium and calcium metals. In the present invention, debismuthizing is carried out with an alloy comprising of essentially magnesium and calcium with the ratio of magnesium to calcium on a weight basis being between 1.2 and 5.2 and in the preferred embodiment of the invention, between 1.9 and 3.0.

The concept of substituting alloys for metallic magnesium and calcium was initially suggested by Betterton in 1930, U.S. Patent No. 1,853,540, who tested alloys comprising of magnesium and lead and calcium, magnesium and lead. T.R.A. Davey "The Physical Chemistry of Lead Refining", Lead-Zinc-Tin 1980, edited by J.M. Cigan et al., Metallurgical Society of AIME, p. 477, mentions the use of a 50% calcium-lead alloy while Kirch and Othmer "Lead", Encyclopedia of Chemical Technology, Vo. 8, The Interscience Encyclopedia Inc., New York, 1952, refer to a 30% calcium-lead alloy. In all of these cases, lead is the principal alloying constituent and is present to lower the melting point of the reagent thus promoting dissolution of magnesium, and in particular calcium, both of which have melting points substantially higher than the lead bath temperature.

In U.S. Patent No. 2,129,445, Rehns mentions that lead can be debismuthized by floating a calcium-magnesium alloy on the surface of a mechanically stirred lead bath. The alloy contained 79.40% magnesium and 20.60% calcium by weight. Rehns specifically points out that when using a calcium-magnesium alloy of the cited composition, it is necessary that the lead bath be raised to a higher temperature, namely 593°C.

Reference to a binary magnesium-calcium phase diagram (Figure 1) shows that the addition of calcium to magnesium will initially lower the melting point of the alloy compared to metallic magnesium. However, once the alloy exceeds 16.20% calcium (i.e. a Mg to Ca ratio of 5.17), its melting point begins to rise due to an increasing concentration in the eutectic of the highly stable intermetallic compound, Mg₂Ca. This stable compound has a melting point of 715°C which is about 200 - 300°C above commercial debismuthizing temperatures.

The same phase diagram, also shows that the 79.40% magnesium, 20.60% calcium alloy suggested by Rehns begins to melt at 516.5°C and is fully molten by about 575°C. By specifying a lead bath temperature of 593°C, Rehns ensures that this alloy will be fully molten and hence its dissolution and the resulting reagent recovery will not be impeded by the presence of any unmelted, highly stable Mg₂Ca intermetallic compound.

Kroll-Betterton type debismuthizing processes usually operate in the 380°C to 500°C range. Rehns specified temperature, 593°C, is thus substantially higher than reported commercial debismuthizing practices.

In the present invention, magnesium-calcium alloys with magnesium to calcium ratios on a weight basis between 1.2 and 5.2, and preferably between 1.9 and 3.0, are added to lead in the commercial temperature range, that is between 380°C to 500°C. As indicated by the relevant phase diagram, all of these alloys have melting points in excess of 516.5°C and, in the range of the preferred embodiment, the alloys do not fully melt until temperatures exceed between 610°C to 685°C which is substantially above the temperature of the lead bath. Contrary to the teachings of the Rehns patent, which ensures that the alloy is completely melted by specifying a higher process temperature of 593°C, in the present invention the alloys do not completely melt and hence the reaction must proceed by dissolving (not melting) a solid into liquid lead. According to the eutectic composition of these alloys, this solid phase is essentially the stable, high melting point Mg₂Ca intermetallic compound. Hence, the present invention differs from that of Rehns since the mechanism of

introducing the reagent into the lead is considerably different, that is melting the reagent alloy in the Rehns patent and solid-liquid dissolution in the current invention. In the former case, the rate of reaction depends only on how fast the alloy melts which in turn depends on the rate of heat transfer from the bath to the reagent. Once melted, any Mg_2Ca compound present in the alloy is completely dissociated and hence available for debismuthizing.

In the present invention, the rate at which the solid Mg_2Ca phase in the alloys eutectic dissolves into the liquid lead depends on thermodynamic and kinetic considerations which are related to the chemical stability of Mg_2Ca relative to magnesium-calcium-bismuth compounds which form during debismuthizing. The rate of dissolution and hence the degree of dissociation of Mg_2Ca in the alloy has significant commercial significance as it will determine processing time and reagent recoveries.

French Patent Application No. 81 19673 assigned to Extramet (Publication No. 25614 786, April 22, 1983) discloses a process for debismuthizing lead by using a mixture of two types of alloy granules. The first type of granule comprises a calcium-magnesium alloy near the calcium-rich eutectic point (approximately 82 weight % calcium) and the second alloy comprises a magnesium-calcium alloy near the magnesium-rich eutectic point (approximately 16.2 weight % calcium). These two types of granules are mixed together in the appropriate amounts to give the ratio of the metals for the best result and are injected into the lead melt to react with the bismuth therein. The composition of the individual alloys are chosen to be near the eutectic points so that they have relatively lower melting points compared to pure magnesium and calcium metals. It is claimed that this speeds up the rate of the reaction at a given processing temperature. The mixture is injected into the lead bath with an inert gas. The temperature of the lead bath is maintained high enough to melt and not simply dissolve the lead granules.

