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# METHOD OF EXTRUSION AND EXTRUSION BILLET THEREFOR

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The invention relates to an improved method of preparing an extrude of magnesium-base alloy and more particularly relates to an improvement in the method of preparing an extrude of precipitation-hardenable magnesium-base alloy from particulated metal and to an improved extrusion billet.

For the purposes of the specification and claims a magnesium-base alloy is defined as an alloy containing at least 75 percent by weight of magnesium.

Heretofore extrudes exhibiting good mechanical strength have been prepared by co-extruding particulated metals such as particulate magnesium-base alloy ZK60 admixed with particulate magnesium-aluminum alloy or aluminum. According to U.S. Patent 2,659,131 such an admixture of particulated metals is placed in the container of a preheated ram extrusion press and promptly die-expressed at relatively low speeds below about 5 feet per minute, then heat treated after extrusion to bring about precipitation hardening. A serious drawback to this procedure is the necessity of employing low extrusion speeds and temperatures, the frequency of surface scoring of the extrude and the low ductility exhibited by the extrude.

It has now been found that, if the alloying constituents are heat treated while in intimate contact whereby a precipitation-hardened magnesium-base alloy is formed, prior to co-extrusion, substantial advantages are obtained.

The so obtained advantages are entirely unexpected because it was not known heretofore that precipitation hardened magnesium-base alloy could be readily worked after precipitation hardening. The more recent work on high strength alloys has been almost entirely centered on alloy systems which harden on being worked and are adversely affected when heat treated before extrusion. Therefore there has been a strong tendency to avoid heat treating extrusion billets before the extrusion thereof.

Appropriate alloying constituents for the present invention must meet the requirements that firstly, the final alloy contain at least 75 percent of magnesium, and secondly, that the other alloying constituents create problems in mutual alloying. Thus, the final alloy will contain at least 75 percent of magnesium and two or more additional alloying components that are mutually insoluble in solidified magnesium.

As used herein the term insoluble refers to solubility in solidified magnesium-base alloy.

This process applies to all magnesium systems which experience interference hardening, incompatibility, or compound formation. In the simplest form of the invention one of the mutually interfering alloying elements is employed as a component of a magnesium-base alloy and the other, desirably the more rapid diffusing of the two, is used in unalloyed form. For example, thorium may be used as a magnesium-base thorium-containing alloy and aluminum may be alloyed therewith according to the method of the invention.

In other modifications of the invention one of the mutually interfering alloying elements is employed as a component of a magnesium-base alloy and two or more alloying components interferring therewith are employed either as physical mixtures, or as alloyed together. The mutually interferring elements may also be brought together as components respectively of a magnesium-base alloy and a magnesium alloy if desired but the dilution of the interferring substances in the additional magnesium increases the heating time required for the diffusion process necessary for precipitation hardening and decreases the concentration of the solid-insoluble precipitates in the product of the invention.



Aluminum may be alloyed by the process of the invention with a magnesium-base alloy containing zirconium. Aluminum metal or magnesium alloys such as those containing from 20 to 30 percent by weight of aluminum may be employed as the source of aluminum. Magnesium-base alloy containing zirconium may be alloyed with binary alloys or physical admixtures of aluminum and silicon, or, of aluminum and zinc. Other possible combinations are tabulated as follows:

MUTUALLY INSOLUBLE COMBINATIONS

| Component of magnesium base alloy: | Other components [1] |
|---|---|
| Zr | Sn, Si, Zn. |
| Mn | Al, Si, Zr. |
| Th | Al. |
| MM [2] | Al. |
| Li | Al. |
| Ca | Al. |

[1] Employed singly or in combination or as a magnesium alloy.
[2] MM=Misch metal.

The magnesium-base alloy employed may also contain non-interferring components which impart desired properties such as ductility, corrosion resistance or higher mechanical strength. As an example, magnesium-base alloy containing up to 0.8 percent zirconium and at least one of the following: up to 4 percent of zinc, up to 6 percent of silver, up to 1 percent of calcium, up to 4 percent of rare earth, up to 4 percent of thorium, up to 5 percent of lithium, may be admixed with aluminum or magnesium-aluminum alloy, and heat treated and extruded according to the invention.

All the metals are employed in particulated form. The magnesium-base alloy is conveniently used as atomized pellets such as those prepared according to U.S. Patent No. 2,676,359. The other metals are generally best used in finely divided form such as that passing about a No. 325 sieve (U.S. Sieve Series). Larger sizes tend to make complete precipitation hardening more difficult, for example, by requiring a longer heat-treating period.

