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ARTICLE OF MAGNESIUM-BASE ALLOY AND METHOD OF MAKING

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The invention relates to die-expressed articles of magnesium-base alloy. It more particularly concerns an improved method of producing die-expressed articles of dispersion hardened magnesium-base alloys whereby good mechanical properties are attained which are not appreciably lowered by exposure to elevated temperatures.

This application is a continuation-in-part of a prior-filed application, Serial No. 810,257, filed May 1, 1959, now abandoned.

Heretofore high strength magnesium-base alloys have been prepared by alloying magnesium with one or more suitable constituents which are capable of forming solid solutions with magnesium. Such alloys are often further treated, as by cold-working, to increase yield and tensile strength. However, at elevated temperatures the effectiveness of solid solution strengthening is limited and further the benefits of cold-working are soon lost because recovery and recrystallization to a coarser grained condition takes place upon heating the alloys to even rather moderate temperatures. In other attempts to produce high strength magnesium-base alloys having a fine grained crystal structure, fine magnesium powder having a thin oxide coating has been die-expressed to produce an extrude in which magnesium oxide is widely and finely dispersed in a magnesium metal matrix. While so-formed extrudes exhibit good mechanical properties, they tend to be quite brittle and difficult to form even at elevated temperatures. In addition, extremely fine magnesium powder is required to provide sufficiently wide dispersion of the oxide in the extrude as the oxide is present only as a surface coating on the as-particulated metal particles. The preparation of magnesium powder of sufficient fineness for use in the aforesaid method is not only expensive but the fine powder is dangerous to handle because it forms explosive mixtures with air.

appreciably decreased by exposure of the alloy to elevated temperatures.

These and other objects and advantages of the invention will be more fully understood on becoming familiar with the following description and the appended claims.

This invention is predicated on the discovery that, by preparing a magnesium-base alloy containing magnesium and one or more constituents which are each miscible with magnesium in the molten state but substantially insoluble in solidified magnesium and by rapid solidification of said alloy, for example, into a mass of atomized particles, heating, compacting and then die-expressing to form an extrude or die-expressed article, the so-obtained article exhibits exceptionally desirable mechanical properties. For the purpose of the specification and appended claims the term "solidified magnesium" is to be understood to include solidified magnesium-base alloy.

In carrying out the invention, a magnesium-base alloy containing at least 70 percent of magnesium is prepared by alloying, according to well known methods, magnesium and one or more constituents having the hereinafter defined specific properties. An essential constituent must have sufficient solubility in molten magnesium at reasonable alloying temperatures, for example 650 to 900° C., but a solid solubility in magnesium of less than 0.1 atomic percent. As to the solid solubility in magnesium, those elements which on cooling form an intermetallic compound with magnesium and which are insoluble in solid magnesium are employed. The insoluble phase must remain suspended in the rapidly cooled and solidifying magnesium. It is further desired that the molten alloy have a narrow solidification range so that the size of the intermetallic compound particle is minimized. It is desired that the intermetallic particles dispersed in the solid magnesium have a maximum diameter of about .0001 inch or less, preferably as small as about .00005 inch or less, since the smaller particle size, the more the improvement in properties that results. A few particles having larger diameters can be tolerated, but they should be kept to a minimum to avoid adversely affecting the properties of the final product. Suitable metal constituents that may be used singly or in combination in the practice of the invention include barium, cobalt, copper, germanium, antimony, nickel, silicon and strontium, the pertinent properties of which are listed in Table I.

TABLE I

Alloying Constituent	Solubility in Mg, Wt. percent	Liquid Solubility in Mg at 800° C., Wt. percent	Solidus Temperature of Mg Binary, ° C.	Intermetallic Compound Formed With Mg	Wt. percent of Constituent to Form 10% by Volume of Intermetallic Compound
Ba	0.08	ca. 100	634	Mg_9Ba	ca. 5.
Co	nil	ca. 12	633	Mg_2Co	ca. 8.
Ge	nil	ca. 25	635	Mg_2Ge	ca. 10.
Sb	<0.02	ca. 50	629	Mg_3Sb_2	ca. 18.
Si	0.003	4	638	Mg_2Si	ca. 13.
Sr	0.01	ca. 100	582	Mg_9Sr	ca. 3.

