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(54) **COMBINATION OF CASTING PROCESS AND ALLOY COMPOSITION**

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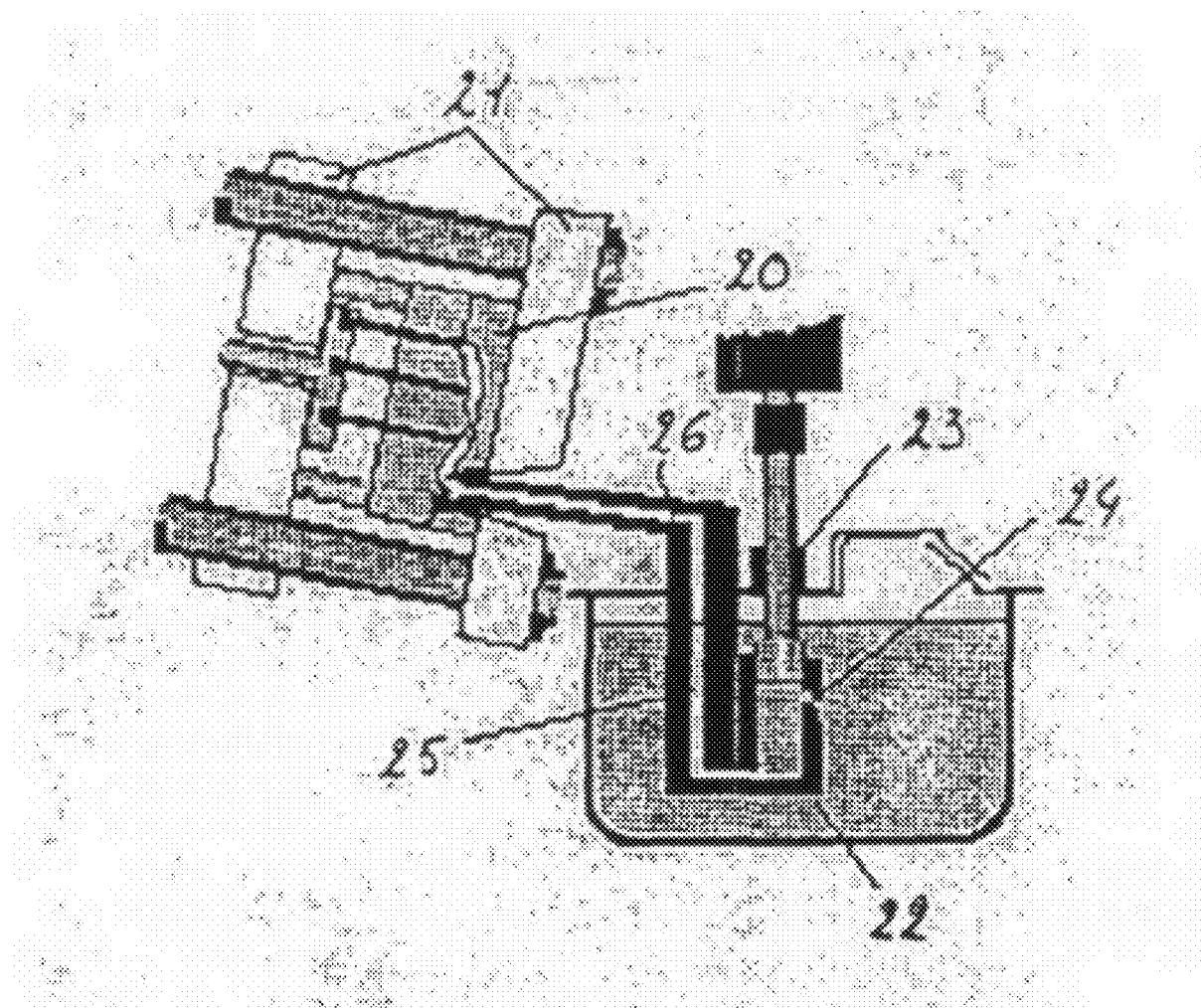
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(57) **ABSTRACT**

A process for casting a magnesium alloy consisting of 10.00-13.00% by weight of aluminium, 0.00-10.00% by weight of zinc, and 5.00-13.00% by weight of aluminium, 10.00-22.00% by weight of zinc, also containing 0.10-0.5% by weight of manganese, and the balance being magnesium and unavoidable impurities, the total impurity level being below 0.0% by weight, wherein the alloy is cast in a die in which the temperature is controlled in the range of 150-340° C., the die is filled in a time which expressed in milliseconds is equal to the product of a number between 2 and 300 multiplied by the average part thickness expressed in millimetre, the static metal pressures being maintained during casting between 20-70 MPa and may subsequently be intensified up to 180 MPa.



