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(54) **High strength magnesium-based alloy materials and method for producing the same**

Hochfeste Werkstoffe auf Legierungen auf Magnesiumbasis und Verfahren zur Herstellung dieser Werkstoffe

Matériaux à base d'alliages de magnésium, à haute résistance mécanique et procédé de fabrication de ces matériaux

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Description

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to high strength magnesium-based alloy materials having superior mechanical properties and a method for producing the same.

2. Description of the Prior Art

As conventional magnesium-based alloys, there are known Mg-Al, Mg-Al-Zn, Mg-Th-Zr, Mg-Th-Zn-Zr, Mg-Zn-Zr, Mg-Zn-Zr-RE (RE: rare earth element), etc. and these known alloys have been extensively used as light-weight structural component materials in a wide variety of applications, according to their properties. Further, as rapidly solidified materials, there are known alloys disclosed in Japanese Patent Laid-open No. 3-47,941.

However, under the present circumstances, known various types of magnesium-based alloys, as set forth above, have a low hardness and strength. Although the alloys disclosed in Japanese Patent Laid-open No. 3-47,941 have superior hardness and tensile strength, they still leave some room for further improvement in thermal stability and ductility. Further, in the Japanese Patent specification, there is no specific mention about Mg-Nd-Zn alloys, which are contemplated by the present invention, and most of the alloys disclosed therein are alloys including Mg in an amount of 70-80 atomic %.

Further, WO-A-89/11552 discloses a method of superplastic forming (extrusion, forging, rolling, etc.) of bulk articles which are made by consolidation of the powder of rapidly solidified magnesium base metal alloys consisting essentially of the formula $Mg_{bal}Al_aZn_bX_c$, wherein X is at least one element selected from the group consisting of manganese, cerium, neodymium, praseodymium, and yttrium, "a" ranges from about 0 to 15 atom percent, "b" ranges from about 0 to 4 atom percent, "c" ranges from about 0.2 to 3 atom percent, the balance being magnesium and incidental impurities, with the proviso that the sum of aluminum and zinc present ranges from about 2 to 15 atom percent. The alloy used in the known process has a microstructure comprised of a substantially uniform cellular network solid solution phase of a size ranging from 0.2-1.0 µm together with precipitates of magnesium and aluminum containing intermetallic phases of a size less than 0.5 µm.

SUMMARY OF THE INVENTION

In view of the foregoing, it is an object of the present invention to provide magnesium-based alloy materials which have an advantageous combination of properties of high hardness, strength and thermal resistance and which are useful as lightweight and high strength materials (i.e., high specific strength materials) and have a superior ductility.

According to the present invention, there is provided a high strength magnesium-based alloy material having a microcrystalline composite structure, the alloy material consisting of a composition represented by the general formula (I): $Mg_aNd_bZn_c$, wherein a, b and c are, in atomic %, $80 \leq a \leq 99$, $1 \leq b \leq 12$, $0 \leq c \leq 12$ and $a+b+c = 100$, as specified in appended claim 1.

The present invention also provides a high strength magnesium-based alloy material having a microcrystalline composite structure, the alloy material consisting of a composition represented by the general formula (II): $Mg_{a'}Nd_{b'}Zn_{c'}$, wherein a', b' and c' are, in atomic %, $95 < a' \leq 99$, $1 \leq b' \leq 3$, $0 \leq c' \leq 3$ and $a+b+c = 100$, as specified in appended claim 2.

The aforesaid high strength magnesium-based alloy materials are produced by a method comprising:

rapidly solidifying a molten alloy so as to form a fine-grained matrix phase, the molten alloy consisting of the composition represented by the above-defined general formula (I) or (II); and

subjecting the resultant rapidly solidified alloy to plastic working at a prescribed heating temperature for work hardening, thereby forming a microcrystalline composite structure having a uniform dispersion of very fine intermetallic compounds in the matrix.

