METHOD OF PREPARING MELTS OF ZINC BASE ALLOYS AND IMPROVED FLUX THEREFOR

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7 Claims

ABSTRACT OF THE DISCLOSURE

More efficient recovery of usable metal is obtained without objectionable smoke and fumes, iron pick up or loss of magnesium from the alloy by adding to the slush layer of a zinc base alloy bath a flux comprising essentially 20 to 60 percent by weight of magnesium chloride (calculated as anhydrous) and at least 40 percent by weight total of sodium and potassium chlorides, the temperature to which the flux is heated being above the melting point of the flux. The sodium chloride may be present in amounts of 0 to 45 percent by weight and the potassium chloride may be present in amounts of 0 to 60 percent by weight although a superior flux results when sodium and potassium chlorides are each present in amounts of 20 to 40 percent of the total. When the zinc alloy contains aluminum, the improved flux preferably contains a small amount, up to 20 or 25%, of the total of said chlorides of an inorganic fluoride selected from sodium and potassium cryolites and silicofluorides and mixtures of one or more thereof.

The present invention relates to a method of fluxing, melting and maintaining zinc alloys in a form suitable for die casting or other melting of zinc and to an improved flux therefor.

In the melting of zinc base alloys for die casting or other purposes, the metal is heated to a temperature of 780° F. or above, usually at 850° to 1000° F. During the melting operation, parts of the melted metal within the dross on the bath surface are often prevented from coalescing with other parts because of the presence of oxides. The result is that a considerable amount of metal is trapped in the dross layer over the molten metal. This dross is made up primarily of uncoalesced molten particles of the alloy, zinc oxide and an iron-aluminum compound.

In order to facilitate coalescing of major portions of the molten metal so that it is returned to the melt, it is customary to add to the dross layer on the surface of the metal during initial and subsequent meltings, substantial quantities of a flux. The fluxes used heretofore have facilitated coalescence of a major portion or most of the molten metal particles in the dross layer so that the metal is returned to the bath.

The fluxes used heretofore and considered to be most efficient contain large amounts of zinc chloride and ammonium chloride both in mechanical and chemical combination. The zinc chloride-ammonium chloride fluxes cause a strong exothermic reaction in the dross layer and have been considered to do an excellent job of releasing entrapped metal in the dross layer. They produce a desirable dry, powdery dross. The strong exothermic reaction is, however, not desirable for it raises the temperature of the melt above that desired and makes melt temperature hard to control. Both the zinc chloride and the ammonium chloride cause a large amount of smoke (visible and highly objectionable vapors) to be evolved. These vapors are toxic, tend to cause illness, and constitute a health hazard. Authorities concerned with air pollution have objected to the discharge of such smoke into the atmosphere. Compliance with the smoke abatement requirements necessitates the installation and operation of expensive equipment by companies using the prior fluxes.

Zinc die casting alloys contain .02% to .08% of magnesium to increase tolerance of lead, cadmium and tin impurities, and about 4% of aluminum to yield eutectic base alloys. The reactions occurring when fluxes containing zinc chloride-ammonium chloride are used cause a loss of magnesium from the alloy. A decrease of the magnesium content results in the inter granular corrosion of the castings made of such alloy. To compensate for such loss it has been a practice to add some magnesium chloride to the flux.

It is a prime object of the present invention to provide a flux which permits melting of zinc alloys without objectionable smoke or highly toxic fumes.

It is another object of the present invention to provide fluxes for zinc base alloys which produce a finely powdered dross with a higher recovery of metal from such dross than has been obtainable with the prior art.

It is still another object of the invention to provide more efficient fluxes for zinc base alloy baths that produce a powdery dross, increase the recovery of metal therefrom, produce no appreciable exothermic reaction when used, do not cause detrimental consumption or loss of magnesium from the zinc alloy bath, and reduce aluminum loss from the alloy because of the absence of said exothermic reaction.

