Oct. 20, 1953 H. E. DUNN ET AL 2,656,269

MAGNESIUM ALLOYS AND METHOD OF MAKING THE SAME

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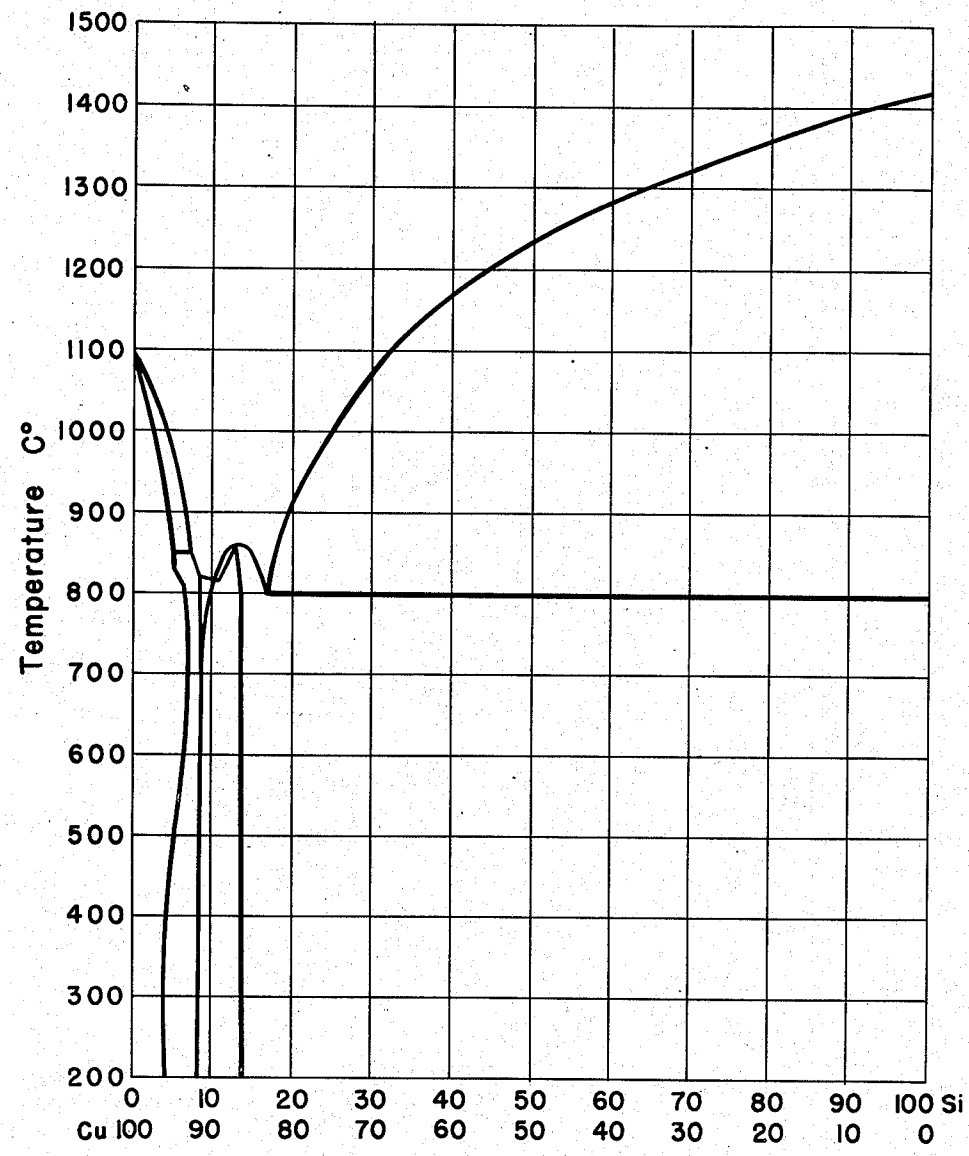


Fig. 1

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MAGNESIUM ALLOYS AND METHOD OF MAKING THE SAME

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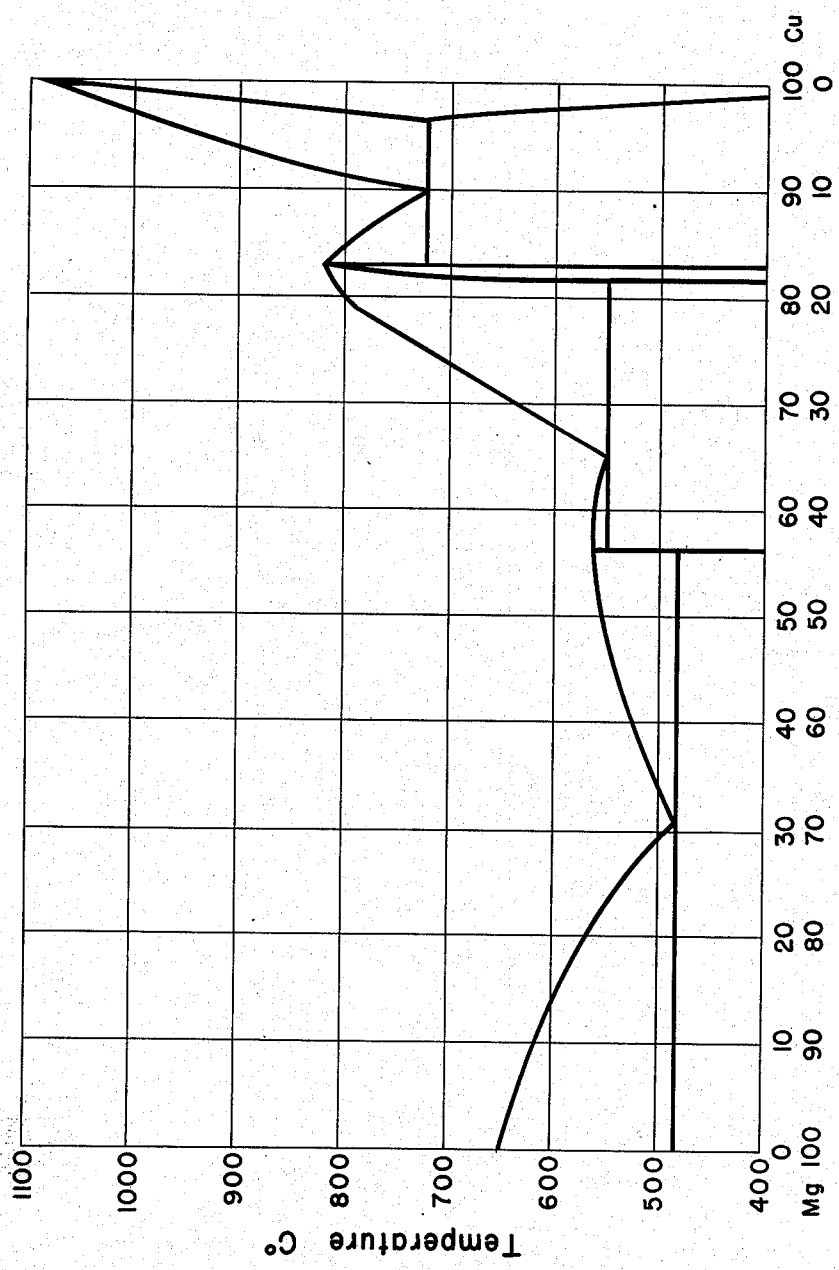


Fig.2

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MAGNESIUM ALLOYS AND METHOD OF MAKING THE SAME

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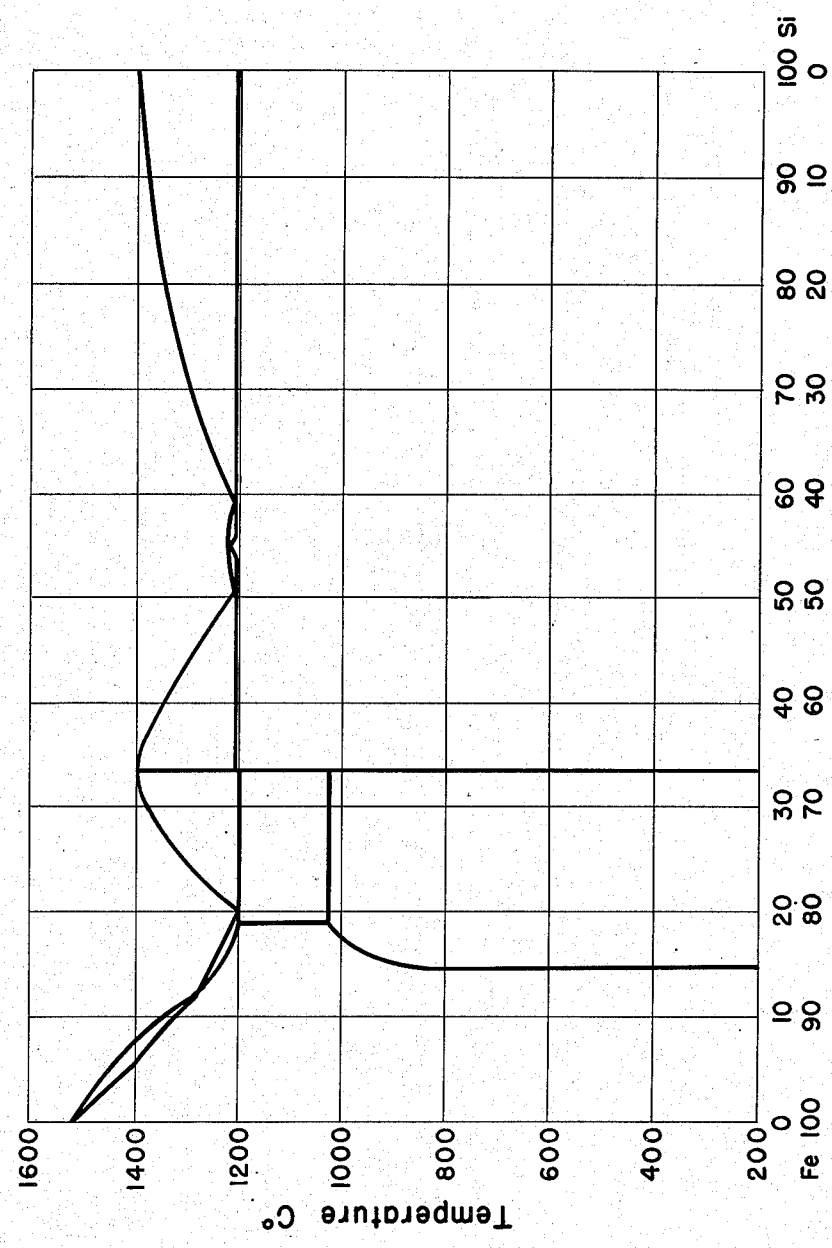


Fig. 3

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UNITED STATES PATENT OFFICE

2,656,269

MAGNESIUM ALLOYS AND METHOD OF MAKING THE SAME

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Application March 8, 1951, Serial No. 214,462

13 Claims. (Cl. 75—135)

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This invention relates to magnesium alloys and to a method of making the same. More specifically, the alloys contain magnesium, copper and silicon, or magnesium, copper, silicon and iron. These alloys are useful in the treatment of cast iron or steel. The final alloys suitable for treating cast iron or steel are generally referred to herein as "treatment alloys" in order to distinguish them from other preliminary alloys used in making the "treatment alloys."

The compositions of typical "treatment alloys" are given in the following Table I, it being understood that these are merely typical examples and that the proportions of the ingredients can be varied quite widely to suit particular conditions.

TABLE I

Type	(1)	(2)	(3)	(4)	(5)	(6)	(7)
Percent Mg	6	6	9	9	9	13	8
Percent Cu	6	7	12	10	10	9	13
Percent Si	34	20	34	24	21	30	27
Percent Fe	54	67	45	57	60	48	52
Ratio Cu/Mg	1.0	1.16	1.33	1.1	1.1	0.7	1.6
Ratio Si/Mg	5.67	3.3	3.8	2.67	2.3	2.3	3.4

The method heretofore employed in making these "treatment alloys" has been to melt a mixture of magnesium metal, copper scrap, silicon metal, and iron punchings and/or ferrosilicon in a covered fuel-fired graphite crucible. Direct melting of the metals in this manner results in a considerable loss amounting in some cases to as much as 50% of the magnesium by volatilization and oxidation. The melting points of the metals involved are as shown in the following Table II:

TABLE II

Metal	Melting Point, ° C.	Boiling Point, ° C.
Magnesium	645	1,097
Copper	1,083	
Silicon	1,420	
Iron	1,535	

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Since the melting points of the "treatment alloys" range in general from 1200 to 1280° C., it is readily seen why there is a considerable loss of magnesium in forming the "treatment alloys" by the direct melting of the metals as heretofore carried out. We have discovered a method whereby this high loss of magnesium can be for the most part and in some cases entirely avoided in forming the "treatment alloys" and have produced alloys not heretofore known.

In the accompanying drawings:

Figure 1 is a phase diagram of copper-silicon alloys;

Figure 2 is a phase diagram of copper-magnesium alloys; and

Figure 3 is a phase diagram of iron-silicon alloys.

In carrying out our preferred method we form a copper-silicon alloy, this alloy being generally referred to hereinafter as "alloy A." This copper-silicon "alloy A" preferably contains copper and silicon in the eutectic proportions of substantially 83.5% copper and 16.5% silicon, which has a melting point of 802° C. We form a magnesium-copper alloy which is hereinafter generally designated as "alloy B." This magnesium-copper "alloy B" preferably contains magnesium and copper in substantially the eutectic proportions of 69.3% magnesium and 30.7% copper having a melting point of 485° C. The eutectic proportions for "alloy A" and "alloy B" are preferred, but, of course, other than the eutectic proportions of the metals can be employed in accordance with the principles herein disclosed.

Having formed the copper-silicon "alloy A" and the magnesium-copper "alloy B," we alloy these two alloys together to produce a ternary magnesium-copper-silicon alloy which is hereinafter generally referred to as "ternary master alloy." This "ternary master alloy" is then alloyed with ferrosilicon to form the "treatment alloy," which may be added to a cast iron or steel bath.

By forming the copper-silicon "alloy A" we provide a copper and silicon containing alloy

having a melting point lower than the melting point of either copper or silicon. Accordingly, magnesium can be alloyed with "alloy A" at a lower temperature than it could be alloyed with either copper or silicon alone or incorporated into a "treatment alloy" by the prior art method. In making the magnesium-copper "alloy B" we provide a magnesium and copper containing alloy having a melting point lower than the melting point of either copper or magnesium. Accordingly, we can alloy solid "alloy A" with molten "alloy B" at a lower temperature initially than we could alloy "alloy A" with molten magnesium alone and we thereby reduce losses of magnesium by volatilization. In addition, the boiling point of the magnesium-copper "alloy B" is higher than the boiling point of magnesium alone so that "alloy A" and "alloy B" can be alloyed together without any substantial loss of magnesium. Of course, the vapor pressure of magnesium alone or when in these magnesium containing "master alloys" is appreciable at temperatures below its boiling point so that there is a tendency to volatilize at these lower temperatures. However, experience has shown that such volatilization does not result in losses of commercial significance and hence it is important, as pointed out herein, to give primary consideration to the boiling point and to avoid closely approaching or exceeding this temperature.

The "ternary master alloy" of magnesium, copper and silicon has a higher melting point and a higher boiling point than the melting points and boiling points of either "alloy A" or "alloy B." Accordingly, the addition of the "ternary master alloy" to molten ferrosilicon in forming the "treatment alloy" results in less loss of magnesium than would be the case were either "alloy A" or "alloy B" added to molten ferrosilicon.

Instead of making "alloy A" by melting silicon metal and copper metal we can replace a part or all of the silicon metal by ferrosilicon, thereby producing an "alloy A" containing silicon, copper and iron in which the iron preferably is relatively low in amount. When this silicon-copper-iron containing "alloy A" is alloyed with the magnesium-copper "alloy B," it results in a quaternary magnesium-copper-silicon-iron alloy which is referred to hereinafter generally as "quaternary master alloy." This "quaternary master alloy" is then alloyed with ferrosilicon to produce the "treatment alloy."

The following examples are illustrative of my invention:

Example 1

Step 1.—30 parts of copper scrap are melted with 6 parts of crushed silicon metal (these are substantially the eutectic proportions of 83.5% copper and 16.5% silicon). The bath is stirred with an iron bar and is either granulated and dried or is cast into an iron chill mold and is then crushed to ½'' by down size. This alloy, which will be designated "alloy A" contains 83.5% copper and 16.5% silicon and has a melting point of about 800° C.

Step 2.—70 parts of magnesium ingot and sufficient flux made up of 60% $MgCl_2$ and 40% NaCl to cover the bath when formed are placed in a covered graphite crucible and the mixture is heated to a temperature of about 670° C. which melts the magnesium and the flux. 30 parts of fine copper turnings are then stirred into the bath. This results in an alloy hereinafter referred to as "alloy B" containing 70% magnesium and 30% copper and having a melting point of about 485° C.

Step 3.—While holding "alloy B" molten, the 36 parts of the copper-silicon "alloy A" are stirred into the 100 parts of the magnesium-copper "alloy B" and as soon as it is dissolved the melt is cast into iron chill molds and crushed to 2'' by down size to give 136 parts of magnesium-copper-silicon alloy, hereinafter referred to as "ternary master alloy" and containing 51.4% magnesium, 44.2% copper and 4.4% silicon.

Step 4.—Molten 37½% ferrosilicon in an amount of 864 parts by weight and at a temperature of 1370 to 1430° C. is placed in a ladle and the 136 parts of the "ternary master alloy" is added as rapidly as possible to the bath of ferrosilicon, preferably in a period of 5 minutes or less, while puddling the surface with an iron bar to submerge lumps of cold alloy. The melt is then cast quickly into an iron chill mold, resulting in a "treatment alloy" having the composition of type 1 alloy shown in Table I.

Even in the final alloying stage of step 4, the operation is not violent but is accompanied by a vigorous boil and some surface burning of magnesium, although much less than when magnesium ingot is added to ferrosilicon or to ferrosilicon in which the copper has been previously dissolved or when all of the metals magnesium, copper, silicon and iron are melted directly.

Example 2

Step 1.—This step is exactly the same as step 1 of Example 1.

Step 2.—This step is exactly the same as step 2 of Example 1.

Step 3.—This step is the same as step 3 of Example 1 except that the silicon content of the copper-silicon alloy is increased to 36.5% Si by adding more silicon metal to the molten copper-silicon alloy, and 54.7 parts of the copper-silicon alloy are stirred into 45.3 parts of the step 2 magnesium-copper alloy, thereby forming a "ternary master alloy" containing 31.69% magnesium, 44.57% copper, and 20% silicon, and having a melting point of 1093° C.

Step 4.—This step is the same as step 4 of Example 1 except that 236 parts of the "ternary master alloy" are added to 764 parts of the molten ferrosilicon containing 37½% silicon. Because of the relatively large amount of "ternary master alloy" added to the molten ferrosilicon, it is necessary to apply heat in order to dissolve all of it so as to form the "treatment alloy."

In carrying out step 4 of this example the operation is less vigorous than in carrying out step 4 of Example 1 and surface burning and flaming of volatilized magnesium is negligible.

Example 3

Step 1.—Instead of using steps 1, 2 and 3 in forming the "ternary master alloy" as in Example 1, the "ternary master alloy" is made by direct melting in a covered graphite crucible of a mixture of magnesium ingot, copper scrap and silicon metal in proportions to produce the "ternary master alloy" of Example 1. The recovery of magnesium by this direct melting method is well over 90% and approximately 95%, as compared with the approximately 100% recovery of magnesium in forming the "ternary master alloy" by the sequential step method of Example 1.

Step 2.—The "ternary master alloy" is alloyed

with ferrosilicon in the same manner as in step 4 of Example 1.

The "ternary master alloys," whether produced by the sequential step methods of Examples 1 and 2 or by the direct melting method of Example 3, may contain from 10 to 55% magnesium, from 12 to 50% copper and from 4 to 60% silicon. The preferred proportions are from 10 to 40% magnesium, from 20 to 50% copper and from 10 to 40% silicon.

The following Table III gives further examples of various suitable magnesium-copper-silicon "ternary master alloys":

TABLE III

Ternary Master Alloy	Composition Ternary Master Alloys			Ratio		Parts Ternary Master Alloy	Parts FeSi	Grade FeSi, Percent Si	Type Treatment Alloy (Table I)
	Percent Mg	Percent Cu	Percent Si	Cu/Mg	Si/Mg				
1	51.4	44.2	4.4	0.8	0.08	13.6	86.4	37.5	1
						16.0	84.0	20.0	2
2	51.4	34.5	14.5	0.7	0.3	26.0	74.0	20.0	3
3	45.0	48.0	7.0	1.1	0.2	15.0	85.0	38.0	1
						22.7	77.3	36.5	3
						15.0	85.0	20.0	2
						18.7	81.3	35.0	1
4	37.0	41.0	22.0	1.1	0.6	17.1	82.9	20.0	2
						28.2	71.8	36.5	3
						22.0	78.0	32.7	1
5	32.0	36.0	32.0	1.1	1.0	33.0	67.0	32.3	3
						19.4	80.6	20.0	2
						33.3	66.7	20.0	4
						24.5	75.5	30.5	1
6	29.0	32.0	39.0	1.1	1.3	36.0	64.0	28.5	3
						21.9	78.1	20.0	2
						37.5	62.5	20.0	4
						26.4	73.6	20.0	1
7	24.0	26.5	49.5	1.1	2.1	45.3	54.7	20.0	3
						26.9	73.1	20.0	1
8	23.0	26.0	51.0	1.1	2.2	46.2	53.8	20.0	3
						30.4	69.6	20.0	1
9	21.0	23.0	56.0	1.1	2.7	52.2	47.8	20.0	3
10	12.0	25.0	63.0	2.1	5.3	48.0	52.0	9.6	1
11	21.8	14.4	63.8	0.7	2.9	48.3	51.7	19.4	3

Table III also shows the parts of "ternary master alloy" and the parts and grade of ferrosilicon which are to be alloyed with the "ternary master alloy" to produce the various types of "treatment alloy" referred to in Table I.

Instead of using magnesium-copper-silicon "ternary master alloys" we may use magnesium-copper-silicon-iron "quaternary master alloys" containing a relatively low percentage of iron. These "quaternary master alloys" may be made by introducing ferrosilicon (preferably 60% silicon grade melting at 1250° C. or 50% silicon grade melting at 1260° C.) into magnesium-copper-silicon "ternary alloys." It may also be made by alloying copper with ferrosilicon to produce a copper-silicon-iron alloy and thereafter alloying such alloy with an alloy of magnesium and copper. Iron does not alloy readily with magnesium. However, a small amount of iron can be introduced into the "master alloy" and is advantageous in that it increases the density of the "master alloy" while (if limited) keeping the melting point of the "master alloy" adequately below the boiling point of magnesium. The amount of iron in the "master alloys" should be less than 20% and the preferred amount is between 3 and 15%.

The following Examples 4 and 5 illustrate the method of making magnesium-copper-silicon-iron "quaternary master alloys" and the making of "treatment alloys" by alloying the "quaternary master alloys" with ferrosilicon.

Example 4

Step 1.—6.6 parts of copper and 1.2 parts of silicon metal are melted to form 7.8 parts of a copper-silicon alloy containing 83.5% copper and 16.5% silicon. The alloy is granulated in water and dried.

Step 2.—6 parts of magnesium is melted and 7.8 parts of step 1 alloy (copper-silicon) are fed into the molten magnesium bath, the temperature of the bath being increased only to the extent required for solution. When solution is complete, 4.8 parts of 60% ferrosilicon are fed to the bath to produce 18.6 parts of "quaternary master alloy" containing 32% magnesium, 35% copper, 22% silicon and 11% iron and having a melting point of 1025° C.

Step 3.—While the step 2 "master alloy" is held molten, 81.4 parts of molten 20% ferrosilicon carrying as little superheat as possible is poured into it. The resultant "treatment alloy" contains 6% magnesium, 6.5% copper, 19.4% silicon and 67.2% iron.

Example 5

Step 1.—80 parts of copper are mixed with 20 parts of ferrosilicon containing 50% silicon and the mixture is melted, thereby producing "alloy A" containing 80% copper, 10% silicon and 10% iron.

Step 2.—An alloy containing 70% magnesium and 30% copper is made according to step 2 of Example 1, this alloy being designated "alloy B."

Step 3.—While holding 60 parts of "alloy B" molten, 40 parts of "alloy A" are stirred into it in the manner described in step 3 of Example 1. This results in a "quaternary master alloy" containing 42% magnesium, 50% copper, 4% silicon and 4% iron.

Step 4.—16 parts of the "quaternary master alloy" from step 3 are alloyed with 84 parts ferrosilicon (25% Si) in the manner given in step 4 of Example 1, thereby producing a "treatment alloy" containing 6% magnesium, 8% copper, 22% silicon, and 64% iron.

Examples of other magnesium-copper-silicon-iron "quaternary master alloys" which can be used in making "treatment alloys" by alloying the "quaternary master alloys" with ferrosilicon are given in the following Table IV:

TABLE IV

Quaternary Master Alloy	Composition Quaternary Master Alloys				Ratio		Parts Quaternary Master Alloy	Parts FeSi	Grade FeSi, Percent Si	Type Treatment Alloy (Table I)
	Percent Mg	Percent Cu	Percent Si	Percent Fe	Cu/Mg	Si/Mg				
1	32.0	44.6	20.0	3.4	1.4	0.63	22.4	77.6	20.0	
2	32.0	35.0	22.0	11.0	1.1	0.69	18.6	81.4	20.0	2
							28.0	72.0	25.0	4
							28.0	72.0	20.0	5
3	33.0	36.1	22.7	8.2	1.1	0.69	19.4	80.6	20.0	2
							29.5	70.5	20.0	5

This table also gives the parts of "quaternary master alloy" and the parts and grade of ferrosilicon which are to be alloyed in producing the "treatment alloys" of the types referred to in Table I.

In place of using straight ferrosilicon for alloying with the "ternary" or "quaternary master alloys" we may use ferrosilicon containing a small amount of copper with advantage. Addition of copper to ferrosilicon lowers the melting point of the ferrosilicon and thus decreases the loss of magnesium in alloying the "master alloy" with the ferrosilicon containing copper. However, the amount of copper allowable in cast iron or steel is limited and therefore the amount of copper in the "treatment alloys" is limited. Copper in the "master alloy" protects the magnesium by raising the boiling point of the "master alloy." Accordingly, a certain amount of copper must be present in the "master alloy" and since the total of the copper in the "master alloy" and the copper in the ferrosilicon is limited, it follows that the amount of copper in the ferrosilicon is limited even though it might be advantageous to increase this amount because of its effect in lowering the melting point of the ferrosilicon. In order to protect the magnesium of the "master alloy" we prefer to use copper in the "master alloy" in such amount that the ratio of the copper to the magnesium is from 0.4:1 to 2:1. With copper in the "master alloy" within the ratio stated, the amount of copper in the ferrosilicon ordinarily should not be in excess of 20% of the silicon content of the ferrosilicon.

As previously stated, the method heretofore employed in making magnesium alloys was to melt the magnesium and all of the other alloying ingredients directly in a covered fuel-fired graphite crucible in order to guard against loss of magnesium. From the standpoint of fuel economy, fuel-fired crucibles are much less efficient than electric furnaces. As shown in Tables III and IV, the "treatment alloys" are made from about 50 to 85% of ferrosilicon and 50 to 15% of "master alloy." Since by our method the ferrosilicon constitutes a large percent of the total weight of the "treatment alloys" and since the ferrosilicon can be made in electric furnaces having high current efficiency, the heating cost of making alloys according to our method is greatly reduced as compared with prior methods in which the entire weight of the ingredients used in making the "treatment alloy" was necessarily melted in covered crucibles in order to protect the magnesium from loss. This saving in heating cost is in addition to the savings effected because of lower losses of magnesium.

The invention is not limited to the preferred embodiments which have been given merely for purposes of illustration but may be otherwise embodied or practiced within the scope of the following claims.

We claim:

1. The method of making an alloy containing magnesium, copper, silicon and iron, which comprises alloying magnesium with copper and silicon to form an alloy containing magnesium, copper and silicon and having a melting point higher than the melting point of magnesium, and thereafter alloying said alloy with ferrosilicon.

2. The method of making an alloy containing magnesium, copper, silicon and iron, which comprises alloying magnesium with copper and silicon to form an alloy containing from 10 to 55% magnesium, from 12 to 50% copper and from 4 to 60% silicon and having a melting point higher than the melting point of magnesium, and thereafter alloying said alloy with ferrosilicon.

3. The method of making an alloy containing magnesium, copper, silicon and iron, which comprises alloying magnesium with copper and silicon to form an alloy containing from 10 to 40% magnesium, from 12 to 50% copper and from 10 to 40% silicon and having a melting point higher than the melting point of magnesium, and thereafter alloying said alloy with ferrosilicon.

4. The method of making an alloy containing magnesium, copper, silicon and iron, which comprises alloying magnesium with copper, silicon, and a substantial amount but less than 20% of iron to form an alloy containing magnesium, copper, silicon and iron and having a melting point higher than the melting point of magnesium, and thereafter alloying said alloy with ferrosilicon.

5. The method of making an alloy containing magnesium, copper, silicon and iron, which comprises alloying magnesium with copper, silicon, and from 3 to 15% of iron to form an alloy containing magnesium, copper, silicon and iron and having a melting point higher than the melting point of magnesium, and thereafter alloying said alloy with ferrosilicon.

6. The method of making an alloy containing magnesium, copper and silicon, which comprises alloying copper and silicon to form a copper-silicon alloy, alloying copper and magnesium to form a copper-magnesium alloy, and alloying said two alloys.

7. The method of making an alloy containing magnesium, copper and silicon, which comprises alloying copper and silicon to form a copper-silicon alloy, alloying copper and magnesium to form a copper-magnesium alloy, and adding said copper-silicon alloy to a molten bath of said copper-magnesium alloy.

8. The method of making an alloy containing magnesium, copper and silicon, which comprises melting a mixture of copper and silicon in such proportions that the resulting copper-silicon alloy has a melting point substantially lower than the melting point of copper, melting a mixture of magnesium and copper in such proportions that the resulting magnesium-copper alloy has a melt-

ing point substantially lower than the melting point of magnesium, and alloying said alloys together.

9. The method of making an alloy containing magnesium, copper and silicon, which comprises melting a mixture of copper and silicon in substantially eutectic proportions to form a copper-silicon alloy, melting a mixture of magnesium and copper in substantially eutectic proportions to form a magnesium-copper alloy, and alloying said alloys together.

10. The method of making an alloy containing magnesium, copper, silicon and iron, which comprises melting a mixture of copper and silicon in such proportions that the resulting copper-silicon alloy has a melting point substantially lower than the melting point of copper, melting a mixture of magnesium and copper in such proportions that the resulting magnesium-copper alloy has a melting point substantially lower than the melting point of magnesium, alloying said alloys together to form a "master alloy" containing magnesium, copper and silicon, and alloying said "master alloy" with ferrosilicon.

11. The method of making an alloy containing magnesium, copper, silicon and iron, which comprises alloying copper and ferrosilicon to form a copper-silicon-iron alloy, alloying copper and magnesium to form a copper-magnesium alloy, and alloying said alloys together.

12. The method of making an alloy containing magnesium, copper, silicon and iron, which comprises alloying copper and ferrosilicon in such proportions that the resulting copper-silicon-iron alloy has a melting point substantially lower than the melting point of copper, alloying copper and magnesium in such proportions that the resulting copper-magnesium alloy has a melting point substantially lower than the melting point of magnesium, and alloying said alloys together.

13. The method of making an iron-rich alloy containing magnesium, copper, silicon and iron, which comprises melting a mixture of copper and ferrosilicon, in substantially eutectic proportions to form a copper-rich silicon-iron alloy, melting a mixture of magnesium and copper in substantially eutectic proportions to form a magnesium-rich copper alloy, dissolving the copper-rich alloy in the molten magnesium-rich alloy, dissolving copper in molten substantially eutectic ferrosilicon to form an iron-rich silicon-copper alloy, and mixing the two molten alloys in the desired proportions to form an iron-rich quaternary alloy of iron-silicon-copper-magnesium.

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