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 patent application 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, and to utilize the formation of intermetallic phases, which electrochemically are more noble than the magnesium matrix, while also improving the mechanical properties, such as increasing the tensile strength and proof stress, as well as reducing the mechanical asymmetry so as to adjust the degradation rate of the implants.

These objects are achieved by a magnesium alloy having the characteristics of claim 1, a method having the characteristics of claim 6, and the use according to the characteristics of claims 10 and 12.

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

The solution 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:
less or equal 4.0% by weight Zn, 2.0 to 10.0% by weight Al, wherein the alloy content of Al in % by weight is greater than or equal to the alloy content of Zn in % by weight,
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 matrix of the alloy is solid solution hardening due to Al and Zn and is also particle hardening due to the intermetallic phases formed of Mg and Al.

Preferably the magnesium alloy according to the this application has a content of Zn less or equal 2.0% by weight, in particular preferably less or equal 1.0% by weight and/or a content of Al in the range of 2.0 to 8.0% by weight, preferably 3.0 to 8.0% by weight and still more preferably 3.0 to 6.0% by weight.

The magnesium alloy according to the subject matter of the patent application has very high corrosion resistance, which is achieved by drastically reducing the content of impurities and the combinations thereof in the magnesium matrix, and by having only those alloying elements present which raise the electrochemical potential of the matrix such that the corrosion resistance of the alloy is considerably increased.

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 the 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.

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; and P <0.0002.
Further preferred in this embodiment, the alloy has additional individual impurities in the following tolerance limits (% by weight): 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;.

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.

It is surprising that the addition of manganese as an alloying element, which is customary in the prior art, can be dispensed with when these tolerance limits are adhered. The formation of the ternary intermetallic phase FeMnSi is suppressed, whereby the corrosion resistance of the alloy is improved.

When the impurity elements are combined, this tolerance limit of the sum of impurities of Fe, Si, Mn, Co, Ni and Cu is no more than 0.003 % by weight, preferably no more than 0.0021% by weight and in particular preferred no m ore than 0.0009% by weight.

The magnesium alloy according to the subject matter of the 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 <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.

These significantly improved mechanical properties can be attributed to the formation of solid solutions between aluminum and zinc in the alloy matrix as well as to the intermetallic phases of magnesium and aluminum occurring in the matrix. The basis for the increased tensile strength is the interaction of the dislocations with the particles, whereby the dislocation movement is adversely impacted and additional tension is required in order to generate the same plastic deformation as in an undisturbed matrix.

The improved mechanical properties of the novel magnesium alloys 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.

For 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 still more 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 less or equal 4.0% by weight Zn, 2.0 to 10.0% by weight Al, wherein the alloy content of Al in % by weight is greater than or equal to the alloy content of Zn in % by weight, 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, 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 matrix of the alloy is solid solution hardening due to Al and Zn and is also particle hardening due to the intermetallic phases formed of Mg and Al;

c) homogenizing the alloy by annealing at a temperature between 150°C and 450°C with a holding period of 4 to 40 hours; and

d) at least single forming of the homogenized alloy in the temperature range between 200°C and 400°C.

Preferably steps c) and d) can be repeated at least once.

After step c) and before step d) an ageing treatment step can be performed. Depending on the alloy composition and/or the amount and/or type of the grains and/or the grain size ageing treatment step can be performed at a temperature between 20°C and 300°C with a holding period of 1h to 168h. Prefereably the ageing treatment can be performed at a temperature between 20°C and 275°C, still more preferably at a temperature of 150°C with a holding period of 120 hours.

In a preferred value range steps c) is performed at a temperature between 250°C and 450°C and/or step d) is performed at a temperature between 225°C and 400°C.

Preferably the magnesium alloy generated by step a) has a content of Zn less or equal 2.0% by weight, in particular preferably less or equal 1.0% by weight and/or a content of Al in the range of 2.0 to 8.0% by weight, preferably 3.0 to 8.0% by weight and still more preferably 3.0 to 6.0% by weight.

b) for the combination of individual impurities in total:
Fe, Si, Mn, Co, Ni, Cu no more than 0.003, preferably no more than 0.0021% by weight and in particular preferred no m ore than 0.0009% by weight.

It is particularly advantageous that the method according to the patent application 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 <10 µm is achieved.

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

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 techniques disclosed herein may allow for provision of a biodegradable magnesium alloy, a method for the production thereof and a use for implants, which may 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, and to utilize the formation of intermetallic phases, which electrochemically are more noble than the magnesium matrix, while also improving the mechanical properties, such as increasing the tensile strength and proof stress, as well as reducing the mechanical asymmetry so as to adjust the degradation rate of the implants.