The proportions of each of the mutually interferring components employed in the process of the invention are not sharply critical. It is essential that a sufficient amount of each be present to cause formation of a solid insoluble precipiate throughout the magnesium-base alloy. When processed according to the present invention with 1 percent by weight of aluminum, a magnesium-base alloy containing as small a proportion of zirconium, such as 0.08 percent by weight, is found to have surprisingly increased strength properties, compared to a magnesium-base alloy containing either the aluminum or zirconium content alone. It is very desirable that the mutually insoluble component or components employed which are not a part of the initial magnesium-base alloy should be used in a small enough particle size and intimate enough dispersion that it will diffuse into the magnesium-base alloy in reasonable times at heat treating temperatures.

The magnesium-base alloy containing one of the mutually insoluble alloying components is brought into intimate contact with the additional insoluble component or components mainly in one of two ways.

The metals to be alloyed according to the invention are thoroughly blended and admixed, while in particulate form, as by tumbling the particles in a cylindrical container for 15 minutes or more. The thoroughly blended admixture is then placed in the preheated container of

a die-extrusion press having a cover plate over the internal face of the die and the particles compacted under heat and pressure to a coherent mass, or extrusion billet. Thereafter the so-formed compact is ejected from the press. Typically a compact is formed at 500 to 800° F. under a pressure of about 50 tons per square inch.

As a modification of the compacting process of forming an extrusion billet the admixture may also be pre-extruded at low reduction ratios such as 5 to 1, and at speeds of 2 feet per minute or less and desirably with a low container temperature to avoid hot shorting. As an example, pre-extrusion may be carried out at 600 to 700° F. with a container temperature of 600° F. and at a speed of about 1 foot per minute.

In another manner of bringing the materials into intimate contact the magnesium-base alloy in solid particulate form may be dipped into, or sprayed with, the other metal or alloy in molten form, or gas plated or vacuum metallized or peen plated whereby a thin film of the other metal or alloy is deposited on substantially each particle of the magnesium-base alloy. An advantage of the plating process is that the plated particles can be heat treated in particulated form if desired, and thereafter extruded into final form thus avoiding a compacting or pre-extrusion step.

The so-prepared compact or pre-extrusion, or the plated particles described above, are then heat-treated for an extended period to cause diffusion of the mutually insoluble alloying components whreby they meet and form solid insoluble particles, generally as intermetallic compounds. Heat treating the metals at 700 to 900° F. for periods of 12 to 48 hours is generally adequate for the purposes of the invention, though shorter times may be used for mixtures formed from extremely fine particulate material. The most advantageous temperatures and times vary somewhat with the magnesium alloy system used and with the diffusion rates and particle sizes of interfering alloying components. The heat-treating conditions should be drastic enough to cause sufficient diffusion into the magnesium-base alloy of any mutually insoluble components originally external thereto that undesired compounds, such as brittle magnesium aluminum intermetallic compound, are dissociated whereby the final extrude does not hot short and also whereby sufficient solid insoluble material is formed to significantly increase the properties of the extrude.

On the other hand, heat treating for overly extended



periods tends to result in grain growth of the magnesium and agglomeration of the solid insoluble material whereby maximum strength is not achieved.

The extrusion billet may be machined to a smaller size, if necessary, to permit easy insertion into the extrusion container.

The heat treated metal, whether in the form of an extrusion billet or particulate metal, is then extruded at temperatures and reduction ratios well understood in the magnesium metal art. Extrusion speeds, however, may be radically increased from about 1 or 2 feet per minute, heretofore used in the extrusion of such particulate admixtures, to speeds as high as 100 feet per minute.

If desired, the extrusion billet formed in the process of the invention may be placed in a close-fitting sleeve formed of either a conventional magnesium-base alloy or an aluminum-base alloy and transformed into rolled form by passing it repeatedly, while at an elevated temperature, between the rolls of a mill. The extrusion billet may also be worked in other ways such as by forging it in a manner well understood in the art.

