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

(11) EP 4 389 924 A1

(12) EUROPEAN PATENT APPLICATION

(43) Date of publication:
26.06.2024 Bulletin 2024/26

(21) Application number: **22214482.6**

(22) Date of filing: **19.12.2022**

(51) International Patent Classification (IPC):
C22C 19/05 *(2006.01)* ***C22F 1/10*** *(2006.01)*

(52) Cooperative Patent Classification (CPC):
C22C 19/057; C22F 1/10

(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 ME MK MT NL NO PL PT RO RS SE SI SK SM TR
Designated Extension States:
BA
Designated Validation States:
KH MA MD TN

(71) Applicant: **Siemens Energy Global GmbH & Co. KG
81739 München (DE)**

(72) Inventor: **Ladru, Francis
13587 Berlin (DE)**

(54) **MICRO ALLOYED SUPERALLOY AND HEAT TREATMENT**

(57) The invention relates to a nickel based superalloy, which comprises (in wt%):
C: 0.05% - 0.16%,
Cr: 8.0% - 9.5%,
Co: 9.0% - 10.5%,
W: 9.0% - 10.5%,
Mo: 0.2% -1.0%,
Ta: 2.5% - 3.5%,
Al: 5.0% - 6.0%,
Ti: 0.5% - 1.5 %,
B: 0.01% - 0.025%,
Hf: 1.0% - 2.0%;
Zr: 0.004% - 0.06%,
Nickel (Ni) and inevitable impurities.

Processed by Luminess, 75001 PARIS (FR)

Description

[0001] The application belongs to the technical field of superalloys and relates to a superalloy with good long-term stability and suitable heat treatments.

[0002] Gas turbines not only have extremely high requirements on the initial machining accuracy and assembly accuracy hot-end components, but also require that failure and fracture cannot occur during long-term service. Alloys for such components are required to have excellent high-temperature long-term stability and performance to avoid part failure before the overhaul period. At present, there are almost no alloys that can fully meet the above requirements in the existing superalloys. Generally, the alloys that can achieve the above mechanical properties have poor long-term stability.

[0003] The present application aims to solve some of the technical problems in the related art at least to a certain extent.

[0004] The problem is solved by claim according to claim 1 and a heat treatment according to claim 11.

[0005] In the dependent claims further advantages are listed which can be combined arbitrarily with each other to yield further advantages.

[0006] Embodiments of the present application propose a superalloy with good long-term stability. This superalloy with good long-term stability not only has excellent mechanical properties, but also has long-term stability and long-lasting life. It fully meets the requirements for the design and use of advanced aero-engines and gas turbines and is suitable for medium- and long-term service parts such as turbine blades, hot-end components of aero-engines and gas turbines.

[0007] The superalloy with good long-term stability according to the embodiment of the present application comprises (in wt%): C: 0.05% - 0.16%, Cr: 8.0% - 9.5%, Co: 9.0% - 10.5%, W: 9.0% - 10.5%, Mo: 0.2% ~ 1.0%, Ta: 2.5% - 3.5%, Al: 5.0% - 6.0%, Ti: 0.5% - 1.5 %, B: 0.01% - 0.025%, Hf: 1.0% - 2.0%; Zr: 0.004% - 0.06%, Nickel (Ni) and inevitable impurities.

[0008] Nickel is especially used for balancing.

[0009] All percentages (%) in the whole description are given or meant in wt% except if ppm is mentioned.

[0010] A special contribution is given by Magnesium (Mg), Manganese (Mn), Silicon (Si) and/or Iron (Fe).

[0011] The superalloys according to the embodiments of the present application have good long-term stability. In the examples of this application, the strengthening element design scheme of high Al, low Ti, and high Ta is adopted.

[0012] The embodiments described below with reference to the accompanying drawings are only exemplary and are intended to be used to explain the present application, but should not be construed as a limitation to the present application.

