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

(11) EP 3 187 616 A1

(12) EUROPEAN PATENT APPLICATION

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

(51) Int Cl.:
C22F 1/16 *(2006.01)* ***C22C 18/02*** *(2006.01)*

(21) Application number: **15460143.9**

(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:
- **Napiora, Tomasz**
  40-872 Katowice (PL)
- **Pawlicha, Stanislaw**
  40-139 Katowice (PL)
- **Knych, Tadeusz**
  30-399 Krakow (PL)
- **Mamala, Andrzej**
  30-650 Krakow (PL)
- **Osuch, Piotr**
  32-087 Zielonki (PL)
- **Walkowicz, Monika**
  25-150 Kielce (PL)
- **Gradkiewicz, Lukasz**
  41-303 Dabrowa Gornicza (PL)
- **Sokol, Radoslaw**
  42-500 Bedzin (PL)

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

(54) FABRICATION METHOD OF STRIPS AND SHEETS MADE OF ZN-CU-TI ALLOYS DESIGNED FOR BUILDING INDUSTRY

(57) A fabrication method of flat-rolled products designed for building industry, made of Zn-Cu-Ti alloy with a chemical composition in accordance with EN-988 standard, composed of at least two basic steps - continuous casting process of metal strip and non-integrated rolling process of finished product in form of sheets, wherein after casting step the metal strip with a thickness from 4 mm to 16 mm and width from 500 mm to 2000 mm is heated up to a temperature ranging from 240°C to 270°C before starting the rolling operation and is being rolled in at least five roll passes until the finished product is obtained. The reduction ratios in the last four roll passes of the rolling process are > 40 % and < 50 % and the rolling rate is not less than 100 mm/min. The sheet temperature following the last roll pass amounts to at least 100 °c (≥ 100 °C).

The Zn-Cu-Ti 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.

The finished product is susceptible to plastic strain in low temperatures ≥ +10 °C.

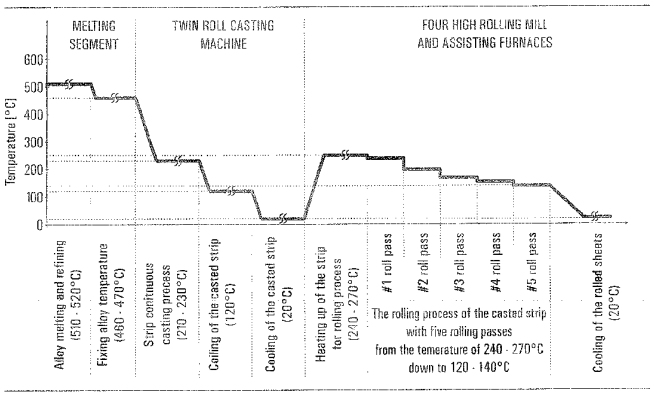

Fig. 3

EP 3 187 616 A1

Description

[0001] The flat-rolled products made of Zn-C-Ti alloys intended for use in building engineering are manufactured in accordance with the EN-988 standard. Multiple manufacturing methods are known, which enable fabrication of sheets made of Zn-Cu-Ti alloys having the desired usable properties, such as mechanical properties, creep resistance and susceptibility to plastic strain of the finished product during installation, also in ambient temperatures as low as +10°C, since the metallic materials made of zinc alloys are known to be susceptible to brittle cracking in low, positive temperatures. The properties of finished sheets are shaped in industrial manufacturing processes of metal plates mainly in the rolling operation of the mill feedstock in form of cast strip obtained most often as a result of the continuous casting process. It is widely known that the technological parameters of the rolling process, such as rolling temperature or deformation speed understood both as a rolling speed and number of roll passes with the reduction ratios resulting from geometric features of the mill feedstock and finished product, determine the mechanical properties of metallic materials in a wide range of their variability, typical for a given chemical composition of Zn-Cu-Ti alloy. Therefore, obtaining of the desired usable properties of the product, described in EN-988 standard is possible through infinite number of the chemical composition combinations of the alloy under consideration and basic parameters of the rolling process.