It is still another object of this invention to provide a method of treating zinc base alloys during the melting, alloying or casting thereof, which method increases the proportion of usable metal over that before obtainable, provides a dross that is powdery and easily removed from the metal and does not cause objectionable smoke.

It is another object of the present invention to provide a method of recovering more efficiently usable metal from the skimming of zinc base alloy baths. Such skimmings being the dross layer which has been removed from the surface of a zinc alloy bath. These skimmings are treated separately with fluxes.

We have found in accordance with the present invention that the above and other objects are obtained by treating the dross upon zinc base alloy baths, with a flux comprising essentially magnesium chloride and at least one chloride selected from sodium and potassium chlorides. Our new flux is preferably obtained by mixing certain proportions of magnesium chloride with both sodium chloride and potassium chloride and, preferably, in cases where aluminum is in the alloy, some inorganic tertiary fluorides compound selected from one or more of cryolite (Na₃AlF₆), potassium cryolite (K₂AlF₆), sodium silicofluoride (Na₂SiF₆) and potassium silicofluoride (K₂SiF₆). These silicofluorides and cryolites can provide a mild exothermic reaction when the flux is added to the surface of a zinc alloy bath.

Our new flux should have little if any zinc chloride and ammonium chloride as even a comparatively small amount of these causes smoking. However, up to 5% or so of each of these materials based on the total weight of MgCl₂, KCl and NaCl present can be tolerated in many applications.

The magnesium chloride (MgCl₂), considered as anhydrous, should constitute at least 20% by weight of the total of the magnesium, sodium and potassium chlorides. When more than 60% of MgCl₂ is present, the dross becomes wet and is hard to manage. When the amount of magnesium chloride is less than 20%, the exothermicity of the flux becomes inordinately high. The preferred amount of magnesium chloride is 25% to 60% of the
total of the magnesium, sodium and potassium chlorides in the flux. The optimum amount depends to some extent on the melting temperature or operational temperature of the melting unit.

The exact function of the sodium and potassium chlorides is not fully understood, but they cooperate with the magnesium in some manner to produce the unique properties in the flux. When the total of these two materials is less than 40% of the total of the MgCl₂ and alkali metal chlorides the dross becomes wet.

We have found that to be effective the flux must melt at or below the operating temperature of the zinc alloy bath. Operational fluxes include, therefore, those mixtures of magnesium chloride with potassium and/or with sodium chlorides which melt at or below the operating temperature of the zinc alloy bath, which is usually from about 780° to 1050° F.

The sodium chloride should constitute about 0% to about 40% of the weight of the total alkali chlorides and MgCl₂ present, and about 20% to about 40% is preferred.

The potassium chloride should be present in a maximum amount of 60% of the weight of the MgCl₂ plus total alkali chlorides present. When at least 40% of these chlorides are made up of sodium, then the potassium chloride may be omitted and still a usable flux obtained, provided the operating temperature of the zinc alloy bath is above the melting point of the flux. Both sodium and potassium chlorides are preferably present, however, and the potassium chloride preferably should be present in amounts of about 15% to about 40% of the total of MgCl₂ and alkali metal chlorides present.

Our new fluxes when applied to the surface of a zinc alloy bath are not even mildly exothermic unless the aforementioned chlorides are present. The application of our fluxes to the surface of a zinc alloy bath serves to release a substantial portion of the free metallic zinc particles entrapped in the surface covering or dross. Subsequently the dross remaining becomes dry and powdery and is easily removed from the surface of the bath. It has been found that these skimings have high heat insulating characteristics such that the remaining spheroids of molten zinc which were not released when the flux was applied to the surface of the bath can be agglomerated and salvaged apart from the melting bath. By simple stirring of the skimings, this free metal accumulates to such an extent that the metallic content thereof is decreased to about 0.5%, or even less. This compares with 0.8% for the best obtainable practice heretofore followed and with the 2% to 3% resulting in the use of ordinary practices. We have found no loss of aluminum and no pick up of iron which melt at or below the operating temperature of the zinc alloy bath.