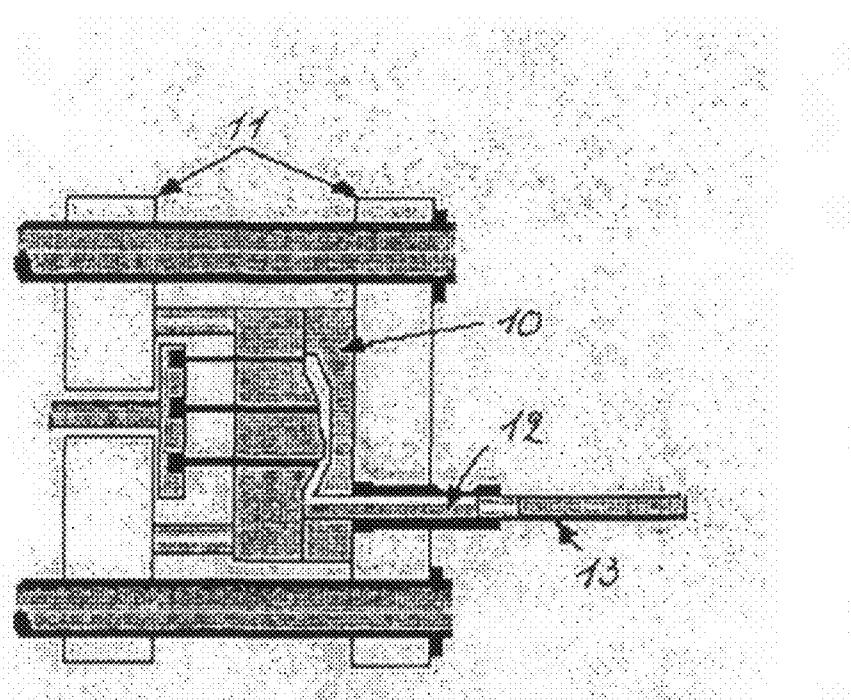


Fig. 1A

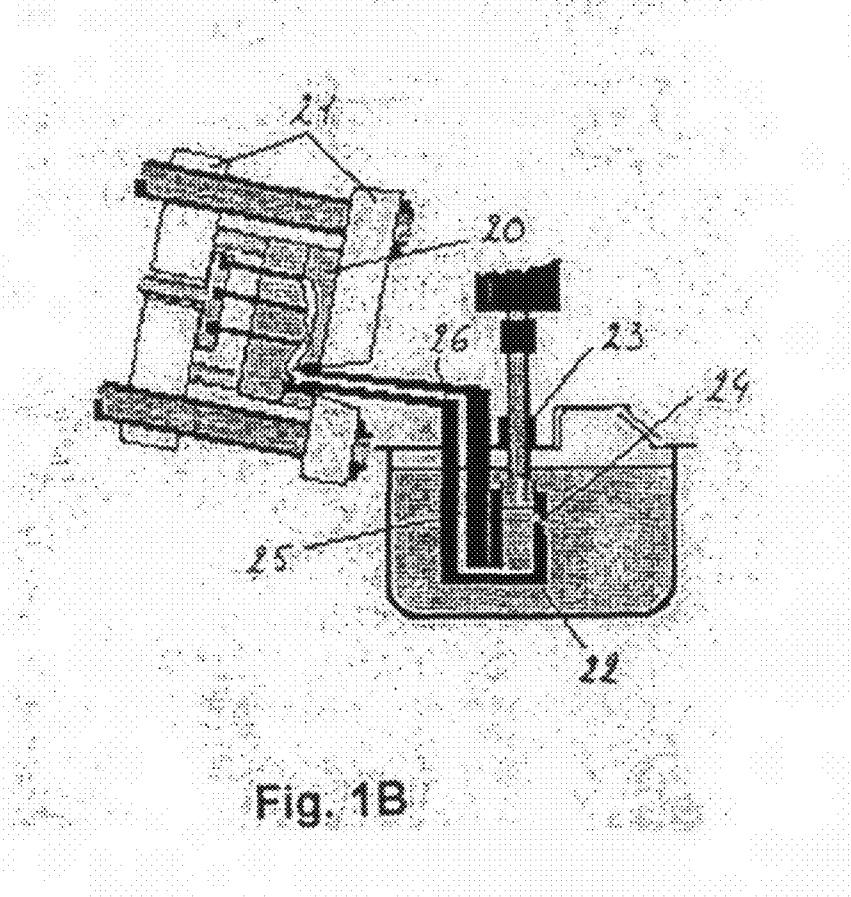


Fig. 1B

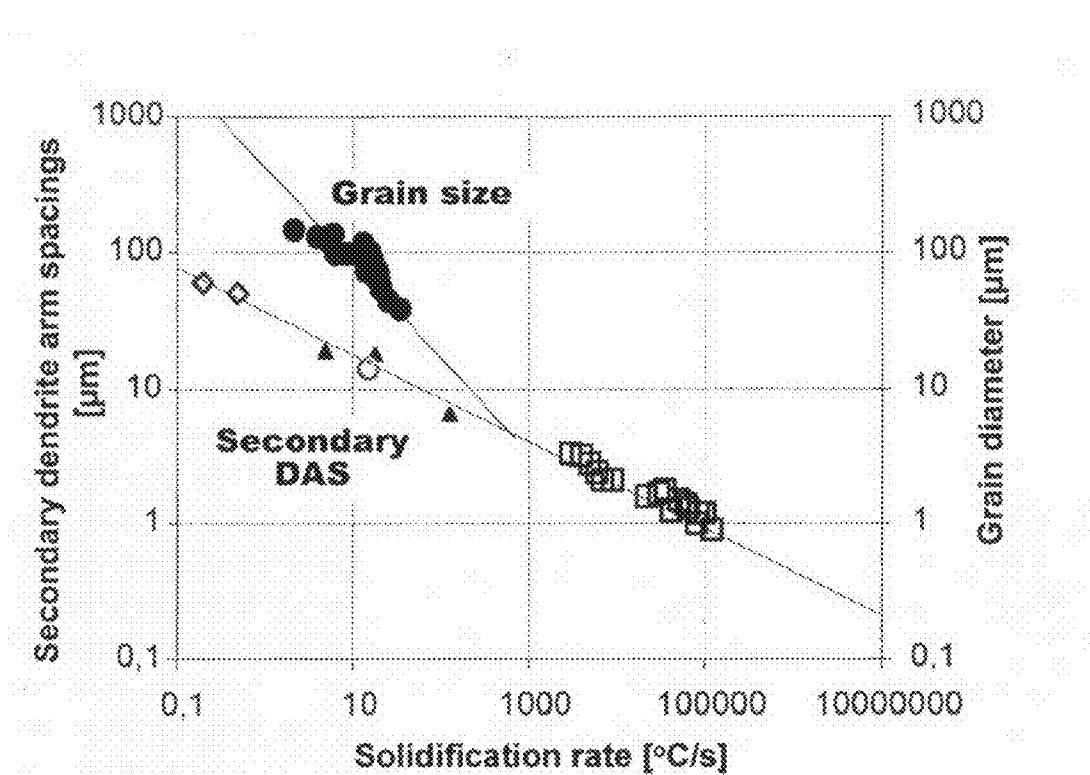


