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(54) **MAGNESIUM ALLOY SHEET PRODUCED BY TWIN ROLL CASTING**

(57) The invention refers to a method of manufacturing a sheet metal product (28) including the steps of:

a) providing a molten magnesium alloy (10, 10') consisting of

- 0.4 wt% to 2 wt% Zn,
- 0.4 wt% to 1 wt% Ca,
- 0.00 wt% to 1.0 wt% rare earth elements and/or Sr,
- unavoidable impurities and
- the balance being Mg

b) forming a strip (10, 10'') in a twin roll casting process,  
c) performing a warm rolling process on the strip (10, 10'') and  
d) performing a subsequent heat treatment on the strip (10, 10'') at 300°C to 450°C for 0,5 min to 60 min.

The invention further refers to a sheet metal product (28), obtained or obtainable by the method of the invention.

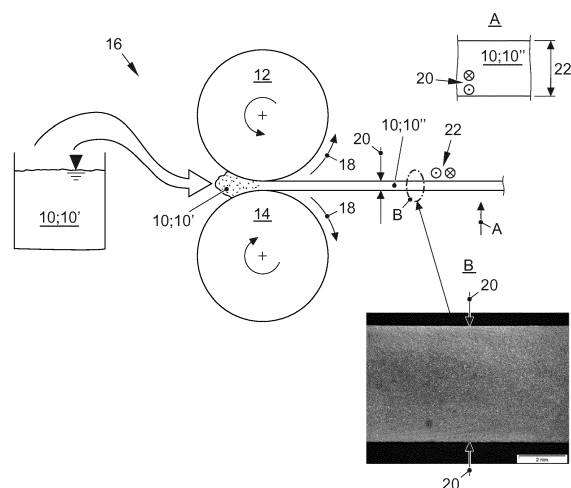


FIG. 1

## Description

[0001] The invention refers to a method of manufacturing a sheet metal product and to a sheet metal product obtainable by the method that results in excellent room temperature stretch formability, corrosion resistance and homogeneous distribution of the alloying elements, while the strength level can be adjusted within a wide range.

[0002] Magnesium alloys have a high potential for light weight construction. Comprising a very low density, even below the density of aluminum and only 25 % of that of steel. Magnesium alloys have a high stiffness, high specific strength and good damping capacity. These and further known advantageous properties of magnesium alloys, such as good machinability, make them highly attractive for light weight design. A major field of application of magnesium alloys is transportation, especially in the automotive and aircraft industry. Here, magnesium alloys are a preferred material for sheet metal products.

## State of the art

[0003] A known manufacturing method for sheet metal products is rolling. State-of-the-art-magnesium-alloys used for industrially established strips, such as AZ31, show a low formability at ambient temperature. As a consequence, it is necessary that the rolling process is conducted at elevated temperatures, often in combination with a low thickness reduction degree of the sheet metal strip per rolling pass. This leads to an increased number of rolling passes and hence higher effort which also results in higher production costs.

[0004] Additionally, as a result of the rolling process performed on conventional magnesium alloys, a strong crystallographic texture is formed in which the basal planes of the grains are preferentially oriented parallel to the rolling plane. Such crystallographic texture significantly hinders the deformability along the strip thickness so that a high planar anisotropy is caused. Thus the mechanical properties of the sheet metal product are adversely affected and strip forming operations become difficult.

[0005] Different attempts are known in the state of the art in order to overcome these two problems.

[0006] Twin roll casting is a manufacturing method that shows good potential for the production of magnesium strips with improved structural and mechanical properties at affordable costs. According to the twin roll casting technology, a thin strip of about 2 to 6 mm in thickness is produced by directly injecting a molten magnesium alloy between an upper and a lower roll. This step is then followed by a warm rolling process with intermediate annealing steps to produce the final sheet metal product of desired thickness. By producing a strip directly from the melt, the required number of subsequent rolling steps can be significantly reduced. This leads to higher cost-efficiency.

[0007] DE 100 52 423 C1 disclose alternative sheet

metal products based on magnesium alloys that are obtainable by a twin roll casting process and subsequent warm rolling. DE 10 2006 013 607 A1 describes a manufacturing line for a magnesium strip comprising a twin roll casting unit and rolling unit.

[0008] A means described in the art to improve the low temperature formability is weakening the crystallographic texture of the magnesium strips.

[0009] For example, the addition of rare earth elements or calcium to the magnesium alloy is known to lead to a reduction of texture intensity. However, the use of rare earth elements is expensive and raises ecological concerns. WO 2013/156523 A1 disclose that texture randomization is achievable by alloying addition of calcium into magnesium alloys. For all such alloys, an inverse relationship between formability and strength has been detected. Hence, magnesium alloys modified using these elements show a high formability, but exhibit a low strength.

[0010] A major problem in twin roll casting of magnesium alloys is the strong segregation of the alloying elements in the center and/or near the surface areas. This leads to a formation of regions of enriched solute and secondary phase content. In other words a strongly inhomogeneous distribution of the alloying elements in the magnesium sheet is observed. Segregation in the twin roll casting process limits the processability of the strip in subsequent thermomechanical treatments due to the embrittlement of the material. However, such treatments are essential in obtaining improved microstructures and mechanical properties.

[0011] It is an objective of the invention to provide a method of manufacturing a sheet metal product based on a magnesium alloy which comprises a high formability at low temperature in combination with a widely adjustable spectrum of mechanical strength, ranging from a low to a high level. Additionally, the object of this invention is to provide this method so that it results in low costs. Additionally, the invention aims at producing a sheet material product absent of any strong segregation within the microstructure.

## Description of the invention

[0012] The invention refers to a sheet metal product consisting of a magnesium alloy and to its production method. The use of the specific magnesium alloy by the method of the invention results in excellent room temperature stretch formability, corrosion resistance and homogeneous distribution of alloying elements of the sheet metal product of the invention, while the strength level can be adjusted within a wide range.

[0013] The manufacturing method of such a sheet metal product includes the steps of:

a) providing a molten magnesium alloy consisting of

- 0.4 wt% to 2 wt% Zn,

- 0.4 wt% to 1 wt% Ca,
- 0.0 wt% to 0.3 wt% Zr,
- 0.0 wt% to 1.0 wt% rare earth elements and/or Sr; and
- unavoidable impurities, and
- the balance being Mg,

- b) forming a strip in a twin roll casting process,
- c) performing a warm rolling process on the strip and
- d) performing a subsequent heat treatment on the strip at 300°C to 450°C for 0.5 min to 60 min.

**[0014]** The combination of the specific magnesium alloy with the given process steps leads to several advantages. One advantage is that the method of the invention allows for manufacturing the sheet metal product with excellent low temperature formability due to a high homogeneity of the microstructure and a weakened crystallographic texture. Due to increased homogeneity of the strip formed in step b) homogenisation annealing prior to the rolling process of step c) becomes redundant. This leads to further advantages in terms of productivity due to a saving of time and to reduced costs due to reduced energy consumption. The term microstructure is well known in the art. The following are only some examples of aspects of the microstructure referred to in this application: segregation effects, the size and shape of single grains as well as the crystal orientation of a number of grains. Depending on the microstructural aspect to be referred to a proper scale is chosen by the person skilled in the art. For example segregation effects are typically observable at a scale of about 1 mm, whereas single grains are typically observable at a scale of less than 30  $\mu\text{m}$ . Another advantage is that the method of the invention allows for manufacturing the sheet metal product with a broad spectrum of mechanical strength only by adjusting certain process parameters. There is no need to change the chemical composition of the magnesium alloy used in the method of the invention in order to change the mechanical strength. This increases production flexibility, for example due to easy changes of the manufactured sheet metal product and reduced set-up effort. Another advantage of the method of the invention is that the sheet metal product can be manufactured at low costs. This is a result of the twin roll casting process. This further increases the possible degree of utilization of production equipment.