The magnesium chloride used need not be anhydrous if care in use of our new flux is practiced. The above percentages are, however, based on anhydrous MgCl₂. Hydrated magnesium chloride (MgCl₂·6H₂O) is considerably less expensive to use than the anhydrous based on magnesium chloride content. When hydrated magnesium chloride is used the flux must be added gradually to the surface of the alloy bath to permit gradual vaporization of the water. One cannot plunge the flux into a molten bath. If such a procedure is used anhydrous MgCl₂ should be used. We have found that the effectiveness of our new flux is increased greatly when it is stirred or worked in the dross on the surface of the molten metal.

The following examples, in which percentages are by weight, illustrate the invention.

### EXAMPLE 1

<table>
<thead>
<tr>
<th>Flux (% Total)</th>
<th>MgCl₂·6H₂O</th>
<th>NaCl</th>
<th>KCl</th>
<th>K₂AlF₆ or Na₂AlF₆</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>42.3</td>
<td>27.3</td>
<td>27.4</td>
<td>3.0</td>
</tr>
<tr>
<td>B</td>
<td>38.5</td>
<td>33.5</td>
<td>25</td>
<td></td>
</tr>
<tr>
<td>O</td>
<td>38.5</td>
<td>33.5</td>
<td>25</td>
<td></td>
</tr>
</tbody>
</table>

The above ingredients are thoroughly mixed and packaged in a closed container.

### EXAMPLE 2

1,000 pounds of a zinc die casting alloy containing about 0.05% of magnesium and 4% of aluminum is placed in a ferrous melting pot of a melting furnace along with 1.8 to 2.0 pounds of the flux of Example 1. The alloy is heated to 850° F. The flux is worked or stirred into the dross on the surface of the molten metal to increase the effectiveness. No noticeable fumes or smoke is evolved and the dross becomes powdery. Upon removal from the furnace and subsequent stirring the metallic content thereof was found to be less than 0.5% of the weight thereof, and the magnesium and aluminum content of the melt remain unchanged.

### EXAMPLE 3

To the ingredients of Example 1 is added 10% (by weight of the original mixture) of Na₃SiF₆. The resultant flux is somewhat superior to that of Example 1 when used in Example 2. The coalescence of the metal is faster.

### EXAMPLE 4

The flux of Example 3 is applied on the surface of a suitable zinc alloy melt, as described in Example 2. The alloy is heated to a temperature of between 780° and 1050° F. No visible fumes are evolved from the flux and the magnesium and aluminum content of the metal remain stable.

### EXAMPLE 5

Three separate fluxes based on MgCl₂·6H₂O were prepared by mixing together the ingredients shown in the following table:

<table>
<thead>
<tr>
<th>Flux (percent)</th>
<th>A</th>
<th>B</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgCl₂·6H₂O</td>
<td>42</td>
<td>38</td>
<td>38</td>
</tr>
<tr>
<td>NaCl</td>
<td>28</td>
<td>28</td>
<td>28</td>
</tr>
<tr>
<td>KCl</td>
<td>28</td>
<td>28</td>
<td>28</td>
</tr>
<tr>
<td>K₂AlF₆ or Na₂AlF₆</td>
<td>10</td>
<td>10</td>
<td>10</td>
</tr>
</tbody>
</table>

### EXAMPLE 6

1,000 grams of skimings, resulting from melting and skimming the dross from zinc die cast gates and sprues were melted in a graphite pot at 1000° F. To these molten skimmings were added 30 grams of Flux B above by slowly mixing the flux into the skimmings. A powdery dross was obtained and 935 grams of free metal alloy were recovered from the skimings, representing a yield of 93.5%.

