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3,182,390

METHOD OF DIE-EXPRESSING A MAGNESIUM-BASE ALLOY

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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 magnesium-base alloys of the dispersion hardened type whereby high values of their high mechanical properties are attained which are not appreciably lowered by exposure to elevated temperatures by virtue of the said alloys remaining in a fine grained condition.

This application is a divisional application of copending 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 for 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.

It is therefore an object of the 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 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.

The 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 or which form an intermetallic compound with magnesium which is similarly insoluble in solidified magnesium and by forming said al-

loy into a mass of atomized particles, heating the mass, compacting the heated mass and then die-expressing the heated compacted mass 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 constituent metals having specific properties. An essential constituent metal 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 weight percent. As to the solid solubility in magnesium, those elements which are soluble in molten magnesium but which on cooling form an intermetallic compound with magnesium which is similarly insoluble in solid magnesium may also be employed. In any case the insoluble phase must remain suspended in the rapidly cooled and solidifying melt. If it settles out, the benefits according to the invention are not obtained. A molten alloy comprising magnesium and the constituent metal should exhibit a high solidus temperature, that is, above about 600° C. whereby articles formed of the alloy are usable at elevated temperatures. It is further desired that the molten alloy have a narrow solidification range. Suitable metal constituents that may be used singly or in combination in the practice of the invention include barium, cobalt, germanium, antimony, silicon and strontium, the pertinent properties of which are listed in Table I.

Table I

Metal Constituent	Solid Solubility in Mg, Wt. Percent	Liquid Solubility in Mg at 800° C., Wt. Percent	Solidus Temperature of Mg Binary, ° C.	Inter-metallic Compound Formed With Mg	Wt. Percent of Metal Constituent to Produce 10% by Volume of Intermetallic Compound
Ba.....	0.08	Ca. 100	634	Mg ₉ Ba.....	Ca. 5
Co.....	nil	Ca. 12	633	Mg ₂ Co.....	Ca. 8
Ge.....	nil	Ca. 25	635	Mg ₃ Ge.....	Ca. 10
Sb.....	<0.02	Ca. 50	629	Mg ₃ Sb ₂	Ca. 13
Si.....	0.003	4	638	Mg ₂ Si.....	Ca. 18
Sr.....	0.01	Ca. 100	582	Mg ₉ Sr.....	Ca. 3

The alloy to be used is brought to the molten state in any convenient manner in preparation for atomizing. 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 is to 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 constituents which are insoluble in magnesium in the solid phase.

The alloy while in the molten state is 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 particles. 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 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 particle sizes, although small, usually results from the atomizing operation. The atomized powder comprises more or less spherical particles for the most part ranging in size from about 10 mesh to smaller than 325 mesh. A preferred range of particle sizes is from —325 mesh to about 140 mesh, though larger sizes may be used for alloys such as Mg—Si.

As a result of the atomizing operation, there is imparted to each particle of the magnesium-base alloy a special heterogeneous microstructure essential in achieving the objects of the 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 phase consisting of the said essential alloying metal or an intermetallic compound thereof with magnesium. This uniformly heterogeneous microstructure is exhibited by all the magnesium-base alloys in atomized form (a frozen dispersion of the melt) containing one or more of the aforesaid alloying metal constituents which are substantially insoluble in solidified magnesium or which form insoluble intermetallic compounds, the insoluble form of the added metal constituent totalling by volume from about 0.5 to 20 percent. A more preferred range is from 5 to 15 percent of the volume of the alloy. The term "atomized metal" as used herein and in the appended claims has the conventional metallurgical meaning of chilled solidified droplets of molten metal produced by any of the known atomizing methods. The size of the droplets that yield the desired microstructure, that is, a fine state of subdivision of the insoluble phase on being chilled to solidification in the atomizing operation appears to be in the range of from 1 to 100 microns average diameter though other sizes may be used. However, atomized particles greater than about 100 microns diameter generally exhibit a microstructure in which the insoluble phase is not so minutely and widely dispersed as in the smaller atomized particles. Extruded articles prepared from such coarse particles accordingly show a larger grain size and less of the dispersion hardening effect. As for extremely fine particles, those particles having an average diameter of less than 1 micron are costly to make and very dangerous to handle on account of the explosive hazard.