**[0015]** The different advantages of the method of the invention are described in more detail below.

**[0016]** It is an advantage of the method of the invention that the used magnesium alloy shows a significantly reduced tendency to form segregation zones. Especially the effects of center line segregation and segregation near the surfaces of the strip of steps b) and c) are lowered. This decreases embrittlement of the material and, more importantly, enables the subsequent rolling and annealing processes to be carried out within larger processing windows without significant embrittlement, observed

on effects such as edge cracking. Extensive research has revealed that in the Mg-Zn-Ca-Zr-material-system multiple secondary phases form beside a Mg-rich matrix. One of these secondary phases is a ternary phase specified by  $\text{Mg}_6\text{Zn}_3\text{Ca}_2$ . This ternary phase was found to cause severe embrittlement during warm forming processes, such as the warm-rolling-process of step c), especially when it is formed directly from the melt. Research has revealed that a Zn content preferably from 0.4 wt% to 2 wt% leads to the effect that another secondary phase specified by  $\text{Mg}_2\text{Ca}$  becomes dominant instead of the ternary phase  $\text{Mg}_6\text{Zn}_3\text{Ca}_2$ . As a result, the tendency towards embrittlement is decreased and low-temperature formability is increased.

**[0017]** Research has revealed that the formation of the  $\text{Mg}_2\text{Ca}$  phase is obtained best by choosing the Zn content within a preferred range from 0.4 wt% to 2 wt%, further preferred from 0.45 wt% to 1.8 wt%, further preferred from 0.5 wt% to 1.5, further preferred from 0.55 wt% to 1.3, further preferred from 0.6 wt% to 1 wt% and further preferred from 0.65 wt% to 0.75 wt%.

**[0018]** A Zn content higher than 2 wt% leads to a large amount of the ternary phase  $\text{Mg}_6\text{Zn}_3\text{Ca}_2$  and lowers the liquidus temperature of the magnesium alloy, which deteriorates the rolling-ability and low temperature formability.

**[0019]** As a result of the beneficial dominance of the  $\text{Mg}_2\text{Ca}$  phase within the preferred compositional range, the sheet metal product features enhanced corrosion resistance. The  $\text{Mg}_2\text{Ca}$  phase is less noble than the Mg-matrix and thus protects it against corrosion as it is dissolved before the Mg-matrix itself is harmed. Another advantage of the method of the invention is that the formed  $\text{Mg}_2\text{Ca}$  phase suppresses grain growth in the magnesium alloy due to Zener pinning, as a small grain size increases the mechanical strength of the material.

**[0020]** Regarding the above stated advantages of the method of the invention, it is beneficial to have a large volume fraction of  $\text{Mg}_2\text{Ca}$  in the magnesium alloy and thus choose a high Ca content. Regarding the protection against corrosion and the limitation of grain growth it is further preferred that the  $\text{Mg}_2\text{Ca}$  is finely dispersed in the total volume of the magnesium alloy. Accordingly, in order to generate a homogeneous and fine distribution of  $\text{Mg}_2\text{Ca}$ , it is advantageous to limit the Ca content. A proper limit is defined by setting the solvus temperature of the  $\text{Mg}_2\text{Ca}$  phase below the solidus temperature of the magnesium alloy. In other words, a fine dispersion of precipitates can best be formed from solid solution rather than directly from the melt, as such phases are typically coarse and do not dissolve completely upon homogenisation.

**[0021]** Thus research can show that a Ca content of at least 0.4 wt% is required. Preferably the Ca content is chosen within a range from 0.4 wt% to 1 wt%, further preferred from 0.45 wt% to 0.9 wt%, further preferred from 0.5 wt% to 0.8 wt%, further preferred from 0.55 wt% to 0.7 wt% and further preferred from 0.55 wt% to 0.65

wt%.

**[0022]** Another advantage of the method of the invention is that due to the Ca in the magnesium alloy, the ignition of the magnesium alloy at high temperatures is retarded. This enhances the processability of the magnesium alloy during twin-roll casting enabling the reduction of cover gases. Additionally, the amount of oxide inclusions is reduced.

**[0023]** Preferably small quantities of Zr are added to the magnesium alloy. Research has revealed that in the magnesium alloy used in the method of the invention Zr advantageously leads to a significant grain refinement, removing to a large extent any directional solidification. Small quantities of Zr lead to heterogeneous nucleation in the entire volume of the magnesium alloy.

**[0024]** Preferably, the magnesium alloy comprises a Zr content of at least 0.03 wt% Zr. Preferably the Zr content is chosen within a range from 0.03 wt% to 0.3 wt%, further preferred from 0.04 wt% to 0.2 wt%, further preferred from 0.05 wt% to 0.15 wt% and further preferred from 0.05 wt% to 0.07 wt%.

**[0025]** A Zr content higher than 0.3 wt% results in Zr segregation in a cast strip and a large amount of ZnZr phases, that is difficult to dissolve during the subsequent processing and deteriorates the rollability.

**[0026]** The addition of Zr leads to an increased number of solidification nuclei. Consequently, any directional solidification is highly suppressed, and hence, equiaxed grains are formed in the strip formed in the twin roll casting process of step b). As an advantageous result, the material features isotropic properties.

**[0027]** Preferably the magnesium alloy contains small quantities of rare earth elements and/or Sr. Some preferred rare earth elements are Sc, Y, La or Gd. Preferably the magnesium alloy comprises 0.1 wt% to 1wt%, further preferred 0.2 wt% to 0.8 wt% and further preferred 0.4 wt% to 0.6 wt% of rare earth elements and/or Sr, related to the total amount of rare elements and Sr.

**[0028]** As an advantage, this additionally weakens the texture and improves the mechanical strength of the manufactured sheet metal product.

**[0029]** In a preferred embodiment of the method of the invention subsequent to the twin roll casting process of step b), an initial heat treatment b') is performed on the strip.

**[0030]** This advantageously dissolves inter-dendritic and inter-granular precipitates.

**[0031]** Preferably the initial heat treatment of step b') is performed at 400 °C to 500 °C for 30 min to 1440 min, preferably 300 min to 1440 min.

**[0032]** In a preferred embodiment of the method of the invention the warm rolling process of step c) is performed at 200 °C to 450 °C, further preferred 250 °C to 450 °C and further preferred 300 °C to 400 °C.

**[0033]** Experiments have shown that rolling a temperature below 250° C causes edge cracking, while grain coarsening occurs at rolling temperatures above 450 °C.

**[0034]** In a preferred embodiment of the method of the

invention the strip formed in the twin roll casting process of step b) and prior to step c) measures 1 mm to 5 mm, preferably 2 mm to 5 mm in thickness and 100 mm to 2000 mm in width. Such range of strip thickness and width, which is available using the specific magnesium alloy composition in the method of the invention, is advantageous in terms of cost efficiency of the sheet metal product production and wide applications, e.g. in various automotive components.

**[0035]** In a preferred embodiment of the method of the invention, a temperature of the molten magnesium alloy is controlled to be 680 °C to 750 °C and a peripheral speed of rolls used in the twin roll casting process of step b) is controlled to be 0.7 m/min to 3.5 m/min, preferably 1 m/min to 3.5 m/min.

**[0036]** This leads to advantageous quality of the strip in combination with a high efficiency of the twin roll casting process of step b).

**[0037]** Microstructures and mechanical properties of the sheet metal product can be flexibly tuned in the warm rolling process of step c) and in the subsequent heat treatment of step d). In the warm rolling process of step c) the thickness of the strip is reduced. Preferably, the warm rolling process of step c) is conducted in multiple passes leading to a stepwise reduction of the thickness of the strip. The thickness of the strip can be reduced to the desired thickness of the sheet metal product.

