(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 3 187 615 A1

(12) EUROPEAN PATENT APPLICATION

(43) Date of publication:
05.07.2017 Bulletin 2017/27

(51) Int Cl.:
C22F 1/16 (2006.01) *C22C 18/00* (2006.01)

(21) Application number: **15460142.1**

(22) Date of filing: **31.12.2015**

(84) Designated Contracting States:
AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR
Designated Extension States:
BA ME
Designated Validation States:
MA MD

(71) Applicant: **ZM Silesia S.A.**
40-155 Katowice (PL)

(72) Inventors:
- **Napióra, Tomasz**
40-872 Katowice (PL)
- **Pawlicha, Stanislaw**
40-139 Katowice (PL)
- **Knych, Tadeusz**
30-399 Kraków (PL)
- **Mamala, Andrzej**
30-650 Kraków (PL)
- **Osuch, Piotr**
32-087 Zielonki (PL)
- **Walkowicz, Monika**
25-150 Kielce (PL)

(74) Representative: **Bogacki, Grzegorz**
Kancelaria Patentowa "PATENTINVENT",
Ul. Andrzeja 10/1/4
40-061 Katowice (PL)

(54) FABRICATION METHOD OF FLAT-ROLLED PRODUCTS MADE OF ZINC-BASE ALLOYS INTENDED FOR USE IN BUILDING ENGINEERING

(57) A fabrication method of flat-rolled products intended for use in building engineering, made of Zn-Cu-Ti alloy with a chemical composition in accordance with the EN-988 standard, composed of at least two basic steps - continuous casting process of metal strip and not integrated rolling process of finished product in form of sheets, is characterized after casting step of metal strip with a thickness from 4 mm to 16 mm and width from 500 mm to 2000 m the strip is submitted to process of heat treatment in soaking-pit at a temperature of 250 °C to 350 °C for a time of 10 minutes to 48 hours, then is subject to cooling down to ambient temperature, whereafter is heated up to a temperature ranging from 160 °C to 200 °C before starting the rolling operation and is being rolled in at least three roll passes until the finished product is obtained.

In the course of rolling process the Zn-Cu-Ti alloy undergoes dynamic recrystallization at initial rolling temperature ranging from 160 °C to 200 °C, through coagulation of the zinc-titanium particles in Zn-Cu-Ti alloy microstructure achieved on the way of heat treatment.

The reduction ratios in individual roll passes of the rolling process are less than 35 %.

A finished product is susceptible to bending at a temperature > +5 °C.

Zn-Cu-Ti alloy contains from 0,08 wt. % to 0,24 wt. % Cu, from 0,06 wt. % to 0,12 wt. % Ti, not more than 0,015 wt. % Al and rest Zn and also tramp elements Cd, Fe, Pb and Sn.

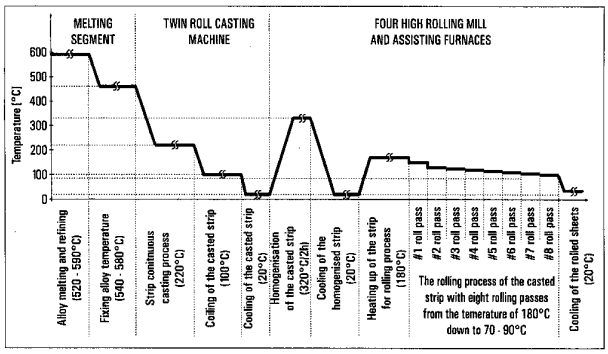

Fig. 6.

EP 3 187 615 A1

Description

[0001] Zn-Cu-Ti alloy sheet metal products designed for the building industry are manufactured in accordance with the EN-988 standard. The finished product has to fulfill several requirements regarding the usable and operational properties. One of the critical requirements is the sheet metal plasticity, also at temperature below 10°C. This fact is conditioned by the way of fitting of the roofing panels on the roof according to the standing seam technique, which requires that the sheet metal be bendable (including bending out) lengthwise in the rolling direction in order to make the joint of individual roofing panels during assembly of metal roof. Furthermore, it is required that the metal panel gives no evidence of cracks and fractures at the bending edge. An additional requirement, which is particularly difficult to be fulfilled in case of Zn-Cu-Ti alloy sheets, is securing the above mentioned technological properties of the sheet metal at outdoor temperatures below 10°C. This requirement is conditioned by the typical outdoor temperatures at the beginning and termination of the building season.

