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EXTRUDED MAGNESIUM-BASE ALLOY

George S. Foerster, Midland, Mich., assignor to The Dow Chemical Company, Midland, Mich., a corporation of Delaware

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7 Claims

ABSTRACT OF THE DISCLOSURE

An extruded alloy article that substantially cannot be made other than by powder metallurgy contains in the overall alloy from 0.1 to .8 percent of zirconium, from 0.1 to 5 percent of aluminum and at least one additional constituent selected from 0.08 to .5 percent calcium, 0.1 to 2.5 percent rare earth metal and 0.1 to 4 percent thorium and the balance magnesium. More preferably the alloy contains from .3 to 3 percent aluminum and most desirably contains from 0.5 to 1.5 percent of aluminum. The alloy is characterized by a sound heterogeneous microstructure consisting of first and second magnesium alloy phases intimately interdispersed. The first phase contains aluminum and zirconium and is a high strength phase. The second phase contains calcium, rare earth metal or thorium, is substantially free of aluminum and is resistant to creep. The article exhibits the properties of each phase to a desirable extent.

The invention relates to magnesium-base alloys containing aluminum and zirconium and more particularly relates to such alloys in extruded form as well as the method of preparing the alloys from particulate metals.

For the purposes of the specification and claims, a magnesium-base alloy is understood to consist of at least 75 percent by weight of magnesium.

In an effort to produce magnesium-base alloy articles having a fine grain size and improved mechanical strength properties, magnesium-base alloys containing aluminum and zirconium have been prepared by admixing magnesium-base alloy in pellet form with particulate or pelletized aluminum or magnesium-aluminum alloy and the mixture extruded. The so-formed powder extrusions exhibit an extremely fine grain size and exceptionally high static strength properties, for example, tensile yield strength and compression yield strength, even when they are fabricated at high temperatures. However, such alloys tend to exhibit poor creep strength even at room temperature, apparently because of their fine grain condition. On the other hand, treating such alloys to increase grain size, e.g., by heat treating the extrusion, or by reducing the zirconium content, while improving creep strength, markedly decreased static strength of the alloy.

It is, therefore, a principal object of the present invention to overcome the disadvantages of the prior alloys and to provide improved extruded alloy articles formed from particulate metal and exhibiting desirable creep properties while at the same time retaining desirably high static strength properties.

This and other objects and advantages of the present invention will be better understood by those skilled in the art upon becoming familiar with the following description and the illustrative examples.

The present invention is based on the discovery that upon providing an extruded article formed of a pellet ex-

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trusion alloy having a sound heterogeneous microstructure characterized by the presence of first and second minute zones intimately and mutually interspersed, each of the first zones comprising a magnesium-base alloy containing zirconium-aluminum intermetallic compound(s) and exhibiting inherently high static strength properties, and each of the second zones comprising magnesium-base alloy containing an alloying constituent selected from the group consisting of at least one of calcium, rare earth metal and thorium and exhibiting inherently good creep strength properties, the resulting extruded alloy article exhibits a highly desirable combination of both high creep strength and desirable static strength properties. The specific amounts of each alloy ingredient employed are hereinafter more fully described.

The term sound heterogeneous microstructure is intended to refer to consolidated metal sufficiently densified by a compressive process to attain substantially the density of cast metal, but having extremely minute heterogeneous composition zones within the consolidated metal, the zones corresponding to the metal particles used to make the consolidated metal.

The present alloy contains as an overall essential composition, by weight, from 0.1 to 0.8 percent of zirconium, from 0.1 to 5 percent of aluminum, an alloying constituent selected from the group consisting of at least one of 0.08 to 0.5 percent of calcium, from 0.1 to 2.5 percent of rare earth metal and 0.1 to 4 percent of thorium and the balance substantially magnesium; more preferably the alloy contains from 0.4 to 0.7 percent of zirconium and from 0.3 to 3 percent of aluminum. An even more preferred range of aluminum is from 0.5 to 1.5 percent. It is also preferred to include one of from about 0.1 to 0.3 percent of calcium, from about 1 to 2 percent of rare earth metal, and from about 1 to 3 percent of thorium. The alloy may also contain up to about 1.5 percent of zinc, and more preferably from 0.3 to 1 percent of zinc.