[0002] 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, wherein a temperature of the mill feedstock ranging from 230 °C to 270 °C and the reduction ratio in the first roll pass amounting to 80 % - 95 % have been indicated as ones of the critical technological parameters, being a requisite of the desired usable properties of the finished product with given chemical composition.

[0003] 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 which ensures the desired usable properties of the finished product.

[0004] 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.

[0005] A similar production technique of Zn-Cu-Ti alloy sheets (cf. FIG. 2) is also known from the Polish patent specification Number PL195253, which differs from the above mentioned method in the number of roll passes reduced to 9 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

[0006] The flat-rolled products made of Zn-Cu-Ti alloys with chemical composition in accordance with the EN-988 standard are manufactured in non-integrated rolling process from the strip cast in a continuous manner according to the Twin Roll Casting (TRC) technique.

[0007] The significance of this invention consists in the fact, that first the geometric parameters of the strip cast in TRC process are chosen, and in particular its thickness, which should be comprised in the range from 4 mm to 16 mm. This requirement is conditioned by achievement of the desired usable properties, distribution of the reduction ratios in the succeeding operation - the rolling process. The width of both cast strip and finished product should be included within the range from 500 mm to 2000 mm. Then, the reheating temperature of cast strip before beginning of the rolling process is being chosen. The heating up operation in hitherto known fabrication methods aims mainly at decreasing of the deformation resistance of the casting during the rolling process. According to the new method, the reheating temperature before rolling plays an essential part in the metallurgical processes shaping the usable properties of the finished sheet through the recrystallization process. Hence, the reheating temperature of the cast strip lies in the range from 240°C to 270°C. In order to obtain the intended effect in form of the desired usable properties of the sheets, it is necessary to secure the appropriate strain rate, both from the point of view of particular reduction ratios, and rate of rolling process itself. Both these factors translate essentially into physical phenomena occurring within the material microstructure in the dynamic conditions of the rolling process, but also determine a finished product

temperature after the last roll pass. It is of great significance, since the processes of recrystallization initiated in the dynamic rolling process conditions will be continued in the static conditions, when the coil of strip weighing several tons is taken away, after rolling, in order to cool down to the ambient temperature. It has been stated that the temperature of the coil of several tons enabling an adequate course of the recrystallization processes in static conditions, and thus the desired usable properties of the finished product, should be not less than 100 °C (≥ 100 °C). In order to obtain such a parameter it is necessary to introduce requirements regarding the distribution of reduction ratios, which should be not less than 40 %, but not greater than 50 %, particularly in the last four roll passes. It enables the optimal equilibrium between the phenomena of microstructural changes in the rolling process and temperature drop of the metal ribbon following successive roll passes caused by the rolling oil emulsion. At the same time, it is admitted that the first roll pass of the rolling process has the reduction ratio less than 40 % in consideration of the fact that the strip having a considerable thickness before the first roll pass gives up the heat relatively more slowly. For similar reasons, in order to obtain the intended effect, it is necessary to conduct the rolling process using the suitable rolling rates. It is assumed that minimum rolling rates allowing to obtain this effect must not be lower than 100 m/min.

[0008] The key factor in the manufacturing process of Zn-Cu-Ti alloy sheets is also a precise choice of its chemical composition. The alloy being the subject of present description 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, Sn.

[0009] The fabrication method of Zn-Cu-Ti alloy sheets described above allows to obtain the finished product with desired usable properties, specified in the EN-988 standard, and also enhanced plastic properties in low temperatures ≥ +10°C, without the necessity of supplementary heat treatment of both cast strip and finished product.

[0010] An exemplary application of the proposed production method of Zn-Cu-Ti alloy sheets is shown schematically in FIG. 3.