[0002] A number of manufacturing methods of Zn-Cu-Ti alloy sheet metal products has been worked out with particular regard to the desired bendability of the finished product, since the usable properties of 2n-Cu-Ti alloy sheet metal, especially the mechanical properties, therein bendability (including bending out), are formed mainly in the course of the rolling process. It is widely known that the technological parameters of the rolling process, such as the rolling temperature or plastic deformation speed, the last one understood as both the rolling speed and number of roll passes during rolling process with the reduction ratios resulting of the mill feedstock and finished product geometry, impart the mechanical properties of metallic materials in wide range of their variability, typical for a given alloy.

[0003] In case of the Zn-Cu-Ti alloys intended for fabrication of the flat-rolled products for the building industry, the patent specification Number GB1191994A discloses a sheet metal manufacture method, wherein the usable properties of Zn-Cu-Ti alloy sheets with the content of the main alloying components in form of Cu (from 0,05 to 2 wt.%), Ti (0,005 wt. % to 0,4 wt. %) and tramp elements such as: Ag, Cd, Fe, In, Pb, Sn are being shaped in the course of rolling process, where the mill feedstock temperature ranging from 230°C to 270°C and the reduction ratio in the first roll pass amounting to 80 % - 95 % were shown to be the most critical technological parameters being a requisite of the desired usable properties of the finished product with given chemical composition.

[0004] Similarly, the U.S. patent specification Number 4051887 discloses a production method of Zn-Cu-Ti alloy sheets with the content of main alloying components in form of Cu (from 1,5 wt. % to 5,5 wt. %), Ti (0,05 wt. % to 0,25 wt. %) and the remainder being Zn, wherein the strip casting process accomplished in continuous way is integrated with the rolling process in such a manner that crystallized strip with a width from 500 mm to 1500 mm and thickness from 6 mm to 24 mm and temperature amounting to 360°C leaving the casting machine undergoes directly the rolling operation in five roll stands positioned one after the other. Each roll stand reduces the thickness of the metal strip by 50, at temperature of plastic deformation amounting to 270°C before the first roll pass what ensures the desired usable properties of the finished product.

[0005] In case of both above mentioned production methods of Zn-Cu-Ti alloy sheets the usable properties of the latter are shaped through dynamic recrystallization of alloy in the course of rolling process, which is a result of relatively high plastic deformation temperature and high values of the reduction ratios.

[0006] Similarly, the Polish patent specification Number PL195433 discloses a production technique of Zn-Cu-Ti alloy sheets designed for use in building engineering though a process consisting of casting operation of Zn-Cu-Tl alloy strip with chemical composition in compliance with EN-988 standard according to the Twin Roll Casting (TRC) method and dis-integrated rolling process being characterized by reheating the strip before rolling operation up to the temperature of 190 °C and following rolling during 11 roll passes with a predetermined value of individual reduction ratios, as shown schematically in FIG. 1. However, this process does not provide fully recrystallized microstructure, and thereby the product obtained in this way does not fulfil the highest expectations regarding the plasticity of sheet metal, especially in temperatures below 10°C.

[0007] From Polish patent specification Number PL195253 it is also known a similar production technique of Zn-Cu-Ti alloy sheets (cf. FIG. 2), which differs from the above mentioned method in reduced to 9 number of roll passes and supplementary heat treatment of the finished product, i.e. sheet metal after rolling process, aiming at recrystallization annealing assumed to improve the usable properties of sheets, and in particular to enable repeated bending and bending out without cracks or fractures, which is not the case in the method coming from patent specification Number PL PL195433.

[0008] The bendability (including bending out ability) of Zn-Cu-Ti alloy sheets is strictly connected with the fraction of recrystallization of metal microstructure in dynamic conditions of the rolling process, which is the case in the techniques disclosed in patent descriptions Number GB1191994A and US4051887 or recrystallization of the finished product in form of sheets in static conditions, which is the case according to the Patent Number PL195253. It is proposed hereby a quite different method of inducing the dynamic recrystallization in the course of rolling process in order to solve the issue of limited plasticity of the sheets fabricated in rolling process from the strips coming mainly from continuous casting operations.

[0009] A restoration of microstructure through recrys-

tallization, particularly in dynamic conditions, consists in two basic steps: nucleation and growth of new grains within the alloy microstructure deformed by the plastic strain. The privileged nucleation sites of the new alloy grains are considered to be the boundaries of original grains, the particles of another phase and also the lattice defects formed in consequence of strain. Since the newly formed grains have lower inner energy than the strained zones, there is a propelling force aiming at growth of the recrystallization nuclei and consumption of neighbouring strained zones. The relocation speed of boundaries of the newly formed grains is a diffusive factor depending strictly on temperature in such a way that the higher is the system temperature the bigger is the propelling force and relocation speed of grain boundaries. The essential factor limiting relocation of the grain boundaries within the material microstructure are the atoms of alloying and tramp elements located in the metallic matrix.