**[0038]** Preferably the strip is heated up to its rolling temperature in-between of different passes of the warm rolling process of step c). Thereby, the warm rolling process of step c) introduces deformation and recrystallization of the strip. A higher deformation energy is introduced by a lower rolling temperature as well as for higher degree of thickness reduction in a pass, which beneficially influences the recrystallization process. A high deformation energy assists a homogeneous formation of recrystallization nuclei that leads to fast recrystallization and a higher homogeneity of the microstructure. Depending on the speed of recrystallization, the microstructural homogeneity of the final sheet metal product obtained by the method of the invention can be easily tuned.

**[0039]** Further, by adjusting a duration of the final heat treatment of step d) the grain size of the material can be tuned. A longer duration of the final heat treatment of step d) leads to an increased grain size and a shorter duration leads to a decreased grain size. Along with an increased size of the grains the mechanical strength of the sheet metal product is decreased. Along with a decreased size of the grains the mechanical strength of the sheet metal product is increased. In this way the mechanical strength of the sheet metal product can be easily tuned.

**[0040]** This means that the method of the invention advantageously allows for tuning the microstructure and homogeneity of the sheet metal product by adjusting the process parameters of the warm rolling process of step c) and the subsequent heat treatment of step d). In this way the mechanical properties of the sheet metal product

can be easily tuned.

**[0041]** In a preferred embodiment of the method of the invention, subsequent to the warm rolling process of step c) a cold rolling process c') is carried out on the strip. This means that a very high amount of deformation energy is introduced to and stored in the strip. Preferably the cold-rolling-process of step c') is performed at a temperature below 150 °C. More preferably the temperature is chosen in a range from 25° C to 100° C, more preferred from 25° C to 50° C. In other words, it is mostly preferred to perform the cold-rolling-process of step c') at ambient temperature.

**[0042]** By performing the cold rolling process of step c'), an advantageous, very fine grain structure with an increased homogeneity of the sheet metal product can be achieved in the final heat treatment of step d), due to a large number of recrystallization nuclei. Additionally, the achievable spectrum of grain sizes (and therefore mechanical strength) is significantly enhanced. This means that the average grain size in the material of the sheet metal product as well as its strength is predominantly determined by the warm rolling process of step c) and duration of the subsequent heat treatment of step d).

**[0043]** In a preferred embodiment of the method of the invention, the thickness of the strip is reduced by a rolling degree of 0.05 to 0.3 in the warm rolling process of step c) and/or the cold rolling process of step c'). The rolling degree refers to the deformation degree introduced by the rolling in one pass. The rolling degree is calculated by  $\ln(t_{n-1}/t_n)$ , wherein  $t_{n-1}$  is the thickness of the strip before the  $n^{\text{th}}$  rolling step and  $t_n$  is the thicknesses of the strip after the  $n^{\text{th}}$  rolling step.

**[0044]** Experiments have shown that this leads to an advantageous ratio of the amount of deformation energy introduced to the strip as well as a reasonable total processing time required to reach the desired thickness. Preferably the rolling degree is 0.05 to 0.3.

**[0045]** The thickness of the sheet metal product is determined by the thickness of the strip in the last rolling pass conducted. Depending on the embodiment of the method of the invention this may be the warm rolling process of step c) or the cold rolling process of step c'). The thickness of the sheet metal product can be adjusted as desired. Preferably the thickness of the final sheet metal product measures 0.2 mm to 3.5 mm, more preferably 0.8 mm to 2.0 mm.

**[0046]** This is a proper range of thickness for most applications, for example in the automotive industry.

**[0047]** In a preferred embodiment of the method of the invention the content of unavoidable impurities is less than 50 ppm in total in all process steps. The tolerable value individually refers to the content of each unavoidable impurity contained in the magnesium alloy. Some very critical impurities are Fe, Cu and Ni. The content of the unavoidable impurities is preferably controlled in all process steps a) to d), as well as b') and c') of the method of the invention.

**[0048]** The invention further refers to a sheet metal

product, obtained or obtainable by the method of the invention.

**[0049]** In a preferred embodiment of the sheet metal product of the invention an ultimate tensile strength is in the range from 200 MPa to 325 MPa and/or a yield strength is in the range from 125 MPa to 275 MPa while a low-temperature formability measures at least 6 on the Erichsen index.

**[0050]** The tensile strength of the sheet metal product can be tested at room temperature and a strain rate of  $10^{-3}/\text{s}$  using a tensile sample having a gauge length of 25 mm. The Erichsen index is referred to as an index indicating formability of a sheet metal sample. The Erichsen index is the displacement of a spherical punch obtained at the moment of fracture of the sheet metal sample fixed at a blank holding force of 10 kN. The spherical punch has a diameter of 20 mm and moves at speed of 5 mm/min.

**[0051]** It is an advantage of the sheet metal product of the invention that a broad range of mechanical properties is covered while the low-temperature formability remains on a very high level throughout. This makes the sheet metal product of the invention highly attractive for applications in the transportation industry. In a vehicle structure, for example a car body, each component bears different mechanical specifications thus requiring a broad range of mechanical properties referring to the sheet metal product used for the component. Some examples are mounting structures and outer skin panel parts. The sheet metal product of the invention is thus capable of covering a wide spectrum of requirements and fields of applications without the need of changing the alloy system.

**[0052]** In a preferred embodiment the sheet metal product of the invention comprises a grain size in a range from 3  $\mu\text{m}$  to 30  $\mu\text{m}$ . As the mechanical strength of the sheet metal product of the invention strongly depends on the grain size, a wide spectrum of mechanical strength can be covered.

**[0053]** In a preferred embodiment the sheet metal product of the invention comprises a corrosion rate of less than 0.25 mm/year. The corrosion rate is indicated by a neutral salt spray test at room temperature.

**[0054]** This enhances the durability of the sheet metal product of the invention. Especially in the automotive industry this is an important requirement as the duration of a life cycle of a vehicle is often limited by corrosion effects.

**[0055]** In a preferred embodiment, the sheet metal product of the invention comprises at least one mechanical property that does not vary by more than 30 % in all planar directions of the sheet metal product. The term mechanical property herein refers to actual material properties, rather than to sheer geometrical properties. Preferably a number of mechanical properties do not vary by more than 30 %. Preferably the mechanical property or the mechanical properties do not vary by more than 20 %, further preferred 10 % and further preferred 5 %. In

other words, the sheet metal product of the invention advantageously comprises isotropic properties. Some important mechanical properties referred to are the ultimate strength, the yield strength and the low-temperature formability.

**[0056]** Further preferred embodiments are represented by the features described by the depending claims.

**[0057]** All embodiments mentioned in this application can be advantageously combined as long as nothing is stated to the contrary.

**[0058]** The invention is further described by the following embodiments and the figures according to the embodiments. It is illustrated in:

Figure 1 a preferred embodiment of steps a) and b) of the method of the invention;

Figure 2 a preferred embodiment of step b') of the method of the invention;

Figure 3 a preferred embodiment of steps c) and c') of the method of the invention;

Figure 4 a rolling schedule of a preferred embodiment of steps c) and c') of the method of the invention as shown in Figure 3;

Figure 5 a preferred embodiment of step d) of the method of the invention and

Figure 6 an overview of preferred mechanical properties of a sheet metal product obtainable by a method of the invention.

**[0059]** A combination of the figures 1 to 4 delivers a preferred embodiment of the entire method of the invention.

**[0060]** Figure 1 shows a preferred embodiment of steps a) and b) of the method of the invention wherein a magnesium alloy 10 is provided as a melt 10' and a strip 10" is formed in a twin roll casting process.