It is therefore an object of the present invention to provide an improved method of forming a fine grained magnesium-base alloy which remains in the fine grained state even at elevated temperatures and exhibits superior physical and mechanical properties.

A further object is to provide an improved method of preparing a fine grained magnesium-base alloy which retains its fine grained character at elevated temperatures but is still readily formable.

A still further object of the invention is to provide an improved fine grained magnesium-base alloy having superior mechanical and physical properties which are not

The alloy to be used is brought to the molten state in any convenient manner in preparation for rapid solidification. Temperatures in the order of 25 to 50 centigrade degrees above the melting point of the alloy are desirable although other temperatures may be used at which the alloy is in the molten state. It is preferable to use the lower temperature of a molten state not only so as to reduce the degree of hazard involved in handling the molten alloy but also to reduce the amount of heat which must be removed to permit the molten alloy to return to the solid state. It is highly desirable for reasons hereinafter more fully discussed that the solidification of the

atomized alloy take place quickly in order to minimize aggregation or crystal growth of intermetallic compounds which are insoluble in magnesium in the solid phase.

The alloy while in the molten state may be subjected to a dispersion and chilling operation whereby the metal is obtained in atomized form, that is in the form of fine individually frozen discrete pellets. There are various ways in which atomization may be performed and any one of them may be used. A convenient method appears to be directing a jet of an inert cooling gas against an unconfined stream of the molten alloy as described in U.S. Patent No. 2,630,623.

For example, a freely falling stream of the molten alloy may be broken into droplets and solidified by impinging upon the stream an inert gas such as a hydrocarbon gas (e.g., methane, "natural gas," ethane, propane, butane, etc.), argon, helium, hydrogen, the inert gas having a boiling temperature below the melting point of the molten metal. A wide range of pellet sizes, although small, usually results from the atomizing operation. The atomized product comprises more or less spherical pellets for the most part ranging in size from about 10 mesh to smaller than 325 mesh. A preferred range of pellet sizes is from about −325 to about 140 mesh because of the outstanding properties achieved. However, very good properties are achieved with pellet sizes predominating in the 30 to 60 mesh range.

These pellets exhibit very desirable mechanical properties and may be used as pellets per se, for example, to reinforce other metals, as a load support, etc. or may be further fabricated, as by extrusion, rolling and the like.

Of course, other methods of rapidly quenching appropriate alloy compositions, as well as other methods of atomizing magnesium may be employed.

As a result of the atomizing operation, there is imparted to each pellet of the magnesium-base alloy a special heterogeneous microstructure essential in achieving the objects of this invention. This structure is characterized by a magnesium metal matrix having uniformly dispersed therethrough a discontinuous phase made up of very fine crystallites of an insoluble intermetallic compound. The intermetallic compound is present in an amount by volume from about 0.5 to 20 percent. A more preferred range is from about 3 to 15 percent of the volume of the alloy.

In the next step of the method the atomized metal is heated in preparation for compacting and die-expression. Compacting and die-expression may be carried out in conventional apparatus designed for the extrusion of magnesium-base alloy. A suitable method and apparatus for carrying out the die-expression of pelletized magnesium is described in U.S. Patent No. 2,630,623. The temperature to which the metal is heated is within the conventional plastic deformation temperature ranges for magnesium-base alloys, usually between about 300 and 500° C. but always below that temperature which adversely affects the dispersion through agglomeration.

It has been found that the as-atomized magnesium-base alloy may be heated in bulk to the desired temperature merely by placing it in a suitable metal vessel in a heated oven. Or, it is possible to charge the heated container of a die-expressing apparatus, with as-atomized metal and proceed with the operation of the apparatus to effect die-expression with substantially no destruction of the as-atomized structure of the alloy.

The amount of reduction in the cross-sectional dimensions of the compact effected by the extrusion or die-expression is subject to wide variations and may be from about 5 to 1 to as much as 200 to 1 or more (i.e., from about 80 percent to over 99 percent reduction in cross-sectional area).

The so-produced extrude having a uniform dispersion of finely divided intermetallic compound exhibits enhanced properties at both room temperature and elevated temperatures and is less adversely affected by fabrication or heat treatment at high temperatures.