The requisite rapid cooling of the magnesium-base alloy form the molten state in which the alloying metal constituent is miscible to the solid state in which the alloying constituent is insoluble in solidified magnesium is readily achieved in the atomization process and the tendency of growth or agglomeration of the insoluble phase into larger crystals is thereby reduced or substantially prevented. Some magnesium-base alloys containing the aforementioned insoluble phase forming constituents, especially those alloys having a fairly narrow solidification range, e.g., less than about 50 centigrade degrees, may also be satisfactorily prepared for use according to the invention by casting the molten alloy into the form of a billet, extruding the billet into wire form, such as 1/8 inch wire, and thereafter feeding the wire into a conventional metallizing gun employing an oxy-acetylene flame whereby the alloy is melted and atomized by the jet of burning gas. This atomization process is preferably carried out in a chamber or container in which the metal particles are cooled by the ambient atmosphere and solidified before striking the chamber walls. Particles of atomized alloy so-formed are generally rather irregular in shape and size. Further the insoluble metal phase which is not as well dispersed in the extruded rod as in particles atomized directly from the molten alloy, tends not to be completely melted in the flame. However, the dispersion is adequate

for some alloy systems and the use of a metallizing gun may be dictated if more elaborate atomization apparatus is not available. On the other hand, the same alloying composition when cast in massive form, e.g., as an ingot, is generally found to have a grain structure in which the insoluble alloying metal or intermetallic compound thereof has undergone extensive crystal growth whereby there are but few relatively large crystals of the insoluble solid phase dispersed throughout the grain structure. This may be attributed to the fact that in massive form the magnesium-base alloy cannot readily be cooled as rapidly as in the form of atomized particles.

In the next step of the method the atomized metal is heated, preferably in bulk, by contact with a heated metal surface 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 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 290° and 510° C. A preferred range is about 315° to 430° C.

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. Normally it takes but a few seconds for the charge in the die-expression apparatus to reach extrusion temperatures. During this interval of time the charge of metal reaches the plastic deformation temperature and is compacted by the pressure exerted upon the metal by the plunger of the apparatus before extrusion commences. The hot compacted metal extrudes from the die as soon as extrusion pressures are reached which pressures are comparable to conventional extrusion pressures.

The amount of reduction in the cross-sectional dimensions of the compact effected by the extrusion of die-expression is subject to wide variations and may be from about 8 to 1 to as much as 2,500 to 1 or more (i.e., from about 85 percent to over 99 percent reduction in cross-sectional area) depending upon the strength of the apparatus as is well understood in the art.

The extrude so produced is possessed of a uniformly microheterogeneous structure characterized by unusually high values of strength and toughness which are not appreciably decreased upon repeatedly heating the extrude to elevated temperatures, such as 540° C. for 1 hour, yet the extruded material is sufficiently ductile to be readily formable at elevated temperatures by conventional forming techniques.

The enhancement of the physical properties of magnesium-base alloy by the presence of the herein described fine insoluble solid phase particles is not entirely understood but it is believed that the dispersion is instrumental in inhibiting grain growth of the magnesium thereby keeping the magnesium matrix in a fine grained state or condition. This belief is strengthened by the discovery that the change in properties of a magnesium-base alloy upon a metal constituent forming a solid insoluble phase is more directly related to the volume of insoluble phase formed than to the percent by weight of alloying metal constituent added.