[0013] The superalloy according to the embodiment of the present application comprises: C: 0.06% to 0.09%, Cr: 8.0% - 8.5%, Co: 9.0% - 9.5%, W: 9.1% - 9.8%, Mo: 0.3% - 0.7%, Ta: 3.0% - 3.5%, Al: 5.3% - 5.8%, Ti: 0.5% - 1.0%, B: 0.01% - 0.02%, Hf: 1.1% - 1.7%, Zr: 0.005% - 0.02%.

[0014] Nickel is especially used for balancing.

[0015] The role of each main element in the superalloy of the embodiment of the present application is as follows: Carbon: C mainly suppresses the growth of austenite grains during heating by forming MC-type carbides at the end of solidification in nickel-based superalloys and forms MC along grain boundaries during heat treatment. Various types of carbides, which play a role in strengthening grain boundaries, delaying the initiation, expansion and merging of microcracks, thereby improving the high-temperature durable life of the alloy. When the C content is less than 0.05%, it is not enough to form enough MC. When the C content is too high, the size of MC formed is larger, and it will consume too much Mo, Cr, Ti and Ta in the alloy. On the one hand, it not only reduces the solid solution strengthening effect of Mo and Cr, on the other hand, it is used to form Ni_3 (Al, Ti) and Ni_3 The Ti and Ta of the (Al, Ti, Ta) composite strengthening phase will be reduced, which will adversely affect the high temperature performance and durability of the alloy, so C should be controlled within 0.05% and 0.16%.

[0016] Chromium Cr: The main function of Cr is to improve the oxidation resistance of the alloy and has a certain solid solution strengthening effect. After aging treatment, it can also combine with C to form granular MC distributed along the grain boundaries and plays a role in strengthening the grain boundaries. However, when the Cr content is too high, it is easy to form the TCP phase, which reduces the long-term microstructure and performance stability of the alloy. Therefore, its content generally does not exceed 25%. In the examples of this application, considering the stability of corrosion resistance and long-term microstructure and properties, the Cr content is controlled at 8.0% - 9.5%.

[0017] Cobalt: Co is both an important solid solution strengthening element and an important precipitation strengthening element. Co element can be dissolved in the matrix to provide a good solid solution strengthening effect for the alloy, which can significantly reduce the stacking fault energy of the matrix, widen and expand the dislocation width, so that the dislocation is not easy to bunch up and cross-slip occurs, thereby improving the alloy. creep resistance and longevity. Co can also partially replace Ni_3 Al-type precipitation of elements in the strengthening phase improves the stability of the phase in long-term service; Co can also reduce the solid solubility of Al and Ti elements in the matrix, promote the precipitation of γ' strengthening phase and increase the number of precipitation and solid solution. temperature. When the Co content is lower than 9%, the high temperature strength is low.

[0018] When the Co content is higher than 11%, it is easy to form an η phase that affects its performance in long-term service, so the Co content is controlled at 9.0% - 10.5%.

[0019] Tungsten and Molybdenum: W and Mo: W and Mo are one of the main solid-solution strengthening elements, which can be solid-dissolved in the alloy matrix and in the γ' strengthening phase and at the same time can improve the bonding force between atoms, increase the diffusion activation energy and recrystallization temperature, so as to effectively improve the high temperature strength. However, when Mo is too high, long-term high temperature aging is easy to generate μ phase and reduce alloy toughness. Therefore, the Mo content is controlled at 0.2% - 1.0%. The atomic radius of W is relatively large, more than ten percent larger than the atomic radius of nickel, and the solid solution strengthening effect is obvious. However, W is an element that accelerates high-temperature corrosion, and will form a harmful delta phase during long-term service, reducing the strength and toughness of the alloy.

[0020] Therefore, the W content is controlled at 9.0% - 10.5%.