Example

In accordance with the present invention, a quantity of each of four magnesium-base alloys in atomized form was provided. The compositions of these alloys are listed in Table II for runs No. 1, 2, 3 and 4. In each instance, the atomized pellets contained a uniform dispersion of intermetallic compound in which the intermetallic compound had an average diameter of about 0.00005 inch, substantially none of the intermetallic compound having a diameter greater than 0.0001 inch. In each case the quantity of atomized material was charged into a cylindrical container 3 inches in internal diameter, the container being at 400° C. The charge had a depth of about 6 inches and was compacted at 400° C. in the container to a compact about 4 inches long. The compact was then die-expressed at the same temperature at a rate of 5 feet per minute into a strip having a rectangular cross section 1¼ inches by 1/16 inch, the reduction in area being about 90:1. The so obtained die-expressed articles were subjected to physical testing at 24° C., 315° C. and 427° C. The results of the tests are listed in Table II.

Table II

Run No.	Composition [1]				Properties at 24° C.				Properties at 316° C.			Properties at 427° C.		
	Percent Si	Percent Ba	Percent Zn	Percent Zr	Percent E	TYS	CYS	TS	Percent E	TYS	TS	Percent E	TYS	TS
1	2.1	------	------	------	4	36	34	46	13	3.2	5.0	------	------	------
2	------	4.5	------	------	4	46	35	53	23	4.0	7.1	44	1.3	2.2
3	------	8.3	------	------	1	51	48	54	28	4.4	7.4	35	1.6	2.5
4	4	------	------	------	5	45	30	50	24	5.3	8.2	23	2.2	3.6
5	------	------	6	0.5	15	40	40	50	ca 100	1.0	2.0	infinite	nil	nil

[1] Balance magnesium.
Percent E = Percent elongation in 2 inches.
TYS = Tensile yield strength in thousands of lbs. per sq. in.
CYS = Compression yield strength in thousands of lbs. per sq. in.
TS = Ultimate tensile strength in thousands of lbs. per sq. in.

By way of comparison the atomized form of a conventional alloy, having the ASTM designation ZK 60 and a nominal composition of 6 weight percent of zinc, 0.5 weight percent of zirconium (thus, essentially no insoluble intermetallic compound), the balance magnesium, was similarly charged into the same heated die-expression apparatus and similarly extruded into 1¼ inches by 1/16 inch strip. The so-obtained strip was subjected to physical testing at 24° C., 315° C. and 427° C. The results of this comparison test are listed in Table II as run No. 5.

To further show the advantages of the process of the present invention, using a uniform dispersion of fine particles of intermetallic compound (in this instance Mg_2Si), in contrast to large particles of intermetallic compound, pellets and ingots were extruded at 5 feet per minute in the same manner above described and the properties of

the resulting extrude determined. These results are summarized in Table III.

TABLE III

Percent Si	Percent Zn	Form	Size[1]	Percent E	TYS	CYS	TS
1.4	1.0	Ingot	.0005	10	24	16	37
1.4	1.0	Pellet (35/65 mesh).	.00005	3	43	36	50
1.4	1.0	Pellet (−100 mesh).	.00001	3	47	41	54

[1] Size of uniformly dispersed Mg_2Si intermetallic compound in inches.

In another embodiment of the invention, a magnesium-base alloy is prepared by making suitable additions to magnesium of a metal constituent, which forms an insoluble phase therewith as described hereinabove as well as one or more metals which increase the strength of magnesium in a well known conventional manner such as by solution and precipitation hardening. It has thus been found that the benefits of dispersion hardening may be combined with the benefits of increasing the strength of the matrix about the finely dispersed crystallites of solid insoluble phase. Further, the problem of grain refining magnesium alloys is largely eliminated. This is especially important in the case of alloys of magnesium with manganese which tend to crystallize in a coarse grain structure, but in the fine grained condition exhibit excellent physical properties. Metals which may be added variously to increase the matrix strength include:

	Weight percent
Mn	0–2.5
Al	0–13
Zn	0–9
Ag	0–16
Bi	0–11
Ca	0–1
Li	0–15
Sn	0–16
Zr	0–1
Th	0–8
Rare earth metals	0–2

Combinations of the above listed elements which are mutually insoluble in molten magnesium to the extent that they form precipitates which settle out of the melt include Al—Th, Al—Zr, and Mn—Zr. It is within the skill of the metallurgist to check desired combinations for mutual insolubility. In general, any conventional magnesium-base alloy system may be employed, such as Mg—Al, Mg—Zn, Mg—Al—Zn, Mg—Zn—Zr, or Mg—Al—Mn, in combination with one or more of the previously mentioned metals which form a solid insoluble phase in solidified magnesium.

