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3,537,844

PROCESS FOR PREPARING RARE EARTH METAL AND SILICON ALLOYS

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No Drawing. Filed Oct. 2, 1967, Ser. No. 671,939

Int. Cl. C22b 59/00

U.S. Cl. 75—84

7 Claims

ABSTRACT OF THE DISCLOSURE

Master alloys of rare earth metals and silicon are commonly prepared by reducing ores of the rare earth metals with metal silicides at elevated temperatures to obtain, after separation and solidification of the alloy, a cast master alloy product suitable for use in iron and steel making and the like. The inclusion in the molten alloy product of the reduction reaction of at least 15% by weight of metallic iron results in a master alloy which resists physical disintegration due to light impact and the disintegrating effect of reaction with moist air.

BACKGROUND OF THE INVENTION

The rare earth metals are the 15 elements of the lanthanide series having atomic numbers 57–71 inclusive, although the element yttrium (atomic number 39) is commonly found with and included in this group of metals. The most common alloy of the rare earth metals which contains the metals in the approximate ratio in which they occur in their most common naturally occurring ores is known as misch metal, and intermetallic compounds of rare earth metals and silicon are known as misch metal silicides.

The rare earth metals, and particularly cerium which is the most plentiful of these metals, are valuable alloying additives for improving the metallurgical properties of alloyed and unalloyed steel, cast iron, and other metals. However, as the rare earth metals are extremely reactive, particularly at high temperatures, the direct addition of these metals (for example, as misch metal) to molten iron or steel may result in excessively high loss of the added rare earth metals if improper technique is employed. As a result, the rare earth metals may be added to the molten metal in the form of silicon alloys or silicides containing a relatively small proportion of rare earth metals. Typical master alloys contain from 35 to 50% silicon, up to 15% rare earth metals, and the remainder other metallic impurities.

United States Pat. 3,250,609 discloses a process for preparing substantially phosphorus-free alloys of rare earth metals and silicon in the form of small particles or granules. The process involves reducing phosphate-containing rare earth metal ores with a metal silicide, such as calcium silicide, at an elevated temperature to obtain a molten slag and the desired rare earth metal and silicon master alloy. After separation and solidification of the master alloy product, the metal regulus is allowed to react with atmospheric moisture to convert the metal phosphide contained therein to phosphine. Evolution of phosphine results in the formation of a substantially phosphorus-free granular or powdered alloy product which is recovered. The master alloy product thus obtained is a valuable additive for use in the production of iron and

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steel and other metals. However, under certain circumstances use of granular or powdered alloy additives creates problems for the operator and leads to inefficient use of the master alloy. Accordingly, it is desirable under the latter circumstances to prepare the master alloy in the form of relatively large lumps which resist disintegration during storage and which have sufficient mechanical strength to resist physical disintegration when handled and when dumped into the molten ferrous metal being treated.

One procedure that can be used to form mechanically sturdy lumps of master alloy is to briquet the alloy particles or powder. However, this is a costly procedure since special briquetting machines and auxiliary equipment are required. Moreover, such a procedure involves use of organic binders, such as lignite syrup, sugar, molasses, and the like, to act as a binder for the powdery master alloy. However, the use of such organic binders is undesirable in that they tend to form gas when introduced to iron, steel or other melts thereby creating porosity in the metal product.

SUMMARY OF INVENTION

After an intensive investigation of the problem of making rare earth metal and silicon master alloys that do not disintegrate when handled or stored, we have made the surprising discovery that when metallic iron, as this term is hereinafter defined, is introduced into the molten master alloy the iron will serve as a binder so that when the alloy is cooled and solidified, the resulting solid alloy has a high degree of resistance to physical disintegration during storage and the normal course of handling in transit and in the foundry. Specifically, our improvement in the process of producing master alloys by the reduction of rare earth metal ores with metal silicides at elevated temperatures comprises incorporating in the molten master alloy product of the reduction reaction an amount of metallic iron equal to at least about 15% by weight based on the total of the weight of the rare earth metal ores and the metal silicide initially present plus the weight of said metallic iron.

The metallic iron can be introduced into the molten master alloy either by adding the iron to the initial reaction mixture of rare earth metal ores and metal silicides or by adding the metallic iron directly to the molten master alloy product of the reduction reaction. However, it is important that the iron be added in the form of the metal itself (for example, as scrap iron or steel) rather than in the form of an iron compound (for example, as iron silicide). The amount of the metallic iron that is introduced in the molten alloy must, as noted, be at least about 15% by weight of the total weight of initial reactants plus iron, and it can amount to about 50% by weight of this total weight. In addition, for best results, the reductant is an alkaline earth metal silicide such as calcium silicide, and the reaction is carried out in the presence of a flux selected from the group consisting of the alkaline earth metal and alkali metal chlorides and fluorides.

