United States Patent [19]
Derham, deceased et al.

[11] **3,754,897**
[45] **Aug. 28, 1973**

[54] MELTING OF METALS

[76] Inventors: **Leslie Jack Derham, deceased,** late of Avonmouth, England; **by Michael Gordon Derham, administrator,** 20 Ridgehill, Henleaze, England

[22] Filed: **Nov. 5, 1971**

[21] Appl. No.: **196,234**

Related U.S. Application Data

[63] Continuation of Ser. No. 810,088, March 21, 1969, abandoned.

[52] **U.S. Cl.** **75/96,** 75/68, 75/77, 75/85, 75/86, 75/94, 148/26
[51] **Int. Cl.** **C22b 9/10,** C22b 21/06, C22h 13/06
[58] **Field of Search** 75/65, 67, 68, 78, 75/88, 93, 94; 148/26

[56] **References Cited**

UNITED STATES PATENTS

2,723,928	11/1955	Fisher	148/26
3,186,881	6/1965	Robbins	75/68 R
2,184,705	12/1939	Willmore	75/68 R
2,013,926	9/1935	Pacz	75/68 R
3,650,730	3/1972	Derham	75/68
3,667,934	6/1972	Derham	75/94

Primary Examiner—L. Dewayne Rutledge
Assistant Examiner—Peter D. Rosenberg
Attorney—Lane, Aitken, Dunner & Ziems

[57] ABSTRACT

A method of purifying or preventing oxidation of metals is achieved by covering the metals in the molten state with a flux containing a molten double salt of sodium chloride and aluminum chloride. Other alkali or alkaline earth metal halides may additionally be included in the flux.

12 Claims, No Drawings

MELTING OF METALS

This is a continuation, of application Ser. No. 810,088 filed Mar. 21, 1969 now abandoned.

This invention relates to methods of melting and purifying metals, and in particular to fluxes used in such processes.

In a variety of metallurgical operations involving such metals as zinc, aluminum, lead and copper, it is desirable to be able to cover the liquid metal surface with a layer of liquid flux, so that oxidation and dross formation can either be avoided or minimised. Of the many materials that could be used, the fluxes at present in commercial use, for zinc, are based upon zinc chloride, ammonium chloride, or a mixture of these two, known commerically as ZAC. This last is by far the most usual, but it has a number of disadvantages.

The prime disadvantage is that any oxide which enters the flux tends to form zinc oxychloride; this is insoluble in either component or ZAC, and thus causes the flux to "stiffen" and lose its fluidity. Ultimately it will form a solid dross. To overcome this, more ZAC has to be used. This is not a cheap material, and hence a pasty, rather than a liquid, flux layer is the general rule. In use this has two implications: clean separation of the flux from the metal is not easy, and separation of trapped metal from within the flux layer is very inefficient. Where the flux is being used in a waste metal recovery operation this loss is important, particularly if the feedstock is small or particulate: e.g., oversize material from the preparation of zinc dust or aluminium flake.

This invention consists in a method of preventing or reducing oxidation of molten metals by covering the metal with a flux layer containing a molten double salt of sodium chloride and aluminium chloride.

The method is particularly applicable to processes involving melting of zinc, aluminium, lead, tin or copper or alloys of these metals. For instance, in re-melting oversize zinc dusts a high metal recovery can be attained and the flux does not stiffen to a mrked degree as its oxide content increases.

The invention further consists in a fluxing material for preventing the oxidation of molten metals, which material is formed by mixing sodium chloride and aluminium chloride and subsequently fusing the mixture formed.

This material has the advantages that a very fluid flux is formed so that removal of the flux layer is relatively simple in that the flux is easily tapped. Thus less flux needs to be used and very little metal is trapped in the flux when it is removed from the metal.

The invention further consists in a method for the recovery of metals involving a melting step in which the metal is covered with a flux layer containing a molten double salt of sodium chloride and aluminium chloride while in its molten condition.

This flux can advantageously be used for zinc and aluminium and in our copending application Ser. No. 810,086, we describe an improved aluminium chloridization process based upon its use, but its use is not limited to these two metals. It can with advantage be used also for example, with lead, tin and various other metals. Further, we prefer largely for simplicity, to use this flux alone; but it can equally well be used admixed with other fluxes, particularly those of the metallic halide type: for example in its use with aluminium, it could be admixed with fluxes of the cryolite (Na_2AlF_6) type.