Fig. 2

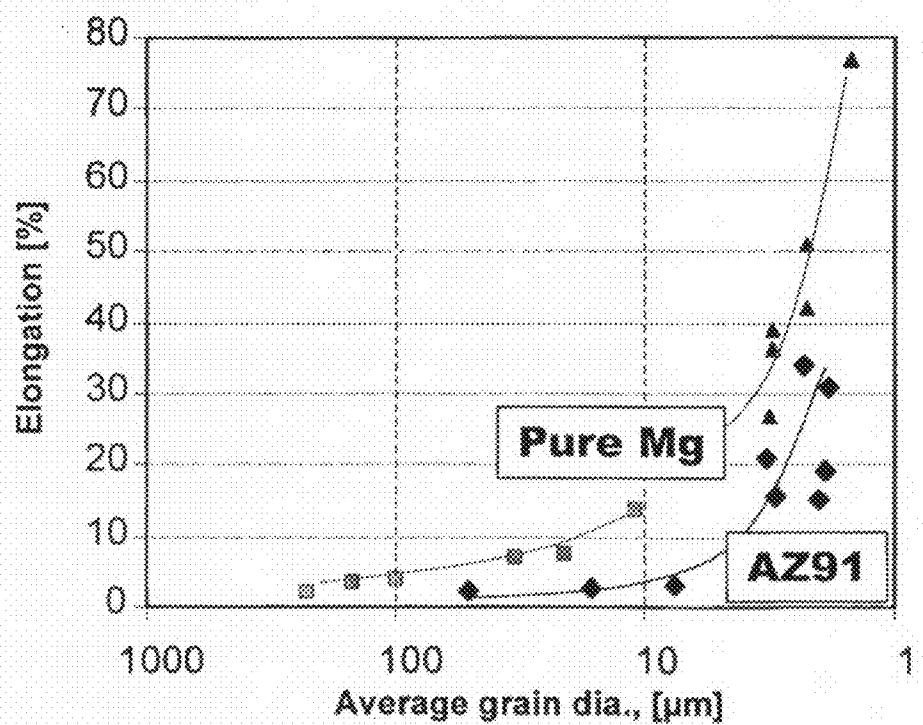


Fig. 3

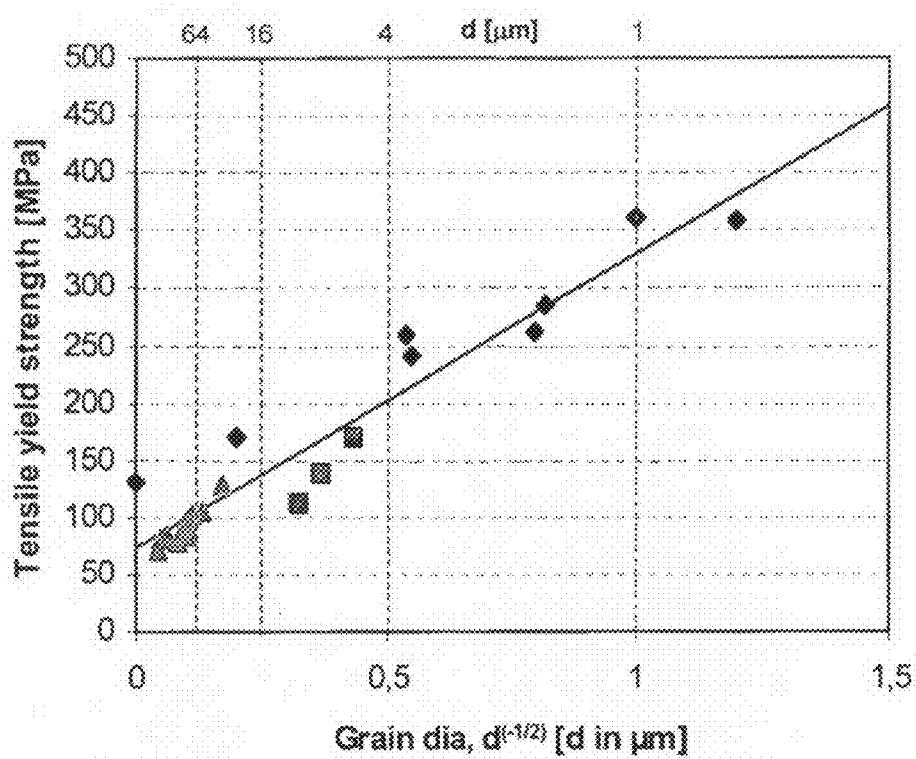
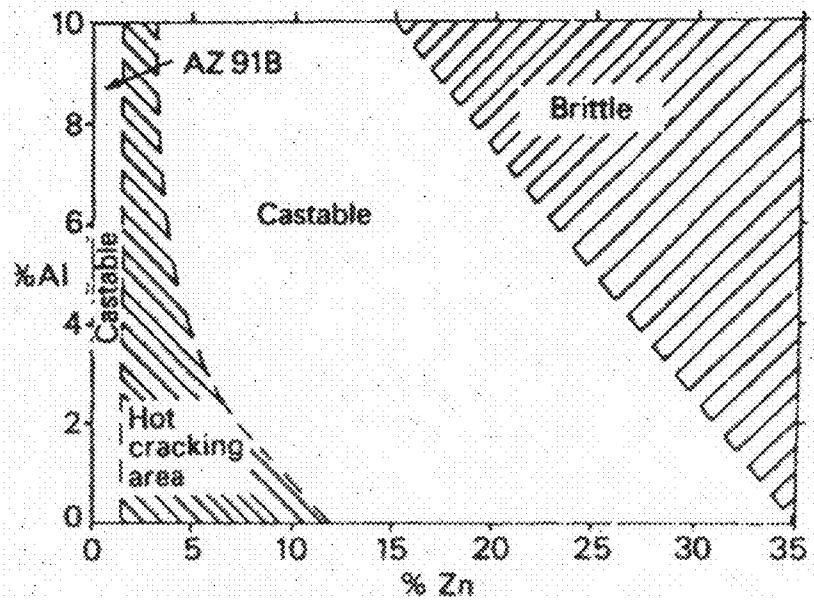