This heterogeneous mixture of magnesium-rich calcium-rich alloy granules is still susceptible to poor reagent recovery because the calcium-rich alloy granules will behave in much the same way as pure calcium metal. Because of the composition of calcium-rich eutectic alloy granules, the eutectic may contain up to almost 2/3 of finely divided calcium metal with the remainder being the Mg_2Ca intermetallic compound. The high proportion of calcium metal in the eutectic causes the calcium-rich alloy granules to react with atmospheric oxygen and humidity in much the same way as calcium metal. Tests with ingots cast at the calcium-rich eutectic composition have shown that this alloy reacts with atmospheric oxygen and humidity and, hence, is not stable in air.

Because of the reactive nature of the calcium-rich granules, the heterogeneous granule mixture of magnesium-rich granules and calcium-rich granules must be packaged under dry, inert gas in a similar fashion to calcium metal. Contamination of the calcium-rich granules with oxygen or moisture prior to treatment will result in lower reagent recoveries and unpredictable final bismuth levels. The calcium-rich granules are also susceptible to oxidation during treatment with the lead in much the same way as calcium metal, especially if they float to the surface before they have completely reacted due to large differences in density between lead and calcium. The injection of the granules into the lead bath with an inert gas carrier adds additional turbulence to the melt, increasing the amount of oxidation and emissions from the lead bath.

In the present invention, the difficulties associated with the use of calcium metal or granular mixtures containing calcium-rich alloy granules are avoided by using a single magnesium-calcium alloy of the desired composition. In this invention, the alloy is primarily made up of magnesium and calcium but may contain one or more minor amounts of other alloying elements.

The present invention will now be described in more detail in conjunction with the accompanying drawings, in which:

Figure 1 is the known binary magnesium-calcium phase diagram;

Figure 2 is a graph showing the effect of the Mg/Ca ratio on the quantity of alloy required to reduce the bismuth concentration to prescribed amounts;

Figure 3 is a graph showing the effect of the same ratio on incremental cost;

Figure 4 is a graph showing the effect of the same ratio on the melting temperature of the alloy; and

Figure 5 is a graph showing the effect of the same ratio on the percentage of Mg_2Ca intermetallic compound contained in the alloy.

In the present invention, an alloy for use in lead refining is provided which is rich in magnesium and has magnesium to calcium ratios on a weight basis between 1.2 and 5.2; the lower ratio corresponding to the intermetallic compound Mg_2Ca . In a preferred embodiment of the invention, the alloy has a magnesium to calcium ratio between about 1.9 to 3.0.

Figure 1 illustrates the binary magnesium-calcium phase diagram and shows that the addition of calcium to magnesium will initially lower the melting point of the alloy compared to metallic magnesium. However, once the alloy exceeds 16.2% calcium (i.e. a Mg to Ca ratio of 5.17), its melting point begins to rise due to an increasing concentration in the eutectic of the highly stable intermetallic compound, Mg_2Ca . This stable compound has a melting point of 715°C which is between about 200 - 300°C above commercial debismuthizing temperatures.

In Kroll-Betterton processes, magnesium and calcium are first dissolved in liquid lead at temperatures usually between 415°C to 500°C. Subsequent cooling of the lead precipitates a solid compound, $CaMg_2Bi_2$, which is separated out in the dross. The lead is eventually cooled to just above its liquidus temperature; however, some calcium, magnesium and bismuth will still be retained in solution in the lead.

T.R.A. Davey in "The Physical Chemistry of Lead Refining" published in 1980 by The Metallurgical Society of

the AIME indicates that at a specific final bismuth concentration, the amount of calcium and magnesium retained in solution in the lead at the liquidus temperature is given by equation (1):

$$\log (\% \text{Ca}) + 2 \log (\% \text{Mg}) + 2 \log (\% \text{Bi}) = -7.37 \quad (1)$$

The inventors have calculated the theoretical alloy requirements to chemically remove bismuth, based on the stoichiometry of the bismuth containing intermetallic, CaMg_2Bi_2 , and the solubility relationship given in equation (1).

Figure 2 illustrates the effects of alloy composition on the quantity of alloy needed to remove bismuth to 0.005% and 0.020% which represents the range of final bismuths in most commercial treatments.

As indicated in Figure 2, for both final bismuth levels, the amount of alloy required increases exponentially as the calcium content of the alloy decreases below 35% (a Mg to Ca weight ratio of about 1.9). Conversely, a higher calcium content (i.e. 40% Ca) does not significantly reduce the quantity of alloy needed to remove bismuth. Hence, based on this analysis, an alloy with a Mg to Ca weight ratio of about 1.9 is chemically optimum for removing bismuth from lead.

From a commercial standpoint, however, calcium is between 1.5 to 2.0 times more costly than magnesium. Hence, the most cost effective commercial alloy will depend both on the chemical requirements to remove bismuth and the proportion of costly calcium relative to less expensive magnesium in the alloy.

Figure 3 illustrates the effects of alloy composition on the percentage change in the lead refiners' cost relative to an alloy containing 60% calcium. These data are based on the amount of alloy required to chemically remove bismuth and the cost of the magnesium and calcium components in the alloy. It can be seen that, depending on the final bismuth level, the lead refiners' costs are lowest for alloys containing between 25% to 35% calcium (a Mg to Ca weight ratio between 3.0 to 1.9).