However, mixed fluxes of this type need to be treated with some caution: addition of other salts will generally raise the melting point of the flux. In this context, only broad guide lines can be given, since the fluidity is temperature dependent. Thus a mixture of sodium aluminium choride and 2 percent by weight of sodium chloride has a melting point of approximately 650° C: it is suitable for use on aluminium at about 730° C. Addition of about 5 percent of cryolite has the same effect.

Mixed fluxes based on other alkali metal chlorides, and alkaline earth metal chlorides, are especially useful. Thus a very good flux can be obtained by mixing aluminium chloride, sodium chloride and potassium chloride, the latter two salts being taken in approximately equal quantities by weight. In this way fluxes with melting points almost anywhere between 650° C and about 200° C can be prepared.

We have discovered that the fluidity of this flux appears to depend upon the aluminium chloride content of the sodium chloride containing flux. Once the flux is in use, fluidity and melting point can both be easily controlled:

to make more fluid: add more aluminium chloride, either as such, or as the double salt;

to make less fluid: add either chloride or fluoride of an alkali or alkaline earth metal, or a complex fluoride, such as cryolite.

The actual melting point of the flux will be determined by the melting point of the metal or by the temperature of operation. The melting points of the commoner non-ferrous metals are quite low: zinc, 421°C, lead 327°C and tin 232°C, with the exception of aluminium, 660°C, and copper 1,083°C. Therefore in the low melting metal cases the flux will consist substantially of the double salt, whereas for copper the flux will only contain sufficient of the double salt to give the desired fluidity.

The invention will now be further described by reference to the following non-limiting Examples.

EXAMPLE 1

Method of Preparation of Flux

It is of prime importance that both constituents be dry; in the case of sodium chloride this is achieved simply by powdering and heating in an oven; in the case of aluminium chloride it may involve distillation in suitable apparatus if the material has deteriorated in storage. The two dry salts were mixed in a ratio of 3 parts by weight sodium chloride to 7 parts by weight aluminium chloride and added to a bottom heated steel pot maintained at an internal temperature of 300°C. Very quickly a liquid pool was formed. To this pool was added further salt mixture at such a rate that a liquid condition was maintained throughout. It is preferred that the mix be used immediately, and this preparation in situ is preferred, but the flux can be cast into suitable moulds and stored for a short period before use.

EXAMPLE 2

Recovery of Zinc from Oversize Zinc Dust

Approximately 100 lb. of the flux was prepared in a large steel pot; the oversize dust was then added to the pool at such rate that it would melt and the flux would remain liquid. Stirring occasionally with a steel rabble ensured adequate mixing. As more zinc was added so also was more flux, in order to maintain an adequate liquid layer on the surface of the melt. The zinc pool was maintained at about 450°C. When all the zinc had been added, the whole was well stirred, left to stand for 15 minutes, the flux tapped off and the zinc cast into ingots. Quantities used: Oversize dust: 4,462 lb.

flux 250 lb. (5.6 percent of wt. of Zn treated)

Quantity of zinc recovered: 4,208 lb.

Metal recovery: 94.8 percent

This operation took a total of 3½ hours; the time is directly linked to the rate of melting of the zinc.

The process of Example 2 is batchwise; it need not be so, and can by suitable adaptation be made continuous. In that case periodic tapping of the flux and its replenishment will also be necessary.

EXAMPLE 3

Recovery of Aluminum from Melting Furnace Drosses

A mixture was made of equal parts by weight of the furnace drosses after powdering, and solid sodium aluminium chloride and the whole then slowly heated in a steel pot to approximately 750°C (external temperature). After a short period the pot was tapped and the liquid metal run off: metal recovery was 75 percent by weight of the drosses taken.

Note—These drosses are a mixture of free metal trapped in a skin of alumina, which it is almost impossible to analyse for free metal: hence a theoretical metal recovery figure cannot be given. Repeats of this process, on a small scale, give metal recoveries varying from 70–85 percent, based on dross weight taken. The only other method used to recover the metal is by a wet-milling process: metal recovery then is at about 45 percent by weight of the dross.

EXAMPLE 4

Removal of Tellurium from Lead

The lead used in these experiments contained approximately 0.02 percent tellurium. In both cases, the experiments were carried out by the following technique. In one case no flux was used but in the other a sodium chloride flux was used.