[0011] The Zn-Cu-Ti alloy with chemical composition containing 0,15 wt. % Cu; 0,07 wt. % Ti; 0,003 wt. %. Al and rest tramp elements such as 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 following technological step the metal strip is guided to the soaking-pit in order to heat it up to the rolling temperature, which amounts to 250 °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 reversing system. The rolling process of metal strip with input thickness is carried out until the thickness of 0,65 mm is obtained, in 5 roll passes with reduction ratios amounting to ≥ 40%. The rolling rate in first roll pass amounts to 120 m/min, whereas in the last four passes 160 m/min. After the rolling process the coil of strip has a temperature of about 120°C and cools down in ambient temperature.

Claims

1. A fabrication method of flat-rolled products designed for building industry, made of Zn-Cu-Ti alloy with a chemical composition in accordance with EN-988 standard, composed of at least two basic steps - continuous casting process of metal strip and non-integrated rolling process of finished product in form of sheets, **wherein** after casting step the metal strip with a thickness from 4 mm to 16 mm and width from 500 mm to 2000 mm is heated up to a temperature ranging from 240°C to 270°C before starting the rolling operation and is being rolled in at least five roll passes until the finished product is obtained.

2. A method of claim 1, **wherein** the reduction ratios in the last four roll passes of the rolling process are > 40 % and < 50 %.

3. A method of claim 2, **wherein** the rolling rate is not less than 100 m/min.

4. A method of claim 3, **wherein** the sheet temperature following the last roll pass of the rolling process is ≥ 100°C

5. A method of claim 4, **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,015 wt. % Al and rest Zn and tramp elements, such as : Cd, Fe, Pb, Sn.

6. A method of claim 5, **wherein** the finished product is **characterized by** the susceptibility to plastic strains in low temperatures ≥ +10°C.

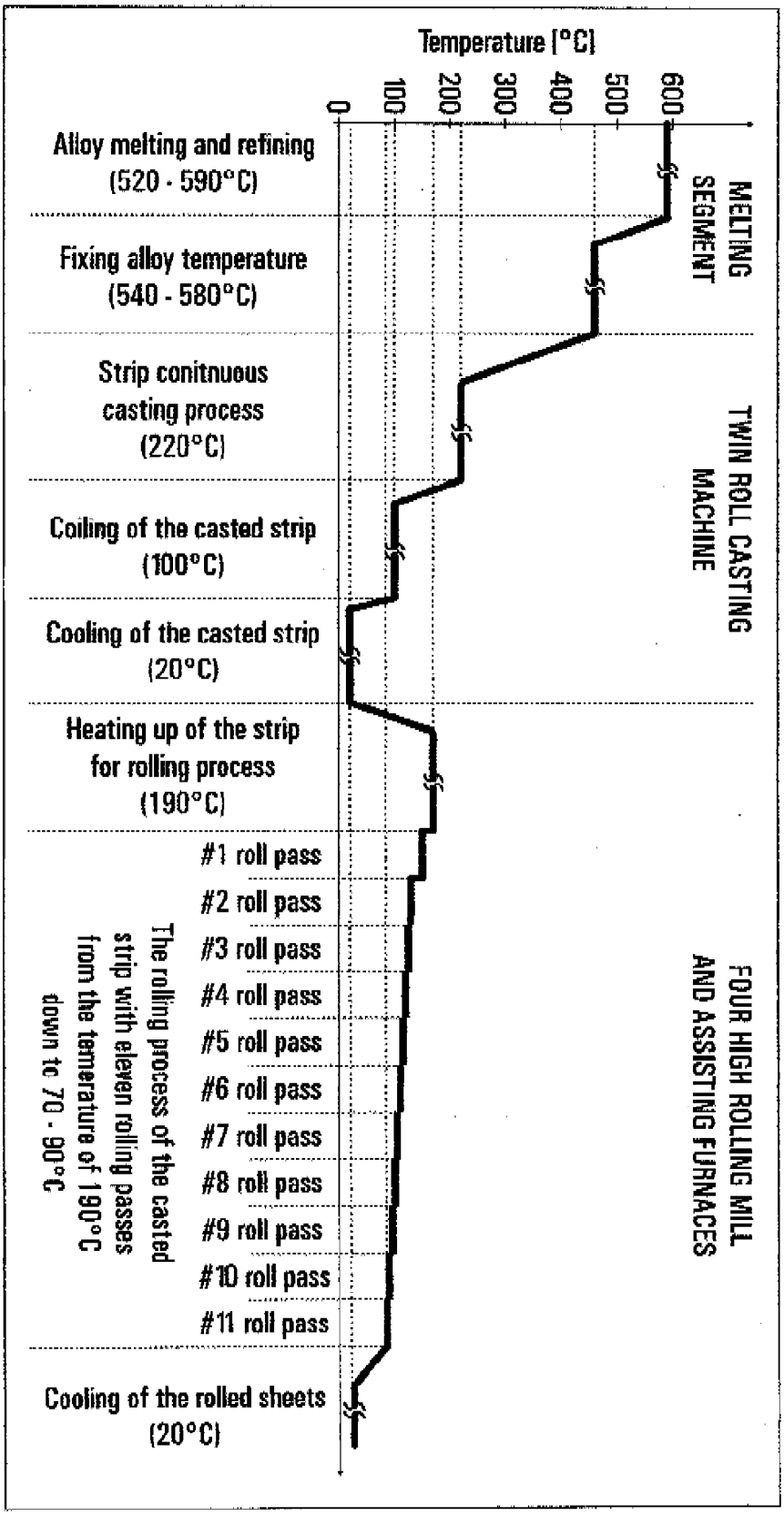
Temperature [°C]
0
100
200
300
400
500
600
Alloy melting and refining (520 - 590°C)
Fixing alloy temperature (540 - 580°C)
Strip conitnuous casting process (220°C)
Coiling of the casted strip (100°C)
Cooling of the casted strip (20°C)
Heating up of the strip for rolling process (190°C)
#1 roll pass
#2 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)
MELTING SEGMENT
TWIN ROLL CASTING MACHINE
FOUR HIGH ROLLING MILL AND ASSISTING FURNACES

