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(54) Title: MAGNESIUM ALLOY, METHOD FOR THE PRODUCTION THEREOF AND USE THEREOF

(57) Abstract: The patent application relates to a magnesium alloy and to a method for the production thereof and to the use thereof, the magnesium alloy comprising: 1.5 to 7.0% by weight Zn, 0.5 to 3.5% by weight Al, the remainder being magnesium which contains impurities, which promote electrochemical potential differences and/or the formation of precipitations and/or intermetallic phases, in a total amount of no more than 0.0063% by weight of Fe, Si, Mn, Co, Ni, Cu, Zr, Y, Sc or rare earths having the ordinal numbers 21, 57 to 71 and 89 to 103, Be, Cd, In, Sn and/or Pb as well as P.

MAGNESIUM ALLOY, METHOD FOR THE PRODUCTION THEREOF AND USE THEREOF

This patent application relates to a magnesium alloy and to a method for the production thereof and to the use thereof.

It is known that the properties of magnesium alloys are decisively defined by the type and quantity of the alloying elements and impurities as well as the production conditions. The effects of the alloying elements and impurities on the properties of the magnesium alloys have been known for a long time to a person skilled in the art and illustrate the complex nature of determining the properties of binary or ternary magnesium alloys for the use thereof as implant materials.

The alloying element used most frequently for magnesium is aluminum, resulting in increased tensile strength due to solid solution and precipitation hardening and fine grain formation, but also in microporosity. Moreover, in the melt aluminum shifts the iron precipitation boundary toward drastically lower iron contents at which the iron particles precipitate or form intermetallic particles together with other elements.
Undesirable accompanying elements in magnesium alloys include iron, nickel, cobalt and copper, which cause a considerable increase in the corrosion tendency due to the electropositive nature thereof.
Manganese can be found in all magnesium casting alloys and binds iron in the form of AlMnFe precipitations, whereby the formation of local elements is reduced. On the other hand, manganese is not able to bind all the iron, and therefore a remainder of iron and a remainder of manganese are always left in the melt.

Silicon lowers the castability and viscosity, and as the content of Si rises, a worsened corrosion behavior is to be expected. Iron, manganese and silicon have a very high tendency to form an intermetallic phase.

The electrochemical potential of this phase is very high and can thus act as a cathode controlling the corrosion of the alloy matrix.

As a result of solid solution hardening, zinc improves the mechanical properties and results in grain refining, however it also leads to microporosity with a tendency toward hot cracking starting at a content of 1.5 to 2% by weight in binary Mg-Zn and ternary Mg-Al-Zn alloys.

Alloying additions made of zirconium increase the tensile strength without lowering the expansion and lead to grain refining, but also to a strong impairment of dynamic restrystallization, which is manifested in an increase of the recrystallization temperature and therefore requires high energy expenditure. Moreover, zirconium cannot be added to melts containing aluminum and silicon because the grain refining effect is lost.

Rare earths such as Lu, Er, Ho, Th, Sc and In all exhibit a similar chemical behavior and form eutectic systems with partial solubility on the magnesium-rich side of the binary phase diagrams such that precipitation hardening is possible.

The addition of further alloying elements, in conjunction with the impurities, is known to cause the formation of different intermetallic phases in binary magnesium alloys. For example, the intermetallic phase $Mg_{17}Al_{12}$ forming on the grain boundaries is brittle and limits the ductility. As compared to the magnesium matrix, this intermetallic phase is more noble and able to form local elements, whereby the corrosion behavior worsens.

In addition to these influencing factors, the properties of the magnesium alloys also decisively depend on the metallurgical production conditions. Conventional casting methods automatically introduce impurities when adding, by alloying, the alloying elements. The prior art (US 5,055,254 A) therefore defines tolerance limits for impurities in magnesium casting alloys, which, for example for a magnesium-aluminum-zinc alloy containing approximately 8 to 9.5% by weight Al and 0.45 to 0.9% by weight Zn, mentions tolerance limits of 0.0015 to 0.0024% by weight Fe, 0.0010% Ni, 0.0010 to 0.0024% by weight Cu and no less than 0.15 to 0.5% by weight Mn.

Tolerance limits for impurities in magnesium and the alloys thereof as well as the production conditions are mentioned in many known documents and listed as follows in % by weight:

Alloy	Production	State	Fe	Fe/Mn	Ni	Cu
Pure Mg	no information		0.017		0.005	0.01
AZ 91	Die casting	F		0.032	0.005	0.040
	High-pressure die casting			0.032	0.005	0.040
	Low-pressure die casting			0.032	0.001	0.040
		T4		0.035	0.001	0.010
		T6		0.046	0.001	0.040
	Gravity die casting	F		0.032	0.001	0.040
AM60	Die casting	F		0.021	0.003	0.010
AM50	Die casting	F		0.015	0.003	0.010
AS41	Die casting	F		0.010	0.004	0.020
AE42	Die casting	F		0.020	0.020	0.100

It has been found that these tolerance definitions are not sufficient to reliably exclude the formation of corrosion-promoting intermetallic phases, which in terms of electrochemistry have a more noble potential than the magnesium matrix.

Biodegradable implants (orthopedics, traumatology, cardiovascular implants) require a load-bearing function and consequently strength, together with sufficient expandability, during the physiologically necessary support periods thereof. However, especially in this respect, the known magnesium materials cannot come even close to the properties achieved by permanent implants such as titanium, CoCr alloys and titanium alloys. The ultimate tensile strength R_m for permanent implants is approximately 500 MPa to >1000 MPa, while that of magnesium materials is <275 MPa so far, and in most cases <250 MPa.

Another drawback of many technical magnesium materials is that the difference thereof between ultimate tensile strength R_m and proof stress R_p is only small. In the case of implants that allow plastic deformation, such as cardiovascular stents, this means that no further resistance exists against deformation after initial deformation of the material, and the regions that have already been deformed are deformed further without any load

increase, whereby overstretching of parts of the component may be caused and fracture may occur.

Many magnesium materials, such as the alloys containing 3 to 10% by weight Al and less than 1% by weight Zn and Mn (AZ group), for example, additionally exhibit a clearly pronounced mechanical asymmetry, which is manifested in the difference in the mechanical properties, especially the proof stress R_p with tension load and compression load. Such asymmetries are created, for example, during forming processes such as extrusion, rolling and drawing, which are used to produce suitable semi-finished products. A difference between the proof stress R_p during tension and the proof stress R_p during compression that is too large may result in inhomogeneous deformation of a component, such as a cardiovascular stent, which later undergoes multiaxial deformation, and may cause cracking and fracture.

Because of the low number of crystallographic slip systems, magnesium alloys can generally also form textures during forming processes such as extrusion, rolling and drawing used to produce suitable semifinished products by orienting the grains during the forming process. Specifically, this means that the semifinished product has different properties in different directions in space. For example, high deformability or elongation at fracture occurs in one direction in space after forming, and reduced deformability or elongation at fracture occurs in another direction in space. The formation of such textures should likewise be avoided, because a stent is subjected to high plastic deformation, and reduced elongation at fracture increases the risk of failure of the implant. One method for substantially avoiding such textures during forming is to adjust as fine a grain as possible prior to forming. Because of the hexagonal lattice structure of magnesium materials, the ability of these materials to deform at room temperature is low, which is characterized by slip in the base plane. If the material additionally has a coarse microstructure, which is to say a coarse grain, so-called twinning is forcibly produced upon further deformation, at which shear strain occurs, which transforms a crystal region into a position that is mirror symmetrical to the starting position.

The resulting twin grain boundaries constitute weak points in the material, where incipient cracking starts, especially with plastic deformation, which ultimately leads to the destruction of the component.

If the grain of the implant materials is sufficiently fine, the risk of such implant failure is drastically reduced. Implant materials should therefore have as fine a grain as possible so as to prevent such undesirable shear strain.

All available technical magnesium materials for implants are subject to high corrosion in physiological media. Attempts have been made in the prior art to curb the corrosion tendency by providing the implants with a corrosion-inhibiting coating, for example made of polymeric materials (EP 2 085 100 A2, EP 2 384 725 A1), an aqueous or alcoholic conversion solution (DE 10 2006 060 501 A1) or an oxide (DE 10 2010 027 532 A1, EP 0 295 397 A1).

The use of polymeric passivation layers is highly contested, because virtually all appropriate polymers also cause strong inflammations in the tissue at times. Thin structures without such protective measures do not reach the required support periods. The corrosion on thin-walled traumatological implants is often times accompanied by an excessively fast loss of tensile strength, which poses an additional burden by forming excessive amounts of hydrogen per unit of time. The consequences are undesirable gas inclusions in the bones and tissue.

In the case of traumatological implants having larger cross-sections, there is a need to be able to deliberately control the hydrogen problem and the corrosion rate of the implant by way of the structure thereof.

Specifically with biodegradable implants, there is a desire for maximum biocompatibility of the elements, because all the chemical elements that are contained are absorbed by the body after decomposition. In any case, highly toxic elements such as Be, Cd, Pb, Cr and the like should be avoided.

Degradable magnesium alloys are especially suitable for implementing implants which have been employed in a wide variety of forms in modern medical technology. Implants are used, for example, to support vessels, hollow organs and vein systems (endovascular

implants, such as stents), for fastening and temporarily fixing tissue implants and tissue transplantations, but also for orthopedic purposes, such as nails, plates or screws. A particularly frequently used form of an implant is the stent.

The implantation of stents has become established as one of the most effective therapeutic measures for the treatment of vascular diseases. Stents have the purpose of assuming a supporting function in hollow organs of a patient. For this purpose, stents featuring conventional designs have a filigree supporting structure comprising metal struts, which is initially present in compressed form for introduction into the body and is expanded at the site of the application. One of the main application areas of such stents is to permanently or temporarily widen and hold open vascular constrictions, particularly constrictions (stenosis) of coronary blood vessels. In addition, aneurysm stents are known, which are used primarily to seal the aneurysm. The support function is additionally provided.