Such composite alloys, that is, those including dispersion hardening as well as conventional strengthening alloying metals, are atomized, compacted and extruded as described above.

Various modifications may be made in the present invention without departing from the spirit or scope thereof, and it is to be understood that I limit myself only as defined in the appended claims.

What is claimed is:

1. Atomized pellets comprising from 0.5 to 20% by volume of solid insoluble particles of magnesium intermetallic compound and the balance magnesium-base alloy; said particles of magnesium intermetallic compound being intimately and uniformly dispersed throughout said magnesium-base alloy; said particles of magnesium intermetallic compound having a maximum diameter of 0.0001 inch; said magnesium intermetallic compound being formed of magnesium and a constituent, said constituent having a solid solubility in magnesium of less than 0.1 atomic percent; said atomized pellets comprising at least 70% of magnesium; and said atomized pellets having diameters smaller than about 10 mesh.

2. Atomized pellets comprising from 0.5 to 20% by volume of solid insoluble particles of magnesium intermetallic compound and the balance magnesium-base alloy; said particles of magnesium intermetallic compound being intimately and uniformly dispersed throughout said magnesium-base alloy; said particles of magnesium intermetallic compound having a maximum diameter of 0.0001 inch; said magnesium intermetallic compound being formed by magnesium with an element selected from the group consisting of barium, cobalt, copper, germanium, antimony, nickel, silicon, strontium and mixtures thereof; and said atomized pellets having diameters smaller than about 10 mesh.

3. Atomized pellets as in claim 2 comprising from 3 to 15% by volume of solid insoluble particles of magnesium intermetallic compound having a maximum diameter less than about 0.00005 inch.

4. Atomized pellets consisting essentially of from 0.5 to 20% by volume of solid insoluble particles of magnesium intermetallic compound and the balance magnesium-base alloy; said particles of magnesium intermetallic compound being intimately and uniformly dispersed throughout said magnesium-base alloy; said particles of magnesium intermetallic compound having a maximum diameter of 0.0001 inch; said magnesium intermetallic compound being formed of magnesium and a constituent, said constituent having a solid solubility in magnesium of less than 0.1 atomic percent; said atomized pellets comprising at least 70% of magnesium; and said atomized pellets having diameters smaller than about 10 mesh.

5. Atomized pellets consisting essentially of from 0.5 to 20% by volume of solid insoluble particles of magnesium intermetallic compound and the balance magnesium; said particles of magnesium intermetallic compound being intimately and uniformly dispersed through said magnesium; said particles of magnesium intermetallic compound having a maximum diameter of 0.0001 inch; said magnesium intermetallic compound being formed of magnesium and a constituent, said constituent having a solid solubility in magnesium of less than 0.1 atomic percent; and said atomized pellets having diameters smaller than about 10 mesh.

6. Atomized pellets consisting essentially of from 0.5 to 20% by volume of solid insoluble particles of magnesium intermetallic compound, and the balance magnesium-base alloy containing at least one matrix strengthening alloying constituent selected from the group consisting of manganese, aluminum, zinc, silver, bismuth, calcium, lithium, tin, zirconium, thorium and rare earth metal; said particles of magnesium intermetallic compound being intimately and uniformly dispersed throughout said magnesium-base alloy; said particles of magnesium intermetallic compound having a maximum diameter of 0.0001 inch; said magnesium intermetallic compound being formed of magnesium and a constituent, said constituent having a solid solubility in magnesium of less than 0.1 atomic percent; said atomized pellets comprising at least 70% of magnesium; and said atomized pellets having diameters smaller than about 10 mesh.

7. Atomized pellets consisting essentially of from 0.5 to 20% by volume of said insoluble particles of magnesium-silicon intermetallic compound and the balance magnesium-base alloy; said particles of magnesium-silicon intermetallic compound being intimately and uniformly dispersed throughout said magnesium-base alloy; said particles of magnesium-silicon intermetallic compound having a maximum diameter of 0.0001 inch; said atomized pellets comprising at least 70% of magnesium; and said atomized pellets having diameters smaller than about 10 mesh.

References Cited in the file of this patent

UNITED STATES PATENTS

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2,966,736	Towner et al.	Jan. 3, 1961