*Examples*

To illustrate the improved process of the invention various pelletized magnesium-base alloys containing zirconium and having a particle size of about 20 to 140 mesh (U.S. Sieve Series) were thoroughly admixed with fine aluminum powder passing a 325 mesh sieve (U.S. Sieve Series). The mixtures were each compacted into extrusion billets at a temperature of about 650° F. and under a pressure of about 50 tons per square inch. The extrusion billets were each heat treated for 16 hours at a temperature range of 750 to 800° F. The so-treated billets were then scalped to reduce their dimensions slightly so they would fit into the 3 inch diameter container of a ram extrusion press. The billets were each expressed through a die-opening 1/16 by 3/4 inch. The container temperature was 600° F. and the strip was extruded at a temperature of 650° F. Extrusion rates are shown in the table. The mechanical properties of the so-treated extrudes were determined experimentally. The test results and the compositions used are listed in Table I. One of the extrudes was given a Standard ASTM heat treatment, T5, which consisted of heating the extrude for 24 hours at 300° F. The properties of the so-treated extrude are listed as Run No. 18.

TABLE I

| Run No. | Composition of mixture,[1] weight percent Al | Composition of Mg-base alloy,[2] weight percent | | Extrusion speed, ft./minute | Percent E | Physical properties, 1000's p.s.i. | | |
|---|---|---|---|---|---|---|---|---|
| | | Zn | Zr | | | TYS | CYS | TS |
| 1 | 0.25 | 1 | 0.24 | 50 | 4 | 40 | 29 | 47 |
| 2 | 0.25 | 1 | 0.24 | 100 | 4 | 40 | 26 | 47 |
| 3 | 0.5 | 1 | 0.24 | 100 | 5 | 41 | 31 | 48 |
| 4 | 1 | 1 | 0.24 | 50 | 4 | 41 | 36 | 48 |
| 5 | 1 | 1 | 0.24 | 100 | 6 | 42 | 33 | 48 |
| 6 | 2 | 1 | 0.24 | 100 | 9 | 41 | 40 | 48 |
| 7 | 2 | 1 | S 0.24 | 100 | 12 | 41 | 40 | 48 |
| 8 | 3.6 | 1 | 0.24 | 50 | 8 | 45 | 42 | 51 |
| 9 | 3.6 | 1 | 0.24 | 100 | 8 | 44 | 43 | 51 |
| 10 | 4.4 | 1 | 0.24 | 90 | 10 | 47 | 44 | 53 |
| 11 | 6.2 | 1 | 0.24 | 40 | 8 | 48 | 46 | 54 |
| 12 | 1 | 1 | 0.05 | 100 | 11 | 25 | 14 | 36 |
| 13 | 1 | 1 | 0.08 | 100 | 4 | 41 | 22 | 46 |
| 14 | 1 | 1 | 0.32 | 100 | 10 | 41 | 39 | 48 |
| 15 | 1 | 1 | 0.64 | 50 | 6 | 48 | 48 | 55 |
| 16 | 1 | 1 | 0.64 | 100 | 8 | 44 | 45 | 51 |
| 17 | 2 | 4.3 | 0.64 | 40 | 4 | 50 | 51 | 56 |
| 18 | 2 | 4.3 | 0.64 | T5 40 | 6 | 52 | 54 | 49 |
| 19 | 2 | ---- | 0.57 | 100 | 6 | 43 | 45 | 54 |
| Comparison | ---- | 1 | 0.24 | 50 | 9 | 29 | 15 | 37 |
| Do | ---- | 1 | 0.24 | 100 | 10 | 27 | 13 | 36 |
| Do | ---- | 0.6 | [3] | 100 | 11 | 23 | 11 | 34 |

[1] Balance magnesium.
[2] Balance magnesium-base alloy.
[3] 1.3 percent Al, 0.3 percent Mn (AZ11).
Percent E=Percent elongation in 2 inches.
TYS=Tensile yield strength.
CYS=Compression yield strength.
TS=Ultimate tensile strength.
T5=Standard ASTM heat treatment that was used after die-expression of extrude.
S=Sieved, only particles passing number 100 sieve were used.

For purposes of comparison extrudes containing zinc and zirconium but not aluminum, and, aluminum and zinc but not zirconium were prepared and the properties were were determined. The properties are listed in Table I. Also listed for comparison are the properties of an extrude formed by co-extruding magnesium-zirconium alloy with aluminum metal by a process not according to the method of the invention.

In a second series of experiments atomized magnesium-base zirconium alloy, containing one or more additional alloying components was thoroughly admixed with fine particulate aluminum. The so-prepared admixtures were compacted, heat-treated, scalped and extruded in the same manner as the admixtures tested in the first series of experiments. The compositions used, the extrusion speeds and the physical properties of the resulting extrudes are listed in Table II.

