bioactive, bioinert and degradable/resorbable materials in accordance with the response of the biosystem.

Implant materials comprise polymers, metal materials and ceramic materials (for example as a coating). Biocompatible metals and metal alloys for permanent implants include stainless steels for example (such as 316L), cobalt-based alloys (such as CoCrMo cast alloys, CoCrMo forged alloys, CoCrWNi forged alloys and CoCrNiMo forged alloys), pure titanium and titanium alloys (for example cp titanium, TiAl6V4 or TiAl6Nb7) and gold alloys. In the field of biocorrodible stents, the use of magnesium or pure iron as well as biocorrodible master alloys of the elements magnesium, iron, zinc, molybdenum and tungsten is recommended.

The use of biocorrodible magnesium alloys for temporary implants having filigree structures is in particular hindered by the fact that the implant degrades very rapidly *in vivo*. Various approaches are under discussion for reducing the corrosion rate, that is to say the degradation rate. On the one hand, it is attempted to slow down the degradation on the part of the implant material as a result of suitable alloy development. On the other hand, coatings are to temporarily inhibit the degradation. Although the previous approaches were very promising, it has not yet been possible to produce a commercially obtainable product. Rather, irrespective of the previous efforts, there is still an ongoing need for solution approaches that enable at least temporary reduction of the *in vivo* corrosion with simultaneous optimization of the mechanical properties of magnesium alloys.

With this prior art, the objects of the invention are to provide a biologically degradable magnesium alloy and a method for production thereof, which make it possible to keep the magnesium matrix of the implant in an electrochemically stable state over the necessary support time with fine grain and high corrosion resistance without protective layers and to utilize the formation of intermetallic phases that are electrochemically less noble compared to the magnesium matrix with simultaneous improvement of the mechanical properties, such as the increase in strength and proof stress as well as the reduction of the mechanical asymmetry, to set the degradation rate of the implants.

This object is achieved by a magnesium alloy having the features in claim 1 and by a method having the features in claim 12.

Advantageous developments of the magnesium alloy according to the invention and of the method according to the invention for production of said magnesium alloy are possible by means of the features specified in the dependent claims.

The solution according to the invention is based on the awareness of ensuring resistance to corrosion and resistance to stress corrosion and vibration corrosion of the magnesium matrix of the implant over the support period, such that the implant is able to withstand ongoing multi-axial stress without fracture or cracking, and simultaneously to use the magnesium matrix as a store for the degradation initiated by the physiological fluids.

This is achieved in that the magnesium alloy comprises:
no more than 3.0% by weight of Zn, no more than 0.6% by weight of Ca, with the rest being formed by magnesium containing impurities, which favor electrochemical potential differences and/or promote the formation of intermetallic phases, in a total amount of no more than 0.005% by weight of Fe, Si, Mn, Co, Ni, Cu, Al, Zr and P, wherein the alloy contains elements selected from the group of rare earths with the atomic number 21, 39, 57 to 71 and 89 to 103 in a total amount of no more than 0.002% by weight.

The magnesium alloy according to the invention has an extraordinarily high resistance to corrosion, which is achieved as a result of the fact that the fractions of the impurity elements and the combination thereof in the magnesium matrix are extraordinarily reduced and at the same time precipitation-hardenable and solid-solution-hardenable elements are to be added, said alloy, after thermomechanical treatment, having such electrochemical potential differences between the matrix in the precipitated phases that the precipitated phases do not accelerate corrosion of the matrix in physiological media or slow down said corrosion.

Applicant has surprisingly found the following two aspects:

First the alloy contains an intermetallic phase $Ca_2Mg_6Zn_3$ and/or Mg_2Ca in a volume fraction of close to 0 to 2.0% and the phase MgZn is avoided, if the content of Zn is preferably 0.1 to 2.5% by weight, particularly preferably 0.1 to 1.6% by weight, and the content of Ca is no more than 0.5% by weight, more preferably 0.001 to 0.5% by weight, and particularly preferably at least 0.1 to 0.45% by weight.

Second, compared to the conventional alloy matrices, intermetallic phases Mg_2Ca and $Ca_2Mg_6Zn_3$, in particular in each case in a volume fraction of at most 2%, are primarily formed, if the alloy matrix contains 0.1 to 0.3% by weight of Zn and also 0.2 to 0.6% by weight of Ca and/or a ratio of the content of Zn to the content of Ca no more than 20, preferably no more than 10, more preferably no more than 3 and particularly preferably no more than 1.

The alloy matrix has an increasingly positive electrode potential with respect to the intermetallic phase $Ca_2Mg_6Zn_3$ and with respect to the intermetallic phase Mg_2Ca, which means that the intermetallic phase Mg_2Ca is less noble in relation to the intermetallic phase $Ca_2Mg_6Zn_3$ and both intermetallic phases are simultaneously less noble with respect to the alloy matrix. The two phases Mg_2Ca and $Ca_2Mg_6Zn_3$ are therefore at least as noble as the matrix phase or are less noble than the matrix phase in accordance with the subject matter of the present patent application. Both intermetallic phases are brought to precipitation in the desired scope as a result of a suitable heat treatment before, during and after the forming process in a regime defined by the temperature and the holding period, whereby the degradation rate of the alloy matrix can be set. As a result of this regime, the precipitation of the intermetallic phase MgZn can also be avoided practically completely. The last-mentioned phase is therefore to be avoided in accordance with the subject matter of this patent application, since it has a more positive potential compared to the alloy matrix, that is to say is much more noble compared to the alloy matrix, that is to say it acts in a cathodic manner. This leads undesirably to the fact that the anodic reaction, that is to say the corrosive dissolution of a component of the material, takes place at the material matrix, which leads to destruction of the cohesion of the matrix and therefore to destruction of the component. This destruction therefore also progresses continuously, because particles that are more noble are continuously exposed by the corrosion of the

matrix and the corrosive attack never slows, down, but is generally accelerated further as a result of the enlargement of the cathode area.