Fig. 1

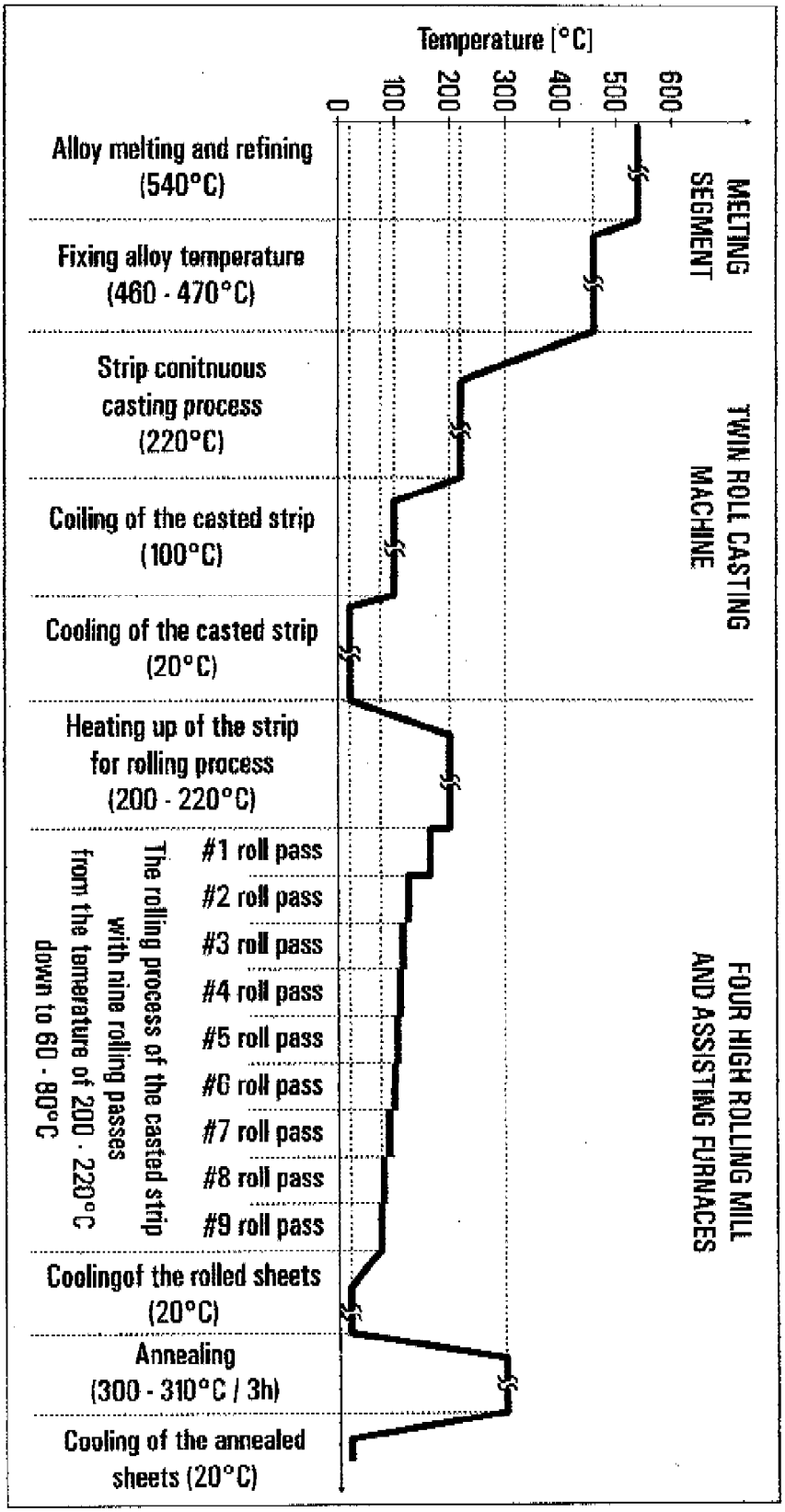
Temperature [°C]
0
100
200
300
400
500
600
Alloy melting and refining (540°C)
Fixing alloy temperature (460 - 470°C)
Strip conitnuous casting process (220°C)
Coiling of the casted strip (100°C)
Cooling of the casted strip (20°C)
Heating up of the strip for rolling process (200 - 220°C)
The rolling process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