Fig. 4



G. S Foerster, "New developments in magnesium die casting",
IMA proceedings, 1976, p. 35-39

Fig. 5

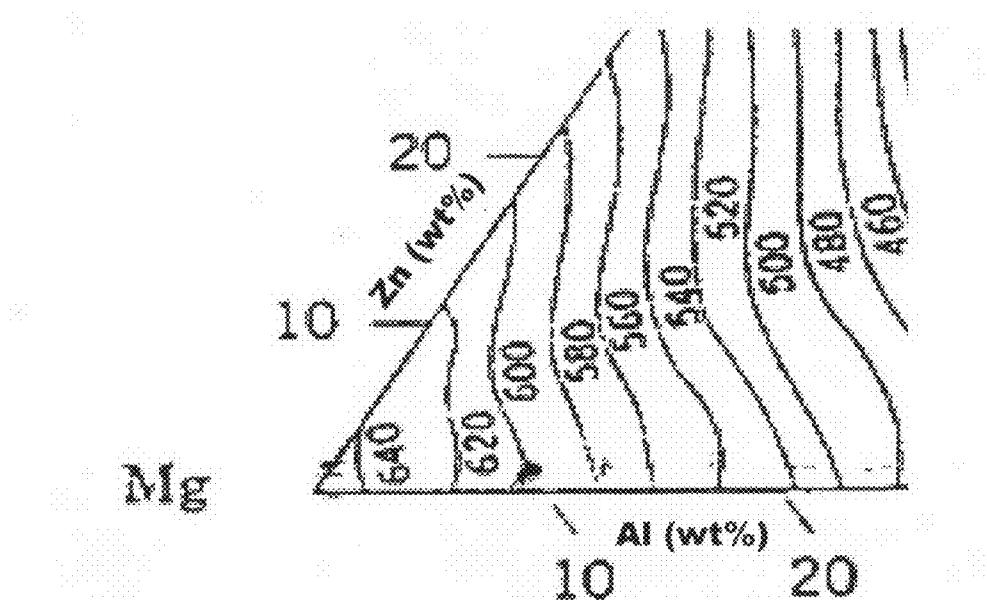


Fig. 6

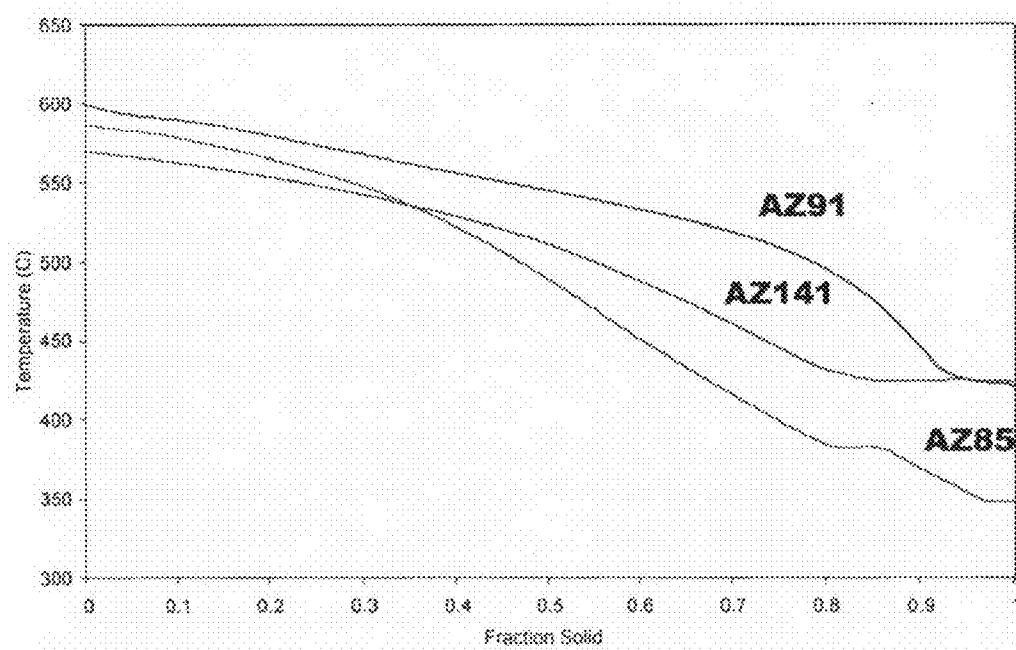


Fig. 7

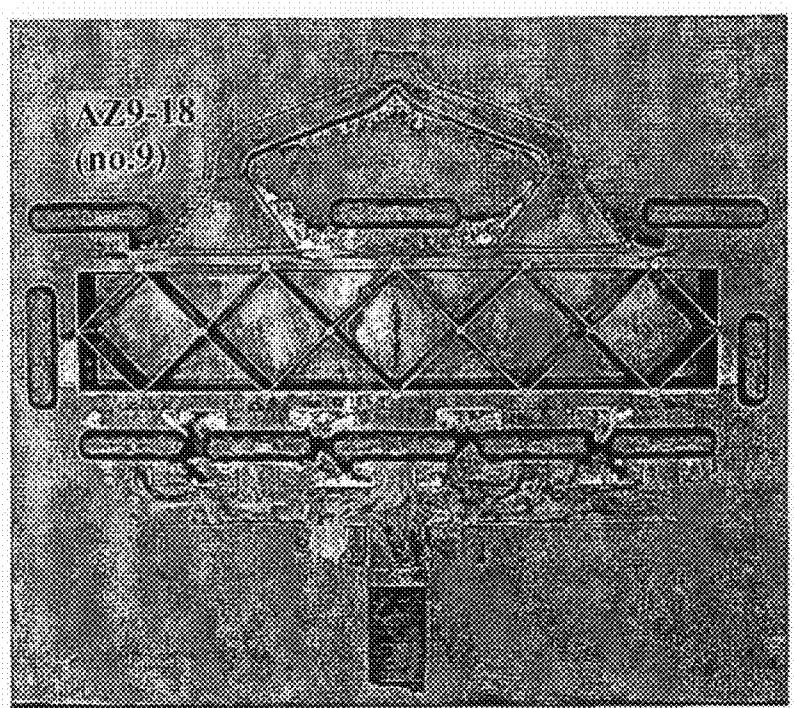


Fig. 8

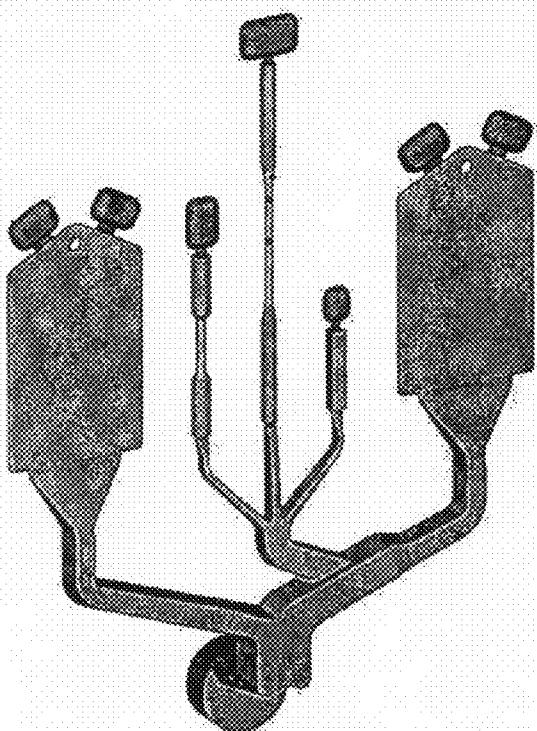


Fig. 9

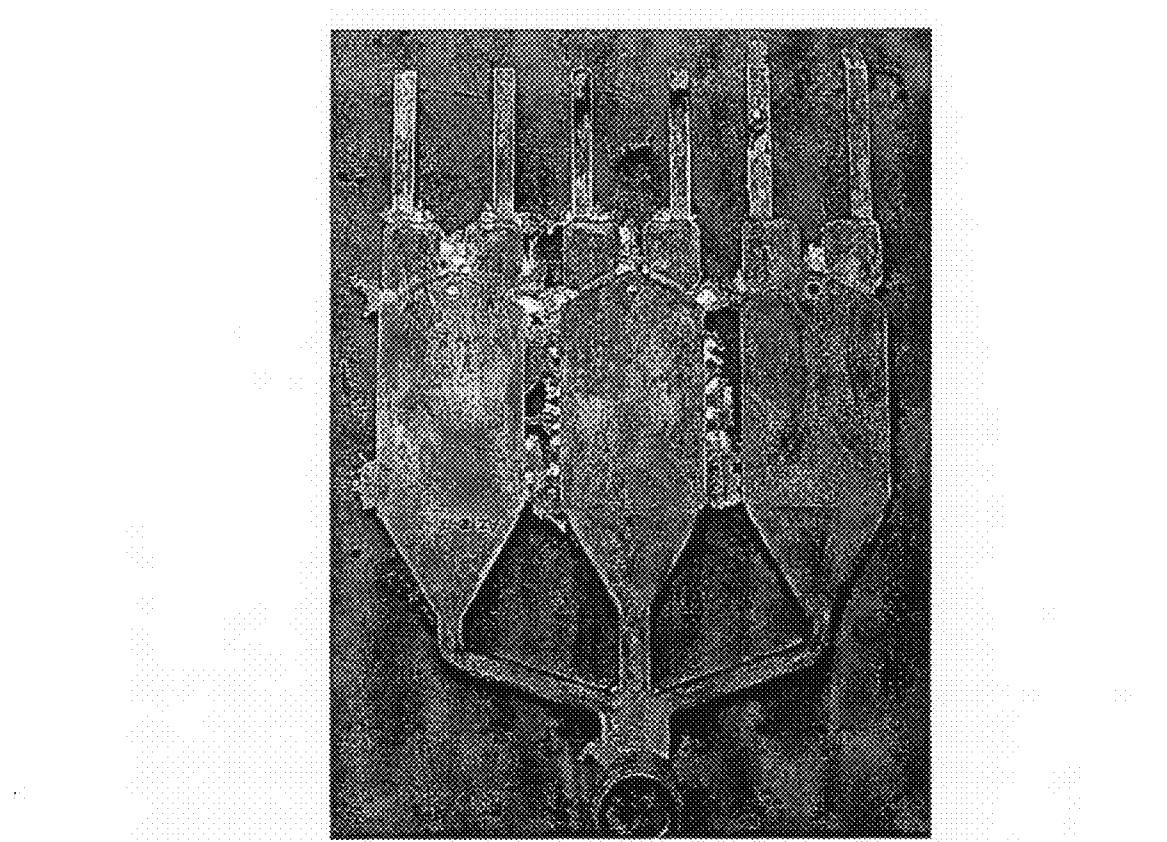


Fig. 10

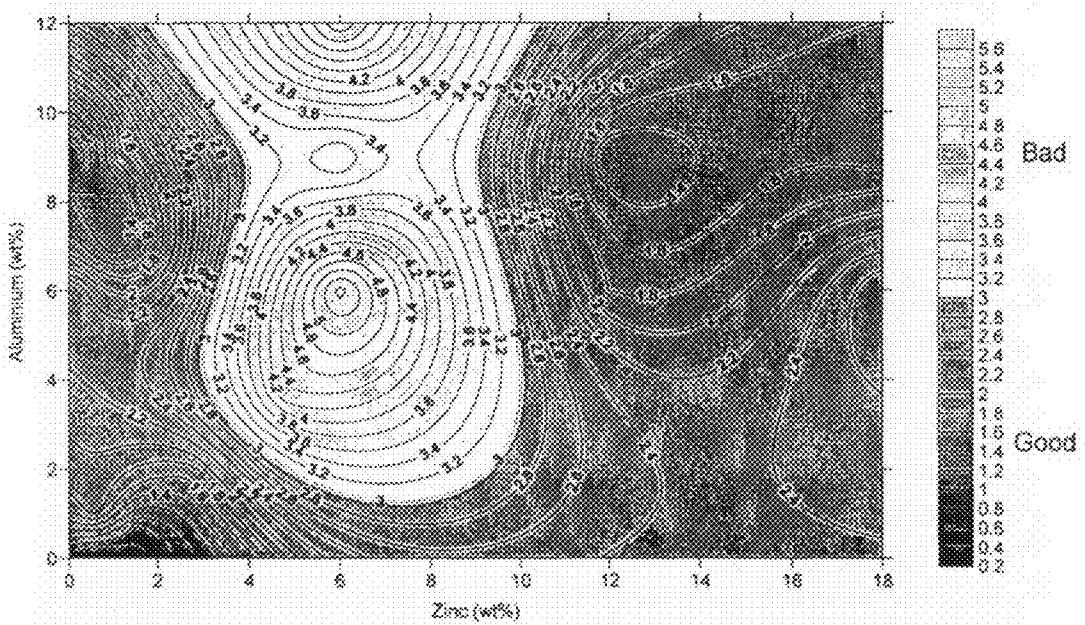


Fig. 11