In the case of the precipitation of particles which are less noble than the matrix, that is to say have a more negative electrochemical potential than the matrix, it is not the material matrix that is corrosively dissolved, but the particles themselves. This dissolution of the particles in turn leaves behind a substantially electrochemically homogenous surface of the matrix material, which, due to this lack of electrochemical inhomogeneities, already has a much lower tendency for corrosion and, specifically also due to the use of highly pure materials, itself has yet greater resistance to corrosion.

A further surprising result is that, in spite of Zr freedom or Zr contents much lower than those specified in the prior art, a grain refinement effect can be achieved that is attributed to the intermetallic phases $Ca_2Mg_6Zn_3$ and/or Mg_2Ca, which block movement of the grain boundaries, delimit the grain size during recrystallization, and thereby avoid an undesirable grain growth, wherein the values for the yield points and strength are simultaneously increased.

A reduction of the Zr content is therefore also particularly desirable because the dynamic recrystallization of magnesium alloys is suppressed by Zr. This result in the fact that alloys containing Zr have to be fed more and more energy during or after a forming process than alloys free from Zr in order to achieve complete recrystallization. A higher energy feed in turn signifies higher forming temperatures and a greater risk of uncontrolled grain growth during the heat treatment. This is avoided in the case of the Mg/Zn/Ca alloys free from Zr described here.

Within the context of the above-mentioned mechanical properties, a Zr content of no more than 0.0003% by weight, preferably no more than 0.0001% by weight, is therefore advantageous for the magnesium alloy according to the invention.

The previously known tolerance limits for impurities do not take into account the fact that magnesium wrought alloys are in many cases subject to a thermomechanical treatment, in particular a relatively long annealing process, as a result of which structures close to equilibrium structures are produced. Here, the metal elements interconnect as a result of

diffusion and form what are known as intermetallic phases, which have a different electrochemical potential, in particular a much greater potential, compared to the magnesium matrix, whereby these phases act as cathodes and can trigger galvanic corrosion processes.

The applicant has found that, if the following tolerance limits of individual impurities are observed, the formation of intermetallic phases of this type is reliably no longer to be expected:

Fe ≤ 0.0005% by weight,

Si ≤ 0.0005% by weight,

Mn ≤ 0.0005% by weight,

Co ≤ 0.0002% by weight, preferably ≤ 0.0001% by weight,

Ni ≤ 0.0002% by weight, preferably ≤ 0.0001% by weight,

Cu ≤ 0.0002% by weight,

Al ≤ 0.001% by weight,

Zr ≤ 0.0003% by weight, preferably ≤ 0.0001,

P ≤ 0.0001% by weight, preferably ≤ 0.00005.

With a combination of the impurity elements, the formation of the intermetallic phases more noble than the alloy matrix then ceases if the sum of the individual impurities of Fe, Si, Mn, Co, Ni, Cu and Al is no more than 0.004% by weight, preferably no more than 0.0032% by weight, even more preferably no more than 0.002% by weight and particularly preferably no more than 0.001% by weight, the content of Al is no more than 0.001% by weight, and the content of Zr is preferably no more than 0.0003% by weight, preferably no more than 0.0001% by weight.

The active mechanisms by which the aforementioned impurities impair the resistance to corrosion of the material are different.

If small Fe particles form in the alloy as a result of an excessively high Fe content, these particles act as cathodes for corrosive attack; the same is true for Ni and Cu.

Furthermore, Fe and Ni with Zr in particular, but also Fe, Ni and Cu with Zr can also precipitate as intermetallic particles in the melt; these also act as very effective cathodes for the corrosion of the matrix.

Intermetallic particles with a very high potential difference compared to the matrix and a very high tendency for formation are the phases formed from Fe and Si and also from Fe, Mn and Si, which is why contaminations with these elements also have to be kept as low as possible.

P contents should be reduced as far as possible, since, even with minimal quantities, Mg phosphides form and very severely impair the mechanical properties of the structure.

Such low concentrations therefore ensure that the magnesium matrix no longer has any intermetallic phases having a more positive electrochemical potential compared to the matrix.

In the magnesium alloy according to the invention, the individual elements from the group of rare earths and scandium (atomic number 21, 39, 57 to 71 and 89 to 103) contribute no more than 0.001% by weight, preferably no more than 0.0003% by weight and particularly preferably no more than 0.0001% by weight, to the total amount.

These additives make it possible to increase the strength of the magnesium matrix and to increase the electrochemical potential of the matrix, whereby an effect that reduces corrosion, in particular with respect to physiological media, is set.

The precipitations preferably have a size of no more than 2.0 μm, preferably of no more than 1.0 μm, particularly preferably no more than 200nm, distributed dispersely at the grain boundaries or inside the grain.

For applications in which the materials are subject to plastic deformation and in which high ductility and possibly also a low ratio yield point (low ratio yield point = yield point/tensile strength) – that is to say high hardening – is desirable, a size of the precipitates between 100 nm and 1 μm, preferably between 200 nm and 1 μm, is particularly preferred. For example, this concerns vascular implants, in particular stents.

For applications in which the materials are subject to no plastic deformation or only very low plastic deformation, the size of the precipitates is preferably no more than 200 nm. This is the case for example with orthopedic implants, such as screws for osteosynthesis implants. The precipitates may particularly preferably have a size, below the

aforementioned preferred range, of no more than 50 nm and still more preferably no more than 20 nm.