The implant, notably the stent, has a base body made of an implant material. An implant material is a non-living material, which is employed for applications in medicine and interacts with biological systems. A basic prerequisite for the use of a material as an implant material, which is in contact with the body environment when used as intended, is the body friendliness thereof (biocompatibility). For the purpose of the present application, biocompatibility shall be understood to mean the ability of a material to induce an appropriate tissue reaction in a specific application. This includes an adaptation of the chemical, physical, biological, and morphological surface properties of an implant to the recipient's tissue with the aim of a clinically desired interaction. The biocompatibility of the implant material is also dependent on the temporal process of the reaction of the biosystem in which it is implanted. For example, irritations and inflammations occur in a relatively short time, which can lead to tissue changes. Depending on the properties of the implant material, biological systems thus react in different ways. According to the reaction of the biosystem, the implant materials can be divided into bioactive, bioinert and degradable or resorbable materials.

Implant materials comprise polymers, metallic materials, and ceramic materials (as coatings, for example). Biocompatible metals and metal alloys for permanent implants comprise, for example, stainless steels (such as 316L), cobalt-based alloys (such as CoCrMo cast alloys, CoCrMo forge alloys, CoCrWNi forge alloys and CoCrNiMo forge alloys), technical pure titanium and titanium alloys (such as cp titanium, TiAl6V4 or TiAl6Nb7) and gold alloys. In the field of biocorrodible stents, the use of magnesium or technical pure iron as well as biocorrodible base alloys of the elements magnesium, iron, zinc, molybdenum, and tungsten are proposed.

The use of biocorrodible magnesium alloys for temporary implants having filigree structures is made difficult in particular in that the degradation of the implant progresses very quickly in vivo. So as to reduce the corrosion rate, this being the degradation speed, different approaches are being discussed. For one, it is attempted to slow the degradation on the part of the implant material by developing appropriate alloys. In addition, coatings are to bring about a temporary inhibition of the degradation. While the existing approaches are promising, none of them has so far led to a commercially available product. Regardless of the efforts made so far, there is rather a continuing need for solutions that make it possible to at least temporarily reduce the corrosion of magnesium alloys in vivo, while optimizing the mechanical properties thereof at the same time.

In light of this prior art, the objects of the invention are that of providing a biodegradable magnesium alloy, a method for the production thereof and a use for implants, which allow the magnesium matrix of the implant to remain in an electrochemically stable state over the required support period with fine grain and high corrosion resistance without protective layers, while also improving the mechanical properties, such as increasing the tensile strength and proof stress, as well as reducing the mechanical asymmetry.

These objects are achieved by a magnesium alloy having the characteristics of claim 1, a method having the characteristics of claim 10, and the use according to the characteristics of claims 19 to 22.

The characteristics listed in the dependent claims allow advantageous refinements of the magnesium alloy according to the invention, of the method for the production thereof according to the invention, and the use.

The solution according to the invention is based on the realization that the corrosion resistance and deformability of the magnesium matrix of the implant must be assured over the support period such that the implant is able to absorb multiaxial permanent load without fracture or cracking, and to also utilize the magnesium matrix as a means for the decomposition triggered by the physiological liquids.

This is achieved by the magnesium alloy comprising:
1.5 to 7.0% by weight Zn, 0.5 to 3.5% by weight Al, the remainder being magnesium which contains impurities, which promote electrochemical potential differences and/or the formation of precipitations and/or intermetallic phases, in a total amount of no more than 0.0063% by weight of Fe, Si, Mn, Co, Ni, Cu, Zr, Y, Sc or rare earths having the ordinal numbers 21, 57 to 71 and 89 to 103, Be, Cd, In, Sn and/or Pb as well as P, wherein the alloy content of Zn in % by weight is greater than or equal to the alloy content of Al in % by weight.

The magnesium alloy according to the invention has extraordinarily high corrosion resistance, which is achieved by drastically reducing the content of impurities and the combinations thereof in the magnesium matrix, and by also adding precipitation and solid solution hardenable elements, which must be present in completely solid solution. The microstructure that is obtained has no electrochemical potential differences between the individual matrix phases after the forming and heat treatment processes, and therefore these differences cannot expedite the corrosion in physiological media.

The applicant surprisingly found that an alloy matrix, which has a content of Zn of preferably 1.5 to 5.5% by weight, and more particularly 3.5 to 5.5% by weight, and a content of Al of preferably at least 0.5 to 2.0% by weight, and more particularly 1.0 to 2.0% by weight, can form, or depending on the treatment forms, a mixed crystal from Zn and Al, which are present completely in solution form, without precipitations, the mixed

crystal having a higher standard potential than unalloyed high-grade magnesium and therefore the alloy being more noble.

Care should be taken that the alloy contents of Zn and Al are exactly adjusted such that the content in solid solution is as high as possible, and therefore maximum corrosion protection is achieved, without exceeding the solubility limit. Typical forming temperatures for this alloy range between 270 and 330°C under these conditions. This prevents particles from forming in the alloy matrix, which could take on the functions of cathodes during the corrosion process and thus promote corrosion.

Another surprising result is that, at a content of Zn of preferably 3.0 to 7.0% by weight, and more particularly 4.0 to 6.0% by weight, and a content of Al of preferably 0.5 to 3.5% by weight, and more particularly 1.5 to 2.5% by weight, an alloy is obtained which contains precipitations in the form of $Mg_3Zn_3Al_2$ und MgZn and has an extremely small grain size, wherein the precipitations having a size of less than 1 µm, and preferably 0.2 µm, are located both on the grain boundaries and in the grain interior.

In this case, the alloying elements may be present in the alloy in amounts even slightly above the solubility limit. Controlled by the cooling conditions during the production of the alloy, the alloying elements are initially present in solution. During forming of the alloy at temperatures below the solubility limit, for example at 250°C, fine particles are precipitated during forming which prevent grain growth and then contribute to an increase in tensile strength, both due to particle hardening and grain refining hardening. Through subsequent aging of the formed semi-finished product at temperatures below the temperature at which the alloying elements go completely into solution, for example 200°C, it is also possible to precipitate fine particles, which continue to remain in the matrix during the later thermomechanical treatment steps so as to prevent grain growth and increase the strength.

The alloy according to the invention has particularly high corrosion resistance. This is achieved by drastically reducing the contents of certain elements, and combinations of certain elements, in the alloy matrix whereby a microstructure is obtained in which, contrary to all known technically available magnesium materials, electrochemical differences in potential no longer occur between the individual matrix phases, and these

therefore no longer play a role in terms of an expedited corrosion of the material in physiological media.

The previously known tolerance limits for impurities do not take into account that wrought magnesium alloys often times are subjected to a thermomechanical treatment, and more particularly to an extended annealing process, which creates near-equilibrium structures. The metallic elements bond by way of diffusion and form what are known as intermetallic phases, which have a different electrochemical potential, notably a considerably higher potential, than the magnesium matrix, and therefore these intermetallic phases act as cathodes and can trigger galvanic corrosion processes.

Because the alloy according to the invention contains Al, it is particularly important to limit not only elements such as Ni, Co or Cu, which in general have a considerable adverse effect on the corrosion resistance of magnesium alloys, but notably the elements Fe, Mn and Si.

When producing such an alloy according to the prior art, both a remainder of Fe and a remainder of Mn are left in the melt. In addition, such melts are not purified with respect to Si. However, Fe, Mn and Si have a very high tendency to form a ternary intermetallic Fe-Mn-Si phase, which has a very positive potential and thus constitutes a very effective cathode for the corrosion of the material. Moreover, Al additionally shifts the boundary in the melt at which iron begins to precipitate as iron particles or intermetallic particles with other elements toward drastically lower iron contents.

The applicant has found that a corrosion-stable alloy matrix can be achieved when complying with the following tolerance limits of individual impurities in % by weight: Fe, Si, Mn, Co, Ni, Cu each with <0.0005; Zr, Y each with <0.0003; Sc or rare earths having the ordinal numbers 21, 57 to 71 and 89 to 103 in total <0.001; Be, Cd, In, Sn and/or Pb each with <0.0003; and P <0.0002.

Preferably the corrosion-staple alloy matrix contains impurities in a total amount of no more than 0.0053 Gew.%, which can be achieved when complying with the following tolerance limits of individual impurities in % by weight:
Fe, Si, Mn each with <0.0005; Co, Ni, Cu each with <0.0002; Zr, Y each with <0.0003; Sc or rare earths having the ordinal numbers 21, 57 to 71 and 89 to 103 in total <0.001; Be, Cd, In, Sn and/or Pb each with <0.0003; and P <0.0001.

In particular preferred the corrosion-staple alloy matrix contains impurities in a total amount of no more than 0.0022 Gew.%, which can be achieved when complying with the following tolerance limits of individual impurities in % by weight:n:
Fe, Si, Mn each with <0.0002; Co, Ni, Cu, Zr, Y each with <0.0001; Sc or rare earths having the ordinal numbers 21, 57 to 71 and 89 to 103 in total <0.0005; Be, Cd, In, Sn and/or Pb each with <0.0001, and P <0.0001.

The formation of precipitations or particles which have a positive potential difference as compared to the matrix is entirely suppressed, or drastically reduced, if the sum of individual impurities consisting of Fe, Si, Mn, Co, Ni and Cu is no more than 0.0030% by weight, preferably no more than 0.0021% by weight, and particularly preferably no more than 0.0009% by weight.
The particular advantage of the alloy according to the invention is that it no longer has any relevant contents of Fe, Si or Mn and only Zn and Al remain in the material, which increase the corrosion resistance of magnesium and increase the strength, however no elements are present which could form effective cathodes for corrosion processes. Such low concentrations moreover no longer allow a formation of intermetallic phases, which have a more positive electrochemical potential as compared to the matrix.

Because the Zr content is considerably below that of the prior art, no Zr-rich phases can form, which are always more noble than the magnesium matrix and thus act as cathodic sites which promote corrosion.