Rare earth metal employed in making up the alloys of the invention is generally obtained either as a commercially available mixture of rare earth metals known as misch metal, or as a substantially binary mixture of neodymium and praseodymium known as didymium.

Methods used to prepare the present improved extruded alloy article must essentially provide a heterogeneous microstructure characterized by stringers of a first alloy with high static strength properties intimately embedded together with stringers of a second alloy exhibiting good creep resistance. The high static strength alloy makes up from about 10 to 90, and more preferably from about 50 to 75, percent by weight of the final alloy, while the high creep strength alloy constitutes the balance. Depending upon the method selected, individual stringers of creep resistant alloy are disposed substantially side by side and roughly parallel to stringers of high static strength alloy, or, the individual stringers of creep resistant alloy are surrounded by an envelope of high static strength alloy.

According to one embodiment of the method of the invention, atomized pellets of magnesium-base alloy containing zirconium and, if desired, up to about 1.5 percent of zinc, are coated with from 0.1 to about 5 percent by weight of particulate aluminum, based on the weight of the pellets, by tumbling or shaking the particulate metals together. Desirably, the aluminum is in the form of fine flakes, e.g., paint grade aluminum. It is also preferred first to wet the atomized pellets with about 1 percent by weight of a liquid such as ethylene glycol before adding the aluminum powder and tumbling the mixture. The use of

ethylene glycol or equivalent liquids in the coating of atomized metal pellets with particulate aluminum is more fully described in co-pending application Ser. No. 524,875, filed Feb. 3, 1966.

The magnesium-base alloy pellets coated with aluminum are dried, if necessary, e.g., to remove liquids such as ethylene glycol. The coated pellets are charged to the container of an extrusion press having the die opening blocked off and the pellets, while at a temperature in the range of about 500 to 800° F., are compacted under sufficient pressure to cause the pellets to form a sound coherent mass. The so-obtained compact is heated to a temperature in the range of about 650° to 900° F. Heating times vary from as short as 1 hour at 900° F. to as long as 4 days at 650° F. Generally, heating times of 4 to 48 hours are suitable at a temperature of about 750–800° F. As a specific example of suitable conditions, the compact may be heated 16 hours at 780° F. As another specific example, the compact may be heat treated in two steps, viz., 780° F. for 16 hours, followed by 850° F. for 2 hours. During the heating period it is essential that the aluminum diffuses substantially throughout substantially each of the compacted pellets and forms well dispersed aluminum-zirconium intermetallic compound(s).

The heat treated compact is then comminuted into particulate form having an average particle size small enough to pass about a No. 20 sieve (U.S. Sieve Series) and preferably with a maximum particle size passing a No. 5 sieve. The comminuted metal is admixed with from about 10 to 90 percent by weight, and more preferably 25 to 50 percent by weight, based on the final composition, of a second magnesium-base alloy essentially containing at least one of from 0.08 to 0.5 percent of calcium, from 0.1 to 2.5 percent of rare earth metal and from 0.1 to 0.8 percent of thorium and the balance substantially magnesium. This second alloy preferably contains from 0.1 to 0.8 percent of zirconium since zones in the final extrusion containing calcium, rare earth metal or thorium and penetrated by aluminum are not high static strength areas unless zirconium is also present. Pellets of the second alloy are subsequently to be transformed into stringers of creep resistant metal during extrusion of the mixture of particles and pellets, though there is some diffusion of aluminum into these pellets during extrusion operations.

The requisite microstructure of the extrusion is obtained by placing a charge of the mixture of comminuted metal particles and the atomized pellets, with or without preheating to about 550° F., into the container of an extrusion press and extruding the mixture at a reduction ratio of at least about 5 to 1 and preferably at least 20 to 1. The resulting extrusion is characterized by the structure described hereinabove and exhibits a highly desirable combination of high static strength properties and good creep resistance. The extrusion is also characterized by the high static strength zones of the heterogeneous microstructure having an average grain diameter less than about 0.0002 inch.

