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(54) **Magnesium alloy containing rare earth metals**

(57) The present invention relates to single-phase solid solution magnesium alloys suitable for the applications as cast or wrought. These alloys are prepared by multi-microalloying with rare earth elements (including gadolinium, yttrium, dysprosium, samarium, lanthanum, cerium, neodymium and praseodymium). Each alloy contains 0.5 to less than 5 wt.% rare earth elements with a content of 0.05-2.0 % by weight. The total amount of rare

earth elements is controlled below 5 % by weight in order for economical considerations. The amount of grain refiner calcium or zirconium is in the range of 0.05-0.6 % by weight. These alloys can be prepared by die casting, permanent casting, chill casting, semi-solid processes, continuous casting and continuous twin roll casting.

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Description**FIELD OF THE INVENTION**

5 **[0001]** The present invention relates to cast and wrought single-phase solid solution magnesium alloys with high mechanical properties, formability and corrosion resistance.

BACKGROUND

10 **[0002]** Magnesium alloys have not yet been widely accepted by car manufacturers. Most of the technical barriers preventing magnesium alloys from widespread applications arise from the low ductility and toughness at low temperatures, poor corrosion and creep resistance at high temperatures. Their present commercial products are normally fabricated by high pressure die casting. The use of wrought magnesium alloys is limited because of its poor formability and corrosion resistance.

15 **[0003]** It will be necessary to improve the low-temperature formability of wrought magnesium alloys in order to obtain a higher acceptance of these alloys in industry. Low ductility and low toughness are due to the intrinsically brittle nature of the hexagonal close-packed crystal structure. A further issue which hinders the acceptance of wrought magnesium alloys is their poor corrosion resistance.

20 **[0004]** Most commercial wrought magnesium alloys belong to magnesium-aluminium (Mg-Al) and magnesium-zinc (Mg-Zn) series. The later developed magnesium-rare earth (Mg-RE) series such as WE43 (Mg-4.1Y-2.2Nd-1Hf-0.5Zr) and WE54 (Mg-5.2Y-1.7Nd-1.7Hf-0.4Zr) alloys were not accepted by the industry due to their high price arising from the high content of rare earth elements.

25 **[0005]** The alloys of magnesium-aluminium series are the most commonly used in wrought applications for their relative ease of extrusion and adequate mechanical properties, but they suffer from both a pronounced asymmetry in the yield behaviour and a relatively narrow processing window. Due to the lower eutectic temperature 437°C for magnesium-aluminium alloys, the hot processing temperatures are normally selected below 350°C and the processing speeds are not so high. If selecting high temperatures more than 350°C with high processing speeds, the eutectic phases dissolve again, leading to the occurrence of hot cracking and bad surface quality of the products. In addition, until now, the methods for refining the as-cast microstructures of magnesium-aluminium alloys are not satisfying and not widely accepted by the industry.

30 **[0006]** Since magnesium-zinc series contain no aluminium, their as-cast microstructure can be effectively refined by the addition of zirconium. However, these magnesium-zinc alloys still have very limited applications because they are susceptible to microporosity during casting. The addition of zinc in magnesium increases the susceptibility to hot tearing. Moreover, due to the high content of zinc, it was considered that these alloys are difficult to be welded.

35 **[0007]** Therefore, at present only AZ31 (Mg-2.9Al-0.8Zn) alloy is used in industry to an significant extent. However, AZ31 (Mg-2.9Al-0.8Zn) alloy exhibits some problems with recrystallisation during the hot working and has insufficient mechanical and corrosion properties.

[0008] It is therefore the object of the present invention to develop new magnesium alloys with high corrosion resistance and formability using innovative alloy design concept.

SUMMARY OF THE INVENTION

40 **[0009]** Accordingly, the present invention provides a magnesium alloy comprising 0.5 wt.% to less than 5.0 wt.% of at least two elements selected from the group consisting of La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu and Y, wherein the content of each of said elements La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu and Y, if present, is from 0.05 to 2.0 % by weight, based on the total weight of the alloy. Preferably, the amount of the at least two elements selected from the group consisting of La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu and Y, is from 1.0 wt.% to less than 5.0 wt.%.