By limiting the yttrium content, the tendency toward stress and vibration corrosion is advantageously decreased, counteracting a rapid weakening of the mechanical strength.

Because the chemical elements of a magnesium alloy from biodegradable implants are absorbed by the human body, additionally the amounts of highly toxic elements such as Be, CD, In, Sn and/or Pb as well as rare earths (elements having the ordinal numbers 21, 57 to 71 and 89 to 103) must be limited in the alloy so as to achieve high biocompatibility, while also suppressing the formation of intermetallic phases between these elements and magnesium, aluminum and zinc.

Such low concentrations thus also ensure that the magnesium matrix no longer contains any, or contains only small amounts of, precipitations or particle phases, which have a more positive electrochemical potential as compared to the matrix.

In the connection with solid solution hardening by Zn and Al, these precipitations or particles of the elements contained in the alloy according to the present application allow the tensile strength of the magnesium matrix to be increased and the electrochemical potential of the matrix to be raised, whereby a corrosion-decreasing effect is created, notably with respect to physiological media. The precipitations preferably have a size of no more than 1 μm, and preferably of no more than 0.2 μm, and are located on the grain boundaries and in the grain interior, whereby the movement of grain boundaries during thermal treatment as well as dislocations during deformation are impaired and the strength of the magnesium alloy is increased.

The magnesium alloy according to the present patent application achieves a tensile strength of >275 MPa, and preferably >300 MPa, a yield point of >200 MPa, and preferably >225 MPa, and a yield ratio of <0.8, and preferably <075, wherein the

difference between the tensile strength and yield point is >50 MPa, and preferably >100 MPa, and the mechanical asymmetry is <1.25.

These significantly improved mechanical properties of the novel magnesium alloy assure that the implants, for example cardiovascular stents, are able to withstand the multiaxial permanent load in the implanted state over the entire support period, despite onsetting degradation of the magnesium matrix due to corrosion.

So as to minimize the mechanical asymmetry, it is particularly important for the magnesium alloy to have a particularly fine microstructure having a grain size of no more than 7.5 μm, preferably < 5 μm, and particularly preferably < 2.5 μm.

The objects are moreover achieved by a method for producing a magnesium alloy having improved mechanical and electrochemical properties. The method comprises the following steps:

a) generating high-purity magnesium by way of vacuum distillation;

b) generating a billet of the alloy by synthesis of the magnesium according to step a) with high-purity Zn and Al in a composition of 1.5 to 7.0% by weight Zn, 0.5 to 3.5% by weight Al, the remainder being magnesium containing impurities, which promote electrochemical potential differences and/or the formation of precipitations and/or intermetallic phases, in a total amount of no more than 0.0063% by weight of Fe, Si, Mn, Co, Ni, Cu, Zr, Y and Sc or rare earths having the ordinal numbers 21, 57 to 71 and 89 to 103, Be, Cd, In, Sn and/or Pb as well as P, wherein the alloy content of Zn in % by weight is greater than or equal to the alloy content of Al in % by weight;

c) homogenizing the alloy by annealing at a temperature between 250°C and 350°C with a holding period of 1 to 60 hours and cooling by exposure to air and in a water bath;

c) at least single forming of the homogenized alloy in the temperature range between 250°C and 350°C; and

d) optionally heat treating the formed alloy in the temperature range between 200°C and 350°C with a holding period of 5 minute to 6 hours.

In a preferred embodiment, step c) is performed alloy in the temperature range between 270°C and 350°C.

A content of Zn of preferably 1.5 to 5.5% by weight, and more particularly 3.5 to 5.5% by weight, and a content of Al of preferably at least 0.2 to 2.0% by weight, and more particularly 1.0 to 2.0% by weight, assures that the microstructure of the alloy is a mixed crystal made of Zn and Al, which are present completely in solution form, without precipitations, the mixed crystal having a higher standard potential than the high-grade magnesium. During subsequent forming, care must be taken that the forming temperature, for example 270°C to 330°C, is adhered to so as to ensure that the solubility limit for the individual elements is not exceeded. This prevents particles from forming in the matrix, which can have a corrosion-accelerating effect.

In contrast, a content of Zn of preferably 3.0 to 7.0% by weight, and more particularly 4.0 to 6.0% by weight, and a content of Al of preferably 0.5 to 3.5% by weight, and more particularly 1.5 to 2.5% by weight means that the alloying element may be present in amounts slightly higher than the solubility limit. The shaping process, after homogenizing annealing, at temperatures of 200°C to 350°C below the solubility limit according to step d) prevents precipitations in the $Mg_{17}Al_{12}$ phase and causes only fine particles to be precipitated in the matrix in the form of $Mg_3Zn_3Al_2$ und MgZn, which impair grain growth and contribute to an increase in the tensile strength of the alloy due to particle hardening and grain refining hardening. Through subsequent aging of the formed semi-finished product below temperatures at which the alloying elements are caused to go completely into solution (typically, these are temperatures of 20°C to 325°C), it is possible to precipitate particles, which continue to remain in the matrix during the later thermomechanical treatment, prevent grain growth processes and further increase the strength.

Vacuum distillation is preferably used to produce a starting material for the alloy according to the present patent application having the required threshold values.

The quantities of the alloying elements Zn and Al as well as the sum of impurities can be selectively adjusted and in % by weight are:

a) for the individual impurities:
Fe, Si, Mn, Co, Ni, Cu each with <0.0005;
Zr, Y each with <0.0003;
Sc or rare earths having the ordinal numbers 21, 57 to 71 and 89 to 103 in total <0.001;
Be, Cd, In, Sn and/or Pb each with <0.0003; and
P <0.0002.

aa) for the individual impurities in a preferred total amount of impurities of no more than 0.0053% by weight,:
Fe, Si, Mn each with <0.0005;
Co, Ni, Cu each with <0.0002;
Zr, Y each with <0.0003;
Sc or rare earths having the ordinal numbers 21, 57 to 71 and 89 to 103 in total <0.001;
Be, Cd, In, Sn and/or Pb each with <0.0003; and
P <0.0001.

ab) for the individual impurities in a particularly preferred total amount of impurities of no more than 0.0022% by weight:
Fe, Si, Mn each with <0.0002;
Co, Ni, Cu, Zr, Y each with <0.0001;
Sc or rare earths having the ordinal numbers 21, 57 to 71 and 89 to 103 in total <0.0005;
Be, Cd, In, Sn and/or Pb each with <0.0001; and
P <0.0001.

b) for the combination of individual impurities in total:
Fe, Si, Mn, Co, Ni and Cu no more than 0.0040, preferably no more than 0.0020, and particularly preferably no more than 0.0010.

It is particularly advantageous that the method described here only requires a small number of forming steps. Extrusion, equal channel angular extrusion and/or multiple forging can thus preferably be employed, which assure that a substantially homogeneous fine grain of <15 µm is achieved.

Because of the artificial aging, precipitations having a grain size of 1 µm, and preferably 0.2 µm, form on the grain boundaries and in the interior of the grains, whereby the tensile strength of the alloy reaches values which at >275 MPa, and preferably >300 MPa, are considerably higher than the prior art.

A third concept of the patent application relates to the use of the magnesium alloy produced according to the method, which has the aforedescribed advantageous composition and structure, in medical technology, notably for the production of implants, for example endovascular implants such as stents, for fastening and temporarily fixing tissue implants and tissue transplantations, orthopedic and dental implants, and neuroimplants.

All implants in the sense of this patent application are in the Cardiovascular field, osteosynthesis field or other areas.

Cardiovascular field in the sense of this application means

- the field of diagnostic, prevention and treatment of all diseases of the cardiovascular system, i.e. heart and blood vessel system,
- by mean of active and non-active implants used to support vessels, and vein systems
- including coronary, cerebral and peripheral vascular implants like stents, valves, closure devices, occluders, clips, coils, staples, implantable regional drug delivery devices,
- implantable electrostimulators (like pacemakers and defibrillators), implantable monitoring devices, implantable electrodes,
- system for fastening and temporarily fixing tissue implants and tissue transplantations
    - field also includes any type of stent as mechanical fix or temporary scaffold to support hollow organs (or bodies?) including bones, intervertebral disks

Osteosynthesis in the sense of this application means

- the field of treatment of fractured bones for internal fixation and stabilization by mechanical devices such as metal plates, pins, rods, wires, screws, clips, nails, staples excluding stent technology

Examples of areas out of the osteosynthesis field or the cardiovascular field are:

- Devices for the treatment of diseases of the sinews, joints, muscles, cartilages,
- oral (including dental) and maxillo facial implants (excl. osteosynthesis means),
- esthetic implants,
- supporting tools out of the body, (examples?)
- tissue engineering,
- soft tissue implants,
- devices for wound care,
- suture material and clamps,
- neurosurgery
- local drug delivery (excl. cardiovascular, i.e. lever)

renal

Exemplary embodiments

Example 1

A magnesium alloy is to be generated which is composed of 5% by weight Zn and 2% by weight Al, the remainder being Mg, in which the alloying elements are present completely in solution form, and which contains the following individual impurities in % by weight:

Fe: <0.0005; Si: <0.0005; Mn: <0.0005; Co: <0.0002; Ni: <0.0002; Cu <0.0002, wherein the sum of impurities consisting of Fe, Si, Mn, Co, Ni and Cu should be no more than 0.0021% by weight, the content of Zr < 0.0003% by weight, the content of Y <0.0001% by weight, the content of rare earths having the ordinal numbers 21, 39, 57 to 71 and 89 to 103 in total should be less than 0.001% by weight, and the contents of Be and Cd should be no more than 0.0001% by weight, respectively, and P <0.0001.

This alloy, produced using magnesium vacuum distillation, is subjected to homogenizing annealing at a temperature of 300°C for a duration of 48 hours, and subsequently to a forming process at a temperature of 275°C to 300°C, which is above the solubility limit. A precision tube for a cardiovascular stent is produced by multiple extrusion and annealing processes above the solubility limit at 275°C so as to prevent the precipitation of $Mg_3Zn_3Al_2$ particles.