The matrix in the composite structure consists of an Mg matrix having a hexagonal close-packed (hcp) structure and intermetallic compounds consisting of a non-equilibrium phase having a face-centered cubic (hcp) structure and/or other intermetallic compound phases, such as an $Mg_{12}Nd$ phase, are finely and uniformly dispersed throughout the matrix .

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

As described above, the present invention provides the above-defined high strength magnesium-based alloy materials consisting of a composition represented by the general formula (I) or (II). In the above-defined general formula (I), the ranges of a, b and c are so limited that the above-defined alloy can be obtained with the aforesaid microcrystalline composite structure by industrial rapid cooling techniques, such as liquid quenching.

The reason why the ranges of a', b' and c' of the general formula (II) are limited as defined above is that since a large amount of intermetallic compounds are formed with a small amount of Nd, the rapidly solidified material obtained from the alloy composition has a high strength on a higher Mg content side as compared with the rapidly solidified material represented by the general formula (I) and is useful as a high specific strength material. Further, the addition of solute elements can be saved.

As a further important reason, in the above-defined compositional ranges, fine hcp-Mg precipitates as a host matrix, and finer intermetallic compounds of a non-equilibrium fcc phase formed from, at least, Mg and Nd and/or $Mg_{12}Nd$ phase, etc. are uniformly and finely distributed throughout the hcp-Mg matrix. Especially, when the intermetallic compounds comprising the non-equilibrium fcc phase, which is formed from, at least, Mg and Nd and which has a good compatibility with the matrix of hcp-Mg, are uniformly and finely dispersed in the matrix, the Mg matrix is strengthened and the strength of the alloy is outstandingly improved. However, when the Mg content is 95 atomic % or less, a very high ductility as obtained in the case of Mg contents exceeding 95 atomic % cannot be expected because the proportion of the intermetallic compounds dispersed in the matrix becomes excessive with respect to the entire alloy.

In the magnesium-based alloys of the present invention, Nd makes it possible to form the above-mentioned composite structure having a dispersion of intermetallic compounds consisting of a non-equilibrium fcc phase, which is formed from, at least, Nd and Mg, and/or other intermetallic compounds, such as an $Mg_{12}Nd$ phase, while suppressing the grain growth of the matrix phase. Since the intermetallic compounds can be formed in large quantities in the presence of a small amount of Nd, it is possible to obtain alloys having a high strength on an Mg-rich side so that high specific-strength materials can be obtained.

Another alloying element Zn transforms the non-equilibrium phase to a more stable non-equilibrium phase of fcc structure so that the intermetallic compounds having a good compatibility with the magnesium matrix (α phase) uniformly and finely disperse in the matrix. As a result, the hardness and strength of the resultant alloys are improved and a high thermal resistance is imparted to the alloys by suppressing coarsening of the microcrystalline structure of the alloys at high temperatures.

In the production of the high strength magnesium-based alloy materials of the present invention, a molten alloy having the above-defined composition is rapidly solidified so as to obtain a fine-grained matrix phase. In the rapidly solidification step, a cooling rate of 10^2-10^6 K/sec is particularly effective. The resultant rapidly solidified alloy is heated to a prescribed temperature and subjected to plastic working. As a result, it is possible to obtain magnesium alloy materials having a microcrystalline composite structure composed of an hcp Mg matrix and, homogeneously distributed in the matrix, intermetallic compounds consisting of a non-equilibrium fcc phase and/or other intermetallic compound phases, such as an $Mg_{12}Nd$ phase formed of Mg and Nd. The non-equilibrium fcc phase may be formed either during rapid solidification or during plastic working. The plastic working is preferably performed at a temperature of 50 to 500°C. A temperature lower than 50°C cannot provide a sound material due to an excessive deformation resistance. On the other hand, a temperature exceeding 500°C causes a considerable grain growth, thereby lowering the strength.

The magnesium matrix and the intermetallic compounds formed by the above production method have a grain size ranging from 200 nm to 600 nm and a particle size ranging from 10 nm to 400 nm, respectively.