[0021] Aluminum, Titanium and Tantalum: Al, Ti and Ta: The three are the forming elements of the strengthening phase γ' in nickel-based alloys. It is generally believed that with the increase of the content of the three, the amount of γ' increases, and the high-temperature creep and durability improve, but too much γ' will cause Deterioration of processability. In addition, Ti and Ta will also combine with C to form MC-type carbides, which hinder the growth of grain boundaries and the sliding of grain boundaries at high temperatures and play a role in improving high-temperature mechanical properties, but too much Ti and Ta will form large-grained MC-type carbides. Carbides are detrimental to the mechanical properties of the alloy. Through research in this application, it is found that the high-temperature mechanical properties of the alloy depend not only on the amount of γ' phase, but also on its composition and characteristics. optimization, the best γ' strengthening effect can be obtained. In the alloys of the examples of the present application, the strengthening element design scheme of high Al, low Ti and high Ta is adopted. $_3$ (Al, Ti) strengthening phase was modified to form Ni with higher Al content and Ta at the same time $_3$ (Al, Ti, Ta), compared to conventional Ni $_3$ The (Al, Ti) strengthening phase is more resistant to high temperatures, thereby improving the tensile properties and long-lasting life of the alloy.

[0022] The specific control range of the three is: Al: 5.0% - 6.0%, Ti: 0.5% - 1.5%, Ta: 2.5% - 3.5%.

[0023] Boron: The role of B is mainly manifested in two aspects. First, because the atomic radius of B is very small, so B atoms are easily enriched at the grain boundaries. The low melting point elements cannot segregate at the grain boundary, which improves the bonding force of the grain boundary; the second is that the boride on the grain boundary can prevent the grain boundary from slipping, the initiation and expansion of voids, and improve the creep resistance and lasting life of the alloy. favorable. However, too much B will deteriorate the hot workability and welding performance of the alloy, so the suitable B content of the alloy in the embodiment of the present application is 0.01% - 0.025%.

[0024] Zirconium: Zr helps to purify the grain boundary and enhance the bonding force of the grain boundary. The compound addition of Zr and B helps to maintain the high temperature strength and long-lasting life of the alloy, but excessive Zr easily reduces the processing performance. The alloys in the examples of this application control Zr at 0.004% - 0.06%.

[0025] Mg, Mn, Si, Fe: the superalloy is micro-alloyed with Mg, Mn, Si and/or Fe.

[0026] The key point to achieve improvement in mechanical high temperature properties and long lifetime are the grain boundaries, phases, and therefore the atoms which segregate there.

[0027] Fe is quite close in the PSE (Periodic system of the elements) to Ni and next to Co. Mn is next to Fe in the PSE. Therefore, these elements Fe, Mn should be controlled.

[0028] Si is next to Al in the PSE and should be controlled, too.

[0029] Mg, Mn, Si, Fe as well as B, C atoms are segregated at grain boundaries, and this segregation is a balanced segregation. The segregation of these atoms at the grain boundary improves the bonding force of the grain boundary and increases the strength of the grain boundary. Mg, Mn, Fe atoms are not only segregated at grain boundaries, but also at carbide phase boundaries, γ' phase boundaries. Mg atoms also enter into γ' and carbides, which have a favorable effect on the mechanical properties. The segregation of a small amount of Mg, Mn, Fe at the grain boundary reduces the grain boundary energy and phase boundary energy, and improves and refines the morphology of other grain boundary precipitation phases at the grain boundary carbide level. For example, carbides can be lumped or spheroidized, effectively inhibiting grain boundary sliding, reducing grain boundary stress concentration, and eliminating notch sensitivity. Mg, Mn, Fe and Sulfur and other harmful impurities form high melting point compounds such as MgS, which purifies the grain boundary, so that the concentration of S, O, P and other impurity elements in the grain boundary is significantly reduced, and the harmful effects of S, O, P and other impurities are reduced.

[0030] A small amount of Mg, Mn, Fe increases durability and plasticity, improves creep properties and high-temperature tensile plasticity, increases impact toughness and fatigue strength, and can also improve hot workability and yield for some alloys. But the content should not be too high, too high will deteriorate the performance.

[0031] Boron and Silicon have the similar effect (melting depressant) and should be controlled.