The grain size that was achieved was < 10 µm, and the magnesium alloy reached a tensile strength of more than 300 MPa and proof stress of < 230 MPa. The yield ratio was 0.72 and the mechanical asymmetry was 1.15.

Example 2

A magnesium alloy is to be produced, which is composed of 5.5% by weight Zn and 3% by weight Al, the remainder being magnesium, in which some of the alloying elements are present as particles in the form of MgZnAl having a size of < 0.5 µm, and which contains the following individual impurities in % by weight:

Fe: <0.0005; Si: <0.0005; Mn: <0.0005; Co: <0.0002; Ni: <0.0002; Cu <0.0002, wherein the sum of impurities consisting of Fe, Si, Mn, Co, Ni and Cu should be no more than 0.0021% by weight, the content of Zr < 0.0003% by weight, the content of Y <0.0001% by weight, the content of rare earths having the ordinal numbers 21, 39, 57 to 71 and 89 to 103 in total should be less than 0.001% by weight, and the contents of Be and Cd should be no more than 0.0001% by weight, respectively, and P <0.0001.

The magnesium alloy is produced in a manner which corresponds to that of Example 1.

So as to precipitate some of the MgZnAl particles, an extrusion process is carried out above the solubility limit at temperatures of ≤ 275°C.

The precision tubes for a cardiovascular stent were produced by multiple extrusion and annealing processes, in part below the solubility limit. The solubility limit was 330°C. This alloy according to the subject matter of the patent application reached the following properties:

- tensile strength of 310 to 340 MPa;
- proof stress of ≤ 230 MPa;
- a yield ratio of 0.69;
- mechanical asymmetry of 1.1; and
- a grain size of < 5 µm.

CLAIMS

What is claimed is

1. A magnesium alloy having improved mechanical and electrochemical properties, comprising:
1.5 to 7.0% by weight Zn, 0.5 to 3.5% by weight Al, the remainder being magnesium which contains impurities, which promote electrochemical potential differences and/or the formation of precipitations and/or intermetallic phases, in a total amount of no more than 0.0063% by weight of Fe, Si, Mn, Co, Ni, Cu, Zr, Y, Sc or rare earths having the ordinal numbers 21, 57 to 71 and 89 to 103, Be, Cd, In, Sn and/or Pb as well as P, wherein the alloy content of Zn in % by weight is greater than or equal to the alloy content of Al in % by weight.

2. The magnesium alloy according to claim 1, characterized in that the content of Zn is preferably 1.5 to 5.5% by weight, and more particularly 3.5 to 5.5% by weight, and the content of Al is preferably at least 0.5 to 2.0% by weight, and more particularly 1.0 to 2.0% by weight, wherein the microstructure of the alloy is a mixed crystal made of Zn and Al, which are present completely in solution form, without precipitations.

3. The magnesium alloy according to claim 1, characterized in that the content of Zn is preferably 3.0 to 7.0% by weight, and more particularly 4.0 to 6.0% by weight, and the content of Al is preferably 0.5 to 3.5% by weight, and more particularly 1.5 to 2.5% by weight, wherein the matrix of the alloy contains only precipitations in the form of $Mg_3Zn_3Al_2$ and MgZn.

4. The magnesium alloy according to claim 1, characterized in that the individual impurities in the total sum of impurities amount to the following in % by weight: Fe <0.0005; Si <0.0005; Mn <0.0005; Co <0.0005; Ni <0.0005; Cu <0.0005; Zr <0.0003; Y <0.0003; Sc or rare earths having the ordinal numbers 21, 57 to 71 and 89 to 103 in total <0.001; Be, Cd, In, Sn and/or Pb each with <0.0003; and P <0.0002.

5. The magnesium alloy according to claim 1, characterized in that when the impurity elements Fe, Si, Mn, Co, Ni, and Cu are combined, the sum of these impurities in % by weight is no more than 0.0030, preferably no more than 0.0021, and particularly preferably no more than 0.0009.

6. The magnesium alloy according to claim 2, characterized in that the alloy has a fine-grained microstructure having a grain size of < 7.5 µm, preferably <5 µm, and still more preferably < 2.5 µm, without considerable electrochemical potential differences between the individual matrix phases.

7. The magnesium alloy according to claim 3, characterized in that the alloy matrix contains only such precipitations which have no potential differences, or potential differences as small as possible, as compared to the matrix, or which are less noble than the matrix.

8. The magnesium alloy according to claim 1, characterized in that the precipitations have a size of 1 µm, and preferably < 0.2 µm, and are dispersely distributed at the grain boundaries or in the grain interior.

9. The magnesium alloy according to claim 1, characterized in that it has a tensile strength of ≥275 MPa, and preferably ≥300 MPa, a yield point of ≥200 MPa, and preferably ≥225 MPa, and a yield ratio of <0.8, and preferably <0.75, wherein the difference between the tensile strength and yield point is ≥50 MPa, and preferably ≥100 MPa, and the mechanical asymmetry is <1.25.

10. A method for producing a magnesium alloy having improved mechanical and electrochemical properties, comprising the following steps:

a) generating high-purity magnesium by way of vacuum distillation;

b) generating a billet of the alloy by synthesis of the magnesium according to step a) with high-purity Zn and Al in a composition of 1.5 to 7.0% by weight Zn, 0.5 to 3.5% by weight Al, the remainder being magnesium containing

impurities, which promote electrochemical potential differences and/or the formation of precipitations and/or intermetallic phases, in a total amount of no more than 0.0063% by weight of Fe, Si, Mn, Co, Ni, Cu, Zr, Y and Sc or rare earths having the ordinal numbers 21, 57 to 71 and 89 to 103, Be, Cd, In, Sn and/or Pb as well as P, wherein the alloy content of Zn in % by weight is greater than or equal to the alloy content of Al in % by weight;

c) homogenizing the alloy by annealing at a temperature between 250°C and 350°C with a holding period of 1 to 60 hours and cooling by exposure to air and in a water bath;

d) at least single forming of the homogenized alloy in the temperature range between 250°C and 350°C, prefereably 270°C and 350°C; and

e) optionally heat treating the formed alloy in the temperature range between 200°C and 350°C with a holding period of 5 minutes to 6 hours.

11. The method according to claim 10, characterized in that the content of Zn is preferably 1.5 to 5.5% by weight, and more particularly 3.0 to 5.5% by weight, and the content of Al is preferably at least 0.2 to 2.0% by weight, and more particularly 1.0 to 2.0% by weight, wherein the microstructure of the alloy is a mixed crystal made of Zn and Al, which are present completely in solution form, without precipitations.

12. The method according to claim 10, characterized in that the content of Zn is preferably 3.0 to 7.0% by weight, and more particularly 4.0 to 6.0% by weight, and the content of Al is preferably 0.5 to 3.5% by weight, and more particularly 1.5 to 2.5% by weight, wherein the matrix of the alloy contains only precipitations in the form of $Mg_3Zn_3Al_2$ and MgZn.

13. The method according to claim 10 or claim 11, characterized in that the alloying elements are not contained in an amount above the solubility limit, and a formation of precipitations in the alloy matrix is suppressed by the forming and heat treatment processes below the solubility limit, the precipitations forming cathodes which expedite corrosion as compared to the alloy matrix.

14. The method according to claim 10 or claim 12, characterized in that the alloying elements are contained in an amount slightly above the solubility limit, and the precipitations from the forming and heat treatment processes at temperatures below the solubility limit, preferably in the range of 200°C to 350°C, are used to adjust the strength.

15. The method according to claim 13 or claim 14, characterized in that the precipitations have a size of 1 µm, and preferably < 0.2 µm, and are dispersely distributed at the grain boundaries or in the grain interior.

16. The method according to claim 10, characterized in that the individual impurities in the total sum of impurities amount to the following in % by weight: Fe <0.0005; Si <0.0005; Mn <0.0005; Co <0.0005; Ni <0.0005; Cu <0.0005; Zr <0.0003; Y <0.0003; Sc or rare earths having the ordinal numbers 21, 57 to 71 and 89 to 103 <0.0010; Be, Cd, In, Sn and/or Pb each with <0.0003; and P <0.0002.

17. The method according to claim 10, characterized in that when the impurity elements Fe, Si, Mn, Co, Ni, and Cu are combined, the sum of these impurities in % by weight is no more than 0.0040, preferably no more than 0.020, and particularly preferably no more than 0.0010.

18. The method according to claim 10, characterized in that the forming process is an extrusion, equal channel angular extrusion (EACE) and/or multiple forging process.

19. Use of a magnesium alloy according to any one of the claims 1 to 9 for producing a biodegradable implant.

20. Use of a magnesium alloy according to claim 19, characterized in that the implant is elected from the group of endovascular implants such as stents, implants for fastening and temporarily fixing tissue implants and tissue transplantations, orthopedic and dental implants, and neuroimplants.

21. Use of a magnesium alloy produced by the method according to any one of the claims 10 to 18 for producing a biodegradable implant.

22. Use of a magnesium alloy according to claim 21, characterized in that the implant is elected from the group of endovascular implants such as stents, implants for fastening and temporarily fixing tissue implants and tissue transplantations, orthopedic and dental implants, and neuroimplants.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2013/062876

A. CLASSIFICATION OF SUBJECT MATTER
INV. C22C23/04 C22F1/00
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C22C C22F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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[X] Further documents are listed in the continuation of Box C. [X] See patent family annex.