Further, by controlling the matrix grain size and the intermetallic compound particle size of the inventive alloys to the above-defined ranges, the alloys may have superior properties as superplastic working materials.

The present invention will be illustrated in more detail by the following examples.

Examples

A molten alloy having a given composition was prepared using a high-frequency melting furnace. The molten alloy was subjected to a single-roller melt-spinning technique, which is one of the rapid solidification techniques, at a cooling of 10^2-10^6 K/sec and a rapidly solidified material comprising a fine-grained matrix phase.

The thus obtained rapidly solidified material was subjected to hot-extrusion at a temperature of 320°C under an applied pressure of 1240-1628 MPa, while suppressing the grain growth of the matrix phase. The thus obtained extruded material had a microcrystalline composite structure having a dispersion of fine intermetallic compounds.

According to the processing conditions as set forth above, test samples (extruded materials) having the compositions (by atomic %) given in Table 1 were produced. Comparative extruded materials having compositions falling outside the compositional range of the present invention were produced under the same processing conditions as described above. The comparative materials are disclosed in Japanese Patent Application Laid-Open No. 3-47,941 hereinbefore described.

Each test sample was subjected to X-ray diffraction and measured for its mechanical properties, i.e., tensile strength (σ_B), plastic elongation (ε_f), Young's modulus (E), specific strength (σ_B/ρ). The results are shown on the right-hand column of Table 1. The specific strength was obtained by dividing tensile strength by density for each sample. Further, the test samples were observed by a transmission electron microscope (TEM). The results of the TEM observation were as follows:

$Mg_{97}Nd_3$ comprised an hcp-Mg matrix having a grain size of 200 nm to 600 nm and, homogeneously distributed in the matrix, an intermetallic compound of $Mg_{12}Nd$ formed of Mg and Nd and having a particle size of 250 nm to 400 nm.

$Mg_{96}Nd_3Zn_1$ was composed of an hcp-Mg matrix having a grain size of 200 nm to 300 nm and, homogeneously distributed in the matrix, non-equilibrium fcc phase intermetallic compounds formed of Mg and Nd and/or Zn with a particle size of 10 nm to 200 nm.

Table 1

No.	Mg	Nd	Zn	Phase	σ_B (MPa)	ε_f (%)	E (MPa)	σ_B/ρ
1	97	3	-	Mg+unknown +$Mg_{12}Nd$	562	0.44	38	285
2	96	3	1	Mg+non-equilibrium fcc	617	3.7	37	307
3	95.5	2.5	2	Mg+non-equilibrium fcc	611	4.7	39	306
4	95	3	2	Mg+non-equilibrium fcc	633	1.0	39	310
Comparative Test Sample								
1	Mg 90	Cu 5	La 5	Mg+Mg_2Cu +Mg_9La	872	0.1	47	382
2	Mg 80	Cu 10	Y 10	Mg+Mg_2Cu +$Mg_{24}Y_5$	901	0.05	52	360

As is evident from Table 1, every test sample of the present invention exhibited superior mechanical properties, i. e., a tensile strength of not less than 500 MPa, a plastic elongation of not less than 0.4%, a Young's modulus of at least 37 GPa and a specific strength of not less than 280 MPa. Particularly, since the magnesium-based alloys of the present invention are superior in plastic elongation over the comparative test samples, they can be successfully subjected to various working operations and exhibit a sufficient durability to permit a high degree of working (plastic working). When the Mg content exceeded 95 atomic % in the Mg-Nd-Zn alloys, the plastic elongation surprisingly increased, although any significant change was hardly detected in the tensile strength, Young's modulus and specific strength.

Since the magnesium-based alloys of the present invention have high levels of strength and heat-resistance, they are very useful as high strength materials and high heat-resistant materials. The magnesium-based alloys are also useful as high specific-strength materials because of their high specific strength. Still further, since the alloys exhibit superior elongation at room temperature and Young's module at room temperature, they can be successfully subjected to various working operations and exhibit a sufficient durability to permit a high degree of working (plastic working).