Here, the precipitates are dispersely distributed at the grain boundaries and inside the grain, whereby the movement of grain boundaries in the event of a thermal or thermomechanical treatment and also displacements in the event of deformation are hindered and the strength of the magnesium alloy is increased.

The magnesium alloy according to the invention achieves a strength of > 275 MPa, preferably > 300 MPa, a yield point of > 200 MPa, preferably > 225 MPa, and a ratio yield point of < 0.8, preferably < 0.75, wherein the difference between strength and yield point is > 50 MPa, preferably > 100 MPa, and the mechanical asymmetry is < 1.25.

These significantly improved mechanical properties of the new magnesium alloys ensure that the implants, for example cardiovascular stents, withstand the ongoing multi-axial load in the implanted state over the entire support period, in spite of initiation of the degradation of the magnesium matrix as a result of corrosion.

For minimization of the mechanical asymmetry, it is of particular importance for the magnesium alloy to have a particularly fine microstructure with a grain size of no more than 5.0 μm, preferably no more than 3.0 μm, and particularly preferably no more than 1.0 μm without considerable electrochemical potential differences compared to the matrix phases.

The object of the invention is also achieved by a method for producing a magnesium alloy having improved mechanical and electrochemical properties. The method comprises the following steps

a) producing a highly pure magnesium by means of vacuum distillation;
b) producing a cast billet of the alloy as a result of synthesis of the magnesium according to step a) with highly pure Zn and Ca in a composition of no more than 3.0% by weight of Zn, no more than 0.6% by weight of Ca, with the rest being formed by magnesium containing impurities, which favor electrochemical potential differences and/or promote the formation of intermetallic phases, in a total amount of no more than 0.005% by weight of Fe, Si, Mn, Co, Ni, Cu, Al, Zr and P, wherein the alloy

contains elements selected from the group of rare earths with the atomic number 21, 39, 57 to 71 and 89 to 103 in a total amount of no more than 0.002% by weight;

c) homogenizing the alloy at least once and, in so doing, bringing the alloy constituents into complete solution by annealing in one or more annealing steps at one or more successively increasing temperatures between 300°C and 450°C with a holding period of 0.5 h to 40 h in each case;

d) optionally ageing the homogenized alloy between 100 and 450°C for 0.5 h to 20 h;

e) forming the homogenized alloy at least once in a simple manner in a temperature range between 150°C and 375°C;

f) optionally ageing the homogenized alloy between 100 and 450°C for 0.5h to 20 h;

g) selectively carrying out a heat treatment of the formed alloy in the temperature range between 100°C and 325°C with a holding period from 1 min to 10 h, preferred from 1min to 6h, still more preferred from 1min to 3h.

A content of from 0.1 to 0.3% by weight of Zn and from 0.2 to 0.4% by weight of Ca and/or a ratio of Zn to Ca of no more than 20, preferably of no more than 10 and particularly preferably of no more than 3 ensures that a volume fraction of at most up to 2% of the intermetallic phase and of the separable phases $Ca_2Mg_6Zn_3$ and Mg_2Ca are produced in the matrix lattice. The electrochemical potential of both phases differs considerably, wherein the phase $Ca_2Mg_6Zn_3$ generally has a more positive electrode potential than the phase Mg_2Ca. Furthermore the electrochemical potential of the $Ca_2Mg_6Zn_3$ phase is almost equal compared to the matrix phase, because in alloy systems, in which only the phase $Ca_2Mg_6Zn_3$ is precipitated in the matrix phase, no visible corrosive attack takes place. The $Ca_2Mg_6Zn_3$ and/or Mg_2Ca phases can be brought to precipitation in the desired scope before, during and/or after the forming in step e) – in particular alternatively or additionally during the ageing process – in a regime preselected by the temperature and the holding period, whereby the degradation rate of the alloy matrix can be set. As a result of this regime, the precipitation of the intermetallic phase MgZn can also be avoided practically completely.

This regime is determined in particular in its minimum value T by the following formula:

$$T > (40 \times (\%Zn) + 50))\,(in.°C)$$

The aforementioned formula is used to calculate the upper limit value determined by the Zn content of the alloy, wherein the following boundary conditions apply however;

- for the upper limit value of the ageing temperature in method step d) and/or f), the following is true for T: 100°C ≤ T ≤ 450°C, preferably T: 100°C ≤ T ≤ 350°C, still more preferred 100°C ≤ T ≤ 275°C.
- in the case of the maximum temperature during the at least one forming step in method step e), the following is true for T: 150°C ≤ T ≤ 375°C.
- in the case of the above-mentioned heat treatment step in method step g), the following is true for T: 100°C ≤ T ≤ 325°C.

Specifically for the production of alloy matrices with low Zn content, attention may have to be paid, in contrast to the specified formula, to ensure that the aforementioned minimum temperatures are observed, since, if said temperatures are not met, the necessary diffusion processes cannot take place in commercially realistic times, or, in the case of method step e), impractical low forming temperatures may be established.

The upper limit of the temperature T in method step d) and/or f) ensures that a sufficient number of small, finely distributed particles not growing too excessively as a result of coagulation is present before the forming step.

The upper limit of the temperature T in method step e) ensures that a sufficient spacing from the temperatures at which the material melts is observed. In addition, the amount of heat produced during the forming process and likewise fed to the material should also be monitored in this case.

The upper limit of the temperature T in method step g) in turn ensures that a sufficient volume fraction of particles is obtained, and, as a result of the high temperatures, that a fraction of the alloy elements that is not too high is brought into solution. Furthermore, as a result of this limitation of the temperature T, it is to be ensured that the volume fraction of the produced particles is too low to cause an effective increase in strength.

