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(54) High strength magnesium-based alloys.

(57) Disclosed are high-strength magnesium-based alloys having a composition consisting of the general formula (I) Mg_aX_b , (II) $Mg_aX_cM_d$, (III) $Mg_aX_cLn_e$ or (IV) $Mg_aX_cM_dLn_e$, wherein X is at least one element selected from the group consisting of Cu, Ni, Sn and Zn; M is at least one element selected from the group consisting of Al, Si and Ca; Ln is at least one element selected from the group consisting of Y, La, Ce, Nd and Sm or misch metal (Mm) which is a composite of rare earth elements; and a, b, c, d and e are, in atomic percentage, $40 \leqq a \leqq 95$, $5 \leqq b \leqq 60$, $1 \leqq c \leqq 35$, $1 \leqq d \leqq 25$ and $3 \leqq e \leqq 25$, the alloy consisting of an amorphous phase forming a matrix containing Mg and the other elements as set forth above and a crystalline phase composed of various intermetallic compounds, which are formed between the matrix-forming elements and/or the above-mentioned elements and finely dispersed throughout the matrix, wherein the crystalline phase is contained in the alloy in a higher volume percentage than the amorphous phase.

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BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to aluminum-based alloys having superior hardness and strength together with high corrosion resistance.

2. Description of the Prior Art

As conventional amorphous magnesium-based alloys, for example, an amorphous magnesium-based alloys has been proposed in Japanese Patent Application Laid-Open No. 3 - 10041. Known magnesium-based alloys have all been produced in order to form an amorphous single-phase structure and thereby obtain an enhanced strength.

The amorphous magnesium based alloy described in the above Japanese Patent Application Laid-Open No. 3 - 10041 exhibits superior properties such as high strength and high hardness, and, thus, it is especially superior as a high strength material. The present inventors considered that the strength and hardness of alloy materials would be still improved by directing their attention to the ratio between the amorphous phase and the crystalline phase in the alloy materials.

SUMMARY OF THE INVENTION

In view of the foregoing, it is an object of the present invention to provide magnesium-based alloys which are further improved in their hardness and strength by investigating in detail the amorphous phase and the crystalline phase existing therein.

According to the present invention, the following high strength magnesium-based alloys are provided:

(1) A high strength magnesium-based alloy having a composition consisting of the general formula

(I) Mg_aX_b ,

wherein:

X is at least one element selected from the group consisting of Cu, Ni, Sn and Zn; and

a and b are, in atomic percentage,

$40 \leqq a \leqq 95$ and $5 \leqq b \leqq 60$,

the alloy consisting of an amorphous phase forming a matrix containing Mg and the X element and a crystalline phase composed of various intermetallic compounds which are formed between the matrix-forming elements and/or the above-mentioned elements and finely dispersed throughout the matrix, wherein the crystalline phase is contained in the alloy in a higher volume percentage than the amorphous phase.

(2) A high strength magnesium-based alloy having a composition consisting of the general formula

(II) $Mg_aX_cM_d$,

wherein:

X is at least one element selected from the group consisting of Cu, Ni, Sn and Zn;

M is at least one element selected from the group consisting of Al, Si and Ca; and

a, c and d are, in atomic percentage,

$40 \leqq a \leqq 95$, $1 \leqq c \leqq 35$ and $1 \leqq d \leqq 25$,

the alloy consisting of an amorphous phase forming a matrix containing magnesium, the X element and the M element and a crystalline phase composed of various intermetallic compounds which are formed between the matrix-forming elements and/or the above-mentioned elements and finely dispersed throughout the matrix, wherein the crystalline phase is contained in the alloy in a higher volume percentage than the amorphous phase.

(3) A high strength magnesium-based alloy having a composition consisting of the general formula

(III) $Mg_aX_cLn_e$,

wherein:

X is at least one element selected from the group consisting of Cu, Ni, Sn and Zn;

Ln is at least one element selected from the group consisting of Y, La, Ce, Nd and Sm or misch metal (Mm) which is a composite of rare earth elements; and
a, c and e are, in atomic percentage,
$40 \leqq a \leqq 95$, $1 \leqq c \leqq 35$ and $3 \leqq e \leqq 25$
the alloy consisting of an amorphous phase forming a matrix containing Mg, the X element and the Ln element and a crystalline phase composed of various intermetallic compounds which are formed between the matrix-forming elements and/or the above-mentioned elements and finely dispersed throughout the matrix, wherein the crystalline phase is contained in the alloy in a higher volume percentage than the amorphous phase.