Fig. 2

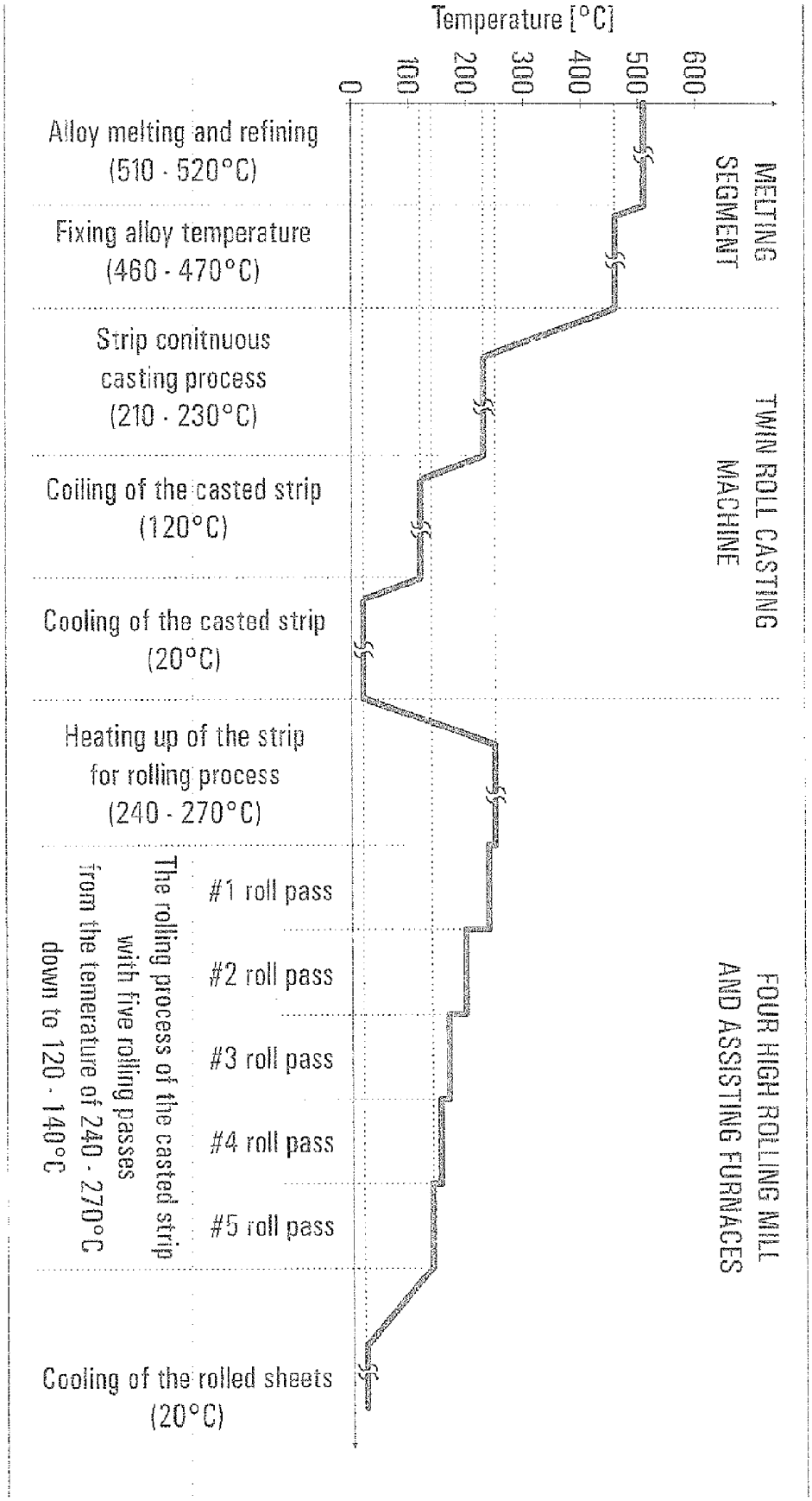
Temperature [°C]
0
100
200
300
400
500
600
MELTING SEGMENT
TWIN ROLL CASTING MACHINE
FOUR HIGH ROLLING MILL AND ASSISTING FURNACES
Alloy melting and refining (510 - 520°C)
Fixing alloy temperature (460 - 470°C)
Strip conitnuous casting process (210 - 230°C)
Coiling of the casted strip (120°C)
Cooling of the casted strip (20°C)
Heating up of the strip for rolling process (240 - 270°C)
The rolling process of the casted strip with five rolling passes from the temerature of 240 - 270°C down to 120 - 140°C
#1 roll pass
#2 roll pass
#3 roll pass
#4 roll pass
#5 roll pass
Cooling of the rolled sheets (20°C)

Fig. 3

Europäisches Patentamt
European Patent Office
Office européen des brevets

EUROPEAN SEARCH REPORT

Application Number
EP 15 46 0143

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
A	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), XP055302946, DOI: 10.1515/amm-2015-0384 * paragraphs [0001], [0002] *	1-6	INV. C22F1/16 C22C18/02
A,D	US 4 051 887 A (GROTH VOLKER ET AL) 4 October 1977 (1977-10-04) * claims 1-5 *	1-6	

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	29 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)

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 15 46 0143

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.

29-09-2016

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 4051887 A	04-10-1977	DE 2510985 A1	23-09-1976
		FR 2303864 A1	08-10-1976
		NL 7600789 A	15-09-1976
		US 4051887 A	04-10-1977

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 **[0002]**
- US 4051887 A **[0003]**
- PL 195433 **[0004] [0005]**
- PL 195253 **[0005]**