

1

3,295,963

ALLOYS CONTAINING RARE EARTH METALS
Paul Désiré Galvin, Chedde, Haute-Savoie, France, assignor to Pechiney Compagnie de Produits Chimiques et Electrometallurgiques, Paris, France
No Drawing. Filed July 25, 1963, Ser. No. 297,695
Claims priority, application France, July 27, 1962, 905,267; Jan. 15, 1963, 921,435
4 Claims. (Cl. 75-122)

This invention relates to metals and alloys containing rare earth metals and it relates more particularly to an alloy system for the incorporation of rare earth metals into metal and alloy compositions.

Rare earth metals have previously been used as elements of addition in various metal systems to improve the characteristics and the properties thereof, as for example in additions to cast iron for the purpose of improving ductility and also for purposes of producing nodular or spherical graphite cast irons. Additions of rare earth metals have also been made to stainless steels, standard steels and special steels, and particularly steels obtained from scrap iron which are usually contaminated with copper, tin and lead, to improve the properties thereof. Other impurities in steels, such as phosphorus, arsenic, oxygen, nitrogen, and especially sulphur and hydrogen, appear to be effectively fixed by rare earth metals such as are made available for misch metal. For such purposes, use has been made of misch metal containing a mixture of cerium and lanthanum in dominant amounts.

The rare earth metals, such as cerium, lanthanum, neodymium, praseodymium, samarium, gadolinium and yttrium, and misch metal can be prepared in a substantially pure state by igneous electrolysis or by thermal reaction of the metal in the presence of reducing agents such as calcium, but the preparation of such metals in a purified state involves careful and costly procedures. Because of the relatively low specific gravity of misch metal, cerium, etc. by comparison with iron, the misch metal, cerium, etc. rare earth metals appear to gather into pools or puddles at the time when introduced in molten iron, whereby solution or uniform distribution into the molten iron or steel is achieved very slowly and with difficulty, and considerable misch metal, etc. is lost from the surface by combustion or oxidation.

The misch metal, cerium, etc. have also been made available for use as alloys but in which relatively large amounts of silicon and/or calcium are also present to render such alloys unsuitable for use in steel making. Large amounts of calcium are particularly undesirable since calcium tends to promote the formation of undesirable inclusions. Thus it is an object of this invention to provide alloys of misch metal and other alloys of the rare earth metals which are capable of being inexpensively produced, easily and rapidly dissolved and uniformly distributed in desired amounts throughout the bath of the molten ferrous based metal or steel or alloy without the introduction of undesirable amounts of such impurities as calcium, silicon, carbon and the like, and in which the misch metal or rare earth metals can be formulated into an alloy system or mixture from which as much as 85-95% of the misch metal or rare earth metal is retained in the final product and wherein such

2

misch metal or rare earth metals in high concentrations are adapted for use in the production of nodular cast iron with the introduction of a minimum amount of misch metal or rare earth metal thereby to enhance effective control of the amounts of rare earth metal introduced without simultaneously introducing excessive amounts of impurities.

The metal alloy produced in accordance with the practice of this invention for addition to ferrous metals and steels is formulated to contain more than 15% by weight of the rare earth metal or metals but not in excess of 65% by weight; at least 12% by weight silicon but less than 45% by weight silicon; up to 6% by weight of calcium; and up to 65% by weight of iron. Within the weight range described for each of the elements, the materials are formulated to be present in the ratios of 1 part by weight silicon to .8-5 parts by weight of the rare earth metals and 1 part by weight of calcium to 5-150 parts by weight of the rare earth metals and the resulting alloy will have a specific gravity of about 4.

The alloy systems of this invention may be sub-divided in accordance to compositions as follows.

Group 1:

	Percent by wt.
Rare earth metals	40-65
Silicon	At least 25
Silicon	Less than 45
Calcium	1-6
Iron	Up to 4

The weight ratio of rare earth metals to silicon is maintained between 1 to 5, or 1 part by weight silicon to 1-5 parts by weight of rare earth metals, and the weight ratio of rare earth metals to calcium is maintained between 5 to 60 or 1 part by weight calcium to 5-60 parts by weight rare earth metals.

Group 2:

	Percent by wt.
Rare earth metals	40-55
Silicon	25-40
Calcium	Up to 1
Iron	5-15

The ratio of components is maintained within the range of 1 part by weight silicon to 1-5 parts by weight rare earth metals and 1 part by weight of calcium to 20-100 parts by weight of rare earth metals.

