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3,216,824

PREPARATION OF MATERIALS OF COMPOSITE STRUCTURE

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The present invention relates to a new process for the preparation of materials of composite structure comprising a compressed powder of magnesium or a magnesium alloy, in which at least one non-metallic phase is dispersed within the metal. The invention also relates to the novel powders and compressed articles obtained according to the process.

The particular properties of metallic materials produced with a composite structure of the metal/oxide type are known and, particularly, all the novel advantages which they have in the field of heat stability under mechanical stress. It is also known that the fineness of dispersion of the non-metallic phase affects these properties; in particular, the resistance to stresses increases with the fineness of dispersion, while the rupture elongation diminishes.

For a given degree of dispersion, the size of the particles of the non-metallic phase has a certain importance. The mechanical resistance initially increases rapidly with this size and then becomes constant, while rupture elongations decrease constantly as the size increases. Also, an optimum size of the non-metallic phases corresponds to each mode of dispersion, which ensures the highest possible values for the resistance and elongation.

In general, the materials in question are manufactured from metallic powders which undergo an oxidation before or during compaction of the powder. The thickness of the oxide films is thus dependent upon the conditions under which this oxidation is carried out.

In the case of composite magnesium/magnesia products, it is difficult to control the thickness of the magnesia film, because of the high reactivity of the metal with regard to oxygen. Also, in order to obtain a sufficiently compact final product, it is necessary to heat the metallic particles to sufficiently high temperatures to favour elimination of the hydrogen derived from water-vapour and organic substances which can be present on the surface of the particles, which has the disadvantage of producing too vigorous an oxidation.

This thus means that the oxidation of the magnesium particles is a difficult operation, more particularly for fine powders, which are precisely those which produce a high mechanical resistance; this also applies to the fine portions of mixtures of powders of varied particle size. With such fine particles or the fine portions of such mixtures, oxidation by known means leads to excessively thick oxide films, because it does not involve, because of uncontrollable elevation of the temperature, a substantially complete oxidation, which thus tends to extend to the whole mass.

The products finally obtained thus have the following defects because it has not been possible to effect the desired oxidation:

(a) Insufficiently high rupture loading, because of the impossibility of using sufficiently fine powders or because of insufficient oxidation;

(b) Low elongation rupture values (under tension), both in the cold and in the hot, due to excessive general or local oxidation;

(c) "Dispersed" properties, namely irregularities, when

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heating of the powders has not been sufficient before compaction to give good elimination of the hydrogen.

The present invention overcomes the foregoing disadvantages and allows the ready production of magnesium or magnesium alloy materials from powders of such metals, having excellent mechanical properties. It also renders possible the gradual and controlled oxidation of the particles of the powder, irrespective of the sizes of the particles.

The free choice of particle size of the powder and thickness of the oxide film thus obtained allows products to be obtained which are characterised by high rupture loadings and elastic limits both at ordinary temperatures and at high temperatures, while preserving relatively enhanced elongation ruptures. Also, for any fineness of the powder, the heating can be carried out at a temperature sufficient to ensure that the hydrogen is eliminated, for example between 350° and 550° C., the time of heating determining the thickness of the film formed on the surface of the particles of the powder.

Also, the invention renders possible the production of products of which the micrographic grain size, after compression, remains remarkably stable, even following prolonged heating at elevated temperature.

The process according to the invention simplifies working of composite materials obtained from powders; as regards rolling or extrusion, the material can be taken directly to the requisite temperature in a single stage, instead of being subjected to a series of successive compressions at increasing temperatures, which has been necessary heretofore.

The novel process according to the invention consists in preparing a material by compression of a powder of magnesium or a magnesium alloy, the metal being subjected to heating in the presence of carbon dioxide gas before, during and/or after compression of the powder.

According to the invention, a thin non-metallic layer is obtained on the particles of the powder, by the action of CO₂ on magnesium, in place of the usual reaction of oxygen on the metal.

This process results in the consideration that the heating of magnesium in an atmosphere of CO₂ leads to the formation of a protective film which considerably decreases the velocity of oxidation and, without the risk of excessive oxidation, allows heating to be carried out at much higher temperatures than in air or in oxygen. Heating under carbon dioxide, applied to magnesium powders, even allows the finest particles to be safely treated and deposits a film of the desired thickness on their surfaces.

Although in fact the film in question can comprise MgO and/or MgCO₃ and possibly even free carbon depending on the temperature and pressure reference will be made below to the oxide, in order to simplify the language of description.

The treatment in carbon dioxide gas in the hot according to the invention can be effected in various ways.

One embodiment consists in heating, in an atmosphere of CO₂, magnesium powder which is to be used for the preparation of materials by compression.

Oxidation of the particles of magnesium powder by heating in a current of carbon dioxide gas can be effected according to known processes for the treatment of powders by gases; an effective and reliable procedure consists in placing the powder in an enclosure which has its walls externally heated and systematically agitating it while under an atmosphere of dry carbon dioxide gas; the temperature, the input of carbon dioxide gas and the duration of treatment are adjusted to suitable values.