The intermetallic phases $Ca_2Mg_6Zn_3$ and Mg_2Ca, besides their anti-corrosion effect, also have the surprising effect of a grain refinement, produced by the forming process, which leads to a significant increase in the strength and proof stress. It is thus possible to dispense with Zr particles or particles containing Zr as an alloy element and to reduce the temperatures for recrystallization.

The vacuum distillation is preferably capable of producing a starting material for a highly pure magnesium/zinc/calcium alloy with the stipulated limit values.
The total amount of impurities and the content of the additive elements triggering the precipitation hardening and solid solution hardening and also increasing the matrix potential can be set selectively and are presented in% by weight:

a) for the individual impurities:
Fe ≤ 0.0005; Si ≤ 0.0005; Mn ≤ 0.0005; Co ≤ 0.0002, preferably ≤ 0.0001% by weight; Ni ≤ 0.0002, preferably ≤ 0.0001; Cu ≤ 0.0002; Al ≤ 0.001; Zr ≤ 0.0003, in particular preferably ≤ 0.0001; P ≤ 0.0001, in particular preferably ≤ 0.00005;

b) for the combination of individual impurities in total:
Fe, Si, Mn, Co, Ni, Cu und Al no more than 0.004%, preferably no more than 0.0032% by weight, more preferably no more than 0.002% by weight and particularly preferably 0.001, the content of Al no more than 0.001, and the content of Zr preferably no more than 0.0003, in particular preferably no more than 0.0001;

c) for the additive elements:
rare earths in a total amount of no more than 0.001 and the individual additive elements in each case no more than 0.0003, preferably 0.0001.

It is particularly advantageous that the method according to the invention has a low number of forming steps. Extrusion, co-channel angle pressing and/or also a multiple forging can thus preferably be used, which ensure that a largely homogeneously fine grain of no more than 5.0 μm, preferably no more than 3.0 μm and particularly preferably no more than 1.0 μm, is achieved.

As a result of the heat treatment, $Ca_2Mg_6Zn_3$ and/or Mg_2Ca precipitates form, of which the size may be up to a few μm. As a result of suitable process conditions during the production process by means of casting and the forming processes, it is possible however to achieve intermetallic particles having a size between no more than 2.0 μm, and preferably no more than 1.0 μm particularly preferably no more than 200 nm.

The precipitates in the fine-grain structure are dispersely distributed at the grain boundaries and inside the grains, whereby the strength of the alloy reaches values that, at > 275 MPa, preferably > 300 MPa, are much greater than those in the prior art.

The $Ca_2Mg_6Zn_3$ and/or Mg_2Ca precipitates are present within this fine-grain structure in a size of no more than 2.0 μm, preferably no more than 1.0 μm.

A size of the precipitates between 100 nm and 1.0 μm, preferably between 200 nm and 1.0 μm, are particularly preferred for applications in which the materials are subject to plastic deformation and in which high ductility and possibly also a low ratio yield point (low ratio yield point = yield point/tensile strength) – that is to say high hardening – is desired. For example, this concerns vascular implants, in particular stents.

Preferably for applications in which the materials are subject to no plastic deformation or only very low plastic deformation, the size of the precipitates is no more than 200 nm. This is the case for example with orthopedic implants, such as screws for osteosynthesis implants. The precipitates may particularly preferably have a size, below the aforementioned preferred range, of no more than 50 nm and most preferably no more than 20 nm.

A third aspect of the invention concerns the use of the magnesium alloy produced by the method and having the above-described advantageous composition and structure in medical engineering, in particular for the production of implants, for example endovascular implants such as stents, for fastening and temporarily fixing tissue implants and tissue transplants, orthopedic implants, dental implants and neuro implants.

Exemplary embodiments

The starting material of the following exemplary embodiments is in each case a highly pure Mg alloy, which has been produced by means of a vacuum distillation method.

Example 7:

A further magnesium alloy having the composition 0.3% by weight of Ca and the rest being formed by Mg with the following individual impurities in% by weight is to be produced:

Fe: < 0.0005; Si: < 0.0005; Mn: < 0.0005; Co: < 0.0002; Ni: < 0.0002; Cu < 0.0002, wherein the sum of impurities of Fe, Si, Mn, Co, Ni, Cu and Al is to be no more than 0.0015% by weight, the content of Al is to be < 0.001% by weight and the content of Zr is to be < 0.0003% by weight, the content of rare earths with the atomic number 21, 39, 57 to 71 and 89 to 103 in total is to be less than 0.001% by weight.

A highly pure magnesium is initially produced by means of a vacuum distillation method; highly pure Mg alloy is then produced by additionally alloying, by means of melting, components Zn and Ca, which are likewise highly pure.

This alloy, in solution, is subjected to a first homogenization annealing process at a temperature of 350°C for a period of 15 h and is then subjected to a second homogenization annealing process at a temperature of 450°C for a period of 10 h, and is then subjected to multiple extrusion at a temperature from 250 to 350°C to produce a precision tube for a cardio vascular stent. Alternatively to these steps, ageing at approximately at 150 to 250°C with a holding period of 1 to 20 hours can take place after the second homogenization annealing process and before the forming process. In addition, an annealing process at a temperature of 325°C can take place for 5 to 10 min as a completion process after the forming process.

As a result of these processes, in particular as a result of the heat regime during the extrusion process, the phase Mg_2Ca can be precipitated being less noble than the matix and thereby providing anodic corrosion protection of the matix.

The grain size can be set to < 2.0 µm as a result of this method.

The magnesium alloy achieved a strength level of > 340 MPa and 0.2 % proof stress of ≤ 275 MPa.

bioactive, bioinert and degradable/resorbable materials in accordance with the response of the biosystem.