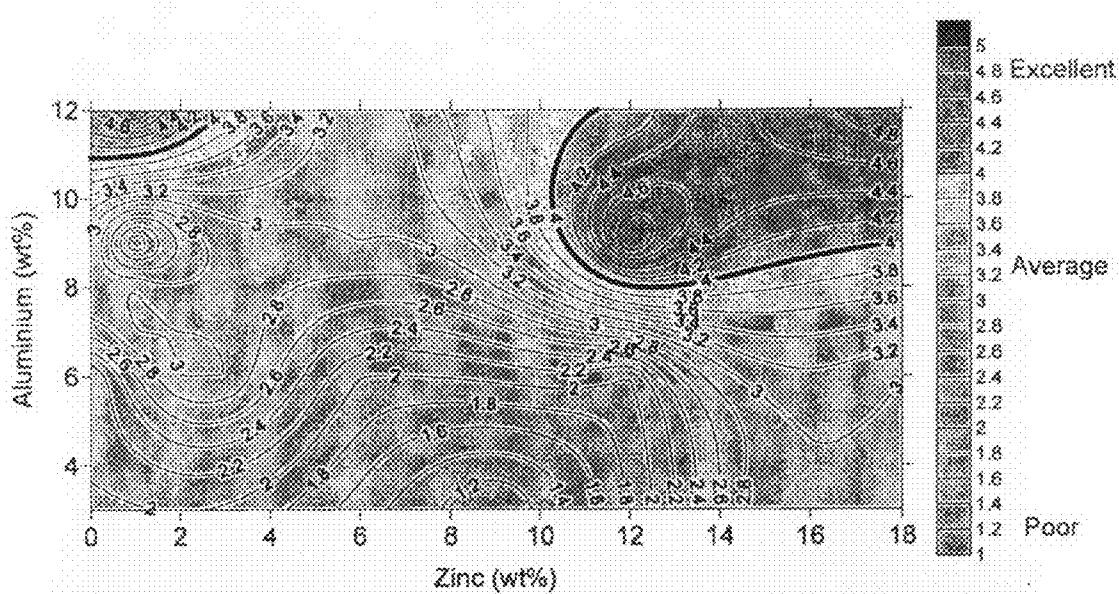


Fig. 12

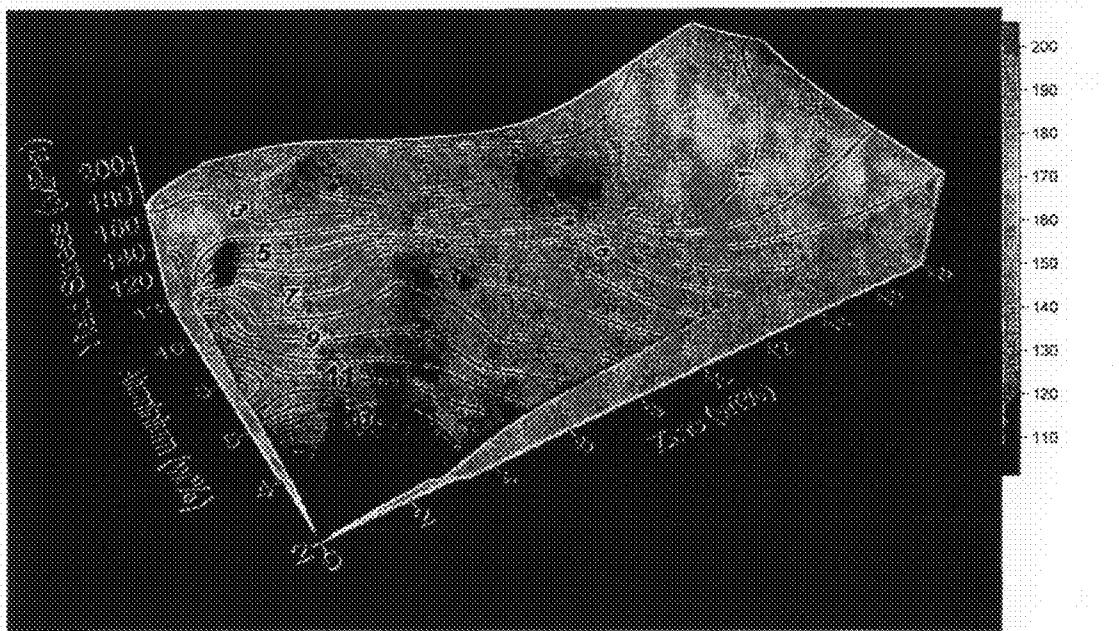


Fig. 13

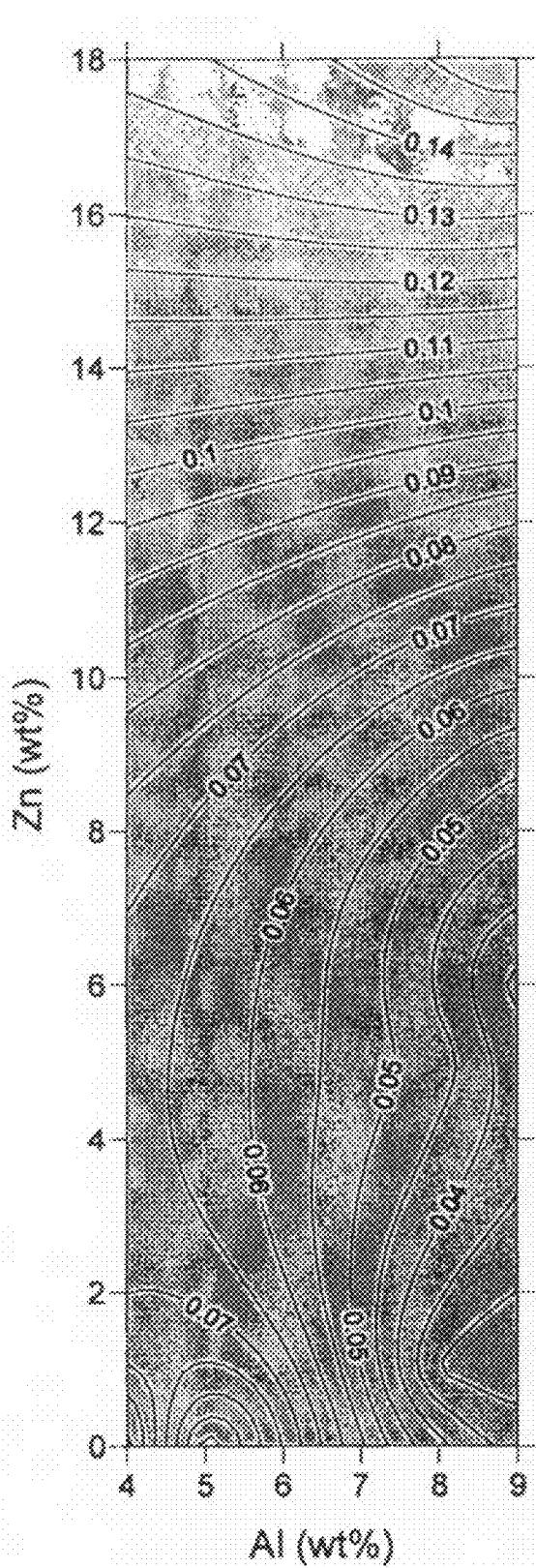


Fig.14

COMBINATION OF CASTING PROCESS AND ALLOY COMPOSITION

[0001] The present invention relates to a process for casting a magnesium alloy consisting of aluminium, zinc and manganese, and the balance being magnesium and unavoidable impurities, the total impurity level being below given % by weight.