These may be achieved by a magnesium alloy, a method, and the use according to the independent claims.

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

The solution may allow for the corrosion resistance and deformability of the magnesium matrix of the implant to 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:
less or equal 4.0% by weight Zn, 2.0 to 10.0% by weight Al, wherein the alloy content of Al in % by weight is greater than or equal to the alloy content of Zn in % by weight,
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 matrix of the alloy is solid solution hardening due to Al and Zn and is also particle hardening due to the intermetallic phases formed of Mg and Al.

Preferably the magnesium alloy according to the this application has a content of Zn less or equal 2.0% by weight, in particular preferably less or equal 1.0% by weight and/or a content of Al in the range of 2.0 to 8.0% by weight, preferably 3.0 to 8.0% by weight and still more preferably 3.0 to 6.0% by weight.

The magnesium alloy according to the subject matter of the patent application may have very high corrosion resistance, which may be achieved by drastically reducing the content of impurities and the combinations thereof in the magnesium matrix, and by having only those alloying elements present which raise the electrochemical potential of the matrix such that the corrosion resistance of the alloy is considerably increased.

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 the 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.

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; and P <0.0002.
Further preferred in this embodiment, the alloy has additional individual impurities in the following tolerance limits (% by weight): 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;.

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 the preferred 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.

It is surprising that the addition of manganese as an alloying element, which is customary in the prior art, can be dispensed with when these tolerance limits are adhered. The formation of the ternary intermetallic phase FeMnSi is suppressed, whereby the corrosion resistance of the alloy is improved.

When the impurity elements are combined, this tolerance limit of the sum of impurities of Fe, Si, Mn, Co, Ni and Cu may be no more than 0.003 % by weight, preferably no more than 0.0021% by weight and in particular preferred no more than 0.0009% by weight.

The magnesium alloy according to the subject matter of the patent application may achieve 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 may be >50 MPa, and preferably >100 MPa, and the mechanical asymmetry may be <1.25.

These significantly improved mechanical properties can be attributed to the formation of solid solutions between aluminum and zinc in the alloy matrix as well as to the intermetallic phases of magnesium and aluminum occurring in the matrix. The basis for the increased tensile strength is the interaction of the dislocations with the particles, whereby the dislocation movement is adversely impacted and additional tension is required in order to generate the same plastic deformation as in an undisturbed matrix.

The improved mechanical properties of the magnesium alloys may allow the implants, for example cardiovascular stents, to be 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.

For 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 still more preferably < 2.5 µm.

In another exemplary technique, there is provided 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 less or equal 4.0% by weight Zn, 2.0 to 10.0% by weight Al, wherein the alloy content of Al in % by weight is greater than or equal to the alloy content of Zn in % by weight, 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, 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 matrix of the alloy is solid solution hardening due to Al and Zn and is also particle hardening due to the intermetallic phases formed of Mg and Al;

c) homogenizing the alloy by annealing at a temperature between 150ºC and 450ºC with a holding period of 4 to 40 hours; and

d) at least single forming of the homogenized alloy in the temperature range between 200ºC and 400ºC.

Preferably steps c) and d) can be repeated at least once.

After step c) and before step d) an ageing treatment step can be performed. Depending on the alloy composition and/or the amount and/or type of the grains and/or the grain size ageing treatment step can be performed at a temperature between 20°C and 300°C with a holding period of 1h to 168h. Preferably the ageing treatment can be performed at a temperature between 20°C and 275°C, still more preferably at a temperature of 150°C with a holding period of 120 hours.

In a preferred value range steps c) is performed at a temperature between 250°C and 450°C and/or step d) is performed at a temperature between 225°C and 400°C.

Preferably the magnesium alloy generated by step a) has a content of Zn less or equal 2.0% by weight, in particular preferably less or equal 1.0% by weight and/or a content of Al in the range of 2.0 to 8.0% by weight, preferably 3.0 to 8.0% by weight and still more preferably 3.0 to 6.0% by weight.

b) for the combination of individual impurities in total:
Fe, Si, Mn, Co, Ni, Cu no more than 0.003, preferably no more than 0.0021% by weight and in particular preferred no m ore than 0.0009% by weight.

It is particularly advantageous that the method according to the patent application 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 <10 µm is achieved.

In another exemplary technique, there is provided a use of the magnesium alloy produced according to the method disclosed herein, which may have 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