**[0061]** The magnesium alloy 10 consists of 0,06 wt% Zr, 0,6 wt% Ca and 0,7 wt% Zn, unavoidable impurities and the balance being Mg. The magnesium alloy 10 does not comprise any rare earth elements or Sr in this embodiment. The content of unavoidable impurities is controlled to be less than 50 ppm regarding each type of impurity. This is the case for all process steps described in the figures 1 to 4. The molten magnesium alloy 10' is directly injected between an upper roll 12 and a lower roll 14 of a twin roll casting tool 16. A temperature of the molten magnesium alloy 10' is controlled to measure 710°C. A peripheral speed 18 of the rolls 12, 14 is controlled to measure 2 m/min. Passing the rolls 12, 14 the molten magnesium alloy 10' solidifies and forms a strip 10". A thickness 20 of the strip 10" measures 4 mm. A width 22 of the strip 10" measures 1500 mm. Detail B of figure 1 illustrates a micrograph of a section the strip 10".

It can be gained from the micrograph (microstructure) that the magnesium alloy 10 in form of the strip 10" shows a homogeneous grain structure regarding the grain size and grain shape. An important aspect is that no segregation in the center line or below the surface areas of the strip 10" can be seen. This is a result of the magnesium alloy 10 in combination with the process of twin roll casting.

**[0062]** Figure 2 shows a preferred embodiment of step b') of the method of the invention wherein an initial heat treatment b') is performed on the strip 10". The step b') is performed subsequent to the steps a) and b). As the steps a), b) and b') refer to the same method of the invention the same reference signs are use. These are valid for both figures 1 and 2.

**[0063]** During the initial heat treatment of step b') thermal energy Q is introduced to the strip 10" that was formed in figure 1. This leads to an increasing temperature of the entire strip 10". The temperature of the strip 10" is elevated to a desired level. The initial heat treatment of step b') is then performed at a constant temperature of the strip 10" of 450 °C for a duration of 960 min. The initial heat treatment of step b') is a homogenization process in this embodiment. Detail A of figure 2 illustrates a micrograph (microstructure) of a section the strip 10" after the initial heat treatment of step b'). The strip has a highly homogeneous grain structure with grain size of about 40 µm.

**[0064]** Figure 3 shows a preferred embodiment of steps c) and c') of the method of the invention wherein a warm rolling process c) followed by a cold rolling process c') is performed on the strip 10". The steps c) and c') are performed subsequent to the steps a), b) and b'). As the steps a), b), b'), c) and c') refer to the same method of the invention the same reference signs are use. These are valid for all figures 1 to 3. As generally in view of this patent application, the technical means illustrated in Figure 3 represent only one example that allows for realizing the method of the invention. Regarding warm rolling and cold rolling, a person skilled in the art is well aware of alternative technical equipment for this purpose. For example it is possible to vary the number of roll pairs and also the feeding direction of the roll pairs.

**[0065]** The strip 10", after the initial heat treatment b') from figure 2, is introduced to a warm rolling process of step c). The thickness 20 of the strip 10" is reduced in one or more rolling passes. Here, just as an example, seven rolling passes I to VII are performed in the warm rolling process of step c). Before each rolling pass I to VII, which means also in-between different rolling passes, thermal energy Q is introduced to the strip 10". In this embodiment the thickness 20 of the strip 10" from figure 2 measures 4 mm. In each rolling pass I to VII the rolling degree  $\varphi_n$  is set in a range from 0.1 to 0.2 so that a thickness 20 of the strip 10" reaches 1.57 mm after rolling pass VII. The temperature of the strip 10" is kept at 370 °C throughout the entire warm rolling process of step c). This requires the preheating and annealing before each

rolling pass I to VII. This reduces the edge cracking. After the warm rolling process of step c) the strip 10" is cold-rolled according to step c'). In this preferred example two passes VIII, IX of the cold rolling process of step c') are performed at a rolling degree  $\varphi_n$  of 0.2. This cold rolling process of step c') is performed at ambient temperature. In the rolling passes VIII, IX of the cold rolling process of step c') the thickness 20 of the strip 10" is reduced to its final value of about 1.0 mm. This cold rolling process of step c') introduces a high amount of deformation energy to the strip 10".

**[0066]** The lower part of figure 3 illustrates the degree of edge cracking achieved in test runs of the warm rolling process of step c). The lower part of figure 3 shows three test strips a, b, c of different magnesium alloys tested.

**[0067]** The magnesium alloy of test strip c is not specified according to the method of the invention but test strip c was manufactured analogically to the steps a) to c) of the method of the invention described in figures 1 to 4. The magnesium alloy 10 of test strip b is composed according to the preferred embodiment of the method of the invention and test strip b was manufactured as described in figures 1 to 4. It is therefore corresponding to the strip 10".

**[0068]** The test strip c consists of a magnesium alloy composed according to the state of the art and comprises a high Zn content. In other words, regarding test strip c the quantities of the alloying elements added to the magnesium matrix are settled outside the range specified by the method of the invention. Test strip c contains little quantity of Zr. Test strip a consists of a magnesium alloy according to the method of the invention comprising a low Zn content and is free of Zr. In comparison to test strip c, test strip a comprises an observably reduced degree of edge cracking.

**[0069]** Test strip b was manufactured according to the preferred embodiment of the method of the invention described in figures 1 to 4. Accordingly it comprises a low Zn content and small quantity of Zr, each within the range specified by the method of the invention.

**[0070]** It can be observed that the magnesium alloy 10 with the low Zn content in combination with the low Zr content fabricated according to the method of the invention leads to significantly improved resistance towards edge cracking of test strip b which means the strip 10" and also to better rollability. This is a result of the absence of the ternary MgZnCa-phase and of enhanced homogeneity of the test strip b/strip 10".

**[0071]** The effects on the test strips a, b, c illustrated in the photo in the lower part of figure 3 are observable after the warm rolling process of step c), as well as after the cold rolling process of step c') of the method of the invention.

**[0072]** Figure 4 shows a rolling schedule of the preferred embodiment of steps c) and c') of the method of the invention analogically to Figure 3 and referring to the same embodiment. So the same reference signs are used. These are valid for all figures 1 to 4. Here, a se-

quence S of the rolling passes I to IX is illustrated along with the respective rolling temperature T and the respective rolling degree  $\varphi_n$  of each rolling pass I to IX. Between rolling pass III and rolling pass VII it is indicated that there may be more or less than seven rolling passes in other embodiments of the method of the invention. Between rolling pass VII and VIII, air cooling 30 is performed on the strip 10" in this embodiment to cool it down to ambient temperature for the cold rolling process of step c').

**[0073]** Figure 5 shows a preferred embodiment of step d) of the method of the invention wherein a subsequent heat treatment is performed on the strip 10". Step d) is performed subsequent to the steps a), b) and b'), c) and c') and refers to the same method of the invention. So the same reference signs are used. These are valid for all figures 1 to 5.

**[0074]** The subsequent heat treatment of step d) is performed on the strip 10" from figure 3 respectively 4 after the cold rolling process of step c'). This is illustrated in figure 5a. This subsequent heat treatment is performed at a temperature of 370 °C and for a duration of 1 min. The high amount of deformation energy stored in the strip 10" of figures 3, 4 after step c') leads to a high recrystallization rate and a weak texture of the strip 10" in the subsequent heat treatment of step d). The short duration of 1 min leads to a small average grain size.

**[0075]** Figure 5b shows a (0002) pole figure of the strip 10" before the subsequent heat treatment of step d). (0002) pole figures are well known in the art. The (0002) pole figure shown in Figure 5b was measured by X-ray diffraction technique at certain crystallographic planes, which are (10.0) / (00.2) / (10.1) / (10.2) / (11.0) / (10.3). Using the measured pole figures, the degree of the preferred grain orientation was calculated such that the recalculated (0002) pole figures could describe quantitatively the texture intensity by multiple random degree. The intensity values in the pole figure represent the degree of orientation of the grains of the texture of the strip 10". With regard the given scale, dark areas corresponding to higher values on the scale represent a higher degree of orientation and brighter areas corresponding to lower values on the scale represent a lower degree of orientation. It can be seen that the magnesium alloy 10 of the strip 10" has a high degree of preferred orientation, respectively a strong texture, after the cold rolling process of step c') which is a result of the deformation of the strip 10". The maximum texture intensity is found at the position corresponding to the tilted (0002) basal planes 24, 26, approximately 15° tilting from the strip 10" normal direction ND to the rolling direction RD.