[0002] Magnesium-based alloys are widely used as cast parts in automotive industries, and with increasing importance in 3C components (3C: computers, cameras and communications). Magnesium-based alloy cast parts can be produced by conventional casting methods, which include die-casting, sand casting, permanent and semi-permanent mould casting, plaster-mould casting and investment casting.

[0003] Mg-based alloys demonstrate a number of particularly advantageous properties that have prompted an increased demand for magnesium-based alloy cast parts in the automotive industry. These properties include low density, high strength-to-weight ratio, good castability, easy machinability and good damping characteristics. Most common magnesium die-casting alloys are such as Mg—Al-alloys or Mg—Al—Zn-alloys with <0.5% Mn, mainly Mg-9% Al-1% Zn (designated AZ91), Mg-6% Al (AM60) and Mg-5% Al (AM50).

[0004] WO 2006/000022 A1 describes a magnesium-based alloy containing zinc, aluminium, calcium and/or beryllium or optionally manganese by which is provided an attempt to improve the surface finish of cast magnesium components. The WO reference is, however, not particularly concerned with the castability of the alloy.

[0005] With the present invention is provided to provide relatively low cost magnesium-based alloy with improved surface finish and improved castability.

[0006] The invention is characterized by an alloy containing

[0007] 10.00-13.00% by weight of aluminium,

[0008] 0.00-10.00% by weight of zinc, and

[0009] 5.00-13.00% by weight of aluminium,

[0010] 10.00-22.00% by weight of zinc,

also containing

[0011] 0.10-0.5% by weight of manganese,

and the balance being magnesium and unavoidable impurities, the total impurity level being below 0.1% by weight, whereby

[0012] the alloy is cast in a die the temperature of which is controlled in the range of 150-340° C.,

[0013] the die is filled in a time which expressed in milliseconds is equal to the product of a number between 2 and 300 multiplied by the average part thickness expressed in millimeter,

[0014] the static metal pressures being maintained during casting between 20-70 MPa and may be subsequently intensified up to 180 MPa, as defined in the attached independent claim 1.

[0015] Dependent claims 2-11 define preferred embodiments of the invention.

[0016] By using the combination of a specified Mg—Al—Zn alloy with the special casting process as defined above, products may be made having excellent surface finish, reasonable ductility and acceptable mechanical properties as well as corrosion properties.

[0017] Preferably the aluminium content is between 5.00 and 13.00% by weight. If less than 10.00% Al is present the Zn content is restricted to 10.00-22.00% by weight. Lower Zn contents give poorer combination of castability and surface finish.

[0018] If more than 10.00% Al is present, the range of Zn can be extended to 0.00-22.00% still giving satisfactory castability and surface finish.

[0019] For applications requiring a minimum of ductility the composition of the alloy is selected in such a way that the aluminium content is between 10.00 and 12.00% by weight and the Zn-content is between 0.00 and 4.00% by weight. Alloys with equivalent castability and surface finish can be prepared if the composition of the alloy is such that the aluminium content is between 6.00 and 12.00% by weight and the Zn-content is between 10.00 and 22.00% by weight. These alloys offer the advantages of lower casting temperature.

[0020] The present invention will be further described in the following by means of examples and with reference to the attached drawings where:

[0021] FIGS. 1A, B each shows schematically cold chamber and hot chamber die casting machines, respectively,

[0022] FIG. 2 is a diagram showing the relationship between the solidification rate and the microstructure (grain size and secondary dendrite arm spacing) of cast Mg alloys,

[0023] FIG. 3 is a diagram showing the grain size vs. ductility of Mg alloys,

[0024] FIG. 4 is a diagram showing the grain size vs. tensile yield strength of Mg alloys,

[0025] FIG. 5 shows a chart from a prior art reference, G. S Foerster; "New developments in magnesium die casting", IMA proceedings 1976 p. 35-39, who split the composition range into a castable—, a brittle—and a hot cracking region,

[0026] FIG. 6 shows the Mg-rich corner of the Mg—Al—Zn phase diagram with lines of constant liquidus temperature,

[0027] FIG. 7 shows a diagram with the fraction solid (expressed in % by weight) on the horizontal axis versus the temperature (OC) on the vertical axis for three different Mg alloys,

[0028] FIGS. 8-10 show three different Mg alloy components being cast with three different dies,

[0029] FIG. 11 is a diagram showing casting defects, average number of cracks and defect ribs on the box die, FIG. 8, plotted as lines of equal number of defects in a diagram, where the Zn content is plotted along the x-axis and the Al content along the y-axis,

[0030] FIG. 12 is a diagram showing surface finish represented as a rating from 1 to 5 on the box die, FIG. 8, plotted as lines of equal rating in a diagram, where the Zn content is plotted along the x-axis and the Al content along the y-axis,

[0031] FIG. 13 is a diagram showing where the z-axis is representing the tensile strength expressed in MPa, while the x and y-axes are representing the Al and Zn contents, respectively, and where the ductility is represented as lines of equal % elongation in the same diagram,

[0032] FIG. 14 is a diagram showing corrosion rates in terms of weight loss being represented as lines of equal corrosion rates (mg/cm²/day), where the Zn content is plotted along the y-axis and the Al content along the x-axis.

[0033] In FIGS. 1A and 1B there are schematically shown cold chamber and hot chamber die castings machines respectively, each machine has a die 10, 20 provided with a hydraulic clamping system 11, 21, respectively.

[0034] Molten metal is introduced into the die by means of a shot cylinder 12, 22 provided with a piston 13, 23, respectively. In the cold chamber system as is shown in FIG. 1A, an auxiliary system for metering of the metal to the horizontal shot cylinder is required. The hot chamber machine, however, shown in FIG. 1 B, uses a vertical piston system 12, 23 directly in the molten alloy.

[0035] To obtain the excellent performance of the Mg—Al—Zn alloys, it is mandatory that the alloys are cast under extremely rapid cooling conditions. This is the case for the high pressure die casting process. The steel die 10, 20 is equipped with an oil (or water) cooling system controlling the die temperature in the range of 200-300° C. A prerequisite for good quality is a short die filling time to avoid solidification of metal during filling. A die filling time in the order of 10^{-2} s × average part thickness (mm) is recommended. This is obtained by forcing the alloy through a gate with high speeds typically in the range 30-300 m/s. Plunger velocities up to 10 m/s with sufficiently large diameters are being used to obtain the desired volume flows in the shot cylinder for the short filling times needed. It is common to use static metal pressures 20-70 MPa and subsequent pressure intensification up to 180 MPa may be used, especially with thicker walled castings. With this casting method the resulting cooling rate of the component is typically in the range of 10-1000° C./s depending on the thickness of the component being cast.