In an additional embodiment of the method of the invention zirconium-containing magnesium-base alloy pellets containing substantially none of added calcium, rare earth metal or thorium, are coated with particulate aluminum in a manner described hereinabove before adding magnesium-base alloy pellets containing at least one of calcium or rare earth metal or thorium. The mixture is placed in the container of an extrusion press, with or without preheating, as may be desired, the die opening of the extrusion press having been blocked off, and the pellets, while at a temperature of about 500 to 800° F., are compressed into a compact. The compact is then placed in a heat treating oven and heat treated at a temperature in the range of about 650° to 900° F. for a period of about 1 hour to 4 days as described above. Preferred heating periods are gauged according to the relative sizes of the pellets of high static strength alloy as compared to the sizes

of the pellets of creep resistant alloy according to the following reasoning.

In order to achieve the objective of the invention it is essential that heat treating be carried out at a sufficiently elevated temperature and for a sufficient time that the aluminum incorporated within the compact diffuses substantially throughout the high static strength alloy. But it is also essential that the aluminum diffuses very little into the creep resistant alloy. It has now been found, surprisingly, that aluminum diffuses very slowly into magnesium-base alloy containing at least one of calcium, rare earth metal or thorium, as compared to the rate at which aluminum diffuses into magnesium-base alloy substantially free of these metals but containing zirconium. It is best to employ pellets of the two alloys having about the same average particle size. Because of the relative rates of diffusion, the method may be successfully carried out using pellets of creep resistant alloy having a somewhat smaller average particle diameter than the pellets of high static strength alloy, provided that the heating times are carefully regulated.

Atomized pellets of magnesium-base alloy obtained by jet atomizing are substantially regular in particle size and jet atomized pellets of differing alloys are generally of sufficiently similar sizes to be satisfactorily used together. Pellets obtained by atomizing magnesium-base alloy on a rotating disc or wheel tend to exhibit an even narrower range of particle sizes and are thus to be preferred.

To assure the requisite degree of diffusion of aluminum into each of the two types of alloy pellets incorporated within the compact, it is advisable to section heat treated compacts made in trial runs and to examine the compacts metallurgically to ascertain the degree of diffusion obtained. Heat treating times are then preselected for subsequent runs as may be indicated.

For the same reasons given hereinabove in describing the first embodiment of the invention, it is preferred to use, as the second type of alloy, magnesium-base alloy containing zirconium, in addition to at least one of calcium, rare earth metal or thorium.

The compact, when properly heat treated, is preheated to about 0 to 100° F. above the container temperature of the extrusion press and then the heated compact is placed in the container and extruded into final form at a temperature in the range of about 500 to 800° F. More generally, the compact is taken directly from the heat treating oven to the container of the extrusion press. The so-obtained extrusion exhibits the combination of static strength properties and creep resistance described hereinabove and the high static strength zones exhibit an average grain diameter not more than about 0.002 inch.

In yet an additional embodiment of the method of the present invention the desired total amount of zirconium as well as the amount of at least one of calcium, rare earth metal or thorium, desired in the completed pellet extrusion alloy are each incorporated into a single magnesium-base alloy. The alloy is atomized according to conventional practices and the so-obtained atomized pellets are then coated with from about 0.2 to 5 percent by weight of particulate aluminum based on the weight of the total composition. The aluminum particles may be made to adhere by tumbling the dry mixture, or, a liquid such as ethylene glycol may be employed in the manner described hereinabove. The mixture of particulate metal is next dried, if necessary, and charged to the container of an extrusion press, with or without preheating, the die opening of the extrusion press having been blocked off. The charge of particulate metal is promptly compressed into a coherent compact at a temperature in the range of about 500 to 800° F.

The so-obtained compact is then heat treated in a highly critical operation in which the aluminum within the compact is caused to penetrate only partially into substantially each of the magnesium-base alloy zones corresponding to the original pellets. Penetration by the alu-

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minum by diffusion desirably corresponds to treatment of about 10 to 90 percent by weight of the magnesium-base alloy portions and more preferably about 50 to 75 percent. The desirable objective is to provide, by the heat treatment, high static strength portions, being the zones into which the aluminum has diffused, in addition to retaining creep resistant zones into which the aluminum has not diffused. Because the extent of diffusion is controlled by pellet sizes, as well as the proportion of calcium, rare earth metal or thorium employed, temperatures and times employed are generally determined by trial and error. However, it has been found in a compact made up from pellets of a magnesium-base alloy containing about 1 percent of rare earth metal, and about 0.6 percent of zirconium, and the pellets used to make the compact being of a particle size passing a No. 20 sieve and substantially retained on a No. 200 sieve (U.S. Sieve Series), that zones corresponding to the original pellets are penetrated to the extent of about 50 to 75 percent by weight upon heat treating the compact at a temperature of about 780° F. for about 16 hours.