Claims

1. A high strength magnesium-based alloy material having a microcrystalline composite structure, the alloy material having a microcrystalline composite structure consisting of an Mg matrix having a hexagonal close-packed structure, and, homogeneously and finely distributed in the matrix, intermetallic compounds consisting of a non-equilibrium phase having a face-centered cubic structure and/or an $Mg_{12}Nd$ phase and consisting of a composition represented by the general formula (I): $Mg_aNd_bZn_c$, wherein a, b and c are, in atomic %, $80 \leq a \leq 99$, $1 \leq b \leq 12$, $0 \leq c \leq 12$ and $a + b + c = 100$.

2. A high strength magnesium-based alloy material having a microcrystalline composite structure, the alloy material having a microcrystalline composite structure consisting of an Mg matrix having a hexagonal close-packed structure, and, homogeneously and finely distributed in the matrix, intermetallic compounds consisting of a non-equilibrium phase having a face-centered cubic structure and/or an $Mg_{12}Nd$ phase and consisting of a composition represented by the general formula (II) : $Mg_{a'}Nd_{b'}Zn_{c'}$, wherein a', b' and c' are, in atomic %, $95 < a' \leq 99$, $1 \leq b' \leq 3$, $0 \leq c' \leq 3$ and $a + b + c = 100$.

3. A high strength magnesium-based alloy material as claimed in Claim 1 or 2, wherein the intermetallic compounds contain at least an intermetallic compound consisting of a non-equilibrium phase having a face-centered cubic structure.

4. A method for producing a high strength magnesium-based alloy material, comprising:

rapidly solidifying a molten alloy so as to form a fine-grained matrix phase, the molten alloy consisting of a composition represented by the general formula (I): $Mg_aNd_bZn_c$, wherein a, b and c are, in atomic %, $80 \leq a \leq 99$, $1 \leq b \leq 12$, $0 \leq c \leq 12$ and $a + b + c = 100$; and
subjecting the resultant rapidly solidified alloy to plastic working at a prescribed heating temperature for work hardening, thereby forming a microcrystalline composite structure consisting of an Mg matrix having a hexagonal close-packed structure, and, homogeneously and finely distributed in the matrix, intermetallic compounds consisting of a non-equilibrium phase having a face-centered cubic structure and/or an $Mg_{12}Nd$ phase.

5. A method for producing a high strength magnesium-based alloy material, comprising:

rapidly solidifying a molten alloy so as to form a fine-grained matrix phase, the molten alloy consisting of a composition represented by the general formula (II): $Mg_{a'}Nd_{b'}Zn_{c'}$, wherein a', b' and c' are, in atomic %, $95 < a' \leq 99$, $1 \leq b' \leq 3$, $0 \leq c' \leq 3$ and $a' + b' + c' = 100$; and
subjecting the resultant rapidly solidified alloy to plastic working at a prescribed heating temperature for work hardening, thereby forming a microcrystalline composite structure consisting of an Mg matrix having a hexagonal close-packed structure, and, homogeneously and finely distributed in the matrix, intermetallic compounds consisting of a non-equilibrium phase having a face-centered cubic structure and/or an $Mg_{12}Nd$ phase.

6. A method as claimed in Claim 4 or 5, wherein the prescribed heating temperature ranges from 50 to 500 °C.

Patentansprüche

1. Hochfestes Legierungsmaterial auf Magnesiumbasis mit einer mikrokristallinen Kompositstruktur, wobei das Legierungsmaterial eine mikrokristalline Kompositstruktur aus einer Mg-Matrix mit einer hexagonal dicht gepackten Struktur und, in der Matrix homogen und fein verteilt, intermetallischen Verbindungen aus einer Nichtgleichgewichtsphase mit einer flächenzentriert kubischen Struktur und/oder einer $Mg_{12}Nd$-Phase aufweist und aus einer durch die allgemeine Formel (I): $Mg_aNd_bZn_c$ dargestellten Zusammensetzung besteht, wobei a, b und c in Atom-% betragen $80 \leq a \leq 99$, $1 \leq b \leq 12$, $0 \leq c \leq 12$ und $a + b + c = 100$.