DETAILED DESCRIPTION

The rare earth metal raw materials to which the process of our invention relates include high grade rare earth metal ores, ore concentrates, and such compounds as the oxides, carbonates, and phosphates of the rare earth metals. The most important naturally occurring ores of

the rare earth metals are monazite and bastnasite, and it is these ores and concentrates thereof that are the principal rare earth raw materials employed in our process. It is known that oxidic rare earth metal ores and compounds can be reduced to the corresponding rare earth metal silicides by reacting them with certain metal silicides such as the alkaline earth metal silicides and aluminum silicide. This known procedure is exemplified by (but is not limited to) the process disclosed in United States Pat. 3,250,609. In the process of this patent the reaction mixture contains sufficient alkaline earth metal silicide to reduce the rare earth metal ores to the corresponding rare earth metal silicides, and advantageously it contains between about 40% and 70% by weight of the metal silicide and between about 30% and 60% of the rare earth raw material. The preferred reducing agent is calcium silicide containing between about 30% and 60% by weight calcium, although other alkaline earth metal silicides may be used. The reduction reaction is carried out at or above the fusion temperature of the rare earth metal silicides and advantageously at a temperature of at least 1400° C. Moreover, the reduction reaction is advantageously carried out in the presence of a flux such as one or more of the alkaline earth metal or alkali metal chlorides or fluorides, the flux combining with the by-products of the reduction reaction to form a slag that is readily separated from the molten rare earth metal and silicon master alloy product of the reaction.

The rare earth metal and silicon master alloy product of the reduction reaction advantageously contains between about 30% and 50% by weight of rare earth metals, and ordinarily is produced in the form of metallic granules or small particles because the alloy tends to crumble or disintegrate into a powder spontaneously in moist air or when subjected to mild impact such as is experienced in the normal handling of these materials. We have found that if metallic iron is incorporated in the molten master alloy product in accordance with the practice of our invention, this iron will serve, when the alloy is cooled and solidified, to prevent the aforesaid physical disintegration of the master alloy.

Our investigations have shown that in order to obtain the desired practical degree of resistance to disintegration, at least about 15% by weight of metallic iron must be introduced into the molten master alloy product, the weight percent of the added iron being based on the total of the weight of the rare earth metal raw material and metal silicides initially present plus the weight of the metallic iron additive. Although the maximum amount of iron incorporated in the rare earth metal and silicide master alloy does not appear to be critical, we have found that the total amount of added iron present advantageously should not exceed about 50% by weight in order to avoid undesirable dilution of the rare earth metal content of the master alloy.

The metallic iron additive can be added to the initial reaction mixture of rare earth metal raw material and metal silicide, or it can be added to the molten master alloy product of the reduction reaction. However, it is important that the iron be added to the reaction mixture or the molten master alloy in metallic form. That is to say, the iron should be in the form of scrap iron or steel, cast iron, and similar forms of metallic iron. The iron should not be added in the form of an iron compound such as iron oxide or iron silicide. The resulting metallic iron-containing rare earth metal and silicon master alloy product is obtained in the form of cast metal which has adequate mechanical strength to resist physical disintegration when struck or subjected to impact in the normal course of handling of these alloys. The cast alloy can be crushed to form lumps of a convenient size for addition to molten steel, iron, or other metals to improve the metallurgical properties of these metals.

The following examples are illustrative but not limitative of the practice of our invention.

Example 1

A reaction mixture comprising 27.5 parts by weight of rare earth metal ore and 34.4 parts by weight of calcium silicide, together with 10 parts by weight of calcium chloride as a flux, were heated to a temperature of about 1500° C. to effect reduction of the ore and to produce a molten rare earth metal and silicon master alloy product and a slag. On completion of the reduction reaction 20 parts by weight of iron in the form of scrap steel were added and thoroughly mixed together with the molten metal. This amount of iron is equal to 24.3% by weight of the total of the weight of the rare earth metal ore and calcium silicide initially present plus the weight of the added iron. The master alloy product was separated from the slag and allowed to solidify in the form of cast ingot of 57.5 parts by weight which contained 30.2% by weight rare earth metal, 28.9% silicon, 40.2% iron, and 0.9% calcium. The slag amounted to 33.5 parts by weight and consisted primarily of unreacted ore, gangue, and the calcium chloride flux. The iron-containing master alloy product had more than sufficient mechanical strength to resist physical disintegration during ordinary storage in open moist air or when struck or when subjected to the repeated impacts encountered in the normal handling of this material.

Example 2

This example illustrates the tendency of rare earth metal master alloys which are prepared by conventional processes to disintegrate into a powder.

A reaction mixture comprising 27 parts by weight of rare earth metal ore concentrate, 33 parts by weight of calcium silicide, together with 15 parts by weight of magnesium fluoride as a flux, were reacted under essentially the same conditions as before to obtain a master alloy product containing 46.2% by weight rare earth metals, 45.8% by weight silicon, 4.0% iron, and 1.3% calcium. The solidified master alloy product disintegrated spontaneously into a mixture of coarse powder and dust.