The following examples serve to illustrate the invention and not to limit the scope thereof.

FIRST SERIES

In a first series of runs wheel-atomized pellets of magnesium-base alloy containing 0.45 percent of zirconium and 1.2 percent of zinc and the balance substantially magnesium were admixed with 1 percent by weight of flake aluminum. The pellets exhibited a particle size range of about 20 to 200 mesh sizes (U.S. Sieve Series). The flake aluminum was fine enough to pass about a No. 325 sieve. The pellets and the flake aluminum were tumbled together for about 5 minutes. Three parts of the mixture was then thoroughly admixed with one part by weight of atomized pellets of magnesium-base alloy containing 2 percent by weight of didymium and about 0.6 percent by weight of zirconium and the balance magnesium by shaking the mixture in a large vessel for about one minute. An additional quantity of aluminum coated pellets was admixed with equal parts by weight of the pellets of rare earth metal (didymium) alloy. In each case a charge of the mixture was placed in the container of an extrusion press having the die opening blocked off. A compact 3 inches in diameter was formed by compressing the charge under a pressure of about 500 tons while the metal was at a temperature of about 600° F. In each case the compact was removed from the press and heat treated at a temperature of 780° F. for a period of 16 hours. The heat treated compacts were then extruded into $\frac{1}{16}$ inch x $\frac{1}{4}$ inch strip at a temperature of 650 to 700° F. at a speed of 50 to 80 feet per minute and at a reduction ratio of about 90 to 1.

Samples of each strip were subjected to testing in order to determine compression yield strength and percent of creep extension. The results of these tests are listed in Table I.

Additional runs were made by way of comparison. In the first comparison run, magnesium-base alloy containing 0.45 percent by weight of zirconium and 1.2 percent of zinc was provided in the form of wheel atomized pellets and the pellets were coated with 1 percent by weight of flake aluminum by shaking the particles together. The so-coated pellets were compacted, heat treated and extruded in the same manner as described above for runs according to the invention.

In a second comparison run, wheel atomized pellets of magnesium-base alloy containing 0.6 percent by weight of zirconium and 2 percent by weight of didymium were not mixed with aluminum nor compacted, but were extruded directly into strip at 700 to 750° F. without heat treating. The extrusion speed was in the range of 50 to 80 feet per minute.

Test samples were taken from strip formed in each of the comparison runs and subjected to physical testing.

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The compression yield strength values and the percent creep extension are also listed in Table I.

Run No.	Composition, ¹ weight percent				CYS, p.s.i.	Percent Creep in 100 hours at 200° F. under 5,000 p.s.i.
	Zr	Al	R.E.	Zn		
Comparison 1.....	0.45	1.0	-----	1.2	39,000	1.00
Comparison 2.....	.60	-----	.2	-----	18,000	0.00
1.....	.59	.75	.3	.5	38,000	.21
2.....	.72	.50	.3	.6	36,000	.01

¹ Balance magnesium.

² Didymium was used as rare metal constituent.

³ Misch metal was used as rare earth metal constituent.

R.E.=rare earth metal.

CYS=compression yield strength.

p.s.i.=pounds per square inch.

SECOND SERIES

In each of two additional runs according to the method of the invention, wheel atomized pellets of magnesium-base alloy containing 2 percent of didymium and about 0.6 percent of zirconium were coated with a small proportion of flake aluminum by shaking the particulate metals together. The coated pellets were compacted at a temperature of about 600° F. in the three inch diameter container of an extrusion press having the die opening blocked off. In each case the compact was heated to a temperature of about 780° F. for a period of about 16 hours. The heat treated compact was placed in the container of an extrusion press and extruded into $\frac{1}{16}$ inch x $\frac{1}{4}$ inch strip at a speed of 75 to 80 feet per minute while the metal was at a temperature of 700 to 750° F. using a reduction ratio of about 90 to 1. Samples taken from strip from each run were subjected to physical testing. The samples exhibited a high degree of creep resistance while retaining desirably high compression yield strength.