(4) A high strength magnesium-based alloy having a composition consisting of the general formula

(IV) $Mg_aX_cM_dLn_e$,

wherein:
X is at least one element selected from the group consisting of Cu, Ni, Sn and Zn;
M is at least one element selected from the group consisting of Al, Si and Ca;
Ln is at least one element selected from the group consisting of Y, La, Ce, Nd and Sm or misch metal (Mm) which is a composite of rare earth elements; and
a, c, d and e are, in atomic percentage,
$40 \leqq a \leqq 95$, $1 \leqq c \leqq 35$, $1 \leqq d \leqq 25$ and $3 \leqq e \leqq 25$,
the alloy consisting of an amorphous phase forming a matrix containing Mg, the X element, the M element and the Ln element and a crystalline phase composed of various intermetallic compounds which are formed between the matrix-forming elements and/or the above-mentioned elements and finely dispersed throughout the matrix, wherein the crystalline phase is contained in the alloy in a higher volume percentage than the amorphous phase.

Among the elements of the above compositions, La, Ce, Nd and Sm may be replaced with misch metal (Mm) which contains these elements as main components.

The term "Mm" used herein is intended to mean a composite comprising, in atomic percentage, 40 to 50% Ce and 20 to 25% La and the balance being other rare earth elements and tolerable levels of impurities (e.g., Mg, Al, Si and Fe, etc.). The Mm may be substituted by the other Ln elements in an Mm : Ln ratio of 1 : 1 (by atomic percent). The Mm is a highly cost-effective source for the Ln alloying elements because of its cheap price.

BRIEF DESCRIPTION OF THE DRAWING

The single figure shows a schematic illustration of a single-roller melt spinning apparatus employed to prepare thin ribbons by rapidly quenching and solidifying alloys of the present invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The magnesium-based alloys of the present invention can be obtained by rapidly solidifying a melt of the alloy having the composition as specified above, employing liquid quenching techniques. The liquid quenching techniques are methods for rapidly cooling a molten alloy and, particularly, single-roller melt-spinning, twin-roller melt-spinning and in-rotating-water melt-spinning are effective. In these techniques, a cooling rate of about 10^4 to 10^6 K/sec can be obtained. In order to produce thin ribbon materials 4 by single-roller melt-spinning or twin-roller melt-spinning, the molten alloy 3 is ejected from the bore 5 of a nozzle 1 onto a roll 2 of, for example, copper or steel, with a diameter of about 30 - 3000 mm, which is rotating at a constant rate within the range of about 300 - 10000 rpm. In such a process, various thin ribbon materials with a width of about 1 - 300 mm and a thickness of about 5 - 500 μm can be readily obtained. Alternatively, in order to produce wire materials by in-rotating-water melt-spinning, a jet of the molten alloy is directed, under application of a back pressure of argon gas, through a nozzle into a liquid refrigerant layer having a depth of about 1 to 10 cm which is held by centrifugal force in a drum rotating at a rate of about 50 to 500 rpm. In such a manner, fine wire materials can be readily obtained. In this process, the angle between the molten alloy ejecting from the nozzle and the liquid refrigerant surface is preferably in the range of about 60° to 90° and the relative velocity ratio of the ejected molten alloy to the liquid refrigerant surface is preferably in the range of about 0.7 to 0.9.

The alloy of the present invention may also be obtained by firstly forming an amorphous alloy in the same procedure as described above, except employing a slightly increased cooling rate, and, then, heating the resultant amorphous alloy to the vicinity of its crystallization temperature (crystallization temperature ±100 °C), thereby causing crystallization. In some alloys, the intended alloys can be produced at temperatures lower than 100 °C less than their crystallization temperature.

Besides the above processes, the alloy of the present invention can also be obtained in the form of a thin film by sputtering. Further, rapidly solidified powder of the alloy composition of the present invention can be obtained by various atomizing processes (e.g., high pressure gas atomizing), spraying, mechanical alloying, mechanical grinding, etc.

In the magnesium-based alloy represented by the general formula (I), a is limited to the range of 40 to 95 atomic % and b is limited to the range of 5 to 60 atomic %. The reason for such limitations is that when a and b are outside the specified ranges, it is difficult to form a supersaturated solid solution containing therein solute elements in amounts exceeding their solid solubility limits and amorphization becomes difficult. Consequently, alloys having properties contemplated by the present invention can not be obtained by industrial rapid quenching processes employing the above-mentioned liquid quenching or the like.