[0010] In case of Zn-Cu-Ti alloys the hitherto known sheet metal production techniques, wherein the usable sheet product properties are obtained owing to the recrystallization taking place in dynamic conditions of the rolling process, we can use a possibility that a moving grain boundary passes through the atoms of alloying components and tramp elements thanks to creation of adequately high temperature in the system, which promotes the displacement of grain boundaries on the way of diffusion mechanisms.

[0011] According to the newly proposed sheet metal fabrication technique the dynamic recrystallization is enabled through removal of obstacles impeding the movement of grain boundaries, i.e. atoms of alloying and tramp elements, without *delivering* additional energy to the system in order to obtain higher temperature of plastic deformation, which is the case in hitherto known sheet metal production methods with utilization of the dynamic recrystallization effect.

[0012] Aiming at accomplishment the above mentioned concept it is necessary to carry out a suitable heat treatment of the strip cast from Zn-Cu-Ti alloy before sheet metal rolling process in order to dear the metallic matrix of alloying and tramp elements randomly scattered in the crystal lattice. The heat treatment process is done in a soaking pit enabling a uniform heating up of metal strip, which in rolling mill conditions is usually wound in a coil weighing a few tons.

[0013] A significance of the invention consists in the following procedure: after continuous casting operation a strip of metal having a thickness from 4 mm to 16 mm and a width from 500 mm to 2000 mm undergoes the heat treatment process in a soaking pit at temperatures from 250 °C to 350 °C during a time from 10 minutes to 48 hours, then the strip is subject to cooling down to ambient temperature, and subsequently undergoes a heating up operation to temperature ranging from 160°C to 200°C before beginning of the rolling process and rolled successively in at least three roll passes until the finished product is obtained. During rolling of Zn-Cu-Ti alloy the strip is subject to dynamic recrystallization at initial rolling temperature in the range of 160°C - 200°C through coagulation of zinc-titanium particles in alloy microstructure achieved by heat treatment. The reduction ratios obtained in particular roll passes of the rolling process are less than 35 %. The finished product is subject to bending at temperature starting from + 5°C. The Zn-Cu-Ti alloy contains from 0,08 wt. % to 0,24 wt. % Cu, from 0,06 wt. % to 0,12 wt. % Ti, not more than 0,015 wt. % Al and rest Zn and tramp elements such as Cd, Fe, Pb and Sn.

[0014] The final microstructure of metal strip cast from Zn-Cu-Ti alloy is composed in principle of two primary phases - zinc matrix and particles of another phase - $Zn_{15}Ti$ - typical for alloys with chemical composition under consideration, occurring in the strips coming from continuous casting operation in form of small particles with sizes from several hundred nm to several μm dissipated in the whole volume of metal strip and possibly in form of big eutectic particles located mainly in the strip axis with sizes of tens μm order, as shown in FIG. 3.

[0015] A production method being subject of present patent application comprises fabrication of Zn-Cu-Ti alloy strip according to the continuous casting technique and its subsequent heat treatment, which leads to coagulation of particles of another phase occurring in microstructure through atomic diffusion, i.e. random thermally-activated movement of alloying and tramp elements atoms, as shown in FIG. 4. Thereby an effect consisting in clearing the metallic matrix from individual atoms of alloying and tramp elements is obtained. During subsequent technological step, i.e. rolling process, a microstructure of this type enables the occurrence of dynamical recrystallization process at significantly lower temperatures than in case of hitherto known production methods and achievement of fully recrystallized microstructure of the finished product, as shown in FIG. 5.

[0016] The Zn-Cu-Ti alloy with a chemical composition containing 0,15 wt. % Cu; 0,07 wt. % Ti; 0,003 %,. Al and remaining tramp elements such as (among other things) Cd, Fe, Pb, Sn and rest Zn is cast in continuous manner according to the Twin Roll Casting (TRC) technique in form of strip with thickness of 8 mm and width of 1100 mm, which is wound in coils weighing 6 tons. The coil has a temperature amounting to 100°C and is cooling down freely to the ambient temperature. In the next technological step the metal strip is subject to heat treatment operation at temperature 320 °C for 2 hours. The coil dwell time in the soaking-pit comprises additionally the time of heating up of the furnace and coil of Zn-Cu-Ti strip until reaching the set temperature. After soaking the coils are removed from the soaking-pit and cool down at ambient temperature for at least 24 hours. After expiration of this time the coil is placed once again in the soaking-pit in order to heat it up to the rolling temperature amounting to 180°C. When the strip placed in soaking-pit reaches the set temperature across the whole coil section, the coil is conducted to the rolling process, which is accomplished by means of roll stand in four-high re-

versing system.