[0032] Therefore, the contents of this microalloying elements are given by:

Mg: 10ppm - 70ppm,
and/or
Si: 20ppm - 300ppm,

especially 30ppm - 300ppm
and/or
Fe: 20ppm - 400ppm,
and/or
Mn: 10ppm - 200ppm;
or more preferably:

Mg: 20ppm - 60ppm
and/or
Si: 30ppm - 200ppm,
especially 40ppm - 200ppm,
and/or
Fe: 30ppm - 300ppm,
especially 40ppm ≤ Fe ≤ 300ppm,
and/or
Mn: 10ppm ≤ Mn ≤ 200ppm.

[0033] Purity of bar or billets of the superalloy are achieved by carefully choosing the raw material of the alloying elements. Some of the raw material comprises all microalloying elements, some raw material only a part of them.

[0034] Regarding the costs of the alloy not every possible purest raw material can be used and should not as these microalloying elements provide also positive effects at a ppm level.

[0035] A special contribution is given by Magnesium (Mg), Manganese (Mn), Silicon (Si) and/or Iron (Fe) especially in combination with Boron (B) and/or Carbon (C): (in wt%).

[0036] Amounts of this microalloying elements are preferably chosen by:

B and Mg are given by 250ppm ≤ B + 10Mg ≤ 750ppm
and/or
Fe and Si are given by 400ppm ≤ Fe + Si ≤ 550ppm
and/or
Mn and Si are given by 400ppm ≤ Si + 2Mn ≤ 500ppm
and/or
C and Si are given by 1000ppm ≤ C + 2Si ≤ 1200ppm
and/or
Fe and C are given by 950ppm ≤ C + 2Fe ≤ 1200ppm
and/or
Si and Mg are given by 250ppm ≤ Si + 10Mg ≤ 750ppm.

[0037] In alloys impurities (Sn, Sb, As, Zn, Hg, U, Th, Ce, Ge, Y, Pt, Au, In, Na, K, La, Ce, Pd, Ba) are generally unavoidable. In the Ni superalloy of the present application, the unavoidable impurities like Phosphorus (P), Sulfur (S), Copper (Cu), Niobium (Nb), Lead (Pb), Selenium (Se), Wismut (Bi), Tellurium (Te), Thallium (Tl), Nitrogen (N), Oxygen (O), Silver (Ag), Vanadium (V), Gallium (Ga), Rhenium (Re), Ruthenium (Ru) are very small, usually below 0.01%, 0.001% or 0.001% or below, or even undetectable.

[0038] Preferably is V ≤ 500ppm and/or Nb < 500ppm and/or Cu < 100ppm.

[0039] More preferably is V: 20ppm ≤ V ≤ 200ppm and/or Nb < 50ppm and/or Cu < 50ppm.

[0040] Furthermore, the particular features, structures, materials or characteristics described may be combined in any suitable manner in any one or more embodiments or examples. Furthermore, those skilled in the art may combine and combine the different embodiments or examples described in this specification, as well as the features of the different embodiments or examples, without conflicting each other.

[0041] The alloy can also only reveal his best properties with an appropriate heat treatment.

[0042] A heat treatment is preferably performed at four different temperatures levels,

especially at three different temperature levels,
very especially only at three different temperature levels. Different temperature levels means at least a difference of 10°C.

[0043] Each temperature level is characterized by increasing the temperature to his desired temperature, holding time and decreasing the temperature, especially near or to room temperature.

[0044] Active cooling can or must be performed depending on the height of the temperature.

[0045] Controlled heating and cooling rates are also needed.

[0046] Higher temperature levels need a careful ramp up, which means that in the beginning the heating rates can be higher, but will be lowered when reaching the desired temperature.

[0047] Gas or vacuum cooling is needed at higher temperature.

[0048] Especially the temperature levels of each subsequent level is decreased.

[0049] First, a solution treatment is performed. The solution temperature is depending on the actual composition, but for this claimed small ranges of the inventive superalloy this solution temperature will between 1220°C and 1250°C.

[0050] Secondly a stabilization treatment is performed at a temperature which is at least 130°C, especially at least 140°C lower than the solution treatment temperature. '

[0051] But preferably the difference should not bigger than 250°C, especially not bigger than 200°C.