In a third series of experiments still an additional embodiment of the invention was carried out. Pellets of magnesium-base alloy containing zirconium were admixed with pellets of magnesium-aluminum alloy and the composition was compacted, heat-treated, scalped and extruded in the manner described in the first series of experiments. The physical properties of the resulting extrudes are determined and are listed in Table III.



experiment pellets of magnesium-base alloy were admixed with aluminum pellets. The admixture was then tumbled in a cylindrical container to peen plate the pellets with aluminum. Both of the above compositions were compacted, heat-treated, scalped and extruded in the manner described in the first series of experiments. The physical properties of these extrudes were determined and are also listed in Table III.

Among the advantages of the invention are the sizeable increase in mechanical strength, ductility and permissible extrusion speed, as well as the freedom from hot shorts and surface imperfections in the extruded material produced according to the method of the invention.

I claim:

1. The improved process of forming a wrought article of magnesium-base alloy which comprises: preparing an intimate admixture consisting essentially of (1) particulate magnesium-base alloy containing at least one first alloying component and (2) at least one additional alloying component in finely divided form which is mutually solid-insoluble with said first alloying component in a magnesium-base alloy system, heat treating the said intimate admixture whereby precipitation hardening takes place, and working the so-heat treated intimate admixture.

2. In the process of forming a wrought article of magnesium-base alloy from particulate metal, the improved sequence of steps which comprises: compacting a thoroughly blended admixture consisting essentially of

TABLE II

| Run No. | Composition of mixture,[1] weight percent Al | Composition of Mg-base Alloy,[2] weight percent | | Other component(s) metal | Weight percent | Extrusion speed, feet/minute | Percent E | Physical properties, 1000's p.s.i. | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | Zr | Zn | | | | | TYS | CYS | TS |
| 20 | 2 | 0.6 | | Bi | 2 | 100 | 4.5 | 48 | 46 | 54 |
| 21 | 2 | 0.6 | | Ca | 1 | 30 | 2 | 46 | 44 | 52 |
| 22 | 2 | 0.6 | | Th | 3 | 100 | 6 | 44 | 49 | 56 |
| 23 | 2 | 0.6 | | Di | 2 | 100 | 8 | 40 | 46 | 54 |
| 24 | 2 | 0.6 | | Di | 2 | 100 | 10 | 49 | 48 | 55 |
| | | | | Ag | 3 | | | | | |
| 25 | 2 | 0.6 | | Di | 2 | 70 | 6 | 46 | 48 | 53 |
| | | | | Ag | 6 | | | | | |
| 26 | 1 | 0.42 | 3.1 | Ag | 3.1 | 20 | 6 | 46 | 48 | 53 |
| 27 | 1 | 0.42 | 3.1 | Ag | 3.1 | T5 20 | 4 | 47 | 51 | 55 |
| 28 | 1 | 0.36 | 2.6 | Ag | 5.6 | 15 | 4 | 45 | 48 | 52 |
| 29 | 2 | 0.48 | | Ag | 2.8 | 100 | 3 | 49 | 49 | 53 |
| 30 | 2 | 0.47 | | Ag | 5.5 | 50 | 7 | 49 | 52 | 56 |
| 31 | 1 | 0.84 | 5.9 | Th | 3.3 | 50 | 9 | 47 | 52 | 57 |
| 32 | 2 | 0.84 | 5.9 | Th | 3.3 | 30 | 8 | 49 | 56 | 58 |
| 33 | 2 | 0.84 | 5.9 | Th | 3.3 | T5 30 | 4 | 50 | 59 | 60 |

[1] Balance magnesium-base alloy.
[2] Balance magnesium.
Di=Mixture containing neodymium, praesodymium and small amounts of other rare earth metals.

TABLE III

| Run No. | Aluminum source | | | | Composition of Mg-base alloy used,[2] weight percent | | Extrusion speed, feet/minute | Percent E | Physical properties, 1000's p.s.i. | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | Metal or alloy | Weight percent [1] | Particle form | Mesh size [c] | Zn | Zr | | | TYS | CYS | TS |
| 34 | Mg 4 Al | 25 | Atomized pellets. | 20 | 1 | 0.24 | 100 | 5 | 39 | 30 | 46 |
| 35 | Mg 10 Al | 10 | do | 20 | 1 | 0.24 | 100 | 6 | 32 | 17 | 39 |
| 36 | Mg 10 Al | 10 | do | 70 | 1 | 0.24 | 100 | 5 | 39 | 28 | 46 |
| 37 | Mg 15 Al | 7 | do | 70 | 1 | 0.24 | 100 | 5 | 32 | 16 | 41 |
| 38 | Mg 33 Al | 3 | do | 20 | 1 | 0.24 | 100 | 2 | 25 | 16 | 31 |
| 39 | Mg 33 Al | 3 | do | 70 | 1 | 0.24 | 50 | 4 | 34 | 25 | 42 |
| 40 | Mg 33 Al | 3 | do | 70 | 1 | 0.24 | 100 | 2 | 32 | 24 | 39 |
| 41 | Al | 1 | Flake | 325 | 1 | [a] 0.5 | 100 | 4 | 42 | 35 | 50 |
| 42 | Al | 2.6 | Atomized pellets. | 325 | 1 | [b] 0.24 | 100 | 5 | 38 | 29 | 45 |