[0017] The rolling process of metal strip with input thickness of 8 mm is carried out until one of the set thicknesses of finished product defined in EN-988 standard is obtained, in 8 roll passes with reduction ratios amounting to 25 % - 35 %. When the rolling operation is completed the coil has a temperature of 70°C and then cools down in ambient temperature. An example of application of the proposed method in fabrication of Zn-Cu-Ti alloy sheets was illustrated schematically in fig 6.

Claims

1. A fabrication method of flat-rolled products intended for use in building engineering, made of Zn-Cu-Ti alloy with a chemical composition in accordance with the EN-988 standard, composed of at least two basic steps - continuous casting process of metal strip and not integrated rolling process of finished product in form of sheets, wherein after casting step of metal strip with a thickness from 4 mm to 16 mm and width from 500 mm to 2000 m the strip is submitted to process of heat treatment in soaking-pit at a temperature of 250 °C to 350°C for a time of 10 minutes to 48 hours, then is subject to cooling down to ambient temperature, whereafter is heated up to a temperature ranging from 160°C to 200°C before starting the rolling operation and is being rolled in at least three roll passes until the finished product is obtained.

2. The method of claim 1, wherein through rolling the Zn-Cu-Ti alloy undergoes dynamic recrystallization at initial rolling temperature ranging from 160°C to 200°C, through coagulation of the zinc-titanium particles in Zn-Cu-Ti alloy microstructure achieved by heat treatment.

3. The method of claim 1, wherein the reduction ratios in individual roll passes of the rolling process are less than 35 %.

4. The method of claim 1, wherein the finished product is susceptible to bending at a temperature > +5 °C.

5. The method of claim 1, wherein the Zn-Cu-Ti alloy contains from 0,08 wt. % to 0,24 wt. % Cu, from 0,06 wt. % to 0,12 wt. % Ti, not more than 0,015 wt. % Al and rest Zn and also tramp elements Cd, Fe, Pb and Sn.

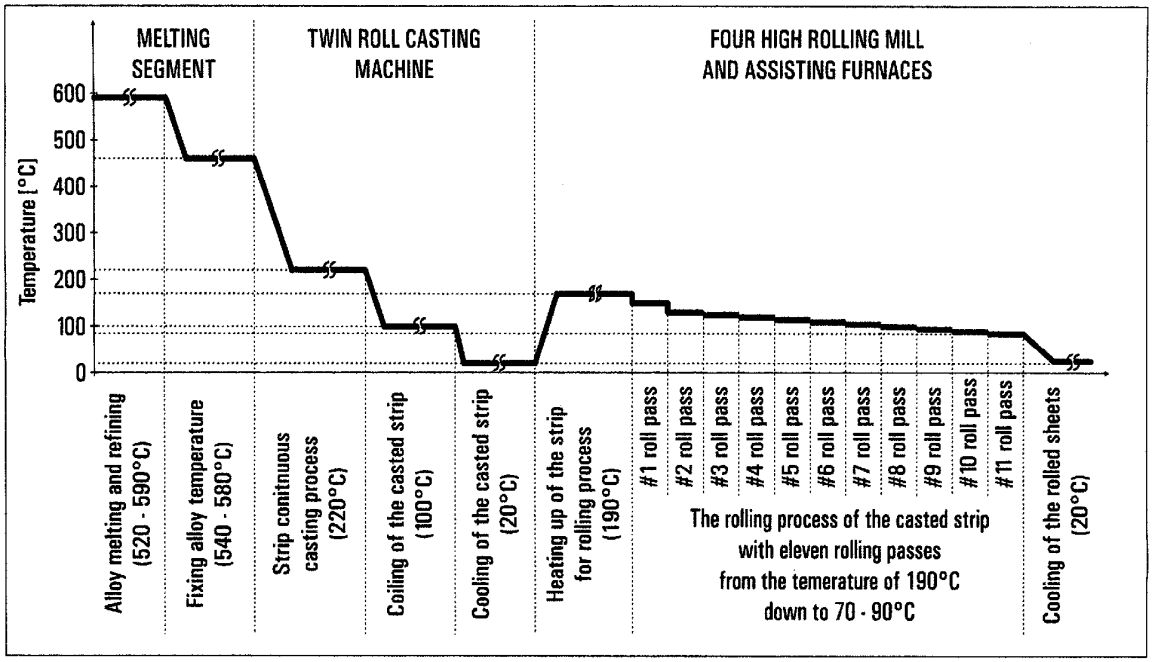
MELTING SEGMENT
TWIN ROLL CASTING MACHINE
FOUR HIGH ROLLING MILL AND ASSISTING FURNACES
Temperature [°C]
600
500
400
300
200
100
0
Alloy melting and refining (520 - 590°C)
Fixing alloy temperature (540 - 580°C)
Strip conitnuous casting process (220°C)
Coiling of the casted strip (100°C)
Cooling of the casted strip (20°C)
Heating up of the strip for rolling process (190°C)
#1 roll pass
#2 roll pass
#3 roll pass
#4 roll pass
#5 roll pass
#6 roll pass
#7 roll pass
#8 roll pass
#9 roll pass
#10 roll pass
#11 roll pass
The rolling process of the casted strip with eleven rolling passes from the temerature of 190°C down to 70 - 90°C
Cooling of the rolled sheets (20°C)