Implant materials comprise polymers, metal materials and ceramic materials (for example as a coating). Biocompatible metals and metal alloys for permanent implants include stainless steels for example (such as 316L), cobalt-based alloys (such as CoCrMo cast alloys, CoCrMo forged alloys, CoCrWNi forged alloys and CoCrNiMo forged alloys), pure titanium and titanium alloys (for example cp titanium, TiAl6V4 or TiAl6Nb7) and gold alloys. In the field of biocorrodible stents, the use of magnesium or pure iron as well as biocorrodible master alloys of the elements magnesium, iron, zinc, molybdenum and tungsten is recommended.

The use of biocorrodible magnesium alloys for temporary implants having filigree structures is in particular hindered by the fact that the implant degrades very rapidly *in vivo*. Various approaches are under discussion for reducing the corrosion rate, that is to say the degradation rate. On the one hand, it is attempted to slow down the degradation on the part of the implant material as a result of suitable alloy development. On the other hand, coatings are to temporarily inhibit the degradation. Although the previous approaches were very promising, it has not yet been possible to produce a commercially obtainable product. Rather, irrespective of the previous efforts, there is still an ongoing need for solution approaches that enable at least temporary reduction of the *in vivo* corrosion with simultaneous optimization of the mechanical properties of magnesium alloys.

The exemplary techniques disclosed herein may provide a biologically degradable magnesium alloy and a method for production thereof, which make it possible to keep the magnesium matrix of the implant in an electrochemically stable state over the necessary support time with fine grain and high corrosion resistance without protective layers and to utilize the formation of intermetallic phases that are electrochemically less noble compared to the magnesium matrix with simultaneous improvement of the mechanical properties, such as the increase in strength and proof stress as well as the reduction of the mechanical asymmetry, to set the degradation rate of the implants.

This may be achieved by a magnesium alloy and by a method having the features of the independent claims.

Advantageous developments of the magnesium alloy and of the method of the independent claims are possible by means of the features specified in the dependent claims.

The solution as disclosed herein may allow for the resistance to corrosion and resistance to stress corrosion and vibration corrosion of the magnesium matrix of the implant over the support period, such that the implant to be able to withstand ongoing multi-axial stress without fracture or cracking, and simultaneously to use the magnesium matrix as a store for the degradation initiated by the physiological fluids.

This is achieved in that the magnesium alloy comprises:
no more than 3.0% by weight of Zn, no more than 0.6% by weight of Ca, with the rest being formed by magnesium containing impurities, which favor electrochemical potential differences and/or promote the formation of intermetallic phases, in a total amount of no more than 0.005% by weight of Fe, Si, Mn, Co, Ni, Cu, Al, Zr and P, wherein the alloy contains elements selected from the group of rare earths with the atomic number 21, 39, 57 to 71 and 89 to 103 in a total amount of no more than 0.002% by weight.

The magnesium alloy as disclosed herein may have an extraordinarily high resistance to corrosion, which may be achieved as a result of the fact that the fractions of the impurity elements and the combination thereof in the magnesium matrix are extraordinarily reduced and at the same time precipitation-hardenable and solid-solution-hardenable elements are to be added, said alloy, after thermomechanical treatment, having such electrochemical potential differences between the matrix in the precipitated phases that the precipitated phases do not accelerate corrosion of the matrix in physiological media or slow down said corrosion.

Applicant has surprisingly found the following two aspects:

First the alloy may contain an intermetallic phase $Ca_2Mg_6Zn_3$ and/or Mg_2Ca in a volume fraction of close to 0 to 2.0% and the phase MgZn is avoided, if the content of Zn is preferably 0.1 to 2.5% by weight, particularly preferably 0.1 to 1.6% by weight, and the content of Ca is no more than 0.5% by weight, more preferably 0.001 to 0.5% by weight, and particularly preferably at least 0.1 to 0.45% by weight.

Second, compared to the conventional alloy matrices, intermetallic phases Mg_2Ca and $Ca_2Mg_6Zn_3$, in particular in each case in a volume fraction of at most 2%, are primarily formed, if the alloy matrix contains 0.1 to 0.3% by weight of Zn and also 0.2 to 0.6% by weight of Ca and/or a ratio of the content of Zn to the content of Ca no more than 20, preferably no more than 10, more preferably no more than 3 and particularly preferably no more than 1.

The alloy matrix may have an increasingly positive electrode potential with respect to the intermetallic phase $Ca_2Mg_6Zn_3$ and with respect to the intermetallic phase Mg_2Ca, which means that the intermetallic phase Mg_2Ca is less noble in relation to the intermetallic phase $Ca_2Mg_6Zn_3$ and both intermetallic phases are simultaneously less noble with respect to the alloy matrix. The two phases Mg_2Ca and $Ca_2Mg_6Zn_3$ are therefore at least as noble as the matrix phase or are less noble than the matrix phase in accordance with the subject matter of the present patent application. Both intermetallic phases may be brought to precipitation in the desired scope as a result of a suitable heat treatment before, during and after the forming process in a regime defined by the temperature and the holding period, whereby the degradation rate of the alloy matrix can be set. As a result of this regime, the precipitation of the intermetallic phase MgZn can also be avoided practically completely. The last-mentioned phase is therefore to be avoided in accordance with the subject matter of this patent application, since it has a more positive potential compared to the alloy matrix, that is to say is much more noble compared to the alloy matrix, that is to say it acts in a cathodic manner. This leads undesirably to the fact that the anodic reaction, that is to say the corrosive dissolution of a component of the material, takes place at the material matrix, which leads to destruction of the cohesion of the matrix and therefore to destruction of the component. This destruction therefore also progresses continuously, because particles that are more noble are continuously exposed by the corrosion of the

matrix and the corrosive attack never slows, down, but is generally accelerated further as a result of the enlargement of the cathode area.