**[0076]** Fig. 5c shows the (0002) pole figure of the strip 10" after the subsequent heat treatment of step d). It can be seen that the magnesium alloy 10 of the strip 10" now has a low texture intensity which is a result of the recrystallization in step d). This can primarily be observed in the tilted (0002) basal planes 24, 26. As a result the strip 10" which is now the final sheet metal product 28 has a randomised texture and excellent low-temperature form-

ability.

**[0077]** Figure 5d shows a graph of the microstructure of the sheet metal product 28 at two different orders of magnitude. A highly homogeneous microstructure is developed across the whole thickness 20 of the sheet metal product 28. It can be gained from figure 5d that the produced sheet metal product 28 in this embodiment has a highly homogenous microstructure and a very small average grain size below 4  $\mu\text{m}$ .

**[0078]** A wide range of the mechanical properties is achieved in the sheet metal product 28 produced in this embodiment of the method of the invention as follows: yield strength in a range from  $R_{p0,2} = 130 \text{ MPa}$  to 260 MPa, ultimate strength in a range from  $R_m = 210 \text{ MPa}$  to 300 MPa while low-temperature formability measures 7 on the Erichsen index IE throughout.

**[0079]** Figure 6 shows an overview of achievable mechanical properties of a sheet metal product 28 obtainable by the method of the invention in a preferred embodiment. Figure 6a illustrates results of testings of the yield strength  $R_{p0,2}$  of the sheet metal product 28 of the invention ranging here from 130 MPa to 260 MPa and generally from 125 MPa to 275 MPa while a strain A ranges from 5 % to 40 % of a fracture strain  $A_{\text{max}}$ .

**[0080]** Figure 6c shows a qualitative stress-strain-curve known in the art just in order to clarify the meaning of the used material specific values regarding mechanical properties.

**[0081]** Figure 6b illustrates results of testings of the ultimate strength  $R_m$  of the sheet metal product 28 of the invention ranging here from 210 MPa to 300 MPa and generally from 200 MPa to 325 MPa while a strain A ranges from 5 % to 40 % of a fracture strain  $A_{\text{max}}$ .

**[0082]** Figure 6d illustrates that a low-temperature formability has values of at least 6 on the Erichsen index throughout the entire spectrum of achievable ultimate tensile strength  $R_m$ .

**[0083]** Referring back to detail A of figure 5a, major planar directions are illustrated: there is a rolling direction RD, a transverse direction TD which is  $90^\circ$  to the rolling direction RD and there is a normal direction ND which is  $90^\circ$  to each, TD and RD. Further there is a direction that is  $45^\circ$  between RD and TD of the sheet metal product 28 can be defined. Here, the ultimate tensile strength  $R_m$  does not vary by more than 10 % in all planar directions TD, RD, ND tested.

## Reference signs

**[0084]**

10	magnesium alloy
10'	melt (molten magnesium alloy 10)
10"	strip
12	upper roll
14	lower roll
16	twin roll casting tool
18	peripheral speed

20	thickness
22	width
24	tilted (0002) basal plane
26	tilted (0002) basal plane
5 28	sheet metal product
30	air cooling
I	rolling pass
II	rolling pass
III	rolling pass
10 IV	rolling pass
V	rolling pass
VI	rolling pass
VII	rolling pass
VIII	rolling pass
15 IX	rolling pass
a	test strip
b	test strip
c	test strip
n	number of rolling pass
20 A	strain
$A_{\text{max}}$	fracture strain
IE	Erichsen index
$R_m$	ultimate strength
$R_{p0,2}$	yield strength
25 ND	normal direction
RD	rolling direction
TD	tilted direction
S	sequence
T	rolling temperature
30 Q	thermal energy
$\varphi_n$	rolling degree in $n^{\text{th}}$ rolling pass

## Claims

- 35 1. Method of manufacturing a sheet metal product (28) including the steps of:
  - 40 a) providing a molten magnesium alloy (10, 10') consisting of
    - 0.4 wt% to 2 wt% Zn,
    - 0.4 wt% to 1 wt% Ca,
    - 0.0 wt% to 0.3 wt% Zr,
    - 0.0 wt% to 1.0 wt% rare earth elements and/or Sr,
    - unavoidable impurities, and
    - the balance being Mg
  - 45 b) forming a strip (10, 10") in a twin roll casting process,
  - c) performing a warm rolling process on the strip (10, 10") and
  - d) performing a subsequent heat treatment on the strip (10, 10") at  $300^\circ\text{C}$  to  $450^\circ\text{C}$  for 0,5 min to 60 min.
- 50 55 2. Method according to claim 1, wherein subsequent



- to the twin roll casting process of step b) an initial heat treatment b'') is performed on the strip (10, 10").
3. Method according to claim 2, wherein the initial heat treatment of step b'') is performed at 400 °C to 500 °C for 30 min to 1440 min. 5
  4. Method according to one of the preceding claims, wherein the warm rolling process of step c) is performed at 200 °C to 450 °C. 10
  5. Method according to one of the preceding claims, wherein the strip (10, 10") formed in the twin roll casting process of step b) and prior to step c) measures 1 mm to 5 mm in thickness (20) and 100 mm to 2000 mm in width (22). 15
  6. Method according to one of the preceding claims, wherein a temperature of the molten Magnesium alloy (10, 10') is controlled to be 680 °C to 750 °C and a peripheral speed (18) of rolls (12, 14) used in the twin roll casting process of step b) is controlled to be 0.7 m/min to 3.5 m/min. 20
  7. Method according to one of the preceding claims, wherein subsequent to the warm rolling process of step c) a cold rolling process c') is carried out on the strip (10, 10"). 25
  8. Method according to claim 7, wherein the cold rolling process of step c') is performed at a temperature below 150 °C. 30
  9. Method according to one of the preceding claims, wherein a thickness (20) of the strip (10, 10") is reduced by a rolling degree ( $\phi_n$ ) of 0.05 to 0.3 in the warm rolling process of step c) and/or a cold rolling process c') carried out on the strip (10, 10") subsequent to the warm rolling process of step c). 35
  10. Method according to one of the preceding claims, wherein the sheet metal product (28) measures 0.2 mm to 3.5 mm in thickness (20). 40
  11. Method according to one of the preceding claims, wherein a content of each unavoidable impurity is less than 50 ppm each in all process steps. 45
  12. Sheet metal product (28), obtained or obtainable by a method of one of the claims 1 to 11. 50
  13. Sheet metal product according to claim 12, with an ultimate strength ( $R_m$ ) in the range from 200 MPa to 325 MPa and/or a yield strength ( $R_{p0.2}$ ) in the range from 125 MPa to 275 MPa while a low-temperature formability measures at least 6 on the Erichsen index (IE). 55
  14. Sheet metal product according to claim 12 or 13, comprising a grain size in a range from 3  $\mu\text{m}$  to 30  $\mu\text{m}$ .
  15. Sheet metal product according to one of the claims 12 to 14, with at least one mechanical property that does not vary by more than 30 % in all planar directions (RD, TD, ND) of the sheet metal product (28).