The compression yield strength values and percent creep extension noted are listed in Table II. The values for comparison run 2 described in the first series are again listed here for easier comparison.

Run Number:	Composition, ¹ weight percent				CYS, p.s.i.	Percent creep in 100 hours at 200° F. under 5,000 p.s.i.
	Zr	Al	R.E.	Zn		
3.....	0.6	0.5	.2	.2	29,000	0.00
4.....	0.6	1.0	.2	.2	33,000	0.05
5.....	0.6	.25	.2	.2	24,000	0.00
Comparison 2.....	0.6	-----	.2	.2	18,000	0.00

¹ Balance magnesium.

² Didymium was used as rare earth metal constituent.

Pellet extrusion alloys according to the invention containing from 0.08 to 0.5 percent of calcium or 0.1 to 4 percent of thorium in place of the rare earth metal of the foregoing examples and prepared in the same manner exhibit similarly high resistance to creep and excellent compression yield strength values.

In yet an additional run a magnesium-base alloy containing about 1 percent of zinc and 0.5 percent of zirconium and the balance substantially magnesium, is provided in wheel atomized form. The atomized metal is admixed with 1.5 percent by weight of flake aluminum. The admixture is compressed into a 3 inch diameter compact at a temperature of 675° F. and under 500 tons load. The compact is heat treated at a temperature of 750° F. for a period of 24 hours. The compact is then comminuted into particles which substantially all pass a No. 10 sieve. Three parts by weight of the comminuted metal are admixed with one part by weight of wheel atomized pellets of magnesium-base alloy containing 1.8 percent by weight of misch metal and 0.7 percent by weight of zirconium. The admixture is charged to the container of an extrusion press and the metal, while at a temperature of 700° F. is extruded directly into $\frac{1}{16}$ inch x $\frac{3}{4}$ inch

strip at a speed of about 70 feet per minute. A test sample of the strip exhibits a compression yield strength of 35,000 p.s.i. and a percent creep extension during 100 hours at 200° F. under a load of 5,000 p.s.i. of 0.11 percent.

I claim:

1. A magnesium base alloy article in extruded form prepared from particulate metal and consisting essentially of:

from 0.1 to 0.8 percent of zirconium, from 0.1 to 5 percent of aluminum, a metal selected from the group consisting of at least one of from 0.08 to 0.5 percent of calcium, from 0.1 to 2.5 percent of rare earth metal and from 0.1 to 4 percent of thorium, and the balance magnesium;

the extruded alloy having a sound heterogeneous microstructure consisting essentially of first and second magnesium base alloy phases, said first phase constituting from about 10 to 90 percent by weight of the extruded alloy and said first phase comprising magnesium-aluminum-zirconium alloy having an average grain diameter less than about 0.0002 inch; and said second phase being a substantially discontinuous phase intimately dispersed with the first phase and comprising an alloying constituent selected from the group consisting of calcium, rare earth metal and thorium and the balance substantially magnesium;

and the article being characterized, after extrusion at a temperature of at least 500° F. by both high compression yield strength and marked resistance to creep extension, and by the aluminum content thereof being diffused substantially throughout the

first phase but aluminum being substantially absent from a substantial part of the second phase.

2. The article as in claim 1 in which the alloy, as extruded, contains 0.1 to 0.3 percent of calcium.

3. The article as in claim 1 in which the alloy as extruded, contains from 0.4 to 0.7 percent of zirconium.

4. The article as in claim 1 in which the alloy, as extruded, contains from 0.5 to 1.5 percent of aluminum.

5. The article as in claim 1 in which the alloy, as extruded, contains in addition up to 1.5 percent of zinc.

6. The article as in claim 1 in which the alloy, as extruded, contains in addition from about 0.3 to 1 percent of zinc.

7. The article as in claim 1 in which the alloy, as extruded, contains from about 50 to 75 percent by weight of the first phase and the balance the second phase.

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