* Special categories of cited documents :

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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"&" document member of the same patent family

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Name and mailing address of the ISA/	Authorized officer
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INTERNATIONAL SEARCH REPORT

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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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INTERNATIONAL SEARCH REPORT

International application No
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INTERNATIONAL SEARCH REPORT

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International application No
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权利要求书3页 说明书10页

(54)发明名称

镁合金、其生产方法及其用途

(57)摘要

本专利申请涉及镁合金，并且涉及其生产方法以及涉及其用途，该镁合金包含：按重量计1.5%至7.0%的Zn，按重量计0.5%至3.5%的Al，其余是镁，其包含促进电化学电势差和/或促进形成沉淀和/或金属间相的杂质，其总量为不大于按重量计0.0063%的Fe、Si、Mn、Co、Ni、Cu、Zr、Y、Sc或具有21、57至71和89至103序数的稀土、Be、Cd、In、Sn和/或Pb以及P。

CN 104284993 A

1. 一种具有改进的机械和电化学特性的镁合金，包含：

按重量计 1.5%至 7.0%的 Zn，按重量计 0.5%至 3.5%的 Al，其余部分是包含杂质的镁，所述杂质促进电化学电势差和 / 或促进形成沉淀和 / 或金属间相，总量为不大于按重量计 0.0063%的 Fe、Si、Mn、Co、Ni、Cu、Zr、Y、Sc 或具有序数 21、57 至 71 和 89 至 103 的稀土、Be、Cd、In、Sn 和 / 或 Pb 以及 P，其中所述合金 Zn 含量以按重量%计大于或等于以按重量%计的所述合金 Al 含量。

2. 根据权利要求 1 所述的镁合金，其特征在于所述 Zn 含量优选地是按重量计 1.5%至 5.5%，并且更特别是按重量计 3.5%至 5.5%，以及所述 Al 含量优选地是按重量计至少 0.5%至 2.0%，并且更特别是按重量计 1.0%至 2.0%，其中所述合金的微结构是由 Zn 和 Al 形成的混合晶体，Zn 和 Al 完全以溶液形式存在而没有沉淀。

3. 根据权利要求 1 所述的镁合金，其特征在于所述 Zn 含量优选地是按重量计 3.0%至 7.0%，并且更特别是按重量计 4.0%至 6.0%，以及所述 Al 含量优选地是按重量计 0.5%至 3.5%，并且更特别是按重量计 1.5%至 2.5%，其中所述合金的基质仅包含以 $Mg_3Zn_3Al_2$ 和 MgZn 形式的沉淀。

4. 根据权利要求 1 所述的镁合金，其特征在于在杂质总和中单一杂质占以下重量 %：Fe<0.0005；Si<0.0005；Mn<0.0005；Co<0.0005；Ni<0.0005；Cu<0.0005；Zr<0.0003；Y<0.0003；Sc 或具有序数 21、57 至 71 和 89 至 103 的稀土总计 <0.001；Be、Cd、In、Sn 和 / 或 Pb 每一个 <0.0003；并且 P<0.0002。

5. 根据权利要求 1 所述的镁合金，其特征在于当将所述杂质元素 Fe、Si、Mn、Co、Ni 和 Cu 结合时，这些杂质总数以重量%不大于 0.0030、优选不大于 0.0021、并且特别优选不大于 0.0009。

6. 根据权利要求 2 所述的镁合金，其特征在于所述合金具有细晶粒微结构，其具有 <7.5μm、优选地 <5μm 以及还更优选地 <2.5μm 的晶粒尺寸，在单一基质相之间没有相当大的电化学电势差。

7. 根据权利要求 3 所述的镁合金，其特征在于所述合金基质仅包含这种沉淀，所述沉淀与所述基质相比不具有电势差或具有尽可能小的电势差，或其比所述基质较不惰性。

8. 根据权利要求 1 所述的镁合金，其特征在于所述沉淀具有尺寸是 1μm，并且优选地 <0.2μm，并且分散地分布在晶界处或晶粒内部中。

9. 根据权利要求 1 所述的镁合金，其特征在于其具有拉伸强度≥ 275MPa、并且优选地≥ 300MPa，屈服点≥ 200MPa、并且优选地≥ 225MPa，以及屈服比 <0.8、并且优选地 <0.75，其中拉伸强度与屈服点之间的差是≥ 50MPa、并且优选地≥ 100MPa，以及机械不对称性 <1.25。

10. 一种具有改进的机械和电化学特性的镁合金的生产方法，包括以下步骤：

a) 通过真空蒸馏生成高纯度镁；

b) 通过根据步骤 a) 的镁与高纯度 Zn 和 Al 的合成生成所述合金的坯料，以组成按重量计 1.5%至 7.0%的 Zn，按重量计 0.5%至 3.5%的 Al，其余是包含杂质的镁，所述杂质促进电化学电势差和 / 或促进形成沉淀和 / 或金属间相，总量为不大于按重量计 0.0063%的 Fe、Si、Mn、Co、Ni、Cu、Zr、Y、Sc 或具有序数 21、57 至 71 和 89 至 103 的稀土、Be、Cd、In、Sn 和 / 或 Pb 以及 P，其中所述合金 Zn 含量以按重量%计大于或等于以按重量%计的所述合金

Al 含量；

c) 通过在 250℃与 350℃之间的温度以 1 至 60 个小时的保持时间退火并且通过暴露于空气以及在水浴中冷却而将所述合金均化；

d) 将所述均化的合金在 250℃与 350℃之间、优选 270℃与 350℃之间的温度范围内至少一次成形；并且

e) 任选地在 200℃与 350℃之间的温度范围内以 5 分钟至 6 个小时的保持时间热处理所述成形的合金。

11. 根据权利要求 10 所述的方法，其特征在于所述 Zn 含量优选地是按重量计 1.5％至 5.5％、并且更特别是按重量计 3.0％至 5.5％，并且所述 Al 含量优选地是按重量计至少 0.2％至 2.0％、并且更特别是按重量计 1.0％至 2.0％，其中所述合金的微结构是由 Zn 和 Al 形成的混合晶体，Zn 和 Al 完全以溶液形式存在而没有沉淀。

12. 根据权利要求 10 所述的方法，其特征在于所述 Zn 含量优选地是按重量计 3.0％至 7.0％、并且更特别是按重量计 4.0％至 6.0％，并且所述 Al 含量优选地是按重量计 0.5％至 3.5％、并且更特别是按重量计 1.5％至 2.5％，其中所述合金的基质仅包含以 $Mg_3Zn_3Al_2$ 和 MgZn 形式的沉淀。

13. 根据权利要求 10 或权利要求 11 所述的方法，其特征在于所述合金元素不以高于溶解限度的量被包含，并且所述合金基质中沉淀的形成被所述溶解限度以下的成形和热处理过程抑制，所述沉淀形成与所述合金基质相比加速腐蚀的阴极。

14. 根据权利要求 10 或权利要求 12 所述的方法，其特征在于所述合金元素以稍微高于所述溶解限度的量被包含，并且在所述溶解限度以下的温度、优选在 200℃至 350℃的范围内使用来自所述成形和热处理过程的所述沉淀来调节强度。

15. 根据权利要求 13 或权利要求 14 所述的方法，其特征在于所述沉淀具有尺寸是 1μm，并且优选地 <0.2μm，并且分散地分布在晶界处或晶粒内部中。

16. 根据权利要求 10 所述的方法，其特征在于在杂质总和中单一杂质占以下重量％：Fe<0.0005；Si<0.0005；Mn<0.0005；Co<0.0005；Ni<0.0005；Cu<0.0005；Zr<0.0003；Y<0.0003；Sc 或具有序数 21、57 至 71 和 89 至 103 的稀土 <0.0010；Be、Cd、In、Sn 和 / 或 Pb 每一个 <0.0003；并且 P<0.0002。

17. 根据权利要求 10 所述的方法，其特征在于当将所述杂质元素 Fe、Si、Mn、Co、Ni 和 Cu 结合时，这些杂质总数以重量％不大于 0.0040、优选不大于 0.020、并且特别优选不大于 0.0010。

18. 根据权利要求 10 所述的方法，其特征在于所述成形过程是挤压、等通道转角挤压 (EACE) 和 / 或多次锻造。

19. 根据权利要求 1 至 9 中的任一项所述的镁合金用于生产可生物降解的植入物的用途。

20. 根据权利要求 19 所述的镁合金的用途，其特征在于所述植入物选自：血管内植入物，比如支架；用于紧固或暂时性固定组织植入物和组织移植物的植入物；整形外科和牙科植入物、以及神经植入物。

21. 通过根据权利要求 10 至 18 中的任一项所述的方法生产的镁合金用于生产可生物降解的植入物的用途。

22. 根据权利要求 21 所述的镁合金的用途，其特征在于所述植入物选自：血管内植入物，比如支架；用于紧固或暂时性固定组织植入物和组织移植物的植入物；整形外科和牙科植入物、以及神经植入物。

镁合金、其生产方法及其用途

[0001] 本专利申请涉及镁合金，并且涉及其生产方法以及涉及其用途。

[0002] 已知镁合金的特性由合金元素和杂质的类型和量以及生产条件明确地限定。合金元素和杂质对镁合金特性的影响是本领域技术人员长时间来已知的并且阐明了确定二元或三元镁合金的特性其作为植入物材料的用途的复杂性质。

[0003] 最常用于镁的合金元素是铝，由于固溶体和沉淀硬化以及细晶粒形成导致增加的拉伸强度，但是也导致了微孔性。此外，在熔体中铝将铁沉淀界限朝向显著更低的铁含量移动，在该铁含量处铁颗粒沉淀或与其他元素一起形成金属间颗粒。镁合金中不希望的伴生元素包括铁、镍、钴和铜，这些元素由于其正电的性质引起了腐蚀倾向的显著增加。

[0004] 在所有镁铸造合金中可以发现锰并且以 AlMnFe 沉淀的形式结合铁，由此降低了局部元素的形成。另一方面，锰不能结合所有的铁，并且因此剩余的铁和剩余的锰总是留在熔体中。

[0005] 硅降低了可铸造性和粘度，并且随着 Si 含量升高，预期了一种恶化的腐蚀行为。铁、锰和硅具有非常高的形成金属间相的倾向。

[0006] 这种相的电化学电势非常高并且因此可以作为控制合金基质的腐蚀的阴极。

[0007] 作为固溶体硬化的结果，锌改进机械性能并且导致晶粒细化，然而它还导致在二元 Mg-Zn 和三元 Mg-Al-Zn 合金中以按重量计 1.5 至 2％的含量开始的具有倾向于热裂化的微孔性。