[0036] In FIG. 2 there is shown the relationship between the solidification range and the microstructure of a cast alloy. On the horizontal axis there is shown the solidification rate expressed as ° C./s and on the left hand vertical scale the secondary dendrite arm spacing expressed in μm is shown, whereas on the right hand vertical scale the grain diameter expressed in μm is shown. Line 30 indicates the grain size obtained, whereas line 31 is the obtained value for the secondary dendrite arm spacing.

[0037] With die casting grain refining is obtained by the cooling rate. As mentioned above cooling rates in the range of 10-1000° C./s are normally achieved. This typically results in grain sizes in the range of 5-100 μm .

[0038] It is well known that fine grain size is beneficial for the ductility of an alloy. This relationship is illustrated in the annexed FIG. 3, in which the relationship between grain size and relative elongation has been shown. On the horizontal axis the average grain size has been represented expressed in μm , whereas the vertical axis gives the relative elongation expressed in %. In the graph there are shown two different compositions, first pure Mg, line 35 and an Mg-alloy designated AZ91 (Mg-9% Al, 1% Zn), line 36.

[0039] It is also well known that fine grain size is beneficial for the tensile yield strength of an alloy. This relationship (Hall-Petch) is shown in the annexed FIG. 4. In the horizontal axis there is represented the grain diameter, expressed as $d^{(-0.5)}$, in which d has been expressed in μm , and in the vertical axis there is shown the tensile yield strength expressed in MPa.

[0040] It is therefore evident that the fine grain size provided by the very high cooling rates facilitated by the die casting process is a necessity for obtaining tensile strength and ductility.

[0041] The castability term describes the ability of an alloy to be cast into a final product with required functionalities and properties. It generally contains 3 categories; (1) the ability to form a part with all desired geometry features and dimensions, (2) the ability to produce a dense part with desired

properties, and (3) the effects on die cast tooling, foundry equipment and die casting process efficiency.

[0042] In the 3C industry extremely thin-walled components for e.g. lap-top and cell phone housings, often less than 0.5 mm, are cast. This puts strong requirements on the ability of the alloy to fill the mould and at the same time provide a smooth and shiny surface. AZ91 is the most common alloy for these applications, mainly due to the better castability compared to AM50 and AM60. However, the surfaces of thin walled components of AZ91 are often not satisfactory. Usually, a conversion coating is applied to these components. With a less shiny surface sometimes including areas with segregation of elements, multiple layers of coating has to be used. Generally, the better surface quality, the less coating is needed.

[0043] Mg—Al—Zn alloys with 0-10 wt % Al and 0-35 wt % Zn were examined in the 1970's (G. S Foerster; "New developments in magnesium die casting", IMA proceedings 1976 pp. 35-39). The chart shown in FIG. 5, from Foerster's paper, split the composition range into a castable—a brittle—and a hot cracking region. The alloys described in Australian patent WO 2006/000022 A1 that provide an attempt to improve the surface finish, are mainly inside the castable region of FIG. 5. The alloy composition ranges of the present invention are mainly outside the composition ranges described in the prior art (FIG. 5) and completely outside those described in patent WO 2006/000022 A1. During the tests that will be explained later it became evident that the alloys of the present invention represent considerable improvements over the earlier described alloys in terms of die filling, die sticking and hot cracking. These are all crucial features in die casting of complex thin-walled components.

[0044] The Mg—Al—Zn alloys with the Al and Zn content as specified in the present invention will start to solidify around 600° C., depending on the Al and Zn content. This is indicated in FIG. 6 where lines of constant liquidus temperature in the Mg-corner of the Mg-Al—Zn phase diagram are shown. As a result, the casting temperature, typically 70° C. above the liquidus, can be significantly lower than for the conventional AM50, AM60 and AZ91 alloys. Due to the fact that the eutectic $\text{Mg}_{17}\text{Al}_{12}$ phase melts at around 420° C., the conventional Mg—Al alloys like AM50, AM60 and AZ91 will have a solidification range of nearly 200° C. as shown in the annexed FIG. 7 which shows the fraction solid (expressed in % by weight) on the horizontal axis versus the temperature (° C.) on the vertical axis for three different alloys. Specifically, AZ91 starts to solidify at 600° C. and is completely solidified at 420° C. Increasing the Al content to 14% as in alloy AZ141, the start of solidification occurs at around 570° C. while solidification is complete at 420° C. Due to the significant presence of Zn the alloy AZ85 solidifies in the range 590-350° C. Since Zn in the Mg—Al—Zn alloy modifies the eutectic $\text{Mg}_{17}\text{Al}_{12}$ phase, the alloy will solidify completely at temperatures significantly lower than 420° C. as is the case for the conventional alloys AM50, AM60 and AZ91.

[0045] In general, increasing aluminium content in Mg—Al die casting alloys improves the die castability. This is due to the fact that Mg—Al alloys have a wide solidification range, which makes them inherently difficult to cast unless a sufficiently large amount of eutectic is present at the end of solidification. This can explain the good castability of AZ91D consistent with the cooling curves shown in FIG. 7. With the large amount of Zn in addition to Al in the present alloys there is an even larger amount of (modified) eutectic present at the

end of solidification, explaining the improved castability of the invented Mg—Al—Zn alloys.

[0046] Magnesium alloys tend to ignite and oxidize (burn) in the molten state unless protected by cover gases such as SF₆ and dry air with or without CO₂, or SO₂ and dry air. The oxidation aggravates with increasing temperature. Usually, small amounts of beryllium (10-15 ppm by weight) are also added to reduce the oxidation. Beryllium is known to form toxic substances and should be used with care. Especially the treatment of dross and sludge from the cleaning of crucibles requires considerable safety precautions due to an enrichment of Be-compounds in dross/sludge. One advantage of the present invention is that the alloy can be cast at temperatures significantly lower than for conventional alloys, thereby reducing the need for cover gases. For the same reason, beryllium additions can be kept at a minimum.

[0047] The lower casting temperatures compared to conventional alloys also offer significant advantages as the lifetime of the metering system, the shot cylinder and the die will all be improved. With hot chamber die casting in particular, the lifetime of the gooseneck will be significantly extended. The alloys with lower casting temperature also have a potential for reducing the cycle time, thereby improving the productivity of the die casting operation.

EXAMPLE 1

[0048] In order to evaluate the influence of the alloying elements and a number of Mg-alloys have been prepared and cast in three different dies:

[0049] The box die with ribs, FIG. 8

[0050] The plate/bar die, FIG. 9

[0051] The three plate die, FIG. 10

[0052] The alloy compositions and the casting temperatures are shown in Table 1 below.

