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MASTER ALLOYS CONTAINING RARE EARTH METALS

Wilbur T. Bolkcom, Allison Park, and William E. Knapp, Pittsburgh, Pa., assignors to American Metallurgical Products Co., Pittsburgh, Pa., a partnership

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This invention relates to alloys and particularly to an addition alloy for steel and the like metals whereby rare earth metal may be more effectively incorporated into the matrix metal. The use of rare earth metals as an additive to metals matrices has long been known. The use of the rare earth metals has, however, been somewhat limited by reason of the relatively low efficiency upon addition to the base or matrix material. Rare earth metals have generally been added to metal matrices in the form of individual pure rare earth metals or in the form of mixtures such as "Misch Metal" which is a mixture of rare earth metals in the proportions in which they normally occur in ore bodies.

We have found that the effectiveness of the rare earth metals can be markedly increased by combining them with one or more metals of the group zirconium, titanium and hafnium in the form of an addition alloy. We have found that zirconium, titanium and hafnium may be admixed with the rare earth metals in the following proportions:

	Percent
Rare earth metals	25 to 93
One or more of the group zirconium, titanium and hafnium	7 to 75

We have found that the rare earth metals and one or more members of the group zirconium, titanium and hafnium in the above proportions may be and preferably is admixed with a diluent to form an addition alloy which has a high density and other desirable properties set out hereinafter. Preferably the diluent is a mixture of metals having a high density and a relatively low melting point. We have found, for example, that manganese and nickel in the proportion of about 1½ parts of manganese to 1 part nickel has a high density and a low melting point of about 1750° F. The diluent, however, may be iron, manganese, nickel, copper or similar metals either alone or in combination, to which are added a rare earth metal or rare earth metal mixture and one or more of the group zirconium, titanium and hafnium. Broadly, the addition alloy of our invention may have the following general composition:

	Percent
One or more of the group zirconium, titanium and hafnium	2 to 25
Rare earth metal	10 to 30
Diluent (preferably 1½ parts of manganese to 1 part nickel)	Balance

Preferably, however, we limited the composition of our addition alloy to a somewhat narrower range. The preferred alloy has the following composition:

	Percent
One or more of the group zirconium, titanium and hafnium	2 to 12
Rare earth metal	10 to 30
Diluent (preferably 1½ parts of manganese to 1 part nickel)	Balance

We have found that the alloy of our invention gives a much greater efficiency than the ordinary misch metal of commerce, for example, in low alloy steel where the rare earth metals are added for improved impact properties, approximately 1 lb. per ton of ordinary misch metal was required in order to achieve a minimum of 20 lbs. impact level on a V notch charpy test at minus 40° F. with a Brinell hardness of 500. Our new alloy of this invention consisting of 45% manganese, 30% nickel, 20% misch metal and 5% zirconium, required a total alloy addition of 1 lb. per ton or only 0.2 lb. per ton of rare earth metal. In short, we are able to obtain an identical result with the use of only ⅕ as much rare earth metal as has been required in the past.

In stainless steel ordinary unprotected misch metal gives a recovery of only approximately 50% of the rare earth elements, whereas the use of the present alloy permits recovery between 80 to 90%. Several stainless steel heats using misch metal in one series and the alloy of this invention (consisting of 45% manganese, 30% nickel, 20% misch metal and 5% zirconium) in the other were prepared and the recovery or rare earth metals determined. The results of this study are set out in Table 1 herein below:

Table I

Grade	Misch Metal Addition, percent	Recovery	Percent Recovery	Addition Alloy of this invention	Recovery	Percent Recovery
304	.05	.02	40	.05	.043	86
310	.15	.06	40	.15	.12	80
316	.10	.03	30	.10	.09	90

The present alloy has the additional advantage that the titanium, zirconium or hafnium, as the case may be, appears to flux out residual dirt which sometimes occurs when rare earth metals are used in steel under unfavorable conditions and which has been a deterrent to the use of rare earth metals.

The effectiveness of rare earth metal additions to a base steel is perhaps most strikingly illustrated by a comparison of V notch charpy tests. A series of samples of a steel having 1.48% manganese, .28% carbon, .35% silicon, .015% sulphur, .011% phosphorus, .63% chromium, .58% molybdenum, .11% nickel and .002% boron were tested both with the addition of our new alloy, standard rare earth misch metal, and without the addition of any rare earth metal at various Brinell hardness level. The results are given in Table 2.

Table 2

V NOTCH CHARPIES FT. LBS. MINUS 40° F.

Brinell Number	No RE Metal Added	.01% RE Metal Added as (An alloy of 45% Mn, 30% Ni, 20% Rare Earth, 5% Zr)	.01% RE Metal Added as Misch Metal (.0025% Zr added separately)
500	6	23	8
400	11	28	14
300	17	47	28

We have found that the addition alloy of the present invention can be made most successfully by incorporating the titanium, zirconium or hafnium in the form of relatively pure metal such as sponge metal or scrap rather than in the form of their ferro alloys. We have found that the usual ferro titanium, ferro zirconium or nickel-silicon-titanium or nickel-silicon-zirconium form high melting intermetallic components when added to the rare earth metals, so that the recovery is relatively low

and is extremely variable. For this reason and other reasons which are apparent from the foregoing disclosure the separate addition of rare earth metals and alloys of zirconium, titanium or hafnium to the molten bath will not produce the unusual advantages characteristic of the addition alloy of our invention.

When we speak of rare earth metals in this application we have reference to that group of metals having atomic members between 58 and 71 of the periodic table. Misch metal is the term commonly used in the industry for a mixture of rare earth metals produced by reduction from naturally occurring rare earth ores and contains an admixture of various rare earth metals in the approximate proportions in which they occur in the ore. The most common rare earth metals are cerium, lanthanum, neodymium and praseodymium and these metals are the principal constituents of misch metal.

We have set out certain preferred compositions of our alloy and have described a preferred method of making the same. It will be understood, however, that the alloy of this invention may be otherwise made and embodied within the scope of the following claims.

We claim:

1. An addition alloy for incorporating rare earth metals into a metal bath consisting essentially of a mixture of about 25% to 93% rare earth metals and about 7% to 75% of one or more metals selected from the group zirconium, titanium and hafnium all incorporated in a sufficient amount of metal diluent of high density compatible with the metal bath to form a mixture whose density is greater than the bath.

2. An addition alloy for incorporating rare earth metals into a metal bath consisting essentially of a mixture of about 45% to 93% rare earth metals and about 7% to 55% of one or more metals selected from the group zirconium, titanium and hafnium all incorporated in a sufficient amount of metal diluent of high density compatible with the metal bath to form a mixture whose density is greater than the bath.

3. An addition alloy for incorporating rare earth metals into a metal bath consisting essentially of about 10% to 30% rare earth metals, about 2% to 25% of one or more metals selected from the group zirconium, titanium and hafnium and the balance a metal diluent of high density compatible with the metal bath.

4. An addition alloy for incorporating rare earth metals into a metal bath consisting essentially of about 10% to 30% rare earth metals, about 2% to 10% of one or more metals selected from the group zirconium, titanium and hafnium and the balance a metal diluent of high density compatible with the metal bath.

5. An addition alloy for incorporating rare earth metals into a metal bath consisting essentially of about 10% to 30% rare earth metals, about 2% to 25% of one or more metals selected from the group zirconium, titanium and hafnium and the balance a metal diluent selected from the group manganese, nickel, copper and iron and mixtures thereof.

6. An addition alloy for incorporating rare earth metals into a metal bath consisting essentially of about 10% to 30% rare earth metals, about 2% to 10% of one or more metals selected from the group zirconium, titanium and hafnium and the balance a metal diluent selected from the group manganese, nickel, copper and iron and mixtures thereof.

7. An addition alloy for incorporating rare earth metals into a metal bath consisting essentially of about 10% to 30% rare earth metals, about 2% to 25% of one or more metals selected from the group zirconium, titanium and hafnium and the balance made up of manganese and nickel in the proportions of 1½ parts of manganese to 1 part of nickel.

8. An addition alloy for incorporating rare earth metals into a metal bath consisting essentially of about 10% to 30% rare earth metals, about 2% to 12% of one or more metals selected from the group zirconium, titanium and hafnium and the balance made up of manganese and nickel in the proportions of about 1½ parts of manganese to 1 part of nickel.

9. An addition alloy for incorporating rare earth metals into a metal bath consisting essentially of about 20% misch metal, 5% zirconium, 30% nickel and 45% manganese.

10. An addition alloy for incorporating rare earth metals into a metal bath consisting essentially of about 20% misch metal, 5% titanium, 30% nickel and 45% manganese.

11. The method of adding rare earth metals to a metal bath comprising the steps of forming a molten bath of the metal to be treated, adding to the bath an alloy consisting essentially of about 25% to 93% rare earth metals and about 7% to 75% of one or more metals selected from the group zirconium, titanium and hafnium.

12. The method of adding rare earth metals to a metal bath comprising the steps of forming a molten bath of the metal to be treated, adding to the bath an admixture consisting essentially of about 10% to 30% rare earth metals, about 2% to 25% of one or more metals selected from the group zirconium, titanium and hafnium and the balance metal diluent of high density compatible with the metal bath.

13. An addition alloy for incorporating rare earth metals into a metal bath consisting essentially of about 10% to 30% rare earth metals, about 2% to 25% of one or more metals seletced from the group zirconium, titanium and hafnium and the balance iron.

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