DETAILED DESCRIPTION OF THE INVENTION

50 **[0010]** The strengthening effects of rare earths in the previous magnesium alloys have been explained by two mechanisms, precipitate strengthening and solid solution strengthening. Precipitate strengthening, especially the age hardening, has been emphasised to improve the mechanical properties. Without being bound to any theory, it is believed that in alloys of the present invention, precipitate strengthening is avoided and that solid solution strengthening is the main mechanism which improves the mechanical properties in the magnesium alloys according to the present invention.

55 **[0011]** It is further believed that the solid solution strengthening depends on the contents of alloying elements in the matrix of magnesium and the difference in atomic radius between the alloying elements and magnesium such that a

high content of alloying elements and large difference in atomic radius increase the effect of solid solution strengthening.

[0012] In addition, it has been found that there exists a synergistic effect caused by the interaction of the different rare earth elements. With the same total content of rare earth elements in the magnesium alloy, the improvement in mechanical properties is higher when two different rare earth elements are present in comparison to the improvement achieved with the presence of only one rare earth element.

[0013] Furthermore, the addition of rare earth elements can purify the melt during casting. The addition of rare earth elements can remove impurity elements such as hydrogen, oxygen, chlorine, etc. Moreover, they interact with iron, cobalt, nickel or copper elements during melting, and these elements are removed by the formation of intermetallic compounds which settle at the bottom of the ingot. The decrease of impurities in the matrix also contributes to the high corrosion resistance.

[0014] Preferably, the magnesium alloy of the present invention further comprises an element selected from the group consisting of Zr, Ca, Zn, and mixtures thereof. The stress corrosion of magnesium alloys could be alleviated by the addition of zirconium (Zr) and rare earth elements. Zirconium (Zr) can be used as an element to decrease the stress corrosion cracking.

[0015] Preferably, the magnesium alloys according to the present invention contain no aluminium; therefore, their as-cast microstructure can effectively be refined by the addition of zirconium or calcium.

[0016] In principle, two groups of rare earth elements can be classified in periodic table: light rare earth elements and heavy rare earth elements. In each group, rare earth elements have the similar chemical and physical properties. Due to the similar properties of yttrium and scandium to heavy rare earth elements, for the purposes of the present invention Y and Sc are treated as they were heavy rare earth elements. The light rare earth elements include samarium, lanthanum, cerium, neodymium, and praseodymium, and the heavy rare earth elements include gadolinium, yttrium and dysprosium. Besides the rare earth elements, zirconium and/or calcium are preferably added as a grain refiner.

[0017] The magnesium alloys of the present invention comprise 0.5 wt.% to less than 5.0 wt.% of at least two rare earth elements with a content of 0.05 to 2.0 % by weight of each of the rare earth elements. The total content of rare earths is maintained below 5 wt.%, mainly for economical reasons. The content of grain refiner calcium and/or zirconium is preferably in the range of 0.05-0.6% by weight.

[0018] The manufacturing processes of the magnesium alloys according to the present invention are not restricted. The alloys can be prepared by die casting, permanent casting, chill casting, semi-solid processes, continuous casting or continuous twin roll casting.

[0019] The magnesium alloys according to the present invention exhibit excellent room temperature ductility with a value of about 25%.

[0020] Tensile tests show that as-cast alloy Mg0.4Gd0.4Y0.4Dy0.2Zr and Mg0.4Gd0.4Y0.4Dy0.2Zn0.2Zr exhibit excellent ductility. The elongation is more than 20%, which is much higher than that of AZ31 alloy. These two alloys have shown a good deformability.

BRIEF DESCRIPTIONS OF THE DRAWINGS

[0021] The above and other characteristics and advantages of the invention will be more readily apparent through the following examples, and with reference to the appended drawings, where:

Figure 1 compares the optical microstructure of the investigated, as cast alloys ((a) Mg, (b) Mg-0.4Y, (c) Mg-0.4Gd-0.4Y, (d) Mg-0.4Gd-0.4Y-0.4Dy, (e) Mg-0.4Gd-0.4Y-0.4Dy-0.2Zr, (f) Mg-0.4Gd-0.4Y-0.4Dy-0.2Zn, (g) Mg-0.4Gd-0.4Y-0.4Dy-0.2Ca, (h) Mg-0.4Gd-0.4Y-0.4Dy-0.2Zn-0.2Zr and (i) AZ31);

Figure 2 shows the grain size, hardness and corrosion properties of the investigated alloys;

Figure 3 shows the tensile properties of selected as-cast alloys; and

Figure 4 shows the microstructural situation and the micro-segregation of the alloying elements.