Group 3:

	Percent by wt.
Rare earth metals	More than 15
Rare earth metals	Up to 35
Silicon	12-35
Calcium	Up to .5
Iron	30-65

The ratio of rare earth metals to silicon is maintained between .8 and 4 and the ratio of rare earth metals to calcium is maintained within the ratio of 50 and 150.

In the alloy groups represented by the foregoing, the carbon content is maintained to be no greater than 0.05% by weight. The iron component can be substituted in whole or in part by nickel or by chromium. The rare earth metal component can be replaced in whole or in

part by yttrium but in which the weight range of the yttrium in the above compositions may be expanded to within the range of .5-65% by weight while the other components remain substantially the same.

When nickel or chromium is substituted in whole or in part for the iron component in the above groups, the resulting alloy is especially well adapted for use in the introduction of rare earth metals into stainless steels which are adapted to contain a nickel and/or chromium or into nickel or chromium alloys or alloys of nickel and chromium, such as an alloy formed of 80% by weight chromium and 20% by weight nickel.

By comparison with the loss by oxidation of as much as 30% of the rare earth metals introduced in the form of light alloys of the type heretofore produced and which rise to the surface of the slag layer, the rare earth metal alloys embodying the features of this invention are of sufficient density and specific gravity to pass through the slag layer into the molten metal bath for admixture therewith or for solution therewith while the covering slag layer protects the introduced rare earth metals against loss by oxidation. Thus the recovery of the rare earth metals introduced as an additive into the steel or other molten metal is maximized to provide yields in excess of 85% and up to 95% or better.

An important feature of this invention resides in the utilization of the alloys described in the fabrication of nodular cast iron of regular or special steels wherein the reliability of the process depends upon the accuracy with respect to the quantity of the rare earth metals retained by the suitably de-oxidized ferrous metal bath. Such accurate control was not heretofore possible because of the large and uncontrolled losses of rare earth metal components by reason of oxidation at the surface. On the other hand, the rare earth metal alloys embodying the features of this invention are relatively free of loss by oxidation thereby to enable more accurate control in the amount of rare earth metal retained by the molten metal bath and thereby to enhance the procedures for addition and uniform distribution of the rare earth metal component.

Another feature of this invention resides in the use of the rare earth metals alloyed in accordance with the practice of this invention for the manufacture of ordinary and special steels wherein the carbon, silicon and calcium content must be maintained at a minimum. Such usage was not available with rare earth metal systems of the type heretofore produced since it was previously unknown to provide a rare earth metal alloy having at most .06 carbon and moderate amounts, such as between 12-40% by weight silicon, and a low concentration, such as at most 1% by weight calcium, and particularly because of the rapid carburization of the alloy having a relatively low silicon content and containing rare earth metals.

The invention also contemplates the use of the aforesaid alloys as mother alloys in the preparation of a number of variations of metal alloys of the type desired within the limits of specific gravity and for use in welding electrodes. A concept of this invention resides also in rare earth metal alloys containing silicon, carbon and iron within the limits described but in which part or all of the rare earth metal component comprises yttrium with the amount of yttrium being within the range of .5-15% by weight and within the ratio of yttrium to silicon and calcium of 1 part by weight silicon to .5-4 parts by weight yttrium and 1 part by weight of calcium to 2-100 parts by weight yttrium.

The important feature of this invention resides in the use of this alloy in the preparation of nodular cast iron and improved steels.

The following examples are given by way of illustration, but not by way of limitation, of the practice of this invention:

EXAMPLE 1

Rare earth metal alloy

	Percent by wt.
Misch metal	54.1
5 Silicon	34.9
Calcium	4.0
Carbon	0.03
Iron	7.0

The foregoing alloy has a specific gravity of 4.6 and a melting point of 1350° C. The alloy is added to a bath of molten steel which has been suitably de-oxidized and which is covered with a slag layer and in which the steel is of the following composition:

	Percent by wt.
15 Carbon	.03
Silicon	.40
Manganese	.60
Chromium	.19
Nickel	.8
20 Iron	Remainder

The addition is made in 1 part by weight of the alloy per 1860 parts by weight of the steel to form a steel having 0.05% by weight misch metal and such small amounts of other materials as 0.03 carbon, traces of calcium and 0.60 silicon. Such small amounts of carbon, calcium and silicon in the steel could previously have been obtained only by the addition of relatively pure misch metal. The rate of solution and distribution of alloy into the molten steel is much more rapid than that obtained with pure misch metal and the alloy remains continuously covered by the slag layer so that little, if any, is lost by oxidation. Thus the yield of misch metal into the final product corresponds to a value of between 92-94% of the misch metal introduced. This indicates accurate control in the amount of rare earth metals introduced into the final product. The small amount of calcium and silicon that remains appears favorably to influence the quality of the steel.

EXAMPLE 2

Mother alloy

	Percent by wt.
Misch metal	55.5
45 Silicon	37.0
Calcium	4.0
Carbon	.02
Iron	3.0

Addition of the mother alloy of this invention is made to an alloy of the following composition in the amount of 100 parts by weight of the mother alloy per 669 parts by weight of the following alloy:

	Percent by wt.
Magnesium	18
55 Iron	26.5
Silicon	55.5

An initial alloy of the following composition is obtained as a product which is adapted for use in the fabrication of nodular cast iron:

	Percent by wt.
60 Magnesium	16
Misch metal	7
Iron	22
Silicon	54

The retention of the rare earth metal is calculated to be about 97%.

EXAMPLE 3

Alloy composition

	Percent by wt.
70 Yttrium	21.0
Rare earth metals	3.5
Silicon	46.0
Calcium	8.0
Iron	21.4
75 Carbon	0.05

5

The alloy, which has a density of 4.2 and a melting point of 1260° C., is adapted for use in the introduction of yttrium in special steels.

Examples 4-7 are set forth in the following table:

Ex. No.	Percent by weight							Density	Melting Point, ° C.
	Misch metal	Si	Misch, Si	Ca	C	P of As for each	Fe		
4-----	49	36	1.36	0.8	0.03	0.03	12	5	1,300
5-----	55	37	1.47	4	0.02	0.03	3	4.4	1,450
6-----	23	22	1.04	0.2	0.05	0.03	53	7	1,050
7-----	27	18	1.5	0.4	0.06	0.03	54	5.8	1,100

In the Examples 4-7, the following lists the rare earth metals in the alloy and their proportion set forth in percent by weight of the rare earth metal component in the alloy:

	Percent
Cerium -----	47
Lanthanum -----	24.5
Neodymium -----	16.5
Praseodymium -----	6
Total of samarium, gadolinium, and yttrium -----	6

It will be understood that numerous changes may be made in the details of formulation of the alloy and its method of preparation and use without departing from the spirit of the invention, especially as defined in the following claims.

I claim:

1. A rare earth metal alloy having the composition consisting essentially of 40-55% by weight of rare earth metals, 25-40% by weight of silicon, up to 1% by weight of calcium, and 5-15% by weight of iron and in which the silicon and calcium are present in the ratio of one part by weight of silicon to 1-5 parts by weight of the rare

6

earth metal component and one part by weight of calcium to 20-100 parts by weight of the rare earth metal component said alloy having a specific gravity of at least 4.

2. A rare earth metal alloy having the composition consisting essentially of 15-35% by weight of earth metals, 12-35% by weight of silicon, up to 0.5% by weight of calcium and 30-65% by weight of iron and in which the silicon and calcium are present in the ratio of one part by weight of silicon to 0.8-4 parts by weight of the rare earth metal component and one part by weight of calcium to 50-150 parts by weight of the rare earth metal component said alloy having a specific gravity of at least 4.

3. A rare earth metal alloy as claimed in claim 1 in which the rare earth metal component is composed at least in part of yttrium present in an amount within the range of 0.5-15% by weight and in which the ratio of silicon and calcium to yttrium is within the range of 1 part by weight silicon to 0.4-4 parts by weight yttrium and 1 part by weight calcium to 2-100 parts by weight yttrium.

4. A rare earth metal alloy as claimed in claim 2 in which the rare earth metal component is composed at least in part of yttrium present in an amount within the range of 0.5-15% by weight and in which the ratio of silicon and calcium to yttrium is within the range of 1 part by weight silicon to 0.4-4 parts by weight yttrium and 1 part by weight calcium to 2-100 parts by weight yttrium.

References Cited by the Examiner

UNITED STATES PATENTS

2,221,781	11/1940	Critchett et al.	75-58
2,280,284	4/1942	Critchett et al.	75-58
3,055,756	9/1962	Kanter et al.	75-123
3,211,549	10/1965	Kusaka	75-123

DAVID L. RECK, *Primary Examiner*.

R. O. DEAN, *Assistant Examiner*.