[0052] Especially for the first level to the second level this difference is not bigger than 190°C.

[0053] Holding time (preferably 100min to 140min) at the stabilization temperature level for the stabilization treatment is least 40% smaller than the holding time at the first temperature level (preferably 220min to 260min) which is the solution treatment temperature.

[0054] Thirdly, an aging treatment is performed at a temperature which is at least 170°C, especially 180°C lower than the temperature of the stabilization treatment temperature. But preferably this difference is not bigger than 250°C.

[0055] Between a first and a second level another level can be performed as an intermediate treatment as an "oversolution" treatment, which has a higher temperature than the solution treatment temperature which means at least 10°C higher but not higher than 50°C, but preferably only three levels are used.

[0056] One exemplary embodiment of the invention: C: 0.072%, Cr: 8.1%, Co: 9.2%, W: 9.5%, Mo: 0.5%, Ta: 3.3%, Al: 5.4%, Ti: 0.5%, B: 0.015%, Hf: 1.2%, Zr: 0.01%.

[0057] Heat treatment at1239°C for 250min, 1085°C for 175min, 880°C for 1day.

[0058] Although the embodiments of the present application have been shown and described above, it should be understood, that the above embodiments are exemplary and should not be construed as limitations to the present application. Embodiments are subject to variations, modifications, substitutions and variations.

Claims

1. A nickel based superalloy,

which comprises (in wt%)
C: 0.05% - 0.16%,
Cr: 8.0% - 9.5%,
Co: 9.0% - 10.5%,
W: 9.0% - 10.5%,
Mo: 0.2% -1.0%,
Ta: 2.5% - 3.5%,
Al: 5.0% - 6.0%,
Ti: 0.5% - 1.5 %,
B: 0.01% - 0.025%,
Hf: 1.0% - 2.0%;
Zr: 0.004% - 0.06%,
Nickel (Ni) and inevitable impurities,
especially the balance is Nickel,
optionally
Mg: 10ppm - 70ppm,
and/or
Si: 20ppm - 300ppm,
and/or
Fe: 20ppm - 400ppm,
and/or
Mn: 10ppm - 200ppm
and/or
V ≤ 500ppm
and/or
Nb < 500ppm
and/or
Cu < 100ppm.

2. Alloy according to claim 1,

which comprises (in wt%),
C: 0.06% to 0.09%
Cr: 8.0% - 8.5%,
Co: 9.0% - 9.5%,
W: 9.1% - 9.8%
Mo: 0.3% - 0.7%
Ta: 3.0% - 3.5%
Al: 5.3% - 5.8%
Ti: 0.5% - 1.0%
B: 0.01% - 0.02%
Hf: 1.1% - 1.7%
Zr: 0.005% - 0.02%.

3. Alloy according to one of the claims 1 or 2,

which comprises
Mg: 20ppm - 60ppm
and/or
Si: 30ppm - 200ppm,
especially 40ppm - 200ppm,
and/or
Fe: 30ppm - 300ppm,
especially 40 ppm ≤ Fe ≤ 300ppm,
and/or
Mn: 10ppm ≤ Mn ≤ 100ppm
and/or
V: 20ppm ≤ V ≤ 200ppm
and/or
Nb < 50ppm
and/or
Cu < 50ppm.

4. Alloy according to any of the previous claims, wherein B and Mg are given by 250ppm ≤ B + 10Mg ≤ 750ppm.

5. Alloy according to any of the previous claims, wherein Fe and Si are given by 400ppm ≤ Fe + Si ≤ 550ppm.

6. Alloy according to any of the previous claims, wherein Mn and Si are given by 400ppm ≤ Si + 2Mn ≤ 500ppm.

7. Alloy according to any of the previous claims, wherein C and Si are given by 1000ppm ≤ C + 2Si ≤ 1200ppm.

8. Alloy according to any of the previous claims, wherein Fe and C are given by 950ppm ≤ C + 2Fe ≤ 1200ppm.

9. Alloy according to any of the previous claims, wherein Si and Mg are