EXAMPLES

[0022] Three rare earth elements gadolinium, yttrium, dysprosium with high solubility in magnesium were selected to develop the single-phase solid solution magnesium alloys. Table 1 lists the compositions of the investigated alloys. A conventional alloy, Mg-3Al-1Zn (AZ31), was included for comparison.

[0023] All alloys were prepared by zone solidification. Their optical microstructures are shown in Figure 1. The average grain size decreases with the increment in the content of rare earths. Compared to the gadolinium and dysprosium, the yttrium element is the most effective element to decrease the grain size. The average grain sizes of E and H alloys containing zirconium are 55 μm and 67 μm . The average grain size of Mg-3Al-1Zn (AZ31) is 480 μm .

Table 1. Nominal compositions of the investigated alloys

Alloys	(Composition (weight percent, wt. %))							
	Mg	Gd	Y	Dy	Zn	Al	Zr	Ca
A-Pure Mg	100	-	-	-	-	-	-	-
B-Mg0.4Y	Bal*	-	0.4	-	-	-	-	-
C-Mg0.4Gd0.4 Y	Bal	0.4	0.4	-	-	-	-	-
D-Mg0.4Gd0.4 Y0.4Dy	Bal	0.4	0.4	0.4	-	-	-	-
<u>E-Mg0.4Gd0.4Y0.4Dy0.2Zr</u>	Bal	0.4	0.4	0.4	-	-	0.2	-
F-Mg0.4Gd0.4 Y0.4Dy0.2Zn	Bal	0.4	0.4	0.4	0.2	-	-	-
G-Mg0.4Gd0.4 Y0.4Dy0.2Ca	Bal	0.4	0.4	0.4	-	-	-	0.2
H-Mg0.4Gd0.4 Y0.4Dy0.2Zn0.2Zr	Bal	0.4	0.4	0.4	0.2	-	0.2	-
I-AZ31	Bal	-	-	-	1.0	3.0	-	-
* Balance.								

Claims

1. A magnesium alloy comprising 0.5 wt.% to less than 5.0 wt.% of at least two elements selected from the group consisting of La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu and Y, wherein the content of each of said elements La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu and Y, if present, is from 0.05 to 2.0 % by weight, based on the total weight of the alloy.
2. The magnesium alloy of claim 1 further comprising an element selected from the group consisting of Zr, Ca, Zn, and mixtures thereof.
3. The magnesium alloy of any of claims 1 or 2 which contains no aluminium.
4. The magnesium alloy of any of the previous claims consisting of (a) Mg; (b) 0.5 wt.% to less than 5.0 wt.% of at least two elements selected from the group consisting of La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu and Y; and (c) optionally Zr, Ca and/or Zn; wherein the content, based on the total weight of the alloy, of each of said elements La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu and Y, if present, is from 0.05 to 2.0 % by weight; and wherein the content, based on the total weight of the alloy, of each of said elements selected from the group consisting of Zr, Ca and Zr, if present, is from 0.05 to 0.6 wt.%; the remainder being magnesium.
5. The magnesium alloy according to any of the previous claims, wherein Gd is present in an amount by weight of 0.05 to 2.0 %.
6. The magnesium alloy according to any of the previous claims, wherein Y is present in an amount by weight of 0.05 to 2.0 %.
7. The magnesium alloy according to any of the previous claims, wherein Dy is present in an amount by weight of 0.05 to 2.0 %.
8. The magnesium alloy according to any of the previous claims, wherein Sm is present in an amount by weight of 0.05 to 2.0 %.
9. The magnesium alloy according to any of the previous claims, wherein La is present in an amount by weight of 0.05 to 0.3 %.
10. The magnesium alloy according to any of the previous claims, wherein Ce is present in an amount by weight of 0.05 to 0.3 %.
11. The magnesium alloy according to any of the previous claims, wherein Nd is present in an amount by weight of 0.05

to 0.3 %.