[0008] 由锆形成的合金添加物提高拉伸强度而没有降低膨胀并且导致晶粒细化，但是还导致对动态重结晶的严重损害，这在重结晶温度的提高中得到证明并且因此要求高能量消耗。此外，锆不能添加到含铝和硅的熔体中，因为损失晶粒细化作用。

[0009] 稀土例如 Lu、Er、Ho、Th、Sc 和 In 均表现出类似的化学行为并且形成在二元相图的富含镁侧上具有部分溶解度的低共熔系统，以便沉淀硬化是有可能的。

[0010] 已知的是另外的合金元素连同杂质的添加引起二元镁合金中形成不同的金属间相。例如，在晶界上形成的金属间相 Mg17Al12 是脆性的并且限制了延展性。与镁基质相比，该金属间相更惰性并且能够形成局部电池 (local element)，由此腐蚀行为恶化。

[0011] 除了这些影响因素之外，镁合金的特性还决定性地取决于冶金生产条件。当通过合金化加入合金元素时，常规的浇铸方法自动引入杂质。因此现有技术 (US 5,055,254 A) 对镁浇铸合金中的杂质限定容许限度，例如，该限度对于包含约按重量计 8％至 9.5％的 Al 和按重量计 0.45％至 0.9％的 Zn 的镁－铝－锌合金，提及容许限度是按重量计 0.0015％至 0.0024％的 Fe、按重量计 0.0010％的 Ni、按重量计 0.0010％至 0.0024％的 Cu 以及按重量计不小于 0.15％至 0.5％的 Mn。

[0012] 在许多已知文献中提及镁及其合金中杂质的容许限度以及生产条件并且如下以按重量计％列出：

[0013]

合金	生产	状态	Fe	Fe/Mn	Ni	Cu

纯 Mg	没有信息		0.017		0.005	0.01
AZ91	压铸	F		0.032	0.005	0.040
	高压压铸			0.032	0.005	0.040
	低压压铸			0.032	0.001	0.040
		T4		0.035	0.001	0.010
		T6		0.046	0.001	0.040
	重力压铸	F		0.032	0.001	0.040
AM60	压铸	F		0.021	0.003	0.010
AM50	压铸	F		0.015	0.003	0.010
AS41	压铸	F		0.010	0.004	0.020
AE42	压铸	F		0.020	0.020	0.100

[0014] 已经发现了这些容许限(tolerance definition)不足以可靠地排除促进腐蚀的金属间相的形成,这就电化学而言比镁基质具有更惰性的电势。

[0015] 可生物降解的植入物(整形外科、创伤学、心血管植入物)在其生理学必须的支持周期期间要求承载功能以及因此强度连同足够的膨胀性。然而,尤其是在此方面,已知的镁材料不能达到甚至接近通过永久性植入物——例如钛、CoCr 合金和钛合金——所实现的特性。永久性植入物的限拉伸强度 R_m 为大约 500MPa 至 >1000MPa,而镁材料的极限拉伸强度迄今为止为 <275MPa,并且大多数情况下 <250MPa。

[0016] 许多工业镁材料的另一个缺点是其极限拉伸强度 R_m 与屈服点 R_p 之间的差异仅仅是小的。在允许塑性形变的植入物的情况下,例如心血管支架,这意味着在材料的初始变形之后对于变形不存在进一步的阻力,并且已经变形的区域在没有任何负载增加的情况下进一步变形,由此可以引起部件的部分的过度拉伸并且可能发生断裂。

[0017] 许多镁材料,比如包含按重量计 3%至 10%的 Al 以及小于按重量计 1%的 Zn 和 Mn(AZ 族)的合金例如另外地表现出明显显著的机械不对称性,这在机械特性差异中证明,尤其是以拉伸负荷和压缩负荷的屈服点 R_p。例如在用于生产适当的半成品的成形过程——例如挤压、辊压和牵引——期间,产生该不对称性。在拉伸期间的屈服点 R_p 与在压缩期间的屈服点 R_p 之间的太大的差异可能导致部件的不均匀变形——比如心血管支架,该部件随后经历多轴变形,并且可能引起开裂和断裂。

[0018] 由于晶面滑移系统的低数值,镁合金一般而言还可在成形过程期间形成纹理,例如在成形过程期间通过将晶粒定向用于生产适当的半成品的挤压、辊压和牵引。具体地,这意味着半成品在空间中在不同的方向上具有不同的特性。例如,在成形之后在空间中的一个方向上出现高可变形性或断裂伸长(elongation at fracture),并且在空间中的另一个

方向上出现降低的可变形性或断裂伸长。该纹理的形成同样应该避免，因为支架经历高塑性形变，并且降低的断裂伸长增加了植入物故障的风险。用于在成形期间基本上避免该纹理的一种方法是在成形之前尽可能细的调节晶粒。因为镁材料的六方晶格结构，这些材料在室温下变形的能力低，特征在于基准平面内的滑移。如果材料另外地具有粗糙的微结构，也就是说粗糙的晶粒，则在进一步变形时被迫产生所谓的孪晶，此时出现剪切应变，这将晶区转变为与起始位置镜面对称的位置。

[0019] 产生的孪晶晶界构成了材料中的薄弱点，在此开始早期开裂，尤其是具有塑性形变，最终导致了部件破坏。

[0020] 如果植入物材料的晶粒足够细，则该植入物故障的风险显著降低。因此植入物材料应具有尽可能细的晶粒以防止该不期望的剪切应变。

[0021] 所有对于植入物可用的工业镁材料在生理学介质中经受高腐蚀。在现有技术中已经进行了尝试来通过提供具有抑制腐蚀涂层的植入物来限制腐蚀倾向，例如，该涂层由聚合物材料(EP 2 085 100 A2,EP 2 384 725 A1)、水或醇转化溶液(alcoholic conversion solution)(DE 10 2006 060 501 A1)或氧化物(DE 10 2010 027 532 A1,EP 0 295 397 A1)制成。

[0022] 聚合物钝化层的使用是高度有争议的，因为几乎所有的适当的聚合物也有时在组织中引起强烈的炎症。没有该保护措施的薄结构不能达到要求的支持周期。薄壁创伤植入物上的腐蚀往往伴随拉伸强度的过快损失，其通过每单位时间形成过多量的氢造成额外的负担。结果是在骨和组织中的不希望的气体内含物。

[0023] 在具有更大横截面的创伤植入物情况下，存在能够通过其结构来有意地控制氢问题和植入物的腐蚀速度的需要。

[0024] 具体地，利用可生物降解的植入物，期望元素的最大生物相容性，因为包含的所有化学元素在分解后都被身体吸收。在任何情况下应该避免高毒性元素，比如Be、Cd、Pb、Cr等等。

[0025] 可降解的镁合金尤其适合于实施已经在现代医学技术中以广泛种类的形式采用的植入物。例如，使用植入物来支持脉管、中空器官和血管系统(血管内植入物，比如支架)，用于紧固和暂时固定组织植入物和组织移植物，而且还用于整形外科的目的，例如钉、板或螺钉。植入物的特别常用的形式是支架。

[0026] 支架的植入已经被确立为用于治疗血管疾病的最有效的治疗措施之一。支架具有在患者的中空器官中承担支持功能的目的。为此目的，特征为常规设计的支架具有包括金属支柱的细丝(filigree)支撑结构，该结构最初以压缩形式存在用于引入到身体中并且在应用的位置膨胀。该支架的主要应用领域之一是永久地或暂时地加宽并且保持打开的血管收缩，特别是冠状血管的收缩(狭窄)。此外，已知动脉瘤支架，其主要用来封闭动脉瘤。另外提供支撑功能。

[0027] 植入物，特别是支架，具有由植入物材料制成的基体。植入物材料是非活体材料，该材料用于医学中的应用并且与生物系统相互作用。作为植入材料使用的材料——其当如预期使用时与身体环境接触——的基本先决条件是其身体友好性(生物相容性)。为了本申请的目的，生物相容性应理解为是指材料在特定应用中诱导适当的组织反应的能力。这包括以临床上期望的相互作用对受体组织的植入物的化学、物理、生物和形态表面性质的

适应性。植入物材料的生物相容性还取决于植入的生物系统的反应的当时的过程。例如，在相对短的时间内发生刺激和炎症，这可能导致组织变化。取决于植入物材料的特性，因此生物系统以不同的方式反应。根据生物系统的反应，植入物材料可以分为生物活性、生物惰性和可降解或可再吸收材料。

[0028] 植入物材料包括聚合物、金属材料和陶瓷材料（例如，作为涂层）。永久性植入物的生物相容的金属和金属合金包括，例如不锈钢（比如316L）、钴基合金（比如CoCrMo浇铸合金、CoCrMo锻造合金、CoCrWNi锻造合金和CoCrNiMo锻造合金）、工业纯钛和钛合金（比如cp钛、TiAl6V4或TiAl6Nb7）以及金合金。在生物可腐蚀支架领域，提出了使用镁或工业纯铁以及元素镁、铁、锌、钼和钨的生物可腐蚀基础合金。

[0029] 具有细丝结构的暂时性植入物的生物可腐蚀镁合金的使用是困难的，特别是因为植入物的降解在体内进行非常快。所以为了降低腐蚀速度，即降解速度，讨论了不同的方法。对于一种方法，尝试了通过开发合适的合金来降低植入物材料的部件上的降解。此外，涂层产生了临时的降解抑制。尽管现有的方法是有前景的，但是它们目前均没有导致可购买的产品。不管迄今为止已经做出的努力，但是对于有可能至少暂时地降低镁合金在体内的腐蚀，同时优化其机械性能的解决方案还有相当持续的需要。