Hence, based on both chemical and cost considerations, alloys containing between 35% to 25% calcium (i.e. Mg to Ca weight ratios between 1.9 to 3.0) are optimum.

In addition to minimizing the alloy requirements needed to chemically remove bismuth, the dissolving rate of the alloy at conventional debismuthizing temperatures has significant commercial implications since it will determine the amount of alloy that can be recovered during the allotted processing time.

As indicated in Figure 4 (which was derived from the phase diagram, Figure 1), all of the alloys in the present invention have final melting points in excess of the eutectic temperature, 516.5°C, and do not fully melt until temperatures exceed between 610°C to 685°C which is substantially above the temperature of the lead bath.

As a result, in the present invention the alloys do not completely melt and hence the reaction proceeds by dissolving (not melting) a solid into liquid lead. According to the eutectic composition of these alloys, this solid phase is essentially the stable, high melting point Mg_2Ca intermetallic compound.

In the present invention, the time required for the alloys to react depends on the dissolving rate of the stable, high melting point of Mg_2Ca which in turn depends on thermodynamic and kinetic considerations related to the stability of Mg_2Ca relative to the CaMg_2Bi_2 dross.

Table I summarizes the results of laboratory tests to determine the effects of composition, temperature and agitation on the dissolving rate of these alloys:

Table I

Results of Laboratory tests to Examine the Effects of Alloy Composition, Temperature and Agitation on the Dissolving Rate of Mg-Ca Alloys in Liquid Lead

| Alloy | | | Temperature °C | Agitation | Dissolving Rate gm/cm ² /hr |
|-------|------|-------|-------------------|-----------|---|
| % Mg | % Ca | Mg/Ca | | | |
| 85 | 15 | 5.6 | 425 | No | 3.5 |
| 70 | 30 | 2.3 | 425 | No | 1.0 |
| 70 | 30 | 2.3 | 500 | No | 4.0 |
| 70 | 30 | 2.3 | 425 | Yes | 3.5 |

These tests indicate that at 425°C, an alloy containing 15% calcium (i.e. a Mg to Ca weight ratio of about 5.6) dissolves about 3.5 times faster than an alloy containing 30% calcium (i.e. a Mg to Ca ratio of 2.3).

As indicated in Figure 4, the 15% calcium alloy is fully molten at 530°C which is 120°C below the melting point for the 30% calcium alloy.

As shown in Figure 5, this lower melting point and hence faster dissolving time can be attributed to the fact that the 15% calcium alloy contains only 33% of the high melting point Mg_2Ca intermetallic in its eutectic compared to 66% Mg_2Ca for the 30% calcium alloy.

The alloy's dissolving rate is also dependent on the temperature of the lead bath. The results shown in Table I indicate that the dissolving rate of a 30% calcium alloy (a Mg to Ca weight ratio of 2.3) increases by about 4 times when the lead temperature is increased from 415°C to 500°C which covers the range of processing temperatures for most commercial debismuthizing operations. Agitating the lead will also increase the alloy's

dissolving rate.

To summarize, magnesium rich-calcium alloys with Mg to Ca weight ratios between 1.9 to 3.0 are superior to other alloy compositions since they combine the optimum chemical reactivity and dissolving characteristics.

Alloys containing about 35% calcium (i.e. a Mg to Ca weight ratio of 1.9) are the most chemically effective since they minimize the amount of alloy needed to remove bismuth from lead. However, the slow dissolving rate of this alloy limits its use commercially to practices which operate at high temperatures (about 500°C) with aggressive agitation.

Conversely, for debismuthizing practices operating at lower temperatures and/or with less agitation, alloys containing as low as 25% calcium (i.e. a Mg to Ca weight ratio of 3.0) are more commercially attractive since they offer significantly faster dissolving rates at an acceptable chemical reactivity with bismuth (see Figures 2 and 3).

Magnesium rich-calcium alloys with Mg to Ca weight ratios outside the 1.9 to 3.0 range are inferior for removing bismuth because they are either too rich in calcium leading to inordinately long processing times and high processing costs or too rich in magnesium to be sufficiently reactive with bismuth.

The alloys of the present invention are prepared by melting the appropriate proportions of calcium and magnesium metals under a protective atmosphere and pouring and solidifying the alloy in the same or similar protective atmospheres. The protective atmosphere may comprise nitrogen, argon or any other gases which are protective or non-reactive when in contact with magnesium and calcium. The temperature used to melt the metals and prepare the alloy is preferably but not necessarily in the range of 680 - 750°C.

In a further aspect of the present invention, a method for achieving the solution of calcium in lead resulting in high recoveries is provided. This method comprises the steps of providing a magnesium and calcium alloy which has a magnesium to calcium ratio between 1.2 and 5.2, and adding this alloy to a lead bath.

Since these magnesium-rich alloys consist of eutectic structures which contain mostly finely divided magnesium metal and Mg₂Ca intermetallic with the complete absence or only minor quantities of finely divided calcium metal, they are not subject to the aforementioned difficulties associated with calcium metal or calcium-rich alloy granules.