Another embodiment of the invention consists in heating, in the presence of CO₂, a more or less compact mass

previously formed by compression of the powder. The mass can have been produced by compression in the cold or also at an elevated temperature, preferably however below 450° C. A non-oxidised compressed powder or, preferably, one which has previously been oxidised, by known methods or by the present novel method, to an oxygen content lower than that desired, can thus be treated.

A particular application is the treatment with CO₂ of a compressed powder material while heating it in order to effect its plastic deformation, for example by rolling or drawing.

It has in fact been found that a fine powder, for example, of not more than 60 microns particle size, oxidised previously to the degree of oxidation desired and then subjected to compression in the cold at 10 to 60 kg./mm.², undergoes a strong oxidation when it is subsequently heated in air at the temperature necessary for extrusion (450° to 550° C. for example); this disadvantage is avoided, if the heating of the material to effect its plastic deformation (rolling, drawing, extrusion, etc.) is effected in an atmosphere of CO₂; there is then the advantage, in accordance with the invention, of effecting hot plastic deformation at the same time as the oxidation treatment with carbon dioxide gas is effected, to the desired degree of oxidation, starting with a non-oxidised powder or one previously oxidised to a lower degree of oxidation than that required.

The powder can be compressed in the cold, for example, in a hollow body to the dimensions of the container for the extrusion press and provided, after compression, with a sealed cover provided with an inlet pipe for purging under vacuum and refilling with carbon dioxide gas. With this protection, a single compression in the cold under a low stress (up to 2 kg./mm.²) is sufficient to obtain a compact product, after extrusion between 450° and 550° C., the compressive force in the hot during extrusion being above 30 kg./mm.².

A particularly advantageous application of the invention consists in oxidising the powder to the desired degree in an atmosphere of CO₂, compressing it into a compact mass and then again operating under CO₂, effecting the subsequent heating of the material for working it to make an object of the desired predetermined form.

Depending on the fineness of the powder, the nature of the magnesium alloy, the temperature and the pressure, the process of the invention can be carried out in an atmosphere of CO₂ alone or in mixture of CO₂ and air, oxygen, nitrogen or other gases. It is necessary, however, for the proportion of CO₂ is the gaseous mixture to be sufficiently high; particularly with air, it is necessary to have at least 5% of carbon dioxide by volume or, preferably, more than 50%. The preferred proportions are of the order of 90% to 100% of CO₂. From this standpoint, excellent results are obtained with industrial carbon dioxide gas containing 99% to 99.7% by volume of CO₂.

The novel process can be carried out at various temperatures; it can be conducted at from 100° C., where a slow superficial oxidation takes place, up to slightly below the fusion point of the metal. However, for reasons of rapidity of operation and the properties of the materials to be obtained, it is preferable to operate between 250° and 600° C. and most preferably between 350° and 500° C.

The composite metallic products of the invention (masses or oxidised powders) can be prepared from non-oxidised powders or insufficiently-oxidised powders of very wide particle size ranges, in particular those in which the particles have dimensions between 1 and 2000 microns; the weight percentage of the non-metallic phase of the product obtained ranges from 0.1% to 20% (this phase is finely distributed in a homogeneous manner in the form of a more or less continuous film, the thickness of which is from about 0.01 to 10 microns, the structure in the form of a continuous film corresponding to that of the powder).

The following examples of application of the new process are given by way of illustration.

EXAMPLE 1

Two different treatments were carried out on a magnesium powder of average dimensions, the particle size of which is between 10 and 100 microns:

- (a) Heating in air at 400° C.;
- (b) Heating for 4 hours at 400° C. under dry CO₂.

The treatment (a) (heating in air) causes flaming of the powder. If attempts are made to avoid flaming by limiting the rate of increase of the temperature, it is found that the finer particles of the mixture oxidise very rapidly and thus heat up the adjacent particles in an excessive manner. After this treatment, the presence of more or less large nodules is also observed, constituted by highly oxidised agglomerations of particles, which it is almost impossible to eliminate from the powder without affecting the properties for which it is to be used; when freed from the powder, these nodules cause a considerable degradation of the cohesion and other properties of the final material.

The treatment (b) gives regular oxidation, without the finest particles undergoing more or less slow combustion. The powder obtained has a homogeneous appearance without blackish nodules of agglomerated oxide and metal. Portions of the powder treated according to process (b) have been compressed in the cold under 40 kg./mm.²; they were then subjected to successive compressions of 300°, 400°, 450° and 500° C. after heating in air.

Other portions of the powder treated according to (b) were subjected to a single compression after heating at 525° C. in an atmosphere of carbon dioxide gas and then to drawing (ratio of the sections before and after drawing: $S/s=16$), in order to obtain round rods. The mechanical properties of the rods have been determined by traction tests at a speed of 4 mm./min.

The same characteristics have been found for the two kinds of rods, namely, those obtained after four successive compressions and those resulting from a single compression.

The following Table I contains the results:

Table I
MECHANICAL PROPERTIES OF RODS FORMED FROM A MAGNESIUM POWDER TREATED BY CO₂ at 400° C. FOR 4 HOURS

Measurements effected at ordinary temperature:

R—kg./mm. ²	33
E—kg./mm. ² (at 2%)	30
A—percent on $\sqrt{67S}$	7
H _B	53

(5 mm. ball; load 31, 250 kg.)