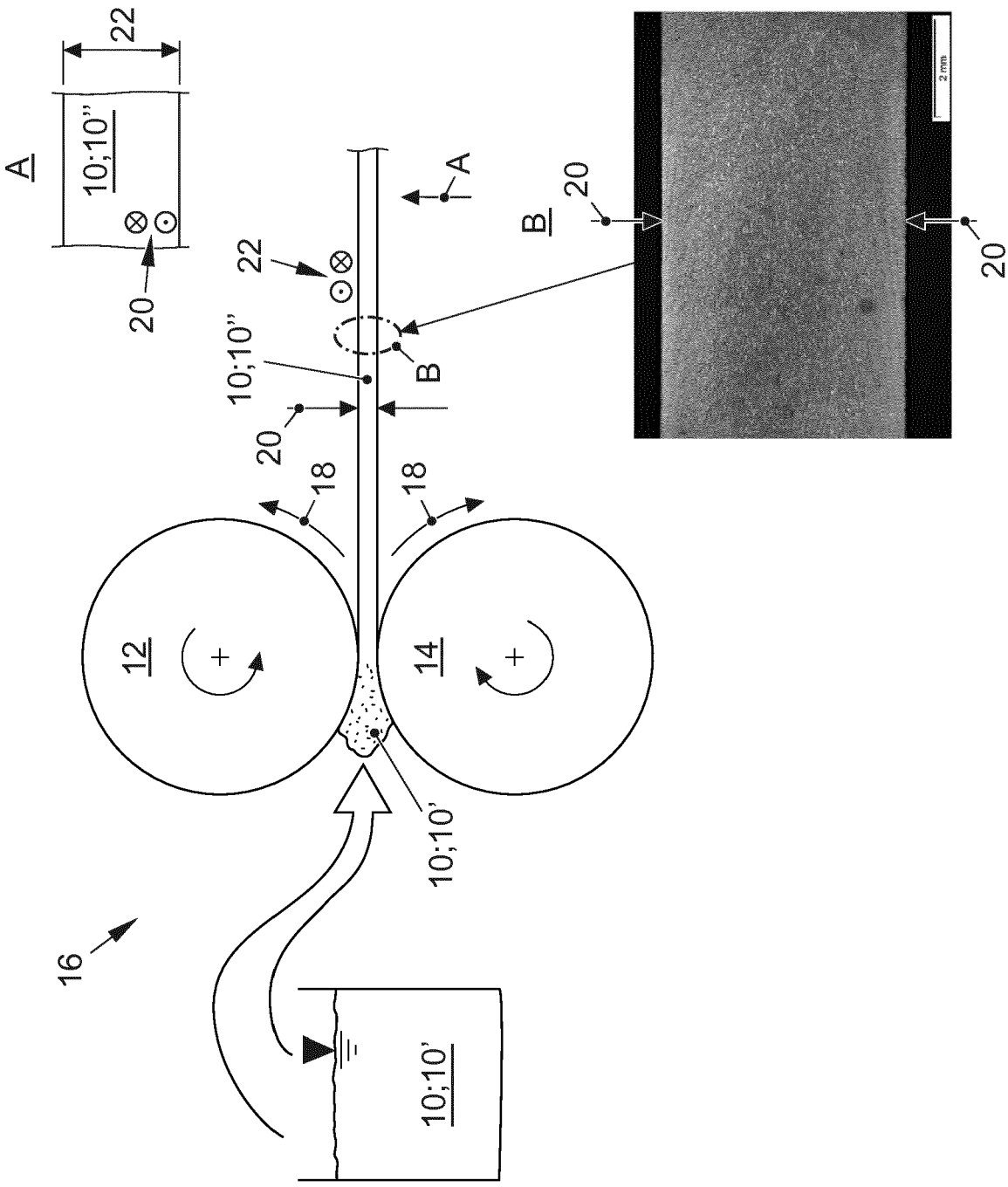


FIG. 1

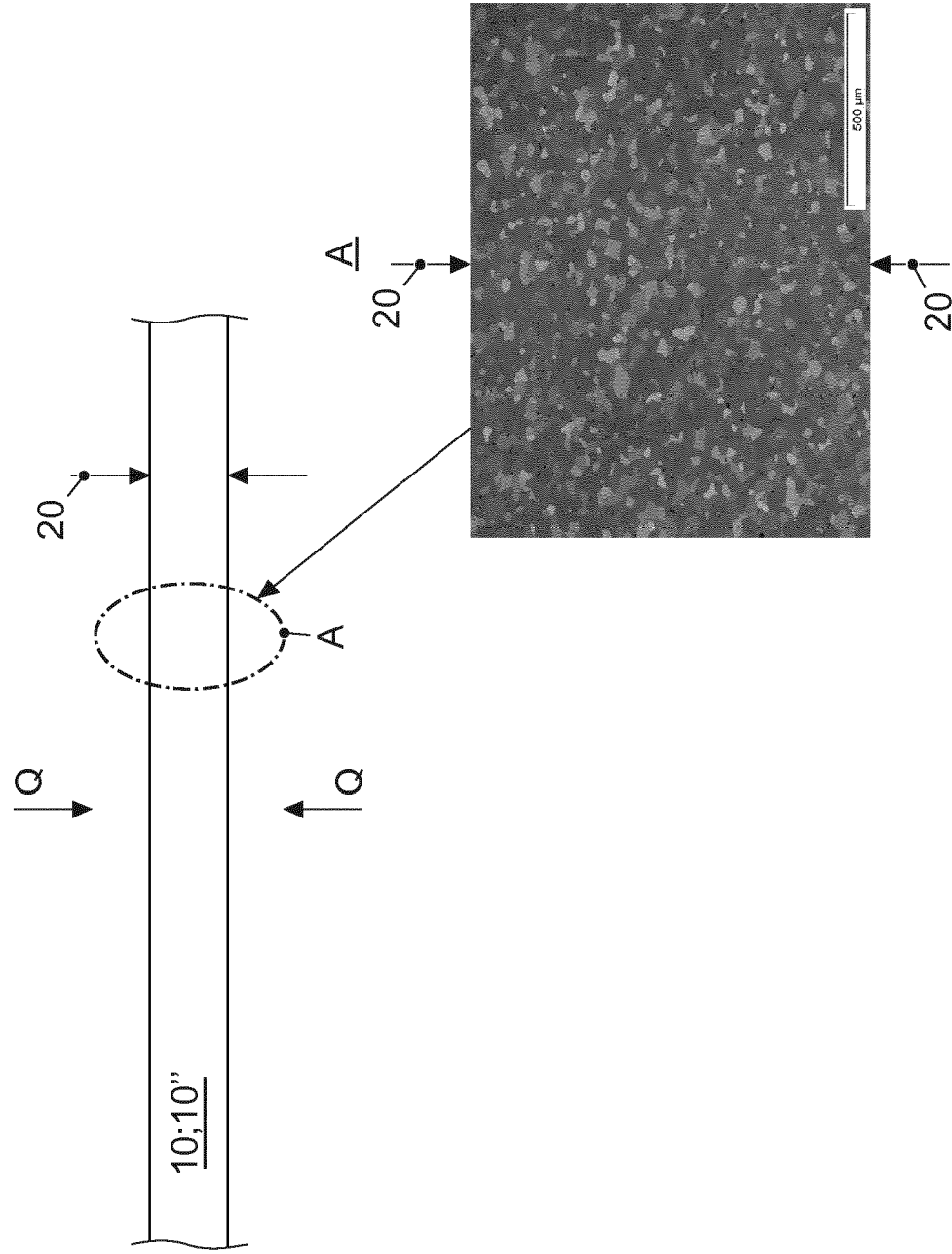


FIG. 2

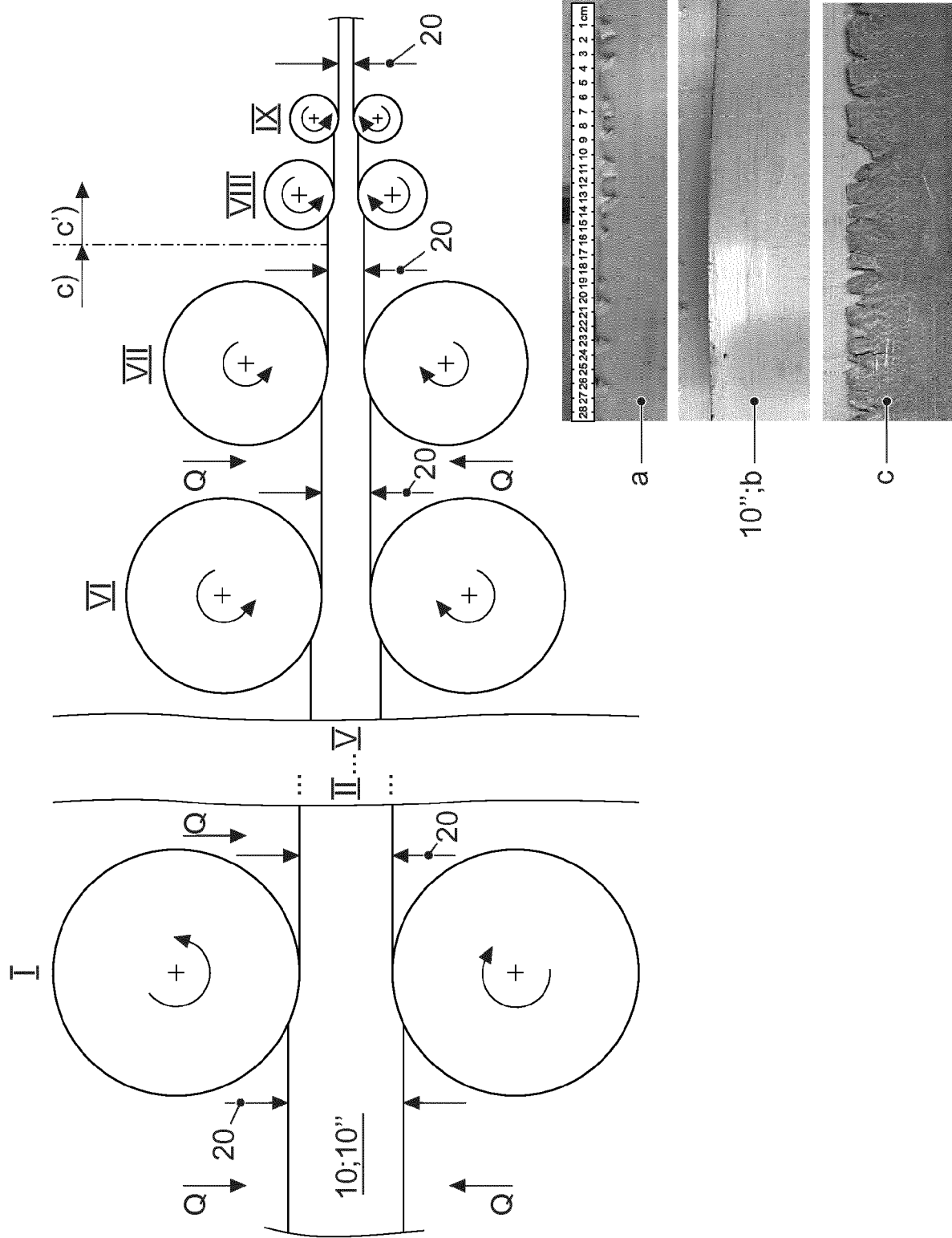


FIG. 3

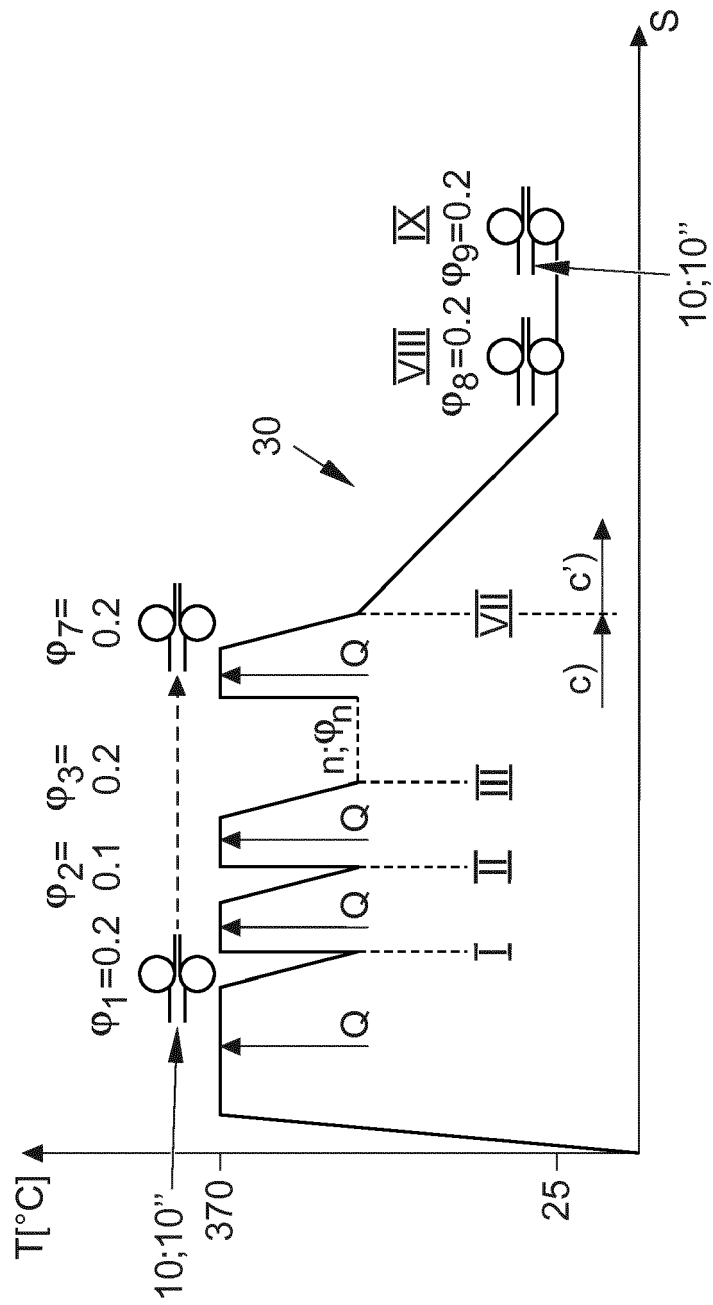


FIG. 4

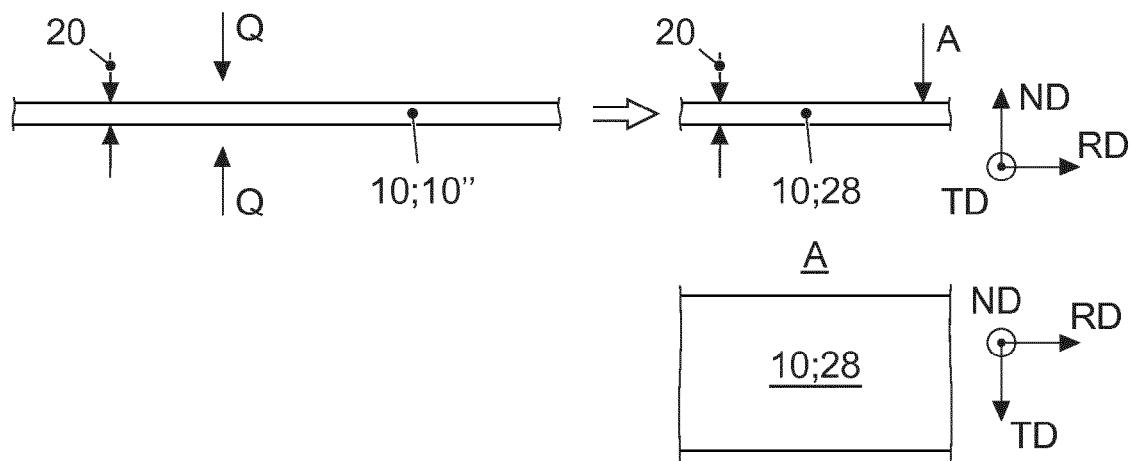


FIG. 5a

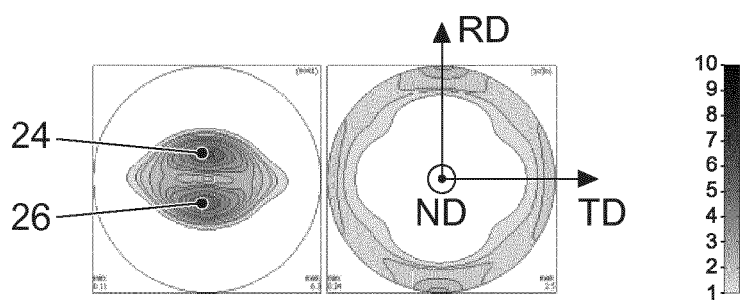


FIG. 5b