Fig. 1.

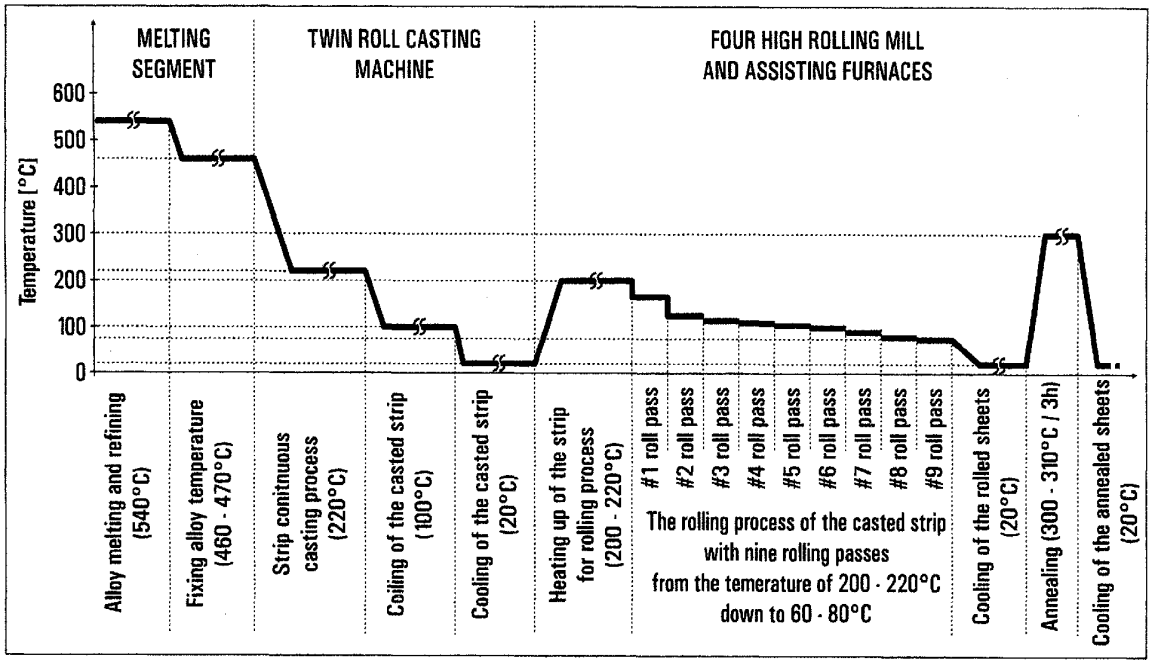
MELTING SEGMENT
TWIN ROLL CASTING MACHINE
FOUR HIGH ROLLING MILL AND ASSISTING FURNACES
Temperature [°C]
600
500
400
300
200
100
0
Alloy melting and refining (540°C)
Fixing alloy temperature (460 - 470°C)
Strip conitnuous casting process (220°C)
Coiling of the casted strip (100°C)
Cooling of the casted strip (20°C)
Heating up of the strip for rolling process (200 - 220°C)
#1 roll pass
#2 roll pass
#3 roll pass
#4 roll pass
#5 roll pass
#6 roll pass
#7 roll pass
#8 roll pass
#9 roll pass
The rolling process of the casted strip with nine rolling passes from the temerature of 200 - 220°C down to 60 - 80°C
Cooling of the rolled sheets (20°C)
Annealing (300 - 310°C / 3h)
Cooling of the annealed sheets (20°C)

Fig. 2.