In the magnesium-based alloy represented by the general formula (II), a, c and d are limited to the atomic percentages ranging from 40 to 95%, 1 to 35% and 1 to 25%, respectively. The reason for such limitations is that when a, c and d are outside the specified ranges, it is difficult to form a supersaturated solid solution containing therein solute elements in amounts exceeding their solid solubility limits and amorphization becomes difficult. Consequently, alloys having properties contemplated by the present invention can not be obtained by industrial rapid quenching processes employing the foregoing liquid quenching or the like.

In the magnesium-based alloy represented by the general formula (III), a, c and e are limited to the atomic percentages ranging from 40 to 95%, 1 to 35% and 3 to 25%, respectively. As set forth above, the reason for such limitations is that when a, c and e are outside the specified ranges, it is difficult to form a supersaturated solid solution containing therein solute elements in amounts exceeding their solid solubility limits and amorphization partially becomes difficult. Consequently, alloys having properties contemplated by the present invention can not be obtained by industrial rapid quenching processes employing the above liquid quenching or the like.

In the magnesium-based alloy represented by the general formula (IV), a, c, d and e are limited to the atomic percentages ranging from 40 to 95%, 1 to 35%, 1 to 25% and 3 to 25%, respectively. As set forth above, the reason for such limitations is that when a, c, d and e are outside the specified ranges, it is difficult to form a supersaturated solid solution containing therein solute elements in amounts exceeding their solid solubility limits and amorphization becomes difficult. Consequently, alloys having properties contemplated by the present invention can not be obtained by industrial rapid quenching processes employing the above-mentioned liquid quenching or the like.

The X element is at least one element selected from the group consisting of Cu, Ni, Sn and Zn. The X element exhibits superior effects in stabilizing the resulting fine crystalline phase and improving the amorphous-forming ability, under the conditions of the preparation of the alloys of the present invention. In addition, the X element has a strengthening effect while retaining the ductility.

The M element is at least one element selected from the group consisting of Al, Si and Ca and forms stable or metastable intermetallic compounds in combination with Mg or other additive elements in the fine crystalline phase of the present invention. The intermetallic compounds thus formed are uniformly and finely distributed throughout a magnesium matrix (α -phase), and, thereby, considerably improve the hardness and strength of the resultant alloys. The M element further prevents coarsening of the fine crystalline phase at high temperatures and provides a good heat resistance. Also, the M element also stabilizes the amorphous phase at relatively elevated temperatures. Among the above elements, Al and Ca have an effect of improving the corrosion resistance and Si improves the fluidity of the molten alloy.

The Ln element is at least one element selected from the group consisting of Y, La, Ce, Nd and Sm or a misch metal (Mm) which is a mixture of rare earth elements. Addition of the Ln element to the Mg-X system or the Mg-X-M system alloys develops a further stabilized fine crystalline phase in these alloys and makes possible great improvement in their hardness. In the amorphous phase, the Ln element exhibits a significant effect of improving the amorphous-phase forming ability.

Since the magnesium-based alloys of the present invention show superplasticity in the vicinity of their crystallization temperature (Tx ± 100 °C), they can be readily processed by extrusion, press working, hot-forging, etc. Therefore, the magnesium-based alloys of the present invention, obtained in the form of thin ribbons, wires, sheets or powder, can be successfully formed into bulk materials by extrusion, press working, hot-forging, etc., within the range of Tx ± 100 °C. Further, some of the magnesium-based alloys of the present invention are sufficiently ductile to permit a high degree of bending.

Example

Molten alloy 3, having a predetermined composition, was prepared using a high-frequency melting furnace and charged into a quartz tube 1 having a small opening 5 (diameter: 0.5 mm) at the tip thereof, as shown in the drawing. After being heated to melt the alloy 3, the quartz tube 1 was disposed right above a copper roll 2. Then, the molten alloy 3 contained in the quartz tube 1 was ejected from the small opening 5 of the quartz tube 1, under the application of an argon gas pressure of 0.7 kg/cm^2, and brought into contact with the surface of the copper roll 2 rapidly rotating at a rate of 5,000 rpm. The molten alloy 3 was rapidly quenched and solidified into an alloy thin ribbon 4.

According to the processing conditions as described above, 20 different alloy thin ribbons (width: 1 mm, thickness: 20 µm) having the compositions (by at.%) as shown in the Table were obtained and test specimens were prepared from the respective thin ribbons. Hardness and tensile strength were measured for each test specimen and the results are shown in a right column of the Table.