12. The magnesium alloy according to any of the previous claims, wherein Pr is present in an amount by weight of 0.05 to 0.3 %.

5 13. The magnesium alloy according to any of the previous claims, wherein Ca is present in an amount by weight of 0.05 to 0.4 %.

10 14. The magnesium alloy according to any of the previous claims, wherein Zr is present in an amount by weight of 0.2 to 0.6 %.

15 15. Use of the magnesium alloys according to any of claim 1 to 14 as casting magnesium alloys, wrought magnesium alloys, or degradable biomaterials.

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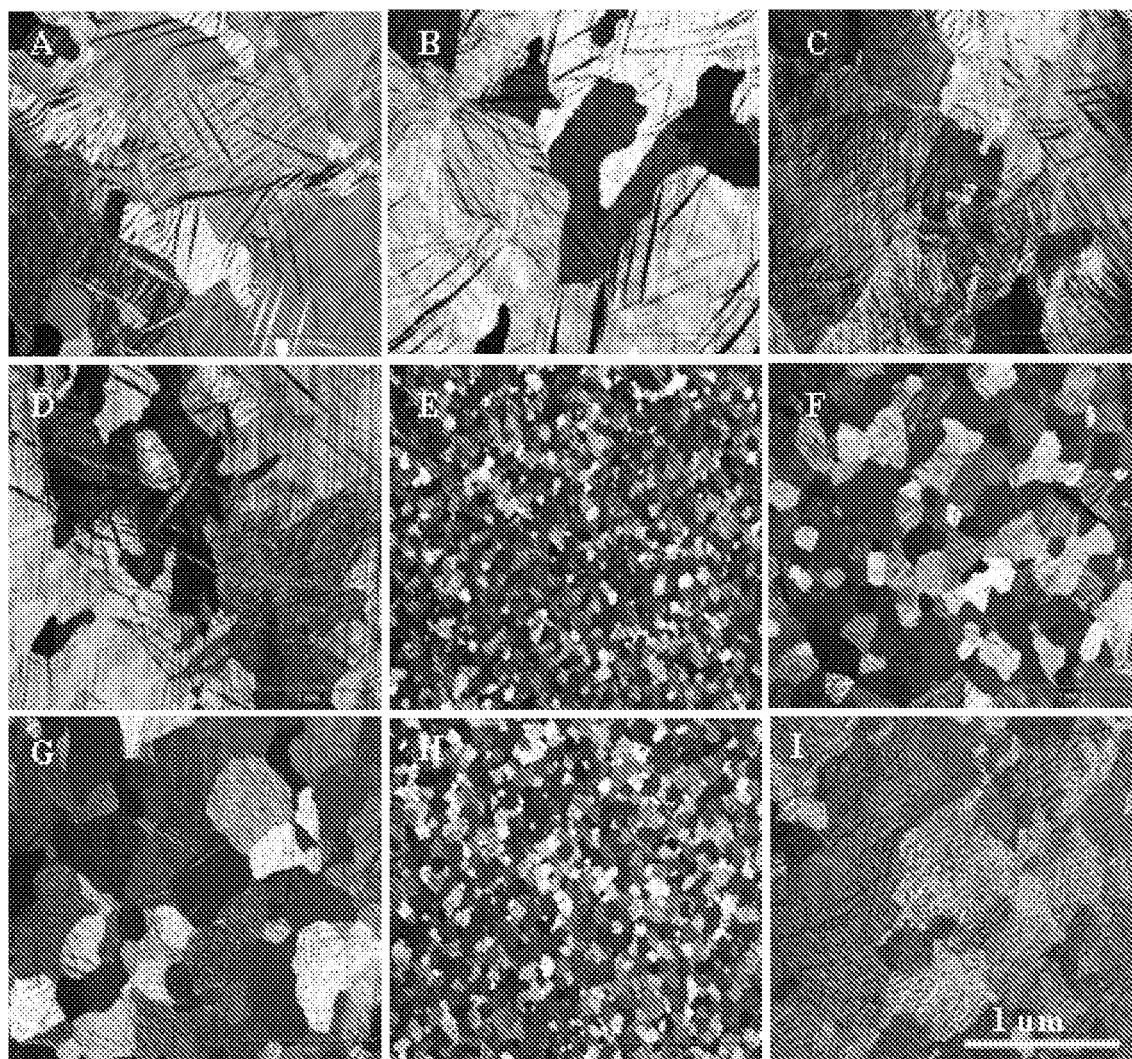