In the present invention, these alloys are stable in air. Since the alloy does not oxidize or hydroxylize in air, it does not require special packaging or protective atmospheres. There is no danger of fire or explosion if these alloys come in contact with moisture. When added to liquid lead, these alloys react with minimal or no oxidation. The reaction is often accompanied by a minor degree of bubbling; however, there is essentially little or no flaring or fume generation. Since the alloys are not prone to contamination from contact with air prior to treatment, reagent recoveries are higher and more predictable than with other reagents. Further, since the alloys do not oxidize readily even if they float to the surface, provided the bath is being agitated no excessive flaring or fuming occurs, which would lead to lower recoveries. This substantially increases the predictability of achieving the desired final bismuth level which is particularly important when aiming at low bismuth levels of less than 0.01%.

The alloy is preferably added to the lead bath in the form of large ingots. Under some circumstances, smaller ingots, large chunks, granules or powder may also be used. The alloys can be added either by plunging or supplied to the surface of an agitated lead bath.

When the alloy is added to the lead bath, the bulk temperature of the melt does not increase as is often the case with calcium metal additions. In this invention, the alloys can be added at commercial debismuthizing temperatures that are between about 380°C to 500°C and are not restricted to the higher temperatures needed to fully melt the alloy as in the case of the prior art discussed. In general, the dissolution rate of these alloys increases with increasing temperature and by agitation. Since there is virtually no flaring and related fume generation with this alloy, even at temperatures as high as 530°C and with agitation, no special fume collection system is required to contain emissions. Agitation is sometimes avoided when calcium metal is utilized as it increases oxidation and flaring.

After the alloy has been added to the lead melt and the dissolution is complete, the lead melt is allowed to cool in the customary fashion of the Kroll-Betterton process to separate out the solid bismuth-rich dross.

The following examples are given to demonstrate the high reagent recoveries that are possible with this alloy. Refined lead low in bismuth was used in all tests to enable investigation of the effects of process conditions on alloy dissolution recoveries without the complications of side reactions with bismuth.

EXAMPLE 1:

Approximately 98.8 grams of a magnesium-calcium alloy with a magnesium to calcium ratio of 2.7 was plunged into a 20 kilogram quiescent lead melt at 419°C. No flaring, oxidation or fume generation was observed. Approximately 45% of the alloy dissolved after 30 minutes with essentially 100% reagent recovery. Final magnesium and calcium analyses were 0.16% and 0.06% respectively.

EXAMPLE 2:

Approximately 98.7 grams of a magnesium-calcium alloy with a magnesium to calcium ratio of 3.0 was plunged into a 20 kilogram agitated liquid lead melt at 415°C. No flaring or fume was observed. Approximately 98% of the alloy dissolved after 23 minutes of stirring with essentially 100% reagent recovery. The final magnesium and calcium analyses were 0.33% and 0.11%, respectively.

EXAMPLE 3:

Approximately 98.8 grams of a magnesium-calcium alloy with a magnesium to calcium ratio of 2.7 was plunged into a 20 kilogram quiescent lead melt at 432°C. Approximately 90% of the sample had dissolved after 30 minutes with essentially 100% reagent recovery. No flaring or fume was observed during the treatment. The final magnesium and calcium analyses were 0.32% and 0.12% respectively.

EXAMPLE 4:

Approximately 97.7 grams of a magnesium-calcium alloy with a magnesium to calcium ratio of 3.0 was plunged into a 20 kilogram quiescent liquid lead melt at 500°C. The reaction was characterized by heavy bubbling; however, no flaring, oxidation or fume generation was evident. The alloy was completely dissolved after 12 minutes with essentially 100% recovery at 0.38% magnesium and 0.13% calcium. Black dross was observed to form on top of the melt after 22 minutes which was accompanied by a 13 - 15% fade in the dissolved magnesium and calcium after 30 minutes to 0.33% magnesium and 0.11% calcium.

In summary, this application has disclosed an invention which improves the dissolution characteristics of magnesium and calcium in lead at commercial debismuthizing temperatures thereby improving the efficiency of bismuth removal from lead. This alloy is stable in atmospheric air and humidity and requires no special protective packaging as does calcium metal. When added to liquid lead at commercial processing temperatures, the alloy dissolves with essentially no oxidation, flaring and fume generation. This results in higher and more consistent reagent recoveries and more predictable final bismuth levels which are particularly important when aiming for final bismuth levels less than about 0.01%. The virtual absence of fume precludes the need for special fume collection systems. The absence of flaring and oxidation enables the alloy to be added with agitation and, if desired, at higher processing temperatures than is customary with calcium metal.

Thus, the present application describes the use of certain magnesium-calcium alloys in Kroll-Betterton type processes for the removal of bismuth impurities from lead. The inventors have found that the use of certain magnesium rich-calcium alloys at commercial debismuthizing temperatures results in a more efficient process since;

(i) in the preferred compositional range, the amount of alloy required to remove bismuth is minimized and the alloy's dissolving rates are fast enough for commercial debismuthizing operations.

(ii) with these alloys there is essentially no burning, flaring or fuming during the lead treatment which results in higher, more predictable reagent recoveries.

(iii) the alloys are resistant to atmospheric oxygen and humidity and, hence, do not require special packaging or protective atmospheres.

(iv) the alloys are sufficiently strong and ductile to enable casting and shipping as ingots of a consistent weight and size, thereby permitting precise additions to the lead bath.