[0030] 就现有技术而言，本发明的目的是提供可生物降解的镁合金、其生产方法以及用于植入物的用途，这允许植入物的镁基质在要求的支持周期内保持电化学稳定状态，具有细晶粒和高耐腐蚀性而无需保护层，同时还改进了机械性能，比如增加了拉伸强度和屈服点，以及降低了机械不对称性。

[0031] 通过具有权利要求1的特征的镁合金、具有权利要求10的特征的方法以及根据权利要求19至22的特征的用途实现这些目的。

[0032] 在从属权利要求中列出的特征允许有利地优化根据本发明的镁合金、其根据本发明的生产方法以及用途。

[0033] 根据本发明的方案基于以下认识，即必须确保在支持周期内植入物的镁基质的耐腐蚀性和变形性，使得植入物能够吸收多轴永久性负荷而不断裂或开裂，并且还能够利用镁基质作为通过生理液体触发的分解的方式。

[0034] 这通过镁合金实现，其包含：

[0035] 按重量计1.5%至7.0%的Zn，按重量计0.5%至3.5%的Al，其余部分是镁，镁包含杂质，杂质促进电化学电势差和/或促进形成沉淀和/或金属间相，总量为不大于按重量计0.0063%的Fe、Si、Mn、Co、Ni、Cu、Zr、Y、Sc或具有序数21、57至71和89至103的稀土、Be、Cd、In、Sn和/或Pb以及P，其中合金Zn含量以按重量%计大于或等于合金Al含量以按重量%计。

[0036] 根据本发明的镁合金具有非常高的耐腐蚀性，这通过显著地降低镁基质中杂质的含量以及其结合，并且还通过加入沉淀和固溶体可硬化元素来实现，这些元素必须以完全固溶体存在。所获得的微结构在成形和热处理工艺之后在单个基质相之间不具有电化学电势差，并且因此这些差异不能在生理学介质中促进腐蚀。

[0037] 申请人出乎意料地发现合金基质可以由Zn和Al形成混合晶体或取决于处理形式可以形成混合晶体，合金基质具有优选地按重量计1.5%至5.5%、并且更特别是按重量计3.5%至5.5%的Zn含量，以及优选地按重量计至少0.5%至2.0%、并且更特别是按重量计

1.0%至2.0%的Al含量，Zn和Al完全以溶液形式存在而没有沉淀，混合晶体比未合金化的高等级镁具有更高的标准电势，并且因此合金是更惰性的。

[0038] 应注意，精确地调节合金Zn和Al的含量使得固溶体中的含量尽可能高，并且因此实现最大的腐蚀保护，而不超出溶解限度。该合金的典型成形温度在这些条件下范围在270与330℃之间。这防止在合金基质中形成颗粒，这会在腐蚀过程期间具有阴极功能并且因此促进腐蚀。

[0039] 另一个出乎意料的结果是，以Zn含量优选地是按重量计3.0%至7.0%，并且更特别是按重量计4.0%至6.0%，并且Al含量优选地是按重量计0.5%至3.5%，并且更特别是按重量计1.5%至2.5%获得了合金，其包含以$Mg_3Zn_3Al_2$和MgZn形式的沉淀并且具有极其小的晶粒尺寸，其中具有尺寸为小于1μm，并且优选地0.2μm的沉淀位于晶界上和晶粒内部中两者。

[0040] 在这种情况下，合金元素可以以比溶解限度甚至稍微高的量存在于合金中。受合金生产期间冷却条件的控制，合金元素最初以溶液存在。在低于溶解限度的温度——例如在250℃——下合金的成形期间，在成形期间沉淀细颗粒，该细颗粒防止晶粒生长并且然后有助于拉伸强度的增加，二者均由于颗粒硬化和晶粒细化硬化。通过在低于合金元素完全进入溶液的温度的温度——例如200℃——下随后老化形成的半成品有可能沉积细颗粒，该细颗在后来的热机械处理步骤期间继续保留在基质中以便防止晶粒生长并且增加强度。

[0041] 根据本发明的合金具有特别高的耐腐蚀性。这通过显著降低合金基质中某些元素的含量以及某些元素的结合来实现，由此获得微结构，其中与所有已知的工业上可得的镁材料相反，在单一的基质相之间不再出现电化学电势差，并且这些因此不再就生理学介质中材料的加速腐蚀起作用。

[0042] 先前已知的杂质的容许限度不考虑锻造的镁合金经常经受热机械处理并且更具体地经受延长的退火过程，这产生接近平衡的结构。金属元素通过扩散的方式结合并且形成已知的金属间相，该金属间相与镁基质相比具有不同的电化学电势，明显地相当更高的电势，并且因此这些金属间相用作阴极并且可以触发电化腐蚀过程。

[0043] 因为根据本发明的合金包含Al，特别重要的是不仅限制一般对镁合金的耐腐蚀性具有显著不利影响的元素，例如Ni、Co或Cu，而且还值得注意地限制元素Fe、Mn和Si。

[0044] 当生产根据现有技术该合金时，剩余的Fe和剩余的Mn均留在熔体中。此外，该熔体未就Si进行纯化。然而Fe、Mn和Si具有非常高的形成三元金属间Fe-Mn-Si相的倾向，这具有非常正的电势并且因此构成非常有效的阴极用于材料的腐蚀。此外，Al另外地将熔体内铁作为铁颗粒或与其他元素的金属间颗粒开始沉淀的界限朝向显著更低的铁含量移动。

[0045] 申请人已经发现当符合以下按重量%计的单一杂质的容许限度时可以获得腐蚀稳定的合金基质：

[0046] Fe、Si、Mn、Co、Ni、Cu每一个<0.0005；Zr、Y每一个<0.0003；Sc或具有序数21、57至71和89至103的稀土总计<0.001；Be、Cd、In、Sn和/或Pb每一个<0.0003；并且P<0.0002。

[0047] 优选地，腐蚀稳定的合金基质包含总量不大于0.0053Gew.%的杂质，这在符合以下按重量%计的单一杂质的容许限度时可以实现：

[0048] Fe、Si、Mn 每一个 <0.0005 ;Co、Ni、Cu 每一个 <0.0002 ;Zr、Y 每一个 <0.0003 ;Sc 或具有序数 21、57 至 71 和 89 至 103 的稀土总计 <0.001 ;Be、Cd、In、Sn 和 / 或 Pb 每一个 <0.0003 ;并且 P<0.0001。

[0049] 特别优选的是，腐蚀稳定的合金基质包含总量不大于 0.0022Gew.％的杂质，这在符合以下按重量％计的单一杂质的容许限度时可以实现：

[0050] Fe、Si、Mn 每一个 <0.0002 ;Co、Ni、Cu、Zr、Y 每一个 <0.0001 ;Sc 或具有序数 21、57 至 71 和 89 至 103 的稀土总计 <0.0005 ;Be、Cd、In、Sn 和 / 或 Pb 每一个 <0.0001 ;并且 P<0.0001。

[0051] 如果由 Fe、Si、Mn、Co、Ni 和 Cu 组成的单一杂质的总量不大于按重量计 0.0030％、优选不大于按重量计 0.0021％并且特别优选不大于按重量计 0.0009％，则与基质相比具有正电势差的沉淀或颗粒的形成被完全抑制，或显著地降低。

[0052] 根据本发明的合金的具体优点是其不再具有任何相关含量的 Fe、Si 或 Mn 并且仅 Zn 和 Al 保留在材料中，这增加镁的耐腐蚀性并且提高了强度，然而不存在可以形成用于腐蚀过程的有效阴极的元素。该低浓度此外不再允许形成金属间相，其与基质相比具有更正的电化学电势。

[0053] 因为 Zr 含量显著地低于现有技术的含量，所以不能形成富含 Zr 的相，这些相通常比镁基质更惰性，并且因此用作促进腐蚀的阴极位点。

[0054] 通过限制钇含量，有利地降低了应力和振动腐蚀 (vibration corrosion) 的倾向，抵制机械强度的迅速弱化。

[0055] 因为来自可生物降解的植入物的镁合金的化学元素被人体吸收，所以另外地合金中高毒性元素比如 Be、CD、In、Sn 和 / 或 Pb 连同稀土（具有序数 21、57 至 71 和 89 至 103 的元素）的量必须被限制以实现高的生物相容性，同时还抑制在这些元素与镁、铝和锌之间形成金属间相。

[0056] 因此该低浓度还确保镁基质不再包含任何或仅仅包含少量的沉淀或颗粒相，其与基质相比具有更正的电化学电势。

[0057] 与通过 Zn 和 Al 的固熔体硬化相关，在根据本申请的合金中包含的元素的这些沉淀或颗粒允许镁基质的拉伸强度增加，并且基质的电化学电势提高，从而产生降低腐蚀的作用，值得注意地是关于生理学介质。沉淀优选地具有不大于 1μm、并且优选不大于 0.2μm 的尺寸，并且位于晶界上和晶粒内部中，从而在热处理期间晶界的移动以及在变形期间的位错受损，并且提高了镁合金的强度。

[0058] 根据本申请的镁合金达到的拉伸强度 >275MPa、并且优选地 >300MPa，屈服点 >200MPa、并且优选地 >225MPa，并且屈服比 <0.8、并且优选地 <0.75，其中拉伸强度与屈服点之间的差 >50MPa、并且优选地 >100MPa，并且机械不对称性 <1.25。

[0059] 新颖的镁合金的这些显著改进的机械性质确保了植入物，例如心血管支架能够在整个支撑周期内经受植入状态的多轴永久性负荷，尽管由于腐蚀开始镁基质的降解。

[0060] 所以为了最小化机械不对称性，特别重要的是镁合金具有特别细的微结构，具有不大于 7.5μm、优选地 <5μm 并且特别优选 <2.5μm 的晶粒尺寸。