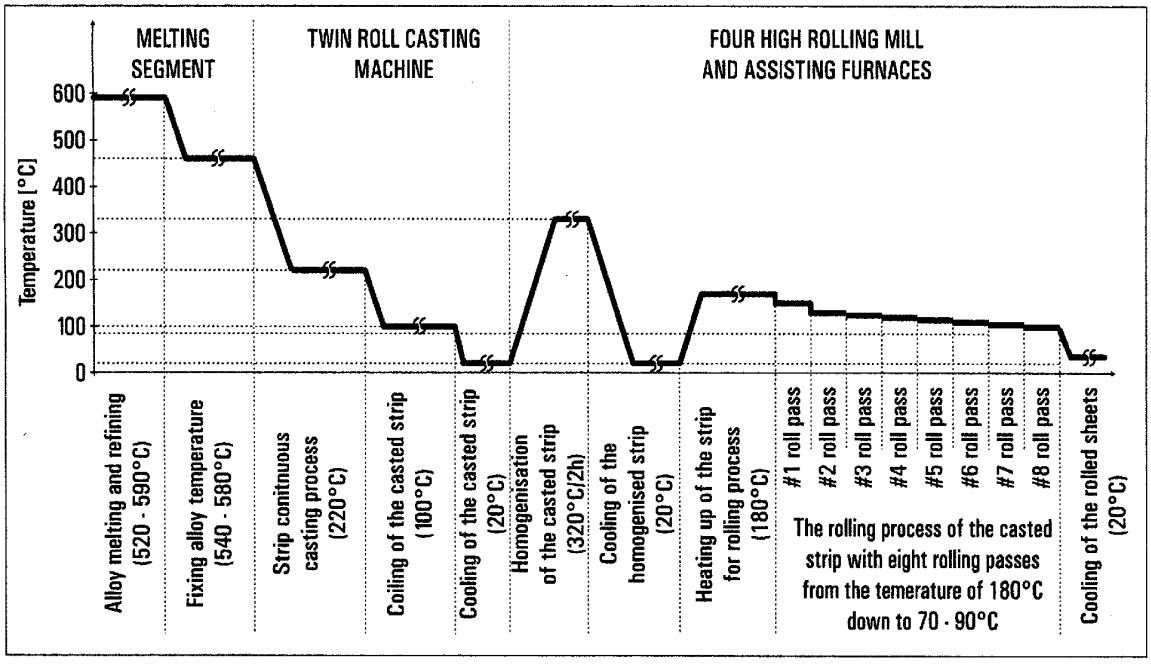
MELTING SEGMENT
TWIN ROLL CASTING MACHINE
FOUR HIGH ROLLING MILL AND ASSISTING FURNACES
Temperature [°C]
600
500
400
300
200
100
0
Alloy melting and refining (520 - 590°C)
Fixing alloy temperature (540 - 580°C)
Strip conitnuous casting process (220°C)
Coiling of the casted strip (100°C)
Cooling of the casted strip (20°C)
Homogenisation of the casted strip (320°C/2h)
Cooling of the homogenised strip (20°C)
Heating up of the strip for rolling process (180°C)
#1 roll pass
#2 roll pass
#3 roll pass
#4 roll pass
#5 roll pass
#6 roll pass
#7 roll pass
#8 roll pass
The rolling process of the casted strip with eight rolling passes from the temerature of 180°C down to 70 - 90°C
Cooling of the rolled sheets (20°C)

Fig. 6.