It has been confirmed through observation by transmission electron microscopy (TEM) that the above alloy thin ribbons were composed of a fine crystalline phase and an amorphous phase and contained the crystalline phase in a higher volume percentage than the amorphous phase.

The hardness (Hv) is indicated by values (DPN) measured using a microVickers hardness tester under a load of 25 g.

As shown in the Table, all test specimens showed a high level of hardness Hv (DPN) of at least 185 which is about 2.0 to 3.0 times the hardness Hv (DPN), i.e., 60 - 90, of the conventional magnesium-based alloys. Further, the test specimens of the present invention all exhibited a high tensile-strength level of not less than 630 MPa and such a high strength level is at least approximately 1.5 times the highest strength level of 400 MPa achieved in known magnesium-based alloys. It can be seen from such results that the alloy materials of the present invention are superior in hardness and strength.

Table

Test Specimen	Hv(DPN)	σ_f(MPa)
1 $Mg_{85}Ni_{10}Zn_5$	220	745
2 $Mg_{85}Ni_5Sn_{10}$	225	760
3 $Mg_{80}Cu_{15}Ca_5$	190	640
4 $Mg_{75}Zn_{20}Al_5$	185	630
5 $Mg_{85}Zn_{10}Ce_5$	210	720
6 $Mg_{86}Ni_8Si_2Mm_4$	235	795
7 $Mg_{85}Ni_8Y_7$	240	810
8 $Mg_{85}Ni_5Zn_{10}$	220	720
9 $Mg_{85}Cu_5Zn_{10}$	190	630
10 $Mg_{80}Ni_{15}Ca_5$	195	670
11 $Mg_{80}Ni_{15}Al_5$	210	690
12 $Mg_{65}Cu_{10}Zn_{10}Al_{15}$	240	780
13 $Mg_{65}Cu_{15}Zn_{15}Ca_5$	225	720
14 $Mg_{75}Ni_{15}Ce_{10}$	205	680
15 $Mg_{70}Cu_{10}Zn_{10}Mm_{10}$	213	710
16 $Mg_{70}Ni_{10}Al_{10}Mm_{10}$	245	730
17 $Mg_{80}Zn_{10}Al_5Mm_5$	260	780
18 $Mg_{65}Cu_{10}Zn_7Al_5Si_5Mm_8$	270	810
19 $Mg_{82}Zn_6Al_{12}$	198	590
20 $Mg_{88}Zn_8Al_4$	167	490

As described above, the magnesium-based alloy of the present invention have a high hardness and a high strength which are, respectively, at least 2.0 times and at least 1.5 times those of a similar type of magnesium-based alloy which has been heretofore evaluated as the most superior alloy and yet also have a good processability permitting extrusion or similar operations. Therefore, the alloys of the present invention exhibit advantageous effects in a wide variety of industrial applications.

Claims

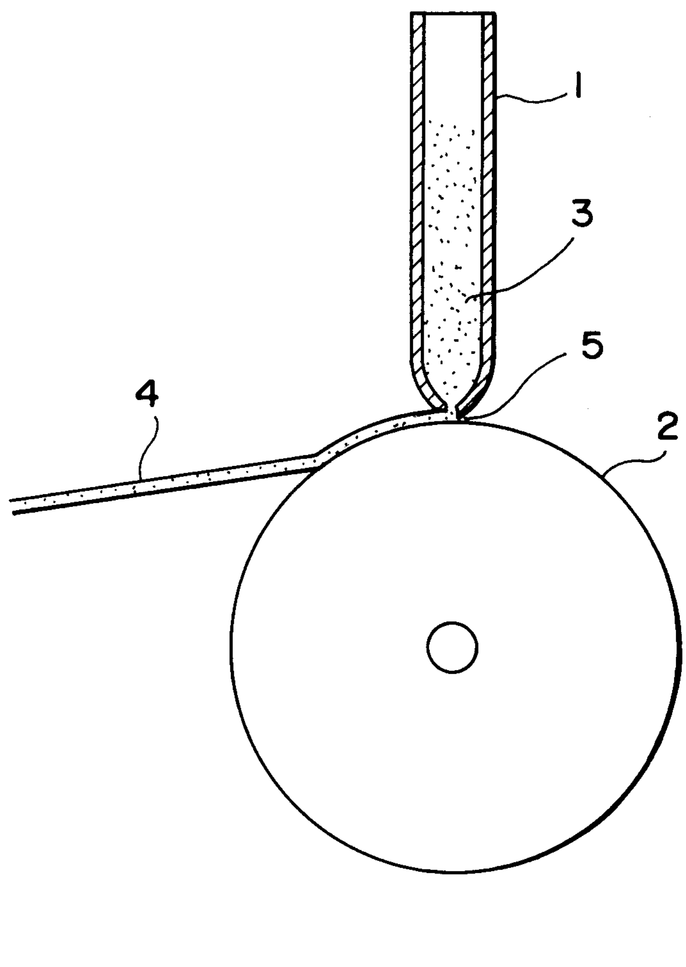
1. A high strength magnesium-based alloy having a composition consisting of the general formula (I) Mg_aX_b , wherein: X is at least one element selected from the group consisting of Cu, Ni, Sn and Zn; and a and b are, in atomic percentage, $40 \leqq a \leqq 95$ and $5 \leqq b \leqq 60$, the alloy consisting of an amorphous phase forming a matrix containing Mg and the X element and a crystalline phase composed of various intermetallic compounds which are formed between the matrix-forming elements and/or the above-mentioned elements and finely dispersed throughout the matrix, wherein the crystalline phase is contained in the alloy in a higher volume percentage than the amorphous phase.