Fig. 1

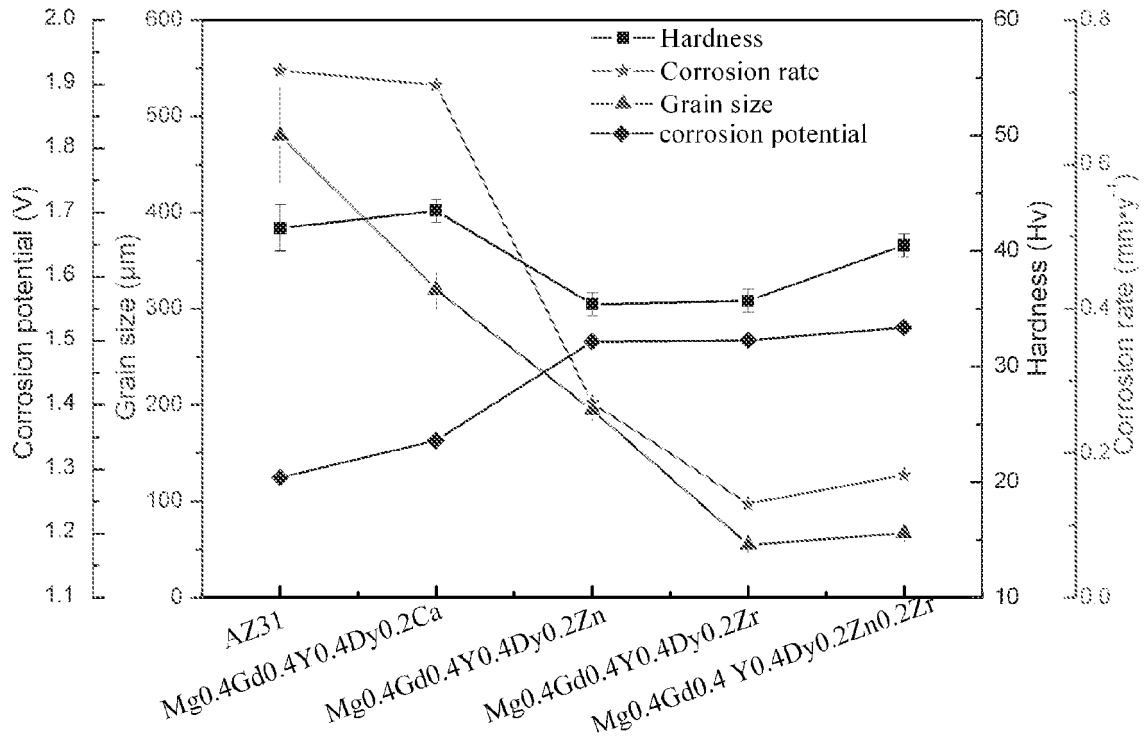


Fig. 2

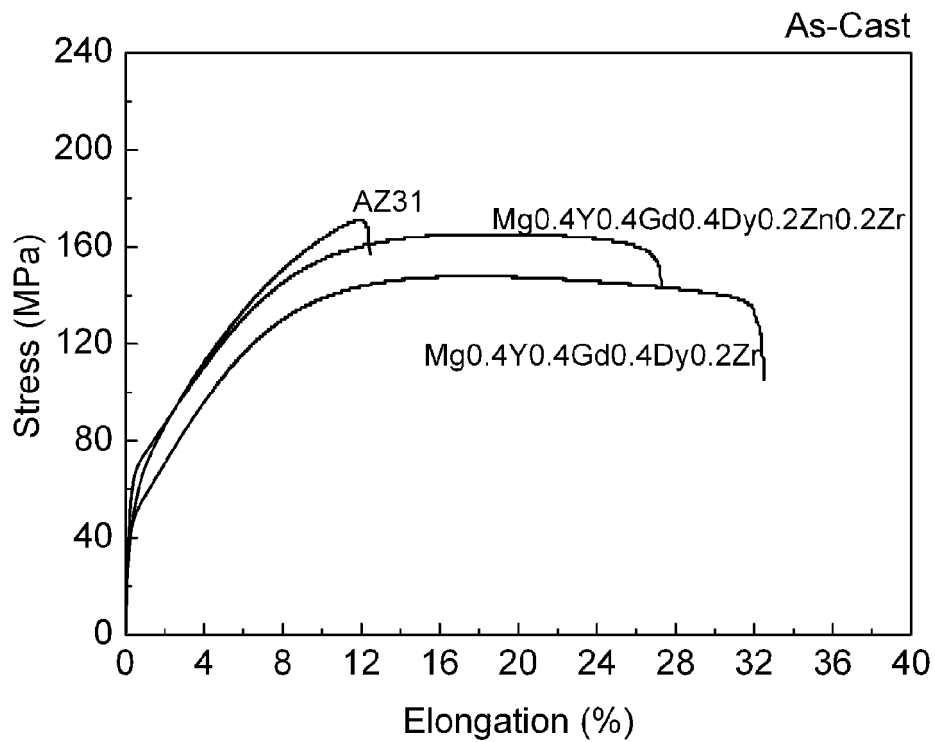


Fig. 3

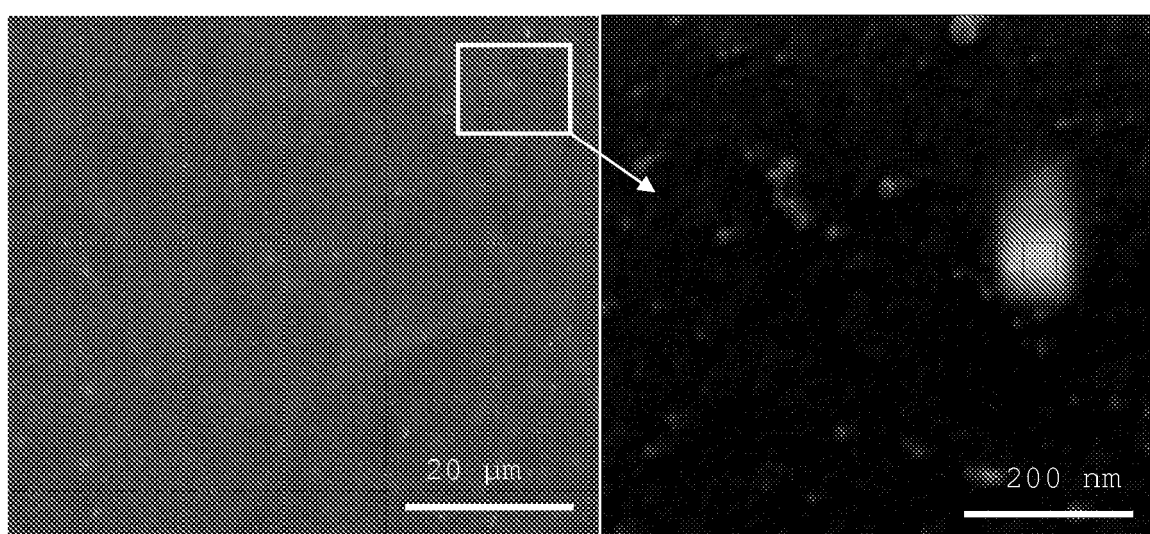


Fig. 4



EUROPEAN SEARCH REPORT

Application Number
EP 11 15 2827

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The present search report has been drawn up for all claims			
Place of search Munich		Date of completion of the search 29 March 2012	Examiner Patton, Guy
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EPO FORM 1503 03/82 (P04C01)

**ANNEX TO THE EUROPEAN SEARCH REPORT
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This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
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