[0061] 目的此外通过用于生产具有改进的机械和电化学特性的镁合金的方法实现。该方法包括以下步骤：

[0062] a) 通过真空蒸馏的方式生成高纯度镁；

[0063] b) 通过合成根据步骤a) 的镁与高纯度Zn和Al生成合金坯(billet)，以组成按重量计1.5%至7.0%的Zn，按重量计0.5%至3.5%的Al，其余是包含杂质的镁，杂质促进电化学电势差和/或促进形成沉淀和/或金属间相，总量为不大于按重量计0.0063%的Fe、Si、Mn、Co、Ni、Cu、Zr、Y和Sc或具有序数21、57至71和89至103的稀土、Be、Cd、In、Sn和/或Pb以及P，其中合金Zn含量以按重量%计大于或等于合金Al含量以按重量%计；

[0064] c) 通过在250℃与350℃之间的温度以1至60个小时的保持时间退火并且通过暴露于空气以及在水浴中冷却而将合金均化；

[0065] c) 将均化的合金在250℃与350℃之间的温度范围内至少一次成形；并且

[0066] e) 任选地在200℃与350℃之间的温度范围内以5分钟至6个小时的保持时间热处理成形的合金。

[0067] 在一个优选实施方式中，在270℃与350℃之间的温度范围内进行步骤c) 合金。

[0068] 按重量计优选1.5%至5.5%、并且更特别按重量计3.5%至5.5%的Zn含量，以及按重量计优选至少0.2%至2.0%、并且更特别按重量计1.0%至2.0%的Al含量确保合金的微结构是由Zn和Al形成的混合晶体，其完全以溶液形式存在而没有沉淀，混合晶体比高等级镁具有更高的标准电势。在随后的成形期间，必须注意保持成形温度，例如270℃至330℃，以便确保不超过单一元素的溶解限度。这防止在基质中形成颗粒，颗粒可以具有加速腐蚀的作用。

[0069] 相比之下，按重量计优选3.0%至7.0%、并且更特别按重量计4.0%至6.0%的Zn含量，以及按重量计优选0.5%至3.5%、并且更特别按重量计1.5%至2.5%的Al含量意味着合金元素可以以稍微高于溶解限度的量存在。根据步骤d) 在低于溶解限度在200℃至350℃的温度下的均化退火之后的成型工艺防止在$Mg_{17}Al_{12}$相中的沉淀，并且仅仅引起细颗粒在基质中以$Mg_3Zn_3Al_2$和MgZn的形式沉淀，这损害晶粒生长，并且由于颗粒硬化和晶粒细化硬化有助于提高合金的拉伸强度。通过在低于引起合金元素完全进入溶液的温度(典型地，这些是20℃至325℃的温度)下随后老化生产的成形半成品，有可能沉淀颗粒，其在随后的热机械处理期间继续保留在基质中，防止晶粒生长过程并且进一步增加强度。

[0070] 优选地使用真空蒸馏以生产具有所要求的阈值的用于根据本专利申请的合金的起始材料。

[0071] 合金元素Zn和Al的量以及杂质的总量可以被选择性地调节并且以按重量%计是：

[0072] a) 对于单一杂质：

[0073] Fe、Si、Mn、Co、Ni、Cu每一个<0.0005；

[0074] Zr、Y每一个<0.0003；

[0075] Sc或具有序数21、57至71和89至103的稀土总计<0.001；

[0076] Be、Cd、In、Sn和/或Pb每一个<0.0003；并且

[0077] P<0.0002。

[0078] aa) 对于单一杂质，杂质的优选总量按重量计不超过0.0053%：

[0079] Fe、Si、Mn每一个<0.0005；

[0080] Co、Ni、Cu每一个<0.0002；

[0081] Zr、Y 每一个 <0.0003；

[0082] Sc 或具有序数 21、57 至 71 和 89 至 103 的稀土总计 <0.001；

[0083] Be、Cd、In、Sn 和 / 或 Pb 每一个 <0.0003；并且

[0084] P<0.0001。

[0085] ab) 对于单一杂质，杂质的特别优选总量按重量计不超过 0.0022%：

[0086] Fe、Si、Mn 每一个 <0.0002；

[0087] Co、Ni、Cu、Zr、Y 每一个 <0.0001；

[0088] Sc 或具有序数 21、57 至 71 和 89 至 103 的稀土总计 <0.0005；

[0089] Be、Cd、In、Sn 和 / 或 Pb 每一个 <0.0001；并且

[0090] P<0.0001。

[0091] b) 对于单一杂质的组合总计是：

[0092] Fe、Si、Mn、Co、Ni 和 Cu 不大于 0.0040，优选不大于 0.0020，并且特别优选不大于 0.0010。

[0093] 特别有利的是在此描述的方法仅仅需要较小数量的成形步骤。因此可以优选地采用挤压、等通道转角挤压 (equal channel angular extrusion) 和 / 或多次锻造，这确保实现 <15μm 的基本上均匀的细晶粒。

[0094] 由于人工老化，在晶界上和在晶粒内部中形成具有 1μm、并且优选地 0.2μm 的晶粒尺寸的沉淀，从而合金的拉伸强度达到 >275MPa、并且优选 >300MPa 的值，这些值显著地高于现有技术。

[0095] 本专利申请的第三个想法涉及根据本方法生产的镁合金在医疗技术中的用途，特别是用于植入物的生产，例如血管内植入物比如支架，用于紧固和暂时地固定组织植入物和组织移植物、矫形和牙科植入物和神经植入物，所述镁合金具有前面描述的有利组成和结构。

[0096] 在本专利申请的意义内的所有植入物在心血管领域、骨接合术领域或其他领域内。

[0097] 在本申请意义内的心血管领域是指

[0098] - 所有心血管系统——即，心脏和血管系统——的疾病的诊断、预防和治疗的领域，

[0099] - 通过用于支撑脉管和血管系统的活性和非活性植入物

[0100] - 包括冠状、脑和周围血管植入物，例如支架、瓣膜、闭合装置、封堵器、夹子、盘管、锁环、可植入局部药物递送装置，

[0101] - 可植入电刺激器（如起搏器和除颤器）、可植入监控装置、可植入电极，

[0102] - 用于紧固和暂时地固定组织植入物和组织移植物的系统

[0103] - 领域还包括作为支撑包括骨、椎间盘的中空器官的机械固定件或暂时性支持架的任何类型的支架。

[0104] 在本申请意义内的骨接合术是指

[0105] - 用于通过除支架技术以外的机械装置比如金属板、销钉 (pin)、杆、线、螺钉、夹具 (clip)、爪 (nail)、钉 (staple) 的内部固定和稳定治疗骨折的领域。

[0106] 在骨接合术领域和心血管领域之外的领域的实例是：

[0107] - 用于治疗腱、关节、肌肉、软骨的疾病的装置

[0108] - 口腔（包括牙科）以及颌面部植入物（除骨接合术装置外），

[0109] - 美容植入物

[0110] - 身体外支撑工具

[0111] - 组织工程学，

[0112] - 软组织植入物，

[0113] - 用于伤口护理的装置，

[0114] - 缝合材料和夹子，

[0115] - 神经外科

[0116] - 局部药物递送（除了心血管，即杆（lever））

[0117] 肾脏

[0118] 示例性实施方式

[0119] 实施例 1

[0120] 生成了镁合金，其由按重量计 5％的 Zn 和按重量计 2％的 Al 组成，并且剩余部分是 Mg，其中合金元素完全以溶液形式存在，并且包含以下按重量％计的单一杂质：

[0121] Fe：<0.0005；Si：<0.0005；Mn：<0.0005；Co：<0.0002；Ni：<0.0002；Cu<0.0002，其中由 Fe、Si、Mn、Co、Ni 和 Cu 组成的杂质的总数应该不大于按重量计 0.0021％，Zr 的含量按重量计 <0.0003％，Y 的含量按重量计 <0.0001％，具有序数 21、39、57 至 71 和 89 至 103 的稀土含量总计应该小于按重量计 0.001％，并且 Be 和 Cd 的含量应该分别不大于按重量计 0.0001％，并且 P<0.0001。

[0122] 将使用镁真空蒸馏生产的这种合金在 300℃的温度下经受均化退火持续 48 小时，并且随后在高于溶解限度的 275℃至 300℃的温度下经受成形过程。通过多次挤压以及高于 275℃下的溶解限度的退火过程以防止 $Mg_3Zn_3Al_2$ 颗粒的沉淀生产用于心血管支架的精密管。

[0123] 实现了 <10μm 的晶粒尺寸，并且镁合金达到了大于 300MPa 的拉伸强度和 <230MPa 的屈服点。屈服比是 0.72 并且机械不对称性是 1.15。

[0124] 实施例 2

[0125] 生产了镁合金，其由按重量计 5.5％的 Zn 和按重量计 3％的 Al 组成，并且剩余部分是 Mg，其中合金元素中的一些以具有 <0.5μm 的尺寸的 MgZnAl 形式的颗粒存在，并且包含以下按重量％计的单一杂质：

[0126] Fe：<0.0005；Si：<0.0005；Mn：<0.0005；Co：<0.0002；Ni：<0.0002；Cu<0.0002，其中由 Fe、Si、Mn、Co、Ni 和 Cu 组成的杂质的总数应该不大于按重量计 0.0021％，Zr 的含量按重量计 <0.0003％，Y 的含量按重量计 <0.0001％，具有序数 21、39、57 至 71 和 89 至 103 的稀土含量总计应该小于按重量计 0.001％，并且 Be 和 Cd 的含量应该分别不大于按重量计 0.0001％，并且 P<0.0001。

[0127] 以对应于实例 1 的方式生产镁合金。以便沉淀一些 MgZnAl 颗粒，在高于溶解限度在≤ 275℃的温度下进行挤压过程。

[0128] 通过多次挤压以及退火工艺部分地低于溶解限度生产用于心血管支架的精密管。溶解限度是 330℃。根据本专利申请的主题的该合金达到了以下特性：

[0129] - 拉伸强度为 310 至 340MPa ;

[0130] - 屈服点为≤ 230MPa ;

[0131] - 屈服比为 0.69 ;并且

[0132] - 机械不对称性为 1.1 ;并且

[0133] - 晶粒尺寸 <5μm。