2. A high strength magnesium-based alloy having a composition consisting of the general formula (II) $Mg_aX_cM_d$, wherein: X is at least one element selected from the group consisting of Cu, Ni, Sn and Zn; M is at least one element selected from the group consisting of Al, Si and Ca; and a, c and d are, in atomic percentage, $40 \leqq a \leqq 95$, $1 \leqq c \leqq 35$ and $1 \leqq d \leqq 25$, the alloy consisting of an amorphous phase forming a matrix containing magnesium, the X element and the M element and a crystalline phase composed of various intermetallic compounds which are formed between the matrix-forming elements and/or the above-mentioned elements and finely dispersed throughout the matrix, wherein the crystalline phase is contained in the alloy in a higher volume percentage than the amorphous phase.

3. A high strength magnesium-based alloy having a composition consisting of the general formula (III) $Mg_aX_cLn_e$, wherein: X is at least one element selected from the group consisting of Cu, Ni, Sn and Zn; Ln is at least one element selected from the group consisting of Y, La, Ce, Nd and Sm or misch metal (Mm) which is a composite of rare earth elements; and a, c and e are, in atomic percentage, $40 \leqq a \leqq 95$, $1 \leqq c \leqq 35$ and $3 \leqq e \leqq 25$ the alloy consisting of an amorphous phase forming a matrix containing Mg, the X element and the Ln element and a crystalline phase composed of various intermetallic compounds which are formed between the matrix-forming elements and/or the above-mentioned elements and finely dispersed throughout the matrix, wherein the crystalline phase is contained in the alloy in a higher volume percentage than the amorphous phase.

4. A high strength magnesium-based alloy having a composition consisting of the general formula (IV) $Mg_aX_cM_dLn_e$, wherein: X is at least one element selected from the group consisting of Cu, Ni, Sn and Zn; M is at least one element selected from the group consisting of Al, Si and Ca; Ln is at least one element selected from the group consisting of Y, La, Ce, Nd and Sm or misch metal (Mm) which is a composite of rare earth elements; and a, c, d and e are, in atomic percentage, $40 \leqq a \leqq 95$, $1 \leqq c \leqq 35$, $1 \leqq d \leqq 25$ and $3 \leqq e \leqq 25$, the alloy consisting of an amorphous phase forming a matrix containing Mg, the X element, the M element and the Ln element and a crystalline phase composed of various intermetallic compounds which are formed between the matrix-forming elements and/or the above-mentioned elements and finely dispersed throughout the matrix, wherein the crystalline phase is contained in the alloy in a higher volume percentage than the amorphous phase.

FIG. 1



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EUROPEAN SEARCH REPORT

Application Number

EP 91 11 3280

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
Y,D	EP-A-0 361 136 (YOSHIDA KOGYO K.K.) * claims 1-4 * *	1-4	C 22 C 1/00
Y,P	EP-A-0 407 964 (YOSHIDA KOGYO K.K.) * complete document* *	1-4	

TECHNICAL FIELDS SEARCHED (Int. Cl.5)

C 22 C

The present search report has been drawn up for all claims

Place of search	Date of completion of search	Examiner
The Hague	14 November 91	LIPPENS M.H.

CATEGORY OF CITED DOCUMENTS

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