In the case of the precipitation of particles which are less noble than the matrix, that is to say have a more negative electrochemical potential than the matrix, it may not be the material matrix that is corrosively dissolved, but the particles themselves. This dissolution of the particles in turn may leave behind a substantially electrochemically homogenous surface of the matrix material, which, due to this lack of electrochemical inhomogeneities, already has a much lower tendency for corrosion and, specifically also due to the use of highly pure materials, itself has yet greater resistance to corrosion.

A further surprising result is that, in spite of Zr freedom or Zr contents much lower than those specified in the prior art, a grain refinement effect can be achieved that is attributed to the intermetallic phases $Ca_2Mg_6Zn_3$ and/or Mg_2Ca, which may block movement of the grain boundaries, delimit the grain size during recrystallization, and thereby avoid an undesirable grain growth, wherein the values for the yield points and strength are simultaneously increased.

A reduction of the Zr content may therefore also be particularly desirable because the dynamic recrystallization of magnesium alloys is suppressed by Zr. This result in the fact that alloys containing Zr may have to be fed more and more energy during or after a forming process than alloys free from Zr in order to achieve complete recrystallization. A higher energy feed in turn signifies higher forming temperatures and a greater risk of uncontrolled grain growth during the heat treatment. This may be avoided in the case of the Mg/Zn/Ca alloys free from Zr described here.

Within the context of the above-mentioned mechanical properties, a Zr content of no more than 0.0003% by weight, preferably no more than 0.0001% by weight, is therefore advantageous for the magnesium alloy disclosed herein.

The previously known tolerance limits for impurities do not take into account the fact that magnesium wrought alloys are in many cases subject to a thermomechanical treatment, in particular a relatively long annealing process, as a result of which structures close to equilibrium structures are produced. Here, the metal elements interconnect as a result of

diffusion and form what are known as intermetallic phases, which have a different electrochemical potential, in particular a much greater potential, compared to the magnesium matrix, whereby these phases act as cathodes and can trigger galvanic corrosion processes.

The applicant has found that, if the following tolerance limits of individual impurities are observed, the formation of intermetallic phases of this type is reliably no longer to be expected:

Fe ≤ 0.0005% by weight,

Si ≤ 0.0005% by weight,

Mn ≤ 0.0005% by weight,

Co ≤ 0.0002% by weight, preferably ≤ 0.0001% by weight,

Ni ≤ 0.0002% by weight, preferably ≤ 0.0001% by weight,

Cu ≤ 0.0002% by weight,

Al ≤ 0.001% by weight,

Zr ≤ 0.0003% by weight, preferably ≤ 0.0001

P ≤ 0.0001% by weight, preferably ≤ 0.00005.

With a combination of the impurity elements, the formation of the intermetallic phases more noble than the alloy matrix then ceases if the sum of the individual impurities of Fe, Si, Mn, Co, Ni, Cu and Al is no more than 0.004% by weight, preferably no more than 0.0032% by weight, even more preferably no more than 0.002% by weight and particularly preferably no more than 0.001% by weight, the content of Al is no more than 0.001% by weight, and the content of Zr is preferably no more than 0.0003% by weight, preferably no more than 0.0001% by weight.

The active mechanisms by which the aforementioned impurities impair the resistance to corrosion of the material may be different.

If small Fe particles form in the alloy as a result of an excessively high Fe content, these particles act as cathodes for corrosive attack; the same is true for Ni and Cu.

Furthermore, Fe and Ni with Zr in particular, but also Fe, Ni and Cu with Zr can also precipitate as intermetallic particles in the melt; these also act as very effective cathodes for the corrosion of the matrix.

Intermetallic particles with a very high potential difference compared to the matrix and a very high tendency for formation are the phases formed from Fe and Si and also from Fe, Mn and Si, which is why contaminations with these elements also have to be kept as low as possible.

P contents should be reduced as far as possible, since, even with minimal quantities, Mg phosphides form and very severely impair the mechanical properties of the structure.

Such low concentrations may therefore ensure that the magnesium matrix no longer has any intermetallic phases having a more positive electrochemical potential compared to the matrix.

In the magnesium alloy disclosed herein, the individual elements from the group of rare earths and scandium (atomic number 21, 39, 57 to 71 and 89 to 103) may contribute no more than 0.001% by weight, preferably no more than 0.0003% by weight and particularly preferably no more than 0.0001% by weight, to the total amount.

These additives make it possible to increase the strength of the magnesium matrix and to increase the electrochemical potential of the matrix, whereby an effect that reduces corrosion, in particular with respect to physiological media, is set.

The precipitations preferably have a size of no more than 2.0 µm, preferably of no more than 1.0 µm, particularly preferably no more than 200nm, distributed dispersely at the grain boundaries or inside the grain.

For applications in which the materials are subject to plastic deformation and in which high ductility and possibly also a low ratio yield point (low ratio yield point = yield point/tensile strength) – that is to say high hardening – is desirable, a size of the precipitates between 100 nm and 1 µm, preferably between 200 nm and 1 µm, is particularly preferred. For example, this concerns vascular implants, in particular stents.

For applications in which the materials are subject to no plastic deformation or only very low plastic deformation, the size of the precipitates is preferably no more than 200 nm. This is the case for example with orthopedic implants, such as screws for osteosynthesis implants. The precipitates may particularly preferably have a size, below the

aforementioned preferred range, of no more than 50 nm and still more preferably no more than 20 nm.