Measurements effected at 450° C.:

R—kg./mm. ²	2.6
E—kg./mm. ² (at 2%)	2.0
A—percent on $\sqrt{67S}$	14

EXAMPLE 2

To show the influence of the thickness of the films on the final properties, three lots of powder of the same particle size as in Example 1 were treated respectively:

- 4 hours at 350° C. under CO₂;
- 4 hours at 400° C. under CO₂;
- 4 hours at 450° C. under CO₂.

After compression in the cold under 40 kg./mm.², heating to 525° C. under CO₂ and extrusion at this temperature with a drawing ratio of 16, the rods obtained were found to have the following properties at ordinary temperature and also at 450° C.

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Table II

Temperature of oxidation of powder	Ordinary temperature			450° C.		
	R kg./mm. ²	E kg./mm. ²	A Per- cent	R kg./mm. ²	E kg./mm. ²	A Per- cent
350° C.-----	32.5	30.5	6	1.8	1.5	14
400° C.-----	33.5	30	5	2.6	2	12.5
450° C.-----	34	31	4	2.7	2.5	13.5

This example clearly shows how the treatment under carbon dioxide gas, by controlling the manner of oxidation of the particles, affects the general properties of the final product.

EXAMPLE 3

Samples of powder of different particle sizes were treated for 4 hours at 400° C. under dry carbon dioxide gas and were then compressed and extruded as in Example 2. The following properties were found on traction of the wire products, at ordinary temperature and at 450° C.

Table III

Particle size range of the powder	Ordinary temperature			450° C.		
	R kg./mm. ²	E kg./mm. ²	A Per- cent	R kg./mm. ²	E kg./mm. ²	A Per- cent
1,500-300 microns-----	23.5	16.5	9	1.2	0.8	27
300-50 microns-----	30	27	5.5	2.3	1.8	14
50-10 microns-----	34.5	33	5	2.85	2.45	12.8

This example shows how, due to the oxidation treatment in the hot under carbon dioxide gas, it is possible to obtain enhanced mechanical properties by utilizing very fine powders; as also shown in Example 1, the oxidation of fine powders is not possible in the air or leads to heterogeneous and fragile products. It is particularly the elongation ruptures, at ordinary and elevated temperature, which are relatively high, if compared with materials of known type, the elongation ruptures of which are lower by more than half the values indicated in the above table.

EXAMPLE 4

A rod was extruded under the following conditions:

(a) Initial powder: particles of dimensions between 10 and 100 microns;

(b) Oxidation treatment in carbon dioxide gas: 4 hours at 400° C., compression in the cold at 40 kg./mm.²;

(c) Heating under carbon dioxide gas and extrusion at 525° C. ($S/s=16$).

After extrusion, micrographic examination showed that the number of particles per mm.² in a section parallel to the axis, was between 25,000 and 50,000. After heating

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for 1000 hours at 500° C., the number of particles was from 12,000 to 25,000. Under the same conditions, the known alloy of magnesium containing 0.4% of zirconium showed 1000 to 2000 particles per mm.² after drawing and 50 to 200 particles per mm.² after 1000 hours at 500° C.

The interest is thus appreciated of magnesium/magnesia composite articles, the properties of which, both in the hot and in the cold, remain stable after long periods of heating.

What we claim is:

1. In a process for the preparation of a composition consisting essentially of metallic magnesium the particles of which are coated with a non-metallic phase consisting essentially of magnesia, the steps of heating and compressing a magnesium powder in an atmosphere containing 90% to 100% of carbon dioxide gas at a temperature from 100° C. to 500° C., the heating step lasting from 2 to 7 hours, the dimensions of the metallic particles ranging from 1 to 2,000 microns, the weight percentage of the non-metallic phase ranging from 0.1% to 10% and the thickness of the coating of magnesia ranging from 0.01 to 10 microns.

2. In a process for the preparation of a composition having a metallic phase consisting essentially of metallic magnesium the particles of which are coated with a non-metallic phase consisting essentially of magnesia, the steps of heating and compressing a magnesium powder in an atmosphere containing 90 to 100% of carbon dioxide at a temperature from 100° C. to 500° C., the heating step lasting from 2 to 7 hours, the dimensions of the metallic particles ranging from 1 to 2,000 microns, the weight percentage of the non-metallic phase ranging from 0.1% to 10% and the coating of magnesia having a thickness of from 0.01 to 10 microns.

3. A process as described in claim 1, the heating step being carried out before, during and after compression of the powder.

4. A process as described in claim 1 in which the powder is heated from 350° to 500° C.

5. A process as described in claim 1 in which the heating step takes place before the compression step.

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**UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION**

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It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

In the heading to the printed specification, after line 9, insert the following:

Claims priority, application France, July 21, 1960,
833,598

Signed and sealed this 19th day of July 1966.

(SEAL)

Attest:

ERNEST W. SWIDER

Attesting Officer

EDWARD J. BRENNER

Commissioner of Patents