[1] Balance of the mixture magesium-base alloy.
[2] Balance magnesium.
[a] Chips machined from ingot; dimensions averaged about 0.020 x ⅜ x ½ inch.
[b] Magnesium-base alloy mixed with the Al pellets and tumbled in cylindrical container to "peen plate" the pellets with Al.
[c] Number of sieve passed.

In an additional experiment aluminum flake passing a 325 mesh sieve was admixed with chips of magnesium-base alloy machined from an ingot. In still an additional

(1) particulate magnesium-base alloy containing at least one first alloying component and (2) at least one additional alloying component in finely divided form which is mutually solid-insoluble with each said first alloying component in a magnesium-base alloy system; heat treating the intimate admixture whereby precipitation hardening takes place in the admixture; and subjecting the heat treated admixture to a wrought operation.

3. In the process of forming a wrought article of magnesium-base alloy from particulate metal, the improved sequence of steps which comprises: preparing an intimate admixture consisting essentially of (1) particulate magnesium-base alloy containing at least one first alloying component and (2) at least one additional alloying component in finely divided form which is mutually solid-insoluble with each said first alloying component in a magnesium-base alloy system; heat treating the intimate admixture whereby precipitation hardening takes place in the admixture; and extruding the heat treated admixture.

4. In the process of forming a wrought article of magnesium-base alloy from particulate metal, the improved sequence of steps which comprises: preparing an intimate admixture consisting essentially of (1) particulate magnesium-base alloy containing at least one first alloying component and (2) at least one additional alloying component in finely divided form which is mutually solid-insoluble with each said first alloying component in a magnesium-base alloy system, said additional alloying component being in a form selected from the group consisting of (a) the substantially pure metal, (b) mixtures and alloys of metals each mutually insoluble with said first alloying component, and (c) magneisum alloys containing at least one said additional alloying component; heat treating the intimate admixture whereby precipitation hardening takes place; and extruding the heat treated admixture.

5. In the process of forming a wrought article of magnesium-base alloy from particulate metal, the improved sequence of steps which comprises: coating (1) particulate magneisum-base alloy containing at least one first alloying component with (2) at least one additonal alloying component which is mutually solid-insoluble with each said first alloying component in a magnesium-base alloy system; heat treating the coated particles of said magnesium-base alloy whereby precipitation hardening takes place; and extruding the heat treated particles.

6. In the process of forming a wrought article of magnesium-base alloy from particulate metal, the improved sequence of steps which comprises: compacting an intimate admixture consisting essentially of (1) particulate magnesium-base alloy containing at least one first alloying component and (2) at least one additional alloying component in finely divided form which is mutually solid-insoluble with each said first alloying component in a magnesium-base alloy system, under sufficient heat and pressure to form a coherent compact; heat treating the compact whereby precipitation hardening takes place therein; and extruding the heat treated compact.

7. In the process of forming a wrought article of magnesium-base alloy from particulate metal, the improved sequence of steps which comprises: pre-extruding an intimate admixture consisting essentially of (1) particulate magnesium-base alloy containing at least one first alloying component and (2) at least one additional alloying component in finely divided form which is mutually solid-insoluble in a magnesium-base alloy system; heat treating the pre-extruded admixture whereby precipitation hardening takes place therein; and extruding the pre-extruded and heat treated admixture.

8. In the process of forming a wrought article of magnesium-base alloy from particulate metal, the improved sequence of steps which comprises: preparing a thoroughly blended admixture consisting essentially of (1) particulate magnesium-base alloy containing zirconium as an alloying component and (2) aluminum in finely divided form; subjecting the intimate admixture to heat and pressure whereby sufficient particles of the admixture are welded together to form a coherent mass; heat treating the coherent mass whereby precipitation hardening takes place; and extruding the so-heat treated admixture.


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