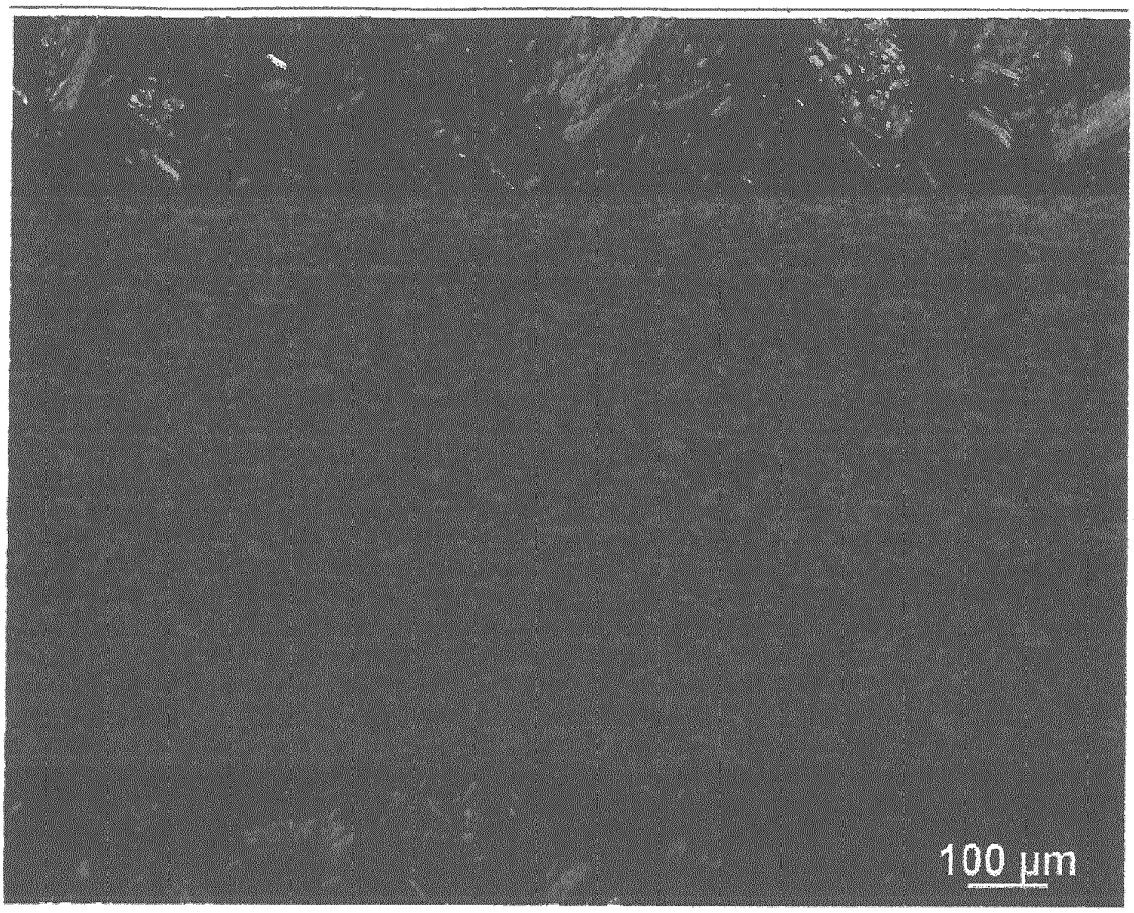

Fig. 5

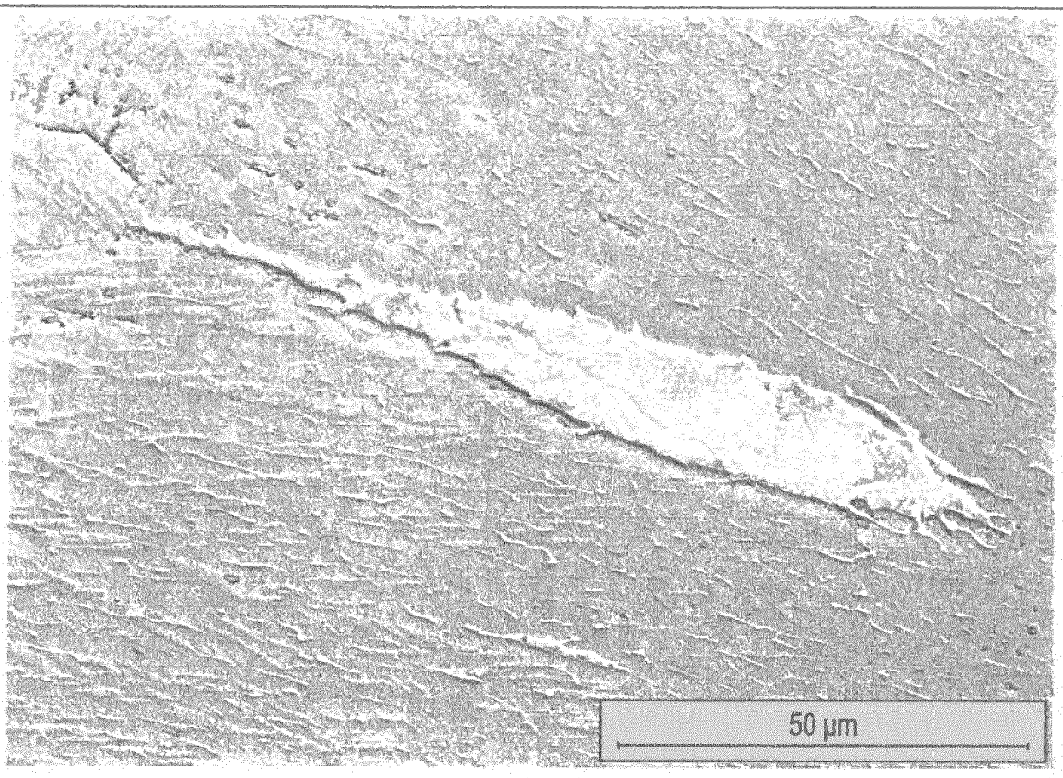

Fig. 3

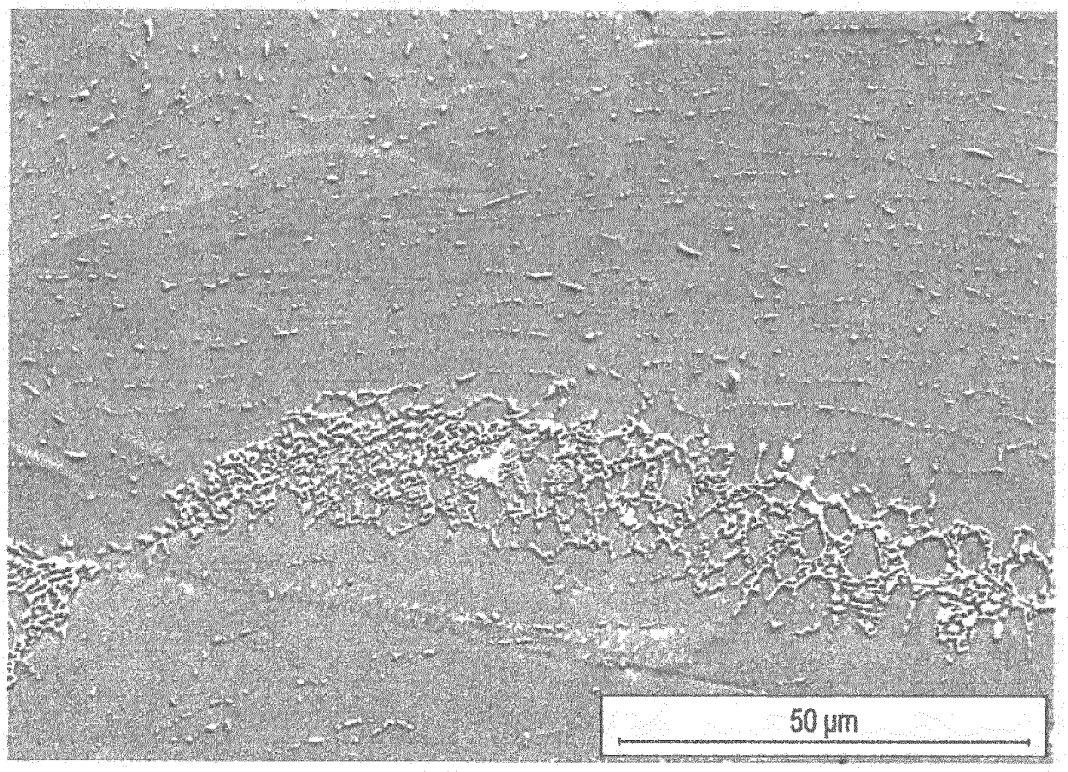

Fig. 4

Europäisches Patentamt
European Patent Office
Office européen des brevets

EUROPEAN SEARCH REPORT

Application Number
EP 15 46 0142

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	G. BOCZKAL ET AL: "THE BRITTLENESS OF Zn-Cu-Ti SHEET ALLOYS", ARCHIVES OF METALLURGY AND MATERIALS, vol. 60, no. 3, 12 September 2015 (2015-09-12), pages 2355-2360, XP055302946, DOI: 10.1515/amm-2015-0384 * page 2355, paragraph 1 - page 2356, paragraph 2 * -----	1-5	INV. C22F1/16 C22C18/00
A	DE 15 58 502 A1 (GRILLO WERKE AG) 16 April 1970 (1970-04-16) * the whole document * -----	1-5	

TECHNICAL FIELDS SEARCHED (IPC)

C22F
C22C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
Munich	19 September 2016	Rischard, Marc

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons
& : member of the same patent family, corresponding document

EPO FORM 1503 03.82 (P04C01)

2

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 15 46 0142

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

19-09-2016

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
DE 1558502 A1	16-04-1970	NONE	

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- GB 1191994 A **[0003] [0008]**
- US 4051887 A **[0004] [0008]**
- PL 195433 **[0006] [0007]**
- PL 195253 **[0007] [0008]**