These magnesium-calcium alloys are superior to other alloy compositions since this preferred range minimizes the amount of alloy required to remove bismuth and gives alloy dissolving rates which are acceptable at commercial debismuthizing temperatures.

The present invention has been described using preferred ratios of magnesium to calcium. Clearly, minor variations in these ratios may be made within the scope of the invention. The alloy may contain other constituents, such as different alkali earth metal, which do not affect the essential nature of the metallurgical process herein disclosed.

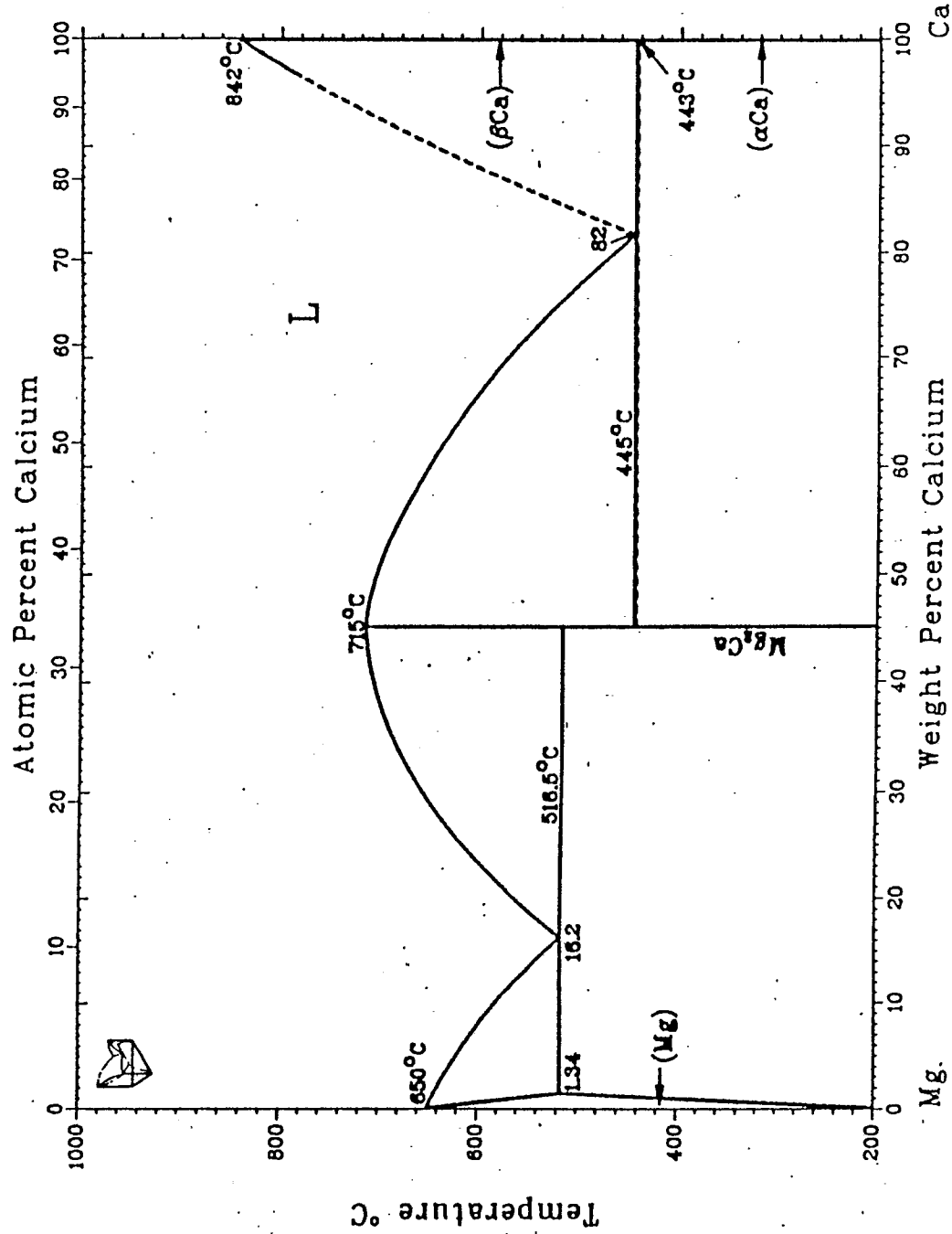
Claims

1. An alloy for use in processing lead, said alloy characterised in that it comprises magnesium and calcium in a ratio of magnesium to calcium between 1.9 and 3.0 on a weight basis.

2. A method for achieving the solution of magnesium and calcium in lead with eventual high recovery comprising the steps of: providing an alloy according to claim 1 adding said alloy to a lead bath at a temperature of approximately 415°C to 500°C whereby the alloy dissolves in the lead; and recovering the magnesium and calcium in association with impurities from the lead bath.

3. A method for achieving the solution of magnesium and calcium in lead with eventual high recovery characterised in that it comprises the steps of: providing an alloy consisting essentially of magnesium and calcium having a ratio of magnesium to calcium between 1.2 and 5.2 on a weight basis; adding said alloy to a lead bath at a temperature of approximately 415°C to 500°C, whereby the alloy dissolves in the lead; and recovering the magnesium and calcium in association with impurities from the lead bath.

4. A method according to claim 2 or 3 further comprising the step of agitating said lead bath.



A.A. Nayeab-Hashemi and J.B. Clark, submitted to the APD Program

FIG. 1

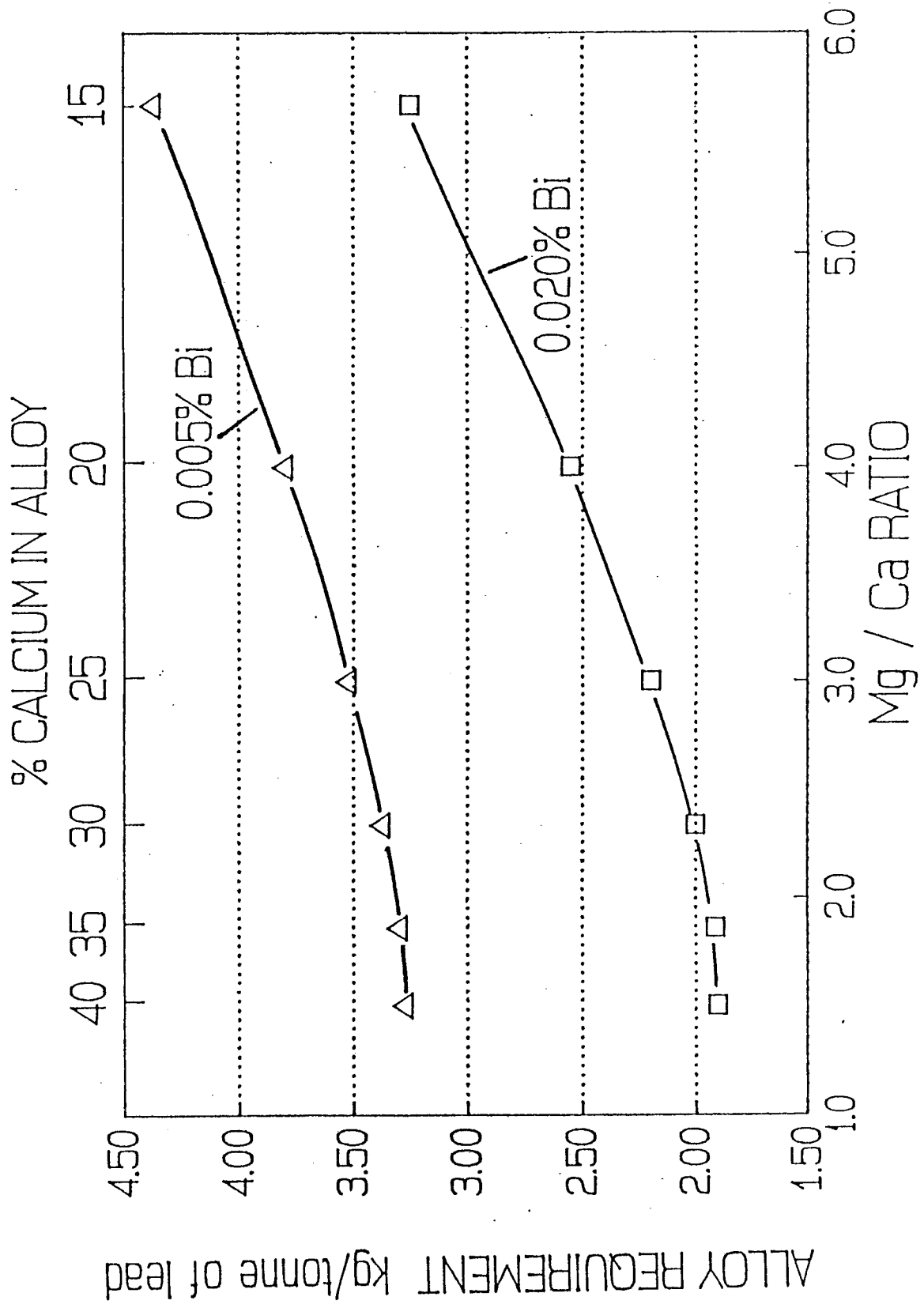


FIG. 2

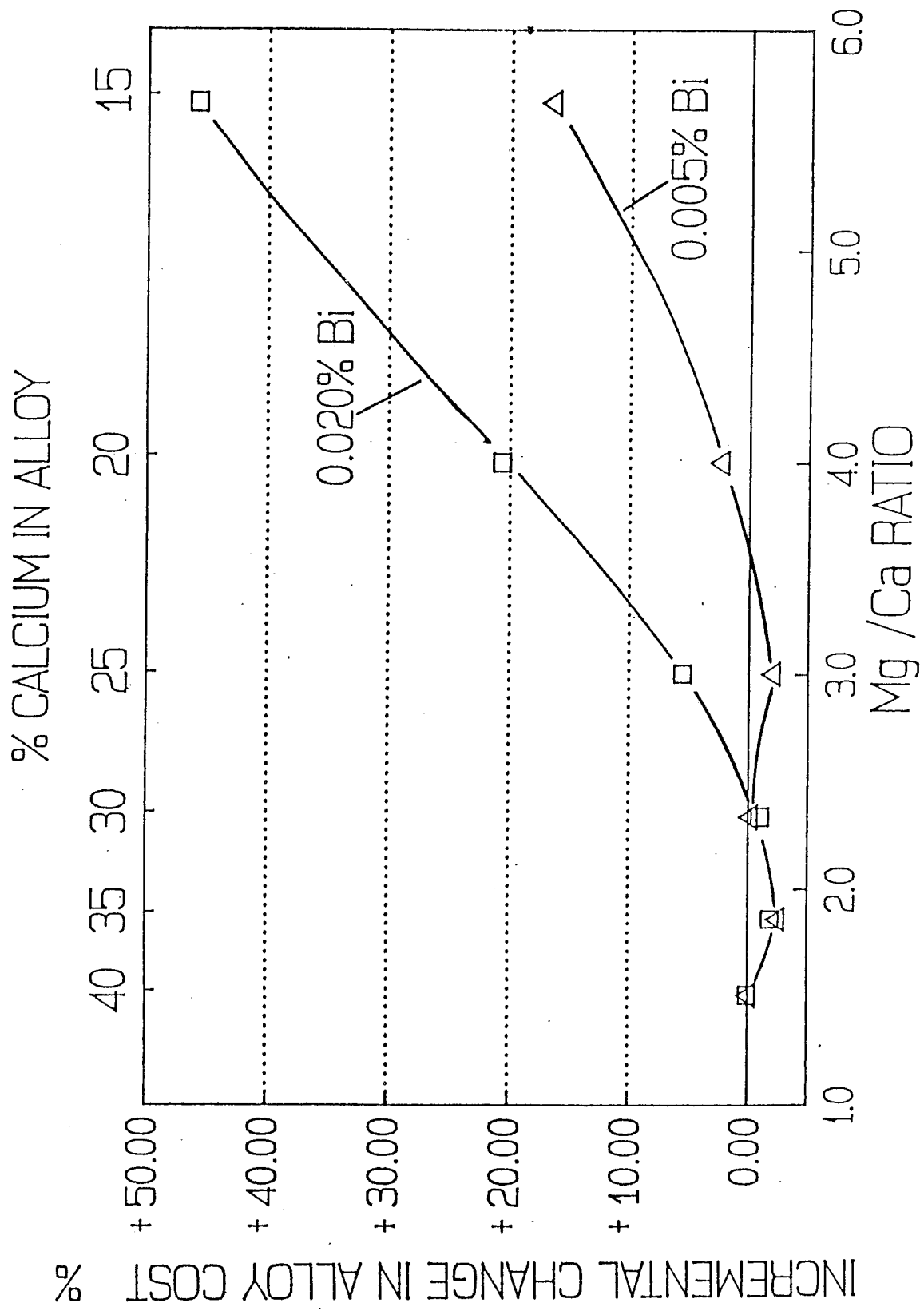


FIG. 3

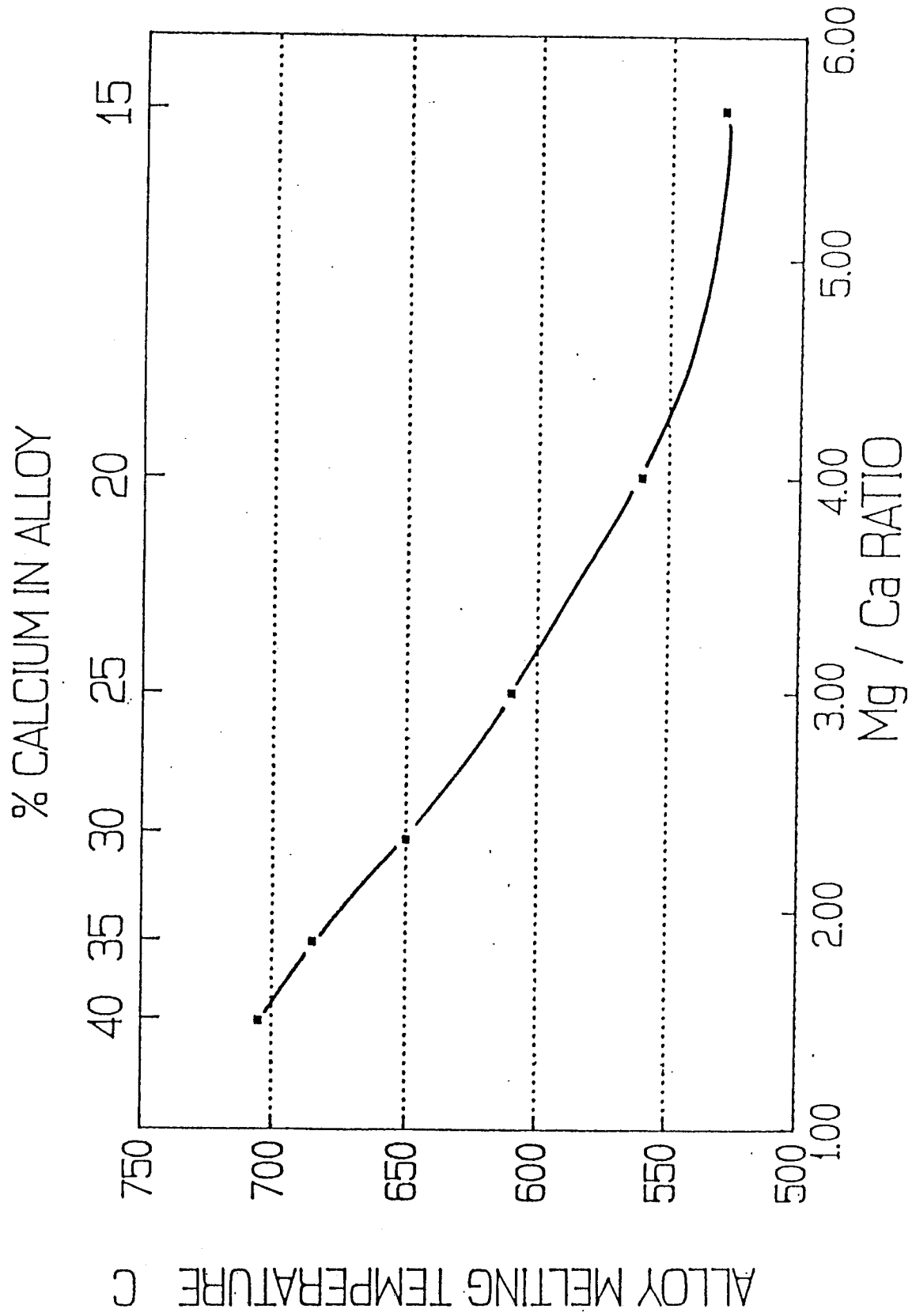


FIG. 4

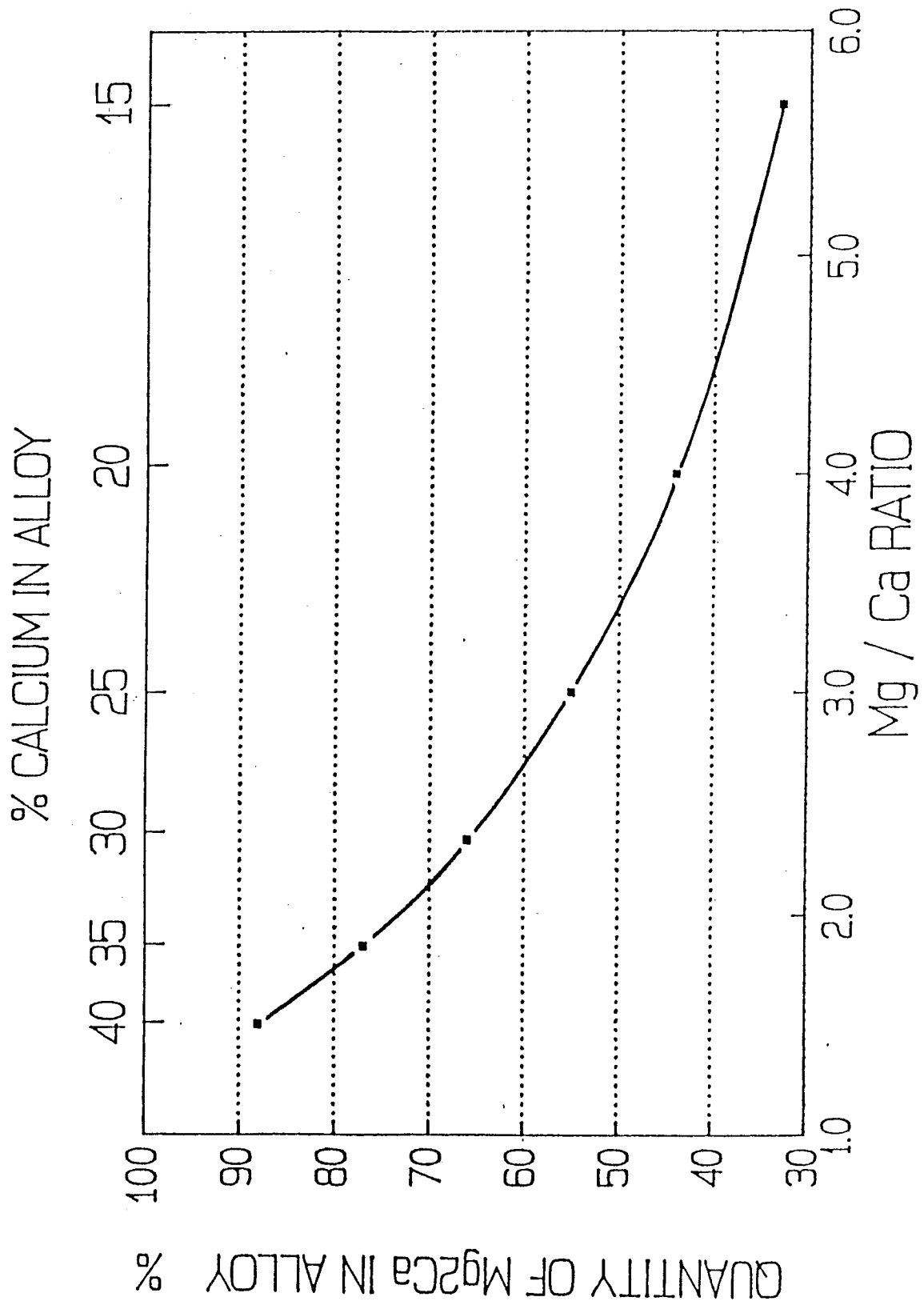


FIG. 5