Here, the precipitates may be dispersely distributed at the grain boundaries and inside the grain, whereby the movement of grain boundaries in the event of a thermal or thermomechanical treatment and also displacements in the event of deformation are hindered and the strength of the magnesium alloy is increased.

The magnesium alloy disclosed herein may achieve a strength of > 275 MPa, preferably > 300 MPa, a yield point of > 200 MPa, preferably > 225 MPa, and a ratio yield point of < 0.8, preferably < 0.75, wherein the difference between strength and yield point may be > 50 MPa, preferably > 100 MPa, and the mechanical asymmetry may be < 1.25.

These significantly improved mechanical properties of the magnesium alloys may allow the implants, for example cardiovascular stents, to withstand the ongoing multi-axial load in the implanted state over the entire support period, in spite of initiation of the degradation of the magnesium matrix as a result of corrosion.

For minimization of the mechanical asymmetry, it may be of particular importance for the magnesium alloy to have a particularly fine microstructure with a grain size of no more than 5.0 µm, preferably no more than 3.0 µm, and particularly preferably no more than 1.0 µm without considerable electrochemical potential differences compared to the matrix phases.

In another exemplary technique, there is disclosed a method for producing a magnesium alloy having improved mechanical and electrochemical properties. The method comprises the following steps

a) producing a highly pure magnesium by means of vacuum distillation;
b) producing a cast billet of the alloy as a result of synthesis of the magnesium according to step a) with highly pure Zn and Ca in a composition of no more than 3.0% by weight of Zn, no more than 0.6% by weight of Ca, with the rest being formed by magnesium containing impurities, which favor electrochemical potential differences and/or promote the formation of intermetallic phases, in a total amount of no more than 0.005% by weight of Fe, Si, Mn, Co, Ni, Cu, Al, Zr and P, wherein the alloy

contains elements selected from the group of rare earths with the atomic number 21, 39, 57 to 71 and 89 to 103 in a total amount of no more than 0.002% by weight;

c) homogenizing the alloy at least once and, in so doing, bringing the alloy constituents into complete solution by annealing in one or more annealing steps at one or more successively increasing temperatures between 300°C and 450°C with a holding period of 0.5 h to 40 h in each case;

d) optionally ageing the homogenized alloy between 100 and 450°C for 0.5 h to 20 h;

e) forming the homogenized alloy at least once in a simple manner in a temperature range between 150°C and 375°C;

f) optionally ageing the homogenized alloy between 100 and 450°C for 0.5h to 20 h;

g) selectively carrying out a heat treatment of the formed alloy in the temperature range between 100°C and 325°C with a holding period from 1 min to 10 h, preferred from 1min to 6h, still more preferred from 1min to 3h.

A content of from 0.1 to 0.3% by weight of Zn and from 0.2 to 0.4% by weight of Ca and/or a ratio of Zn to Ca of no more than 20, preferably of no more than 10 and particularly preferably of no more than 3 ensures that a volume fraction of at most up to 2% of the intermetallic phase and of the separable phases $Ca_2Mg_6Zn_3$ and Mg_2Ca may be produced in the matrix lattice. The electrochemical potential of both phases may differ considerably, wherein the phase $Ca_2Mg_6Zn_3$ generally has a more positive electrode potential than the phase Mg_2Ca. Furthermore the electrochemical potential of the $Ca_2Mg_6Zn_3$ phase may be almost equal compared to the matrix phase, because in alloy systems, in which only the phase $Ca_2Mg_6Zn_3$ is precipitated in the matrix phase, no visible corrosive attack takes place. The $Ca_2Mg_6Zn_3$ and/or Mg_2Ca phases can be brought to precipitation in the desired scope before, during and/or after the forming in step e) – in particular alternatively or additionally during the ageing process – in a regime preselected by the temperature and the holding period, whereby the degradation rate of the alloy matrix can be set. As a result of this regime, the precipitation of the intermetallic phase MgZn can also be avoided practically completely.

This regime may be determined in particular in its minimum value T by the following formula:

$$T > (40 \times (\%Zn) + 50)) \, (in.°C)$$

The aforementioned formula may be used to calculate the upper limit value determined by the Zn content of the alloy, wherein the following boundary conditions apply however;

- for the upper limit value of the ageing temperature in method step d) and/or f), the following is true for T: 100°C ≤ T ≤ 450°C, preferably T: 100°C ≤ T ≤ 350°C, still more preferred 100°C ≤ T ≤ 275°C.
- in the case of the maximum temperature during the at least one forming step in method step e), the following is true for T: 150°C ≤ T ≤ 375°C.
- in the case of the above-mentioned heat treatment step in method step g), the following is true for T: 100°C ≤ T ≤ 325°C.

Specifically for the production of alloy matrices with low Zn content, attention may have to be paid, in contrast to the specified formula, to ensure that the aforementioned minimum temperatures are observed, since, if said temperatures are not met, the necessary diffusion processes cannot take place in commercially realistic times, or, in the case of method step e), impractical low forming temperatures may be established.

The upper limit of the temperature T in method step d) and/or f) may ensure that a sufficient number of small, finely distributed particles not growing too excessively as a result of coagulation is present before the forming step.

The upper limit of the temperature T in method step e) may ensure that a sufficient spacing from the temperatures at which the material melts is observed. In addition, the amount of heat produced during the forming process and likewise fed to the material should also be monitored in this case.

The upper limit of the temperature T in method step g) may in turn ensure that a sufficient volume fraction of particles is obtained, and, as a result of the high temperatures, that a fraction of the alloy elements that is not too high is brought into solution. Furthermore, as a result of this limitation of the temperature T, it may be ensured that the volume fraction of the produced particles is too low to cause an effective increase in strength.