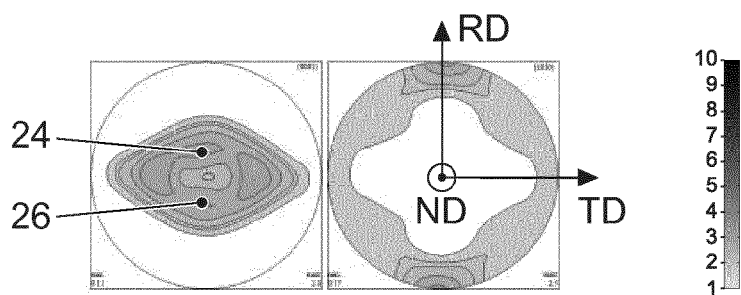


FIG. 5c

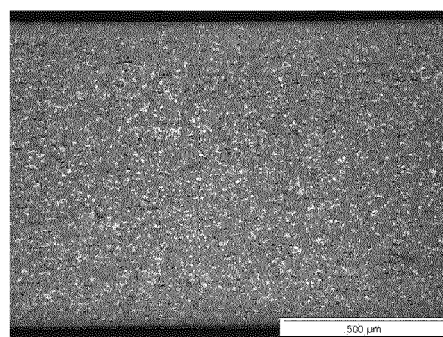
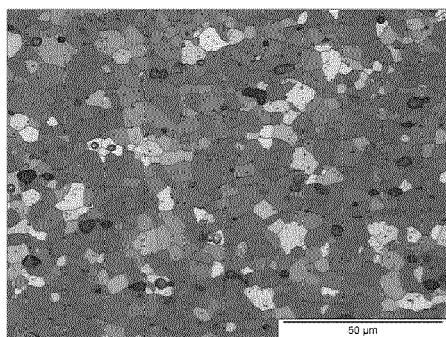


FIG. 5d

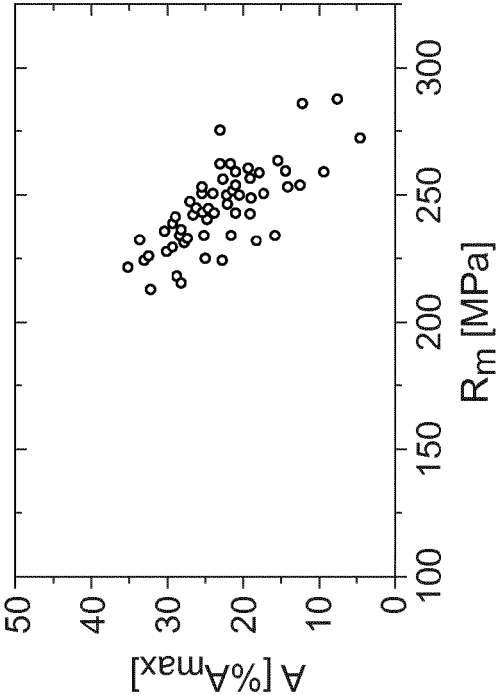


FIG. 6b

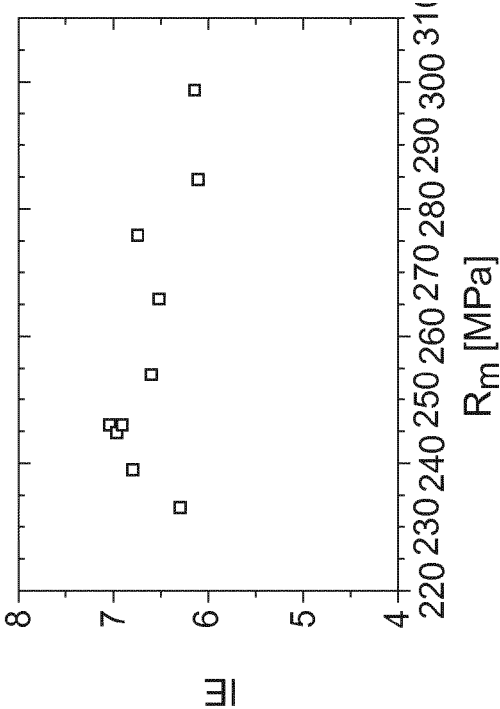


FIG. 6d

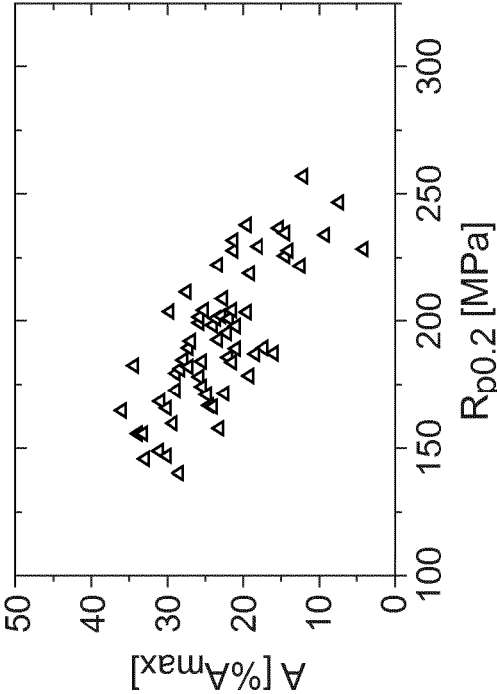


FIG. 6a

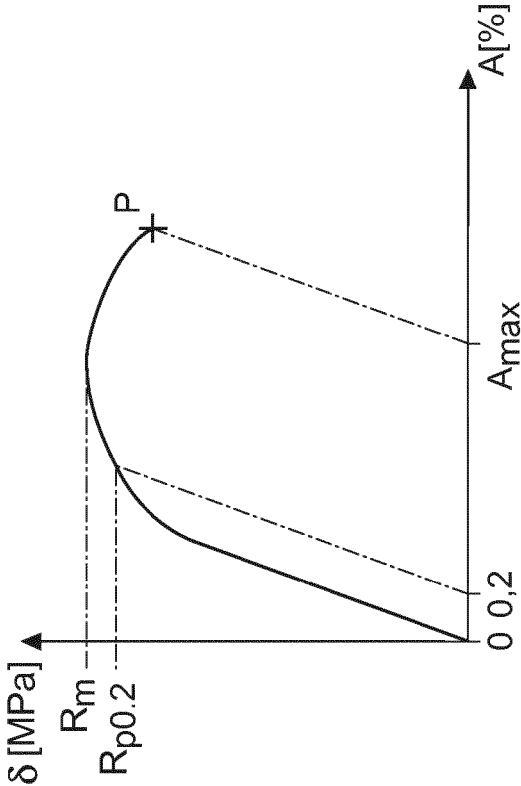


FIG. 6c



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			C22C C22F
The present search report has been drawn up for all claims			
Place of search <b>Munich</b>		Date of completion of the search <b>25 July 2016</b>	Examiner <b>González Junquera, J</b>
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