Aluminium powder was stirred into a pool of molten lead, maintained at 500°–550°C, for 15 minutes. The dross and aluminium powder were then removed, and the lead allowed to cool; a crust which formed was also removed. In the fluxed experiment, this was left on until just before tapping, and the crust removed with it.

	Without Flux	With Flux	With Flux
Weight Lead	8.65 kg.	8.65 kg.	8.65 kg.
" Al powder	0.17 kg.	0.17 kg.	0.04 kg.
" flux	Nil	0.42 kg.	0.22 kg.
"lead recovered	6.41 kg.	7.74 kg.	8.10 kg.
Lead loss, %	15.8%	10.5%	6.3%
Tellurium : before	0.02%	0.02%	0.02%
" after	0.001%	not detectable	

Thus the process is made more efficient by using flux.

EXAMPLE 5

Melting of Tin

Two samples of tin were held molten in a crucible for 12 hours, one being covered with a layer of sodium aluminium chloride. Both crucibles were maintained at 280°–290°C. In the flux covered crucible, the weight lost was 0.38 percent; in the 'open' crucible 1.1 percent.

Various modifications may be made within the scope of the invention as defined by the following claims.

I claim:

1. In a process for the production of a metal selected from the group of lead, tin and zinc including a melting step to form a molten phase of said metal wherein the improvement comprises

a. fusing sodium chloride and aluminum chloride to form a flux containing a member selected from the group consisting of (1) the double chloride salt, sodium aluminum chloride, and (2) a mixture of the double chloride salt, sodium aluminum chloride and sodium chloride and

b. covering the metal during the melting step with said flux to form a separate molten layer of said flux over said molten metal to reduce the oxidation of the molten metal.

2. The process as set forth in claim 1 wherein said metal is zinc.

3. The process as set forth in claim 1 including the step of fusing an additional salt selected from a member of the group consisting of alkali metal halides, alkaline earth metal halides, double halides of an alkali metal and aluminum, and double halides of an alkaline earth metal and aluminum into said flux as a minor portion of said flux.

4. The process as set forth in claim 1 wherein said member is a mixture of the double chloride salt, sodium aluminum chloride and sodium chloride and wherein the sodium chloride is present in said flux as a minor portion of said flux.

5. The process as set forth in claim 3 wherein said additional salt is included in said flux in an amount sufficient to result in a flux with a melting point lower than the melting point of said metal.

6. The process as set forth in claim 5 wherein said additional salt is sodium aluminum floride.

7. In a process for the production of a metal selected from the group of lead, tin and zinc from impure materials containing said metal in which a melting step is utilized to purify said materials and yield said metal in a purified state wherein the improvement comprises

a. fusing sodium chloride and aluminum chloride to form a flux containing a member selected from the group consisting of (1) the double chloride salt, sodium aluminum chloride, and (2) a mixture of the double salt, sodium aluminum chloride and sodium chloride,

b. providing a molten layer of said flux,

c. contacting said layer of molten flux with said material in particulate form and

d. allowing said flux to form a molten flux layer over the molten metal.

8. The process as set forth in claim 7 wherein said metal is zinc.

9. The process as set forth in claim 7 including the step of fusing an additional salt selected from a member of the group consisting of alkali metal halides, alkaline earth metal halides, double halides of an alkali metal and aluminum, and double halides of an alkaline earth metal and aluminum into said flux as a minor portion of said flux.

10. The process as set forth in claim 7 wherein said member is a mixture of the double chloride salt, sodium aluminum chloride and sodium chloride and wherein the sodium chloride is present in said flux as a minor portion of said flux.

11. The process as set forth in claim 9 wherein said additional salt is included in said flux in an amount sufficient to result in a flux with a melting point lower than the melting point of said metal.

12. The process as set forth in claim 11 wherein said additional salt is sodium aluminum fluoride.

* * * * *

PO-1050
(5/69)

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,754,897 Dated August 23, 1973

Inventor(s) Leslie Jack Derham, deceased by Michael Gordon Derham, administrat

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

In the heading on page 1, after the line reading "Ridgehill, Henleaze, England" insert:
--Assignee: Rio Tinto Zinc Corporation of America,
Wilmington, Delaware--

Signed and sealed this 16th day of April 1974.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents