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MAGNESIUM ALLOY

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This invention relates to an alloy comprising pure magnesium as the predominating component.

Light metals are of great interest and are needed not only in aircraft construction but also in many fields where their light weight makes them attractive for special uses, provided the other properties such as resistance to corrosion, mechanical strength, and other physical properties satisfy the particular needs in question. It is essential to keep the alloy as light as possible and at the same time achieve satisfactory physical properties without upsetting the equilibrium between the ingredients which enter into a finally acceptable formula.

Magnesium is abundant in nature and belongs to the group of raw materials which are plentiful in the outer shells of the earth. With its low density of 1.74 it is available for many purposes where such a light metal is desirable. In accordance with my invention I am able to utilize the lightness of magnesium by achieving chemical and physical properties in a magnesium alloy without materially departing from the low density of magnesium. In doing this, I am able to bestow upon the magnesium alloy the physical, chemical and physico-chemical properties which magnesium itself does not possess. I am able to accomplish this, as mentioned above, without departing substantially from the density of the prevailing element in the alloy, i. e., magnesium.

Before proceeding with the description of the present invention the following table of some of the pertinent elements and some of their properties may be noted:

TABLE I

Element	Density	Hardness	D/H	Melting Point (MP), °C.	Boiling Point (BP), °C.	Ratio, BP/MP	Modulas of Elasticity (p. s. i. 10^{-6})
Beryllium	1.85	6.9	.27	1,350	1,550	1.13	43.0
Boron	2.3	9.5	.24	2,300	2,500	1.1	
Magnesium	1.74	2	.87	651	1,110	1.7	6.5
Aluminum	2.7	2.9		659	2,450	3.7	
Silicon	2.4	7.0	.34	1,420	2,600	1.8	16.4
Calcium	1.55	1.5	1.03	845	1,240	1.47	8.5
Antimony	6.68	3.0	2.2	650	1,380	2.2	13.3

From this table it will be seen that magnesium has a desirably low density. However, it has an undesirably low melting point and low boiling points, as well as a low ratio of boiling point to melting point. In addition, it has a relatively low modulus of elasticity.

Aluminum is desirable for many purposes, particularly aircraft needs and can be alloyed in desirable ways. However, notwithstanding the properties that can be achieved by alloying, it is not possible to go very much below its density of 2.7. In instances where a lighter alloy is desirable aluminum cannot be used as the entire base.

In accordance with my invention, I obtain an alloy having a density not appreciably different from the density of magnesium, but having marked improvements over magnesium in terms of physical and chemical properties, which overcome the inherent weaknesses of magnesium as indicated in the above table.

The magnesium alloy of my invention comprises four essential components: (1) pure magnesium as the primary component, a minor part of which may be replaced by aluminum in some instances if the increase density of the alloy for the wanted purpose is not objectionable; (2) a small amount of an interstitial metal; (3) a small but requisite amount of a filler for the interstices of the interstitial metal selected from the group consisting of silicon or boron or both, preferably silicon in most instances, and in some instances antimony alone or in admixture with silicon and/or boron; and (4) a small but requisite amount of an auxiliary metal selected from the group consisting of calcium, beryllium, chromium, cobalt, nickel, manganese and yttrium, which facilitates the incorporation of the silicon or other third component.

The term "interstitial" is used to refer to an element capable of forming a compound with metalloid elements in which the metalloid atoms occupy the interstices between the atoms of the metal lattice.

The following is a brief discussion of each of the four components:

(1) The properties of the pure magnesium, or magnesium a minor portion of which has been replaced by aluminum, are well known together with the manner in which they are made and can be utilized as the primary component of my alloy. These need not be further explained. The magnesium, and aluminum if it is used, must be pure and have boiling points of 1110° C. and 2450° C., respectively.

(2) The interstitial metals which are listed as the second component of my alloy, and their properties are as follows:

TABLE II

	Density (D)	Hardness (H)	D/H	Melting Point (MP), °C.	Boiling Point (BP), °C.	BP/MP	Modulus of Elasticity (p. s. i. 10^{-6})
Titanium	4.5	7	.64	1,800	3,000	1.7	16.8
Zirconium	6.4	7.8	.82	1,900	2,900	1.5	11.0
Hafnium	13.3	7.9	1.68	2,207	3,200	1.41	13.0
Thorium	11.2	6.0	1.87	1,845	>3,000	1.63	12.0
Vanadium	5.87	7.5	.78	1,740	3,000	1.72	15.0
Columbium	8.55	6.5	1.35	2,500	3,700	1.48	25.0
Tantalum	16.6	6.5	2.55	2,996	4,100	1.37	27.0
Molybdenum	10.2	5.5	1.86	2,620	3,700	1.41	50.0
Tungsten	19.3	7.5	2.57	3,370	5,900	1.75	57.0
Uranium	18.7	7.0	2.67	<1,850	3,000	1.60	60.0

All of the elements above listed belong to the so-called transition metals of the periodic table, and are shown in the above listing as they stand in the vertical columns of the fourth, fifth, and sixth groups of the periodic table. Of the interstitial metals I prefer for the purpose of my invention titanium, columbium and tantalum, but any can be used alone or in admixture with each other.

The interstitial metals according to my experience, can all be obtained by reducing their oxides by pure magnesium, with the exception of thoria. Also, their halides are reduced by magnesium and a pure interstitial metal is obtained.

It has long been known that the interstices of the interstitial metals are filled with metalloids and other elements such as hydrogen, oxygen and nitrogen. Halogens may also fill the interstices as well as carbon, sulfur, selenium and tellurium.

(3) In the magnesium alloy of my invention, containing an interstitial metal, I have made the important observation that silicon and/or boron and/or antimony can fill up the interstices of these interstitial metals, thus preventing the air, gases and other elements mentioned above from occupying the instertices. Silicon is generally preferred as the third component of my alloy, although any of the three may be used or mixtures of two or three. Hereinafter I will refer to silicon as representing the best embodiment but it is to be understood that in all references to silicon hereinafter, prior to the illustrative example, boron and antimony or mixtures thereof may be substituted for a part or all of the silicon.

Silicon is of interest in this connection because the interstitial metals can readily be converted to their respective silicides whereby the interstices of the metals are filled with silicon or boron or antimony if these are employed in their purification. It is important during all of such operations to avoid working with products containing moisture, and it should be removed entirely by calcining. Also complete absence of alkaline metals and their compounds and salts is essential.

Silicon is not directly soluble in magnesium, only about 0.003% being soluble at 600° C. While the presence of the silicon increases the hardness of the magnesium alloy up to about 5 for the magnesium silicide, the problem is presented as to the easy incorporation of silicon in magnesium.

(4) It is because of this problem that I introduce the fourth component in my alloy, which plays the important function of facilitating the introduction of silicon into the magnesium alloy. Thus, for instance, calcium is included as a metal representative of the fourth component of the alloy, because it not only lowers the density of the magnesium alloy containing it, but because silicon is easily introduced in calcium with the formation of $CaSi_2$ which has a density of 2.46, a hardness of 3.5 and a melting point of 1020°. This formation is easy and goes according to the following equation:

$$2Si+Ca \rightarrow CaSi_2+224.6 \text{ calories}$$

This calcium silicide is soluble in an excess of silicon which, as will be seen further, is desirable. Magnesium silicide is soluble in the presence of calcium silicide.

In addition to calcium and beryllium, which are the first two mentioned as the fourth component of my alloy, and the properties of which are listed in Table I, I may include as the metals functioning as the fourth component, as mentioned heretofore, chromium, cobalt, nickel, manganese and yttrium. Their properties are shown in the following table:

TABLE III

	Density (D)	Hardness (H)	D/H	Melting Point (MP), °C.	Boiling Point (BP), °C.	BP/MP	Modulus of Elasticity (p. s. i. 10^{-6})
Chromium	7.2	9.0	.81	1,890	2,200	1.16	37.0
Cobalt	8.9	5.5	1.48	1,480	2,500	1.96	37.0
Nickel	8.9	5.5	1.62	1,452	2,900	2.0	30.0
Manganese	7.2	5.0	1.44	1,260	1,900	1.5	23.0
Yttrium	5.5	1.3	4.24	1,490	2,500	1.7	9.0

Chromium, magnesium, cobalt and nickel, in addition to being utilized as their silicides similar to that of the calcium and beryllium, may also be used to increase the modulus of elasticity and the general workability of the alloy. While their density is far greater than that of magnesium or of calcium or beryllium, their introduction so much improves the metal that it can be used for other purposes and the increase in the density is not so great as to make this undesirable for such purposes. In addition only small amounts are used so the increase in density is negligible.

Amongst these metals I should like to mention particularly yttrium, which has the properties of the metals mentioned in the previous paragraph, and is of special interest because it crystallizes in a hexagonal-system like magnesium. This element is often found in the interstitial metals and such minerals as those containing titanium and tantalum, columbium and uranium. Yttria is reduced by magnesium to metal according to the following equation:

$$Y_2O_3+3Mg \rightarrow 2Y+3MgO+77.4 \text{ calories}$$

The silicon plays a number of roles in the alloy which can be summarized as follows: (1) It forms silicides with magnesium, the interstitial metals and the additional metals, in which the ratio of the silicon to the metal is 2:1; (2) silicon fills the interstices of the interstitial metals, such as titanium, zirconium, tantalum, molybdenum, etc., which renders the use of the interstitial metals suitable for the purpose of obtaining the high grade magnesium alloys and solid solutions; (3) the silicon forms a silicide with calcium which facilitates the obtention of the molten alloy providing an even distribution of the individual ingredients whereby the mechanical properties of the alloy are improved; (4) the structure of the silicides are exactly similar to that of the alloy, the bonds of the silicon atoms remaining unaltered and appearing exactly as in the case of silicon; (5) not only does the silicon form silicides with the magnesium and calcium, but also with any other metals that may be included, such as aluminum, chromium, manganese, nickel, cobalt, yttrium, and these may be prepared in the silicide form; (6) the silicon acts as a scavenger in the initial stages of preparing the silicides so that allowance should always be made for a certain percent loss during the process in which silicon is included.

The relative amounts of the ingredients comprising the alloy are generally as follows:

(1) At least 90% of the alloy is magnesium which forms the alloy base, or if a portion of this is substituted by aluminum the magnesium-aluminum mixture comprises at least 90% of which the magnesium in the alloy base is the primary component.

(2) The interstitial metal which comprises the second component of my alloy should be present in an amount of 0.01 to 2.0% preferably 0.01 to 1.0%.

(3) The silicon (or boron or antimony or mixture thereof) may be present in an amount of 1.0 to 5%.

(4) The elements comprising the fourth group vary in amounts depending somewhat upon the metal selected from this group. In the case of calcium larger amounts can be employed, i. e., amounts up to 7.99%. When beryllium is included it may be present in amounts of 0.001% to 0.005%. When the other metals of the fourth component are included they may be present in an amount of 0.01% to 2%, preferably 0.01% to 1.0%.

It is preferred that when beryllium is employed as a component its amount should be kept relatively low in relation to the amount of silicon so that the maximum preferable ratio is 0.01% beryllium to 3% silicon. When chromium is introduced into any specific alloy it preferably should be not more than 1 mol of chromium for 2 mols of silicon. If yttrium is included in the formula its relation to the amount of silicon preferably should be chosen so that not more than one part yttrium is present to 20 parts of silicon.

The method of making the alloy does not involve any particular complications. The ingredients forming the alloy are brought together in a fluid phase, either liquid or gaseous. In view of the nature of magnesium, some of the work must be carried out in an atmosphere of an inert gas such as helium, argon, neon or the like. Working in vacuo, because it is rather expensive, should be avoided if possible, but can be employed if this is feasible mechanically and economically.

In perfecting the alloy, at least a part of the silicon (or boron or antimony) should be added to the bulk of the magnesium in the form of a ternary alloy such as, for instance, a silicon-calcium-magnesium alloy. The interstitial metal or metals can be added in combination with silicon as a silicide. A magnesium-silicon-titanium alloy represents one of the preferred forms containing the first three components of the alloy of my invention. A quaternary alloy can also be produced by introducing calcium silicide or titanium silicide and then introducing the latter into a molten bath containing pure magnesium in addition to which is added a solid solution of the calcium-magnesium alloy.

I intentionally avoid copper as an element in my alloy because copper weakens the resistance of magnesium to corrosion. The following examples are illustrative of the invention:

Example 1

	Percent
Magnesium	95.00
Titanium	.10
Silicon	4.60
Nickel	.15
Chromium	.15

This alloy can be made by first preparing the silicides of nickel, chromium and titanium and adding these to the remaining silicon whereupon this mixture may be introduced into the molten magnesium with the adequate precautionary measures mentioned heretofore. The alloy has a melting point far higher than the melting point of magnesium and has good resistance to corrosion and a substantial increase in modulus of elasticity as compared with magnesium. All of the specific examples hereinafter share in these properties.

Example 2

	Percent
Magnesium	90.00
Tantalum	.01
Silicon	2.35
Calcium	7.50
Manganese	.10
Chromium	.02
Nickel	.02

In this example the introduction of calcium into the alloy greatly simplifies the introduction of silicon. The other metals are prepared as silicides and introduced into the final charge working in an atmosphere of an inert gas. The manganese in this example and in other examples containing it increases the resistance of magnesium to corrosion and facilitates its weldability.

Example 3

	Percent
Magnesium	90.00
Columbium	.02
Silicon	2.35
Calcium	7.50
Yttrium	.23

This example is interesting and important because it introduces the element yttrium, an element as plentiful as vanadium, nickel, and zinc in the outer shell of the earth. In addition, this element often occurs with columbium, tantalum and titanium and can be introduced into the alloy without separation. The low melting magnesium (651° C.) is greatly fortified by the higher melting yttrium (1490° C.). Yttrium, in addition, has the same crystalline structure as magnesium and beryllium, and since it follows the other two metals in the table of electromotive arrangement, it provides a strongly positive alloy.

Example 4

	Percent
Magnesium	90.00
Titanium	.02
Silicon	2.35
Calcium	7.50
Yttrium	.23

This example is similar to Example 1 except for the inclusion of calcium and yttrium and differs from Example 3 by substituting titanium for columbium. The alloy has the advantages imparted by titanium and yttrium and the calcium facilitates the introduction and interaction of these elements into the alloy along with the silicon. It also has a higher melting point and better resistance to wear and tear.

Example 5

	Percent
Magnesium	97.05
Zirconium	.02
Silicon	2.78
Manganese	.10
Chromium	.05

In this example zirconium replaces titanium and all of the metals, zirconium, manganese and chromium are present as silicides.

Example 6

	Percent
Magnesium	98.00
Molybdenum	.01
Silicon	1.90
Chromium	.05
Nickel	.04

In this example molybdenum replaces titanium, zirconium and columbium as the interestitial metal. The alloy is very stable and has excellent physical properties.

Example 7

	Percent
Magnesium	98.00
Vanadium	.02
Silicon	1.95
Manganese	.05

The introduction of manganese, which together with vanadium is first converted into a silicide, greatly facilitates the formation of a stable alloy. The melting point

of vanadium silicide is quite high, namely, 1654° C. and this property is imparted to the alloy. In addition, the alloy has marked hardness as compared with magnesium.

Example 8

	Percent
Magnesium	98.000
Molybdenum	.009
Tungsten	.001
Silicon	1.950
Chromium	.020
Manganese	.020

This example is similar to Example 6 except that a part of the molybdenum is replaced by tungsten, and manganese replaces nickel.

Example 9

	Percent
Magnesium	98.20
Titanium	.01
Columbium	.01
Silicon	1.73
Manganese	.05

This example is somewhat similar to Example 3 except that calcium and yttrium are replaced by manganese and titanium. The alloy is resistant to wear and tear, resist corrosion admirably and has improved mechanical properties. If desired the columbium can be replaced by tantalum.

Example 10

	Percent
Magnesium	98.20
Titanium	.02
Tantalum	.01
Silicon	1.70
Beryllium	.01
Manganese	.06

All of the metals, including beryllium, are present in the form of silicides. The alloy is stable, has a high melting point and resists corrosion. It also has a high and stable modulus of elasticity.

Example 11

	Percent
Magnesium	96.00
Titanium	.02
Boron	1.62
Calcium	2.33
Beryllium	.01
Cobalt	.02

This alloy is unique because calcium and cobalt both have the same crystalline structures. Boron also forms the compound Mg_3B_2 whereby the boron and magnesium unite readily and directly.

Example 12

	Percent
Magnesium	98.00
Titanium	.01
Tantalum	.01
Silicon	1.74
Nickel	.02
Chromium	.02

This alloy is similar to Example 10 except that the beryllium and manganese are replaced by chromium and nickel. All of the metals are present in the form of silicides and give a very efficient alloy.

Example 13

	Percent
Magnesium	65.50
Aluminum	32.50
Tantalum	.01
Silicon	1.70
Manganese	.25
Chromium	.02
Nickel	.02

This alloy is of particular interest since it shows the possibility of incorporating magnesium into aluminum and vice versa, without introducing transition metals other than the interstitial ones.

Example 14

	Percent
Magnesium	60.00
Aluminum	30.00
Titanium	0.20
Silicon	1.75
Calcium	7.40
Manganese	0.25

This example is similar to the previous example except that calcium is introduced into the alloy. Calcium is a splendid diluent and is especially useful in this alloy because it possesses two structures, i. e., that of both magnesium and aluminum.

Example 15

	Percent
Magnesium	96.00
Titanium	.01
Antimony	.25
Silicon	3.49
Titanium	.01

Inasmuch as antimony dissolves in molten silicon it is best prepared the silicide $SbSi_2$. This is then introduced into the molten titanium (which can be replaced by tantalum, columbium, zirconium, or vanadium, separately or in admixtures) followed by introducing the ternary alloy into the molten magnesium adding it in small portions with the stirring after each addition. These alloys show a marked increase in modulus of elasticity, general improvement in mechanical properties, and also greater resistivity to corrosion.

The above light alloys, based on magnesium of high purity, into which small amounts of the specified elements have been introduced, play an important role in light weight metal construction, where resistance to wear and tear and other chemical and physical properties are demanded. These alloys may be processed by recognized techniques such as quenching, annealing, aging, etc., as will be obvious to one skilled in the art.

I claim:

An alloy having the following composition:

	Percent
Magnesium	95.00
Titanium	.10
Silicon	4.60
Nickel	.15
Chromium	.15

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