The intermetallic phases $Ca_2Mg_6Zn_3$ and Mg_2Ca, besides their anti-corrosion effect, also have the surprising effect of a grain refinement, produced by the forming process, which may lead to a significant increase in the strength and proof stress. It is thus possible to dispense with Zr particles or particles containing Zr as an alloy element and to reduce the temperatures for recrystallization.

The vacuum distillation is preferably capable of producing a starting material for a highly pure magnesium/zinc/calcium alloy with the stipulated limit values.
The total amount of impurities and the content of the additive elements triggering the precipitation hardening and solid solution hardening and also increasing the matrix potential can be set selectively and are presented in% by weight:

a) for the individual impurities:
Fe ≤ 0.0005; Si ≤ 0.0005; Mn ≤ 0.0005; Co ≤ 0.0002, preferably ≤ 0.0001% by weight; Ni ≤ 0.0002, preferably ≤ 0.0001; Cu ≤ 0.0002; Al ≤ 0.001; Zr ≤ 0.0003, in particular preferably ≤ 0.0001; P ≤ 0.0001, in particular preferably ≤ 0.00005;

b) for the combination of individual impurities in total:
Fe, Si, Mn, Co, Ni, Cu und Al no more than 0.004%, preferably no more than 0.0032% by weight, more preferably no more than 0.002% by weight and particularly preferably 0.001, the content of Al no more than 0.001, and the content of Zr preferably no more than 0.0003, in particular preferably no more than 0.0001;

c) for the additive elements:
rare earths in a total amount of no more than 0.001 and the individual additive elements in each case no more than 0.0003, preferably 0.0001.

It is particularly advantageous that the method disclosed herein may have a low number of forming steps. Extrusion, co-channel angle pressing and/or also a multiple forging can thus preferably be used, which ensure that a largely homogeneously fine grain of no more than 5.0 µm, preferably no more than 3.0 µm and particularly preferably no more than 1.0 µm, is achieved.

As a result of the heat treatment, $Ca_2Mg_6Zn_3$ and/or Mg_2Ca precipitates may form, of which the size may be up to a few µm. As a result of suitable process conditions during the production process by means of casting and the forming processes, it is possible however to achieve intermetallic particles having a size between no more than 2.0 µm, and preferably no more than 1.0 µm particularly preferably no more than 200 nm.

The precipitates in the fine-grain structure may be dispersely distributed at the grain boundaries and inside the grains, whereby the strength of the alloy reaches values that, at > 275 MPa, preferably > 300 MPa, are much greater than those in the prior art.

The $Ca_2Mg_6Zn_3$ and/or Mg_2Ca precipitates may be present within this fine-grain structure in a size of no more than 2.0 µm, preferably no more than 1.0 µm.

A size of the precipitates between 100 nm and 1.0 µm, preferably between 200 nm and 1.0 µm, are particularly preferred for applications in which the materials are subject to plastic deformation and in which high ductility and possibly also a low ratio yield point (low ratio yield point = yield point/tensile strength) – that is to say high hardening – is desired. For example, this concerns vascular implants, in particular stents.

Preferably for applications in which the materials are subject to no plastic deformation or only very low plastic deformation, the size of the precipitates is no more than 200 nm. This is the case for example with orthopedic implants, such as screws for osteosynthesis implants. The precipitates may particularly preferably have a size, below the aforementioned preferred range, of no more than 50 nm and most preferably no more than 20 nm.

In another exemplary technique, there is provided an use of the magnesium alloy produced by the method and having the above-described advantageous composition and structure in medical engineering, in particular for the production of implants, for example endovascular implants such as stents, for fastening and temporarily fixing tissue implants and tissue transplants, orthopedic implants, dental implants and neuro implants.

Exemplary embodiments

The starting material of the following exemplary embodiments is in each case a highly pure Mg alloy, which has been produced by means of a vacuum distillation method.

Example 7:

A further magnesium alloy having the composition 0.3% by weight of Ca and the rest being formed by Mg with the following individual impurities in% by weight is to be produced:

Fe: < 0.0005; Si: < 0.0005; Mn: < 0.0005; Co: < 0.0002; Ni: < 0.0002; Cu < 0.0002, wherein the sum of impurities of Fe, Si, Mn, Co, Ni, Cu and Al is to be no more than 0.0015% by weight, the content of Al is to be < 0.001% by weight and the content of Zr is to be < 0.0003% by weight, the content of rare earths with the atomic number 21, 39, 57 to 71 and 89 to 103 in total is to be less than 0.001% by weight.

A highly pure magnesium is initially produced by means of a vacuum distillation method; highly pure Mg alloy is then produced by additionally alloying, by means of melting, components Zn and Ca, which are likewise highly pure.

This alloy, in solution, is subjected to a first homogenization annealing process at a temperature of 350°C for a period of 15 h and is then subjected to a second homogenization annealing process at a temperature of 450°C for a period of 10 h, and is then subjected to multiple extrusion at a temperature from 250 to 350°C to produce a precision tube for a cardio vascular stent. Alternatively to these steps, ageing at approximately at 150 to 250°C with a holding period of 1 to 20 hours can take place after the second homogenization annealing process and before the forming process. In addition, an annealing process at a temperature of 325°C can take place for 5 to 10 min as a completion process after the forming process.

As a result of these processes, in particular as a result of the heat regime during the extrusion process, the phase Mg_2Ca can be precipitated being less noble than the matrix and thereby providing anodic corrosion protection of the matrix.

The grain size can be set to < 2.0 µm as a result of this method.

The magnesium alloy achieved a strength level of > 340 MPa and 0.2 % proof stress of ≤ 275 MPa.