TABLE 1

	Al (wt %)	Zn (wt %)	Casting Temp (C.)
AM20	2	0	710
AZ21	2	1	710
AZ22	2	2	705
AZ2-3.5	2	3.5	700
AM40	4	0	700
AZ41	4	1	695
AZ42	4	2	695
AZ4-3.5	4	3.5	690
AZ45	4	5	680
AZ4-14	4	14	650
AZ4-18	4	18	630
AM60	6	0	680
AZ61	6	1	680
AZ62	6	2	680
AZ63	6	3	680
AZ6-3.5	6	3.5	680
AZ65	6	5	670
AZ66	6	6	670
AZ6-12	6	12	640
AZ6-18	6	18	610
AZ71	7	1	680
AZ72	7	2	680
AM80	8	0	680
AZ81	8	1	680
AZ82	8	2	670
AZ8-3.5	8	3.5	670
AZ85	8	5	670
AM90	9	0	670
AZ91	9	1	670
AZ96	9	6	650

TABLE 1-continued

	Al (wt %)	Zn (wt %)	Casting Temp (C.)
AZ99	9	9	640
AZ9-12	9	12	620
AZ9-18	9	18	585
AZ9-22	9	22	560
AM100	10	0	660
AZ10-1	10	1	660
AZ10-2	10	2	660
AZ10-3.5	10	3.5	650
AZ10-5	10	5	650
AM120	12	0	650
AZ12-1	12	1	650
AZ12-2	12	2	640
AZ12-3.5	12	3.5	640
AZ12-5	12	5	630
AZ12-6	12	6	630
AZ12-12	12	12	590
AZ12-18	12	18	550
AM140	14	0	640
AZ14-1	14	1	630
AZ14-2	14	2	630
AZ14-3.5	14	3.5	620
AZ14-5	14	5	610

[0053] Details of the casting parameters are given in Table 2 below.

TABLE 2

	Velocity 1 (m/s)	Velocity 2 (m/s)	Braking (m/s)	Calculated Fill Time (ms)
Die 1 Tensile specimen	0.5	5	3	50
Die 2 Three Plate	0.5	5	2.5	53
Die 3 Box	0.5	5	3	40

[0054] No intensification pressure was used.

[0055] The performed tests are the following:

Evaluation of Casting Defects

[0056] Visual inspection was undertaken on 10 arbitrary boxes from each alloy.

[0057] Defects were grouped as

[0058] Defect ribs including incomplete filling and cold shuts

[0059] Hot tears counted on nodes

[0060] End cracks

Evaluation of Surface Finish

[0061] Surface finish was inspected visually by several persons independently, and rated from 1 to 5 (5 best).

Tensile Strength and Ductility

[0062] Test-bars of 6 mm diameter in accordance to ASTM B557M have been made, and the following test conditions have been used:

[0063] 10 kN Instron test machine

[0064] Room temperature

[0065] At least 10 parallels

[0066] Strain rate

[0067] 1.5 mm/min up to 0.5% strain,

[0068] 10 mm/min above 0.5% strain

[0069] Testing in accordance with ISO 6892

Corrosion Properties

[0070] The corrosion tests were done according to ASTM B117.

EXAMPLE 2

[0071] Casting defects average number of cracks and defect ribs are plotted in FIG. 11 as lines of equal number of defects in a diagram where the Zn content is plotted along the x-axis and the Al content along the y-axis. It is seen that the lowest numbers of cracks are found in the regions with low Zn (<3%) and high Zn ($\geq 10\%$). It is seen that that particularly good alloys in terms of casting defects are found with Al in the range of 8-10% by weight and with Zn<2% by weight; the lower Zn the better. Also, alloys with Al in the range of 7-12% by weight and Zn in the range 12-18% by weight exhibit very few casting defects.

EXAMPLE 3

[0072] Surface finish represented as a rating from 1 to 5 is plotted in FIG. 12 as lines of equal rating in a diagram where the Zn content is plotted along the x-axis and the Al content along the y-axis. It is seen that the best regions in terms of surface finish rating are found with Al>11% by weight and Zn<3% by weight; the lower Zn the better. Also, a region roughly defined by 8-12% Al by weight and >10% Zn by weight provides alloys with superior surface finish.

EXAMPLE 4

[0073] For a number of compositions the strength and elongation have been measured at room temperature. The results are shown in FIG. 13. Here, the z-axis is representing the tensile strength expressed in MPa, whereas the x and y-axes are representing the Al and Zn contents, respectively. The ductility is represented as lines of equal elongation in the same diagram. Generally it is seen that tensile strength expressed in MPa, increases with increasing content of alloying elements. The effect of increasing Al (% by weight) is significantly greater than the effect of Zn. FIG. 13 also indicates that the ductility in terms of % elongation decreases with increasing content of alloying elements. As an example, the line indicating 3% elongation extends almost linearly from 12% Al by weight and 0% Zn to 0% Al and 18% Zn by weight.

EXAMPLE 5

[0074] For a number of compositions the corrosion properties have been defined in accordance to ASTM B117. In this test a great amount of data has been incorporated in order to define the influence of the Zn-content versus the Al-content. The results are shown in FIG. 14.

[0075] In this figure corrosion rates in terms of weight loss is represented as lines of equal corrosion rates (mg/cm²/day), in a diagram where the Zn content is plotted along the y-axis and the Al content along the x-axis. It is seen that for Zn contents lower than approximately 8% by weight, the corrosion rates decrease with increasing Al content and are practically independent of the Zn content, whereas for Zn contents above approximately 12% by weight the corrosion rates increases slightly with increasing Zn content and are practically independent of the Al content. The region defined by 8-12% by weight of Zn represents a transition. Specifically, at 0% Zn the corrosion rate decreases from about 0.09 mg/cm²/day at 4% Al by weight to approximately 0.03 mg/cm²/day at 9% Al by weight. At constant 9% Al by weight the corrosion rate increases to 0.05 mg/cm²/day at 8% Zn by weight and 0.11 mg/cm²/day at 14% Zn by weight.

[0076] From these test results it is clear that a process for casting a magnesium alloy has been provided whereby products are obtained with a superior combination of elevated temperature creep properties, ductility and corrosion performance.

1. A process for casting a magnesium alloy consisting of 10.00-13.00% by weight of aluminium, 0.00-10.00% by weight of zinc, and 5.00-13.00% by weight of aluminium, 10.00-22.00% by weight of zinc, also containing 0.10-0.5% by weight of manganese, and the balance being magnesium and unavoidable impurities, the total impurity level being below 0.1% by weight, wherein the alloy is cast in a die in which the temperature is controlled in the range of 150-340° C., the die is filled in a time which expressed in milliseconds, is equal to the product of a number between 2 and 300 multiplied by the average part thickness expressed in millimeter, the static metal pressures being maintained during casting is between 20-70 MPa and may subsequently be intensified up to 180 MPa.
2. A process according to claim 1, characterized in that the die temperature is controlled to a temperature in the range between 160 and 300° C., preferably in the range between 200 and 270° C.
3. A process according to claim 1, characterized in that the filling time of the die expressed in milliseconds is equal to the product of the average part thickness expressed in millimetre multiplied by a number between 2 and 200, preferably between 3 and 50, most preferably between 3 and 20.
4. A process according to claim 3, characterized in that the static metal pressure during casting is maintained between 30-70 MPa.
5. A process according to claim 4, characterized in that the cooling rate after casting is in the range of 10-1000° C./s.
6. A process according to claim 5, characterized in that the aluminium content is between 10.00 and 13.00% by weight, preferably between 10.00 and 12.00% by weight.
7. A process according to claim 6, characterized in that the Zn content is between 0.00 and 10.00% by weight.
8. A process according to claim 7, characterized in that the aluminium content is between 10.00 and 12.00% by weight and the Zn-content is between 0.00 and 4.00% by weight.
9. The process according to claim 5, characterized in that the aluminium content is between 5.00 and 13.00% by weight, preferably between 6.00 and 12.00% by weight.
10. The process according to claim 9, characterized in that the Zn content is between 10.00 and 22.00% by weight.
11. The process according to claim 10, characterized in that the aluminium content is between 6.00 and 12.00% by weight and the Zn-content is between 10.00 and 18.00% by weight.

* * * * *