2. Hochfestes Legierungsmaterial auf Magnesiumbasis mit einer mikrokristallinen Kompositstruktur, wobei das Legierungsmaterial eine mikrokristalline Kompositstruktur aus einer Mg-Matrix mit einer hexagonal dicht gepackten Struktur und, in der Matrix homogen und fein verteilt, intermetallischen Verbindungen aus einer Nichtgleichgewichtsphase mit einer flächenzentrierten kubischen Struktur und/oder einer $Mg_{12}Nd$-Phase aufweist und aus einer durch die allgemeine Formel (II): $Mg_{a'}Nd_{b'}Zn_{c'}$ dargestellten Zusammensetzung besteht, wobei a', b' und c' in Atom-% betragen $95 \leq a' < 99{,}1 \leq 1 \leq b' \leq 3{,}0 \leq c' \leq 3$ und $a' + b' + c' = 100$.

3. Hochfestes Legierungsmaterial auf Magnesiumbasis nach Anspruch 1 oder 2, bei dem die intermetallischen Verbindungen zumindest eine intermetallische Verbindung aus einer Nichtgleichgewichtsphase mit einer flächenzentriert kubischen Struktur beinhalten.

4. Verfahren zur Herstellung eines hochfesten Legierungsmaterials auf Magnesiumbasis mit den Schritten:

schnell Erstarrenlassen einer geschmolzenen Legierung zur Herstellung einer feinkörnigen Matrixphase, wobei die geschmolzene Legierung aus einer durch die allgemeine Formel (I): $Mg_aNd_bZn_c$ dargestellten Zusammensetzung besteht, wobei a, b und c in Atom-% betragen $80 \leq a \leq 99$, $1 \leq b \leq 12$, $0 \leq c \leq 12$ und $a + b + c = 100$; und

plastisches Bearbeiten der resultierenden schnell erstarrten Legierung bei einer vorbestimmten Heiztemperatur zur Fließverfestigung, wodurch eine mikrokristalline Kompositstruktur aus einer Mg-Matrix mit einer hexagonal dichtgepackten Struktur und, in der Matrix homogen und fein verteilt, intermetallischen Verbindungen aus einer Nichtgleichgewichtsphase mit einer flächenzentriert kubischen Struktur und/oder einer $Mg_{12}Nd$-

Phase gebildet wird.

5. Verfahren zur Herstellung eines hochfesten Legierungsmaterials auf Magnesiumbasis mit den Schritten:

schnell Erstarrenlassen einer geschmolzenen Legierung zur Herstellung einer feinkörnigen Matrixphase, wobei die geschmolzene Legierung aus einer durch die allgemeine Formel (II): $Mg_{a'}Nd_{b'}Zn_{c'}$ dargestellten Zusammensetzung besteht, wobei a', b' und c' in Atom-% betragen 95 ≤ a' ≤ 99,1 ≤b' ≤ 3,0 0 < c' < 3 und a' + b' + c' = 100; und

plastisches Bearbeiten der resultierenden schnellerstarrten Legierung bei einer vorbestimmten Heiztemperatur zur Fließverfestigung, wodurch eine mikrokristalline Kompositstruktur aus einer Mg-Matrix mit einer hexagonal dichtgepackten Struktur und, in der Matrix homogen und fein verteilt, intermetallischen Verbindungen aus einer Nichtgleichgewichtsphase mit einer flächenzentriert kubischen Struktur und/oder einer $Mg_{12}Ng$-Phase gebildet wird.