In accordance with the invention, a quantity of each of four magnesium-base alloys in atomized form was die-expressed. The compositions of these alloys are listed in Table II for runs No. 1, 2, 3 and 4. 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 the rate of 5 feet per minute into a strip having a rectangular cross section 1/4 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.		
	Per- cent Si	Per- cent Ba	Per- cent Zn	Per- cent Zr	Per- cent E	TYS	CYS	TS	Per- cent E	TYS	TS	Per- cent E	TYS	TS
1	2.1				4	36	34	46	13	3.2	5.0			
2		4.5			4	46	35	53	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 lbs. per sq. in. × 1000.

CYS = compression yield strength in lbs. per sq. in. × 1000.

TS = ultimate tensile strength in lbs. per sq. in. × 1000.

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, the balance magnesium, was similarly charged into the same heated die-expression apparatus and similarly extruded into 1/4 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.

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.

What is claimed is:

1. The method of making a die-expressed article of

a magnesium-base alloy comprising at least about 70 percent by weight of magnesium and from 0.5 to 20 percent by volume of a solid insoluble metal phase having a solid solubility in solidified magnesium of less than 0.1 percent by weight which includes the steps of atomizing the requisite alloy so as to convert the same into a mass of fine individually frozen particles having dispersed there-through fine crystallites of the said solid insoluble phase, heating the mass of as-atomized alloy to a temperature within the range of plastic deformation of the alloy, applying pressure upon the heated mass so as to compact the same and ram-extruding the resulting compacted mass at a temperature within the aforesaid range, the reduction in cross-sectional area of the compacted mass effected by the ram extrusion being at least about 80 percent.

2. The method of making a die-expressed article of a magnesium-base alloy comprising at least about 70 percent of magnesium and from 0.5 to 20 percent by volume of a solid insoluble metal phase having a solid solubility in solidified magnesium of less than 0.1 percent by weight and formed by an alloying metal constituent selected from the group consisting of barium, cobalt, germanium, antimony, silicon, strontium and mixtures thereof, which includes the steps of atomizing the requisite alloy so as to convert the same into a mass of fine individually frozen particles having dispersed there-through fine crystallites of the said solid insoluble phase, heating the mass of as-atomized alloy to a temperature within the range of plastic deformation of the alloy, applying pressure upon the heated mass so as to compact the same and ram-extruding the resulting compacted mass at a temperature within the aforesaid range, the reduction in cross-sectional area of the compacted mass effected by the ram-extrusion being at least about 80 percent.

3. The method of making a die-expressed article of a magnesium-base alloy comprising at least about 70 percent of magnesium and from 0.5 to 20 percent by volume of a solid insoluble phase having a solid solubility in solid magnesium of less than 0.1 percent by weight, said solid insoluble phase being selected from the group consisting of Mg₉Ba, Mg₂Co, Mg₂Ge, Mg₃Sb₂, Mg₂Si, Mg₉Sr and mixtures thereof which includes the steps of atomizing the requisite alloy so as to convert the same into a mass of fine individually frozen particles having dispersed there-through fine crystallites of a said solid insoluble phase, heating the mass of as-atomized alloy to a temperature within the range of plastic deformation of the alloy, applying pressure upon the heated mass so as to compact the same, and ram-extruding the resulting compacted mass at a temperature within the aforesaid

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range, the reduction in cross-sectional area of the compacted mass effected by the ram extrusion being at least about 80 percent.

4. The method of making a die-expressed article of a magnesium-base alloy comprising at least 70 percent by weight of magnesium, from 0.5 to 20 percent by volume of a solid insoluble metal phase having a solid insolubility in solidified magnesium of less than 0.1 percent by weight, and at least one matrix strengthening alloying constituent in effective strengthening amount, which includes the steps of particulating the requisite alloy from the molten state so as to convert the same into a mass of fine individually frozen particles having dispersed there-through fine crystallites of the said insoluble phase, heating the mass of as-particulated alloy to a temperature within the range of plastic deformation of the alloy, ap-

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plying pressure upon the heated mass so as to compact the same and ram-extruding the resulting compacted mass at a temperature within the aforesaid range, the reduction in cross-sectional area of the compacted mass effected by the ram-extrusion being at least about 80 percent.

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