Example 3

The following example illustrates the ineffectiveness of the addition of iron in the form of an iron compound to prevent physical disintegration of the master alloy product.

A reaction mixture comprising 27 parts by weight of rare earth metal ore concentrates and 33 parts by weight of calcium silicide, together with 30 parts by weight of iron silicide as an additive and 15 parts by weight of calcium fluoride as a flux, were reacted under essentially the same conditions as before to obtain a master alloy product containing 27.2% by weight rare earth metals, 45.9% silicon, 24.8% iron and 1.9% calcium. The solidified master alloy product disintegrated into a mixture of coarse powder and dust when handled.

Example 4

This example illustrates again the effectiveness of the addition of metallic iron to prevent physical disintegration of the master alloy product.

A reaction mixture comprising 27 parts by weight of rare earth metal ore concentrates and 33 parts by weight of calcium silicide, together with 12 parts by weight of metallic iron as an additive and 30 parts by weight of calcium fluoride as a flux, were reacted under essentially the same conditions as before to obtain a master alloy product containing 38.2% by weight rare earth metals, 34.8% silicon, 24.1% iron and 2.6% calcium. The solidified master alloy product was in the form of a cast ingot which did not disintegrate when struck with a hammer or when handled in normal use.

A number of test batches of master alloy containing rare earth metal and silicon were prepared to determine the effect that the addition or non-addition of metallic iron, and the effect that the quantity of iron included in the

master alloy melt, have on the mechanical strength and impact resistance of the master alloy product. The results of these tests are reported in the following table:

TABLE 1

Starting materials	Master Alloy Test No.										
	1	2	3	4	5	6	7	8	9	10	11
Reaction mixture:											
REM ¹ ore, parts by weight	27	27	27	27	27	27	27	27	27	27	27.5
CaSi ₂ , parts by weight	33	33	33	33	33	33	33	33	33	33	34.4
Additive:											
FeSi, parts by weight			6	15	21	30					
Fe metal, parts by weight							4	8	12	16	20.0
Flux, parts by weight	15	15	15	15	15	15	30	30	30	30	10.0
Reaction mix, weight percent	100	100	90.9	80.0	74.1	66.7	93.8	88.2	83.3	78.9	75.7
Additive, weight percent			9.1	20.0	25.9	33.3	6.2	11.8	16.7	21.1	24.3
Master alloy product, yield, parts by weight	38	39.3	45.2	52	58.5		42.6	46.1	49.4	53.8	57.5
Analyses, weight percent:											
REM ¹	46.2	46.2	43.5	36.0	29.5	27.2	43.5	40.5	38.2	35.4	30.2
Si	45.8	47.0	46.5	42.0	47.4	45.9	44.0	38.2	34.8	31.4	28.9
Fe	4.0	4.0	7.7	21.6	20.3	24.8	9.9	18.5	24.1	30.0	40.2
Ca	1.3	2.3	2.0			1.9	2.3	2.5	2.6	3.5	0.9
Impact resistance	(2)	(2)	(2)	(2)	(2)	(2)	(2)	(2)	(2)	(2)	(3)

¹ Rare Earth Metal.
² Poor.
³ Good.

We claim:

1. In the process for producing master alloys of rare earth metals and silicon wherein oxidic ores of the rare earth metals are reduced at elevated temperatures by metal silicides selected from the group consisting of alkaline earth metal silicides and aluminum silicide to obtain a mixture of a molten slag and said master alloy, and wherein said master alloy is thereupon separated and recovered in the form of cast ingot, the improvement which comprises:
- producing master alloy having sufficient mechanical strength to resist physical disintegration during storage in moist air or when struck by incorporating iron in the form of metallic iron in the molten master alloy product of the reduction reaction in an amount equal to at least about 15% by weight of the total of the weight of the rare earth metal ores and metal silicide initially present plus the weight of said metallic iron.
2. The process according to claim 1 in which the amount of metallic iron introduced into the molten alloy is between about 15% and 50% by weight of said total weight.
3. The process according to claim 1 in which the metallic iron is introduced into the initial reaction mixture of rare earth metal ores and metal silicides.
4. The process according to claim 1 in which the metallic iron is introduced into the molten master alloy on completion of the reduction reaction.
5. The process according to claim 1 in which the initial

reaction mixture contains a flux selected from the group consisting of alkali metal and alkaline earth metal chlorides and fluorides.

6. A master alloy of rare earth metals and silicon containing at least about 15% by weight of essentially metallic iron in the elementary form based on the total weight of the rare earth metal ores and metal silicides initially employed to produce said master alloy plus the weight of said metallic iron, said iron being added to the molten master alloy in the form of metallic iron in the elementary form whereby the mechanical strength of the solid master alloy produced is increased.

7. The master alloy according to claim 6 in which the alloy contains between about 15% and 50% by weight essentially metallic iron on the same basis.

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U.S. Cl. X.R.

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