6. Verfahren nach Anspruch 4 oder 5, bei dem die vorgegebene Heiztemperatur in dem Bereich von 50-500°C liegt.

Revendications

1. Matériaux d'alliages à base de magnésium à haute resistance mécanique ayant une structure composite microcristalline, ce matériau d'alliage ayant une structure microcristalline composite consistant en une matrice de Mg ayant une structure hexagonale compacte, et en des composés intermétalliques, distribués de façon homogène et fine dans le matrice et consistant en une phase en état de non-équilibre ayant une structure cubique à faces centrées et/ou en une phase $Mg_{12}Nd$ et consistant en une composition représentée par la formule générale (I) : $Mg_aNd_bZn_{c,}$ dans laquelle a, b, et c valent, en pourcentage atomique, 80 ≤ a ≤ 99, 1 ≤ b ≤ 12, 0 ≤ c ≤ 12 et a + b + c = 100.

2. Matériaux d'alliages à base de magnésium à haute résistance mécanique ayant une structure composite microcristalline, ce matériau d'alliage ayant une structure microcristalline composite consistant en une matrice de Mg ayant une structure hexagonale compacte et en des composés intermétalliques, distribués de façon homogène et fine dans le matrice et consistant en une phase en état de non-équilibre ayant une structure cubique à faces centrées et/ou en une phase $Mg_{12}Nd$ et consistant en une composition représentée par la formule générale (II) : $Mg_a'Nd_b'Zn_c'$,: dans laquelle a', b', c' valent, en pourcentage atomique, 95 < a' ≤ 99,1 ≤ b' ≤ 3, 0 ≤ c' ≤ 3 et a'+ b' + c' = 100.

3. Matériaux d'alliages à base de magnésium à haute résistance mécanique selon la revendication 1 ou 2, dans lequel les composés intermétalliques contiennent au moins un composé intermétalliques consistant en une phase en état de non-équilibre ayant une structure cubique à faces centrées.

4. Procédé de fabrication d'un matériau d'alliages à base de magnésium à haute résistance mécanique, consistant :

à solidifier rapidement un alliage fondu de manière à former une phase matrice à grains fins, l'alliage fondu consistant en une composition représentée par la formule générale (I) : $Mg_aNd_bZn_c$ dans laquelle a, b, et c valent, en pourcentage atomique, 80 ≤ a ≤ 99, 1 ≤ b ≤ 12, 0 ≤ c ≤ 12 et a + b + c = 100; et
à soumettre l'alliage résultant, solidifié rapidement, à un travail plastique à une température de chauffage prescrite pour un écrouissage, en formant ainsi une structure composite micro-cristalline consistant en une matrice de Mg ayant une structure hexagonale compacte, et en des composés intermétalliques, distribués de façon homogène et fine dans le matrice et consistant en une phase en état de non-équilibre ayant une structure cubique à faces centrées et/ou en une phase $Mg_{12}Nd$.

5. Procédé de fabrication d'un matériau d'alliages à base de magnésium à haute résistance mécanique, consistant :

à solidifier rapidement un alliage fondu de manière à former une phase matrice à grains fins, l'alliage fondu consistant en une composition représentée par la formule générale (II) : $Mg_a,Nd_b,Zn_c,$ $Mg_a,Nd_b,Zn_{c"}$: dans laquelle a', b', c' valent, en pourcentage atomique, 95 < a' ≤ 99,1.≤ b' ≤ 3, 0 ≤ c'≤ 3 et a' + b' + c' = 100; et
à soumettre l'alliage résultant, solidifié rapidement, à un travail plastique à une température de chauffage prescrite pour un écrouissage, en formant ainsi une structure composite microcristalline consistant en une

matrice de Mg ayant une structure hexagonale compacte, et en des composés intermétalliques, distribués de façon homogène et fine dans le matrice et consistant en une phase en état de non-équilibre ayant une structure cubique à faces centrées et/ou en une phase $Mg_{12}Nd$.

6. Procédé selon la revendication 4 ou 5, dans lequel la température de chauffage prescrite se situe dans l'intervalle allant de 50 à 500°C.