### EXAMPLE 7

The procedure of Example 6 was repeated except that Flux C of Example 5 was substituted for Flux B. The free metal alloy recovered was 92.8% of the weight of the skimming.

### EXAMPLE 8

The procedure of Example 6 was repeated except that Flux A of Example 5 was substituted for Flux B. 910 grams of free metal was recovered from the skimmings.

### EXAMPLE 9

To 150 pounds of skimings from a melt of zinc die cast scrap was added 4 pounds of Flux A of Example 5. The mixture was also heated to 1000° F. in a graphite pot while stirring and working the flux into the molten skimings. 135 pounds of free metal alloy were recovered for a yield of 90% based on the weight of the skimming.

In making melts the new fluxes are generally used in amounts of about 15% to 25% of the weight of the zinc base alloys melted, although as little as .05% is effective.
and up to 1.0% or more may be required. In recovering metal from the skimmings from zinc base alloys, fluxes in amounts of 1 to 5%, based on the weight of the skimmings, are usually used, although as little as .5% gives considerable recovery, and even 10% or more may be used. About 2 to 4% is optimum from an economic standpoint.

When the flux is mixed slowly or stirred into the skimmings, heat sufficient to melt the flux must be used and the temperature may vary from 780° F. to 1200° F. Usually the heating is in the presence of molten metal and about 780° F. to 1050° F. is then preferred, although higher temperatures, even 1200° F., may be used.

It is to be understood that in accordance with the provisions of the patent laws, various modifications can be made in the method, procedures, compositions and products of the present invention without departing from the spirit of the same.

We claim:

1. A process of recovering usable metal from the skimmings resulting from melting zinc base alloys which comprises heating the said skimmings in intimate contact with a mixture of MgCl₂ and at least one of the group consisting of NaCl and KCl, said MgCl₂ being present in amounts of 20 to 60 percent by weight and said group members being present in a total of at least 40 percent by weight, 0 to 40 percent of NaCl, and 0 to 60 percent of KCl being present, said heating being at a temperature at least equal to the melting point of said mixture.

2. The process according to claim 1 wherein both NaCl and KCl are present in said mixture in amounts of 20 to 40 percent by weight.

3. The process according to claim 2 wherein 1 to 25% (based on weight of said mixture) of an inorganic fluoride compound, selected from the group consisting of sodium and potassium cryolites, sodium and potassium silico-fluorides and mixtures thereof, is also present in admixture with said mixture of MgCl₂, KCl and NaCl.

4. The process of claim 1 wherein said mixture is free from more than 5% by weight each of zinc and ammonium chlorides.

5. In a process of treating melts of a zinc base alloy wherein the metal is heated to a temperature of between 780° and 1050° F., the steps which comprise applying a flux comprising 20 to 60% by weight of magnesium chloride (calculated as anhydrous) and at least 40% total of sodium and potassium chlorides, the sodium chloride being present in amounts of 0 to 40% and the potassium chloride being present in amounts of 0 to 60%, any zinc chloride and ammonium chloride present being each less than 5% of the total of said magnesium, sodium and potassium chlorides to the surface of the molten metal, stirring the flux on said surface and stirring the resultant powdery dross to agglomerate spheroids of molten metal and return them to the metal bath.

6. In a process of treating melts of a zinc base alloy wherein the metal is heated to a temperature of between 780° and 1050° F., the steps which comprise applying a flux comprising a mixture of MgCl₂ and at least one of the group consisting of NaCl and KCl, said MgCl₂ being present in amounts of 20 to 60 percent by weight and said group members being present in a total of at least 40 percent by weight, 0 to 40 percent of NaCl, and 0 to 60 percent of KCl being present to the surface of the bath, stirring the flux on said surface and stirring the resulting powdery dross to agglomerate spheroids of molten metal and return them to the metal bath.

7. The process of claim 6 wherein the powdery dross is removed from the metallic bath and subsequently stirred to effect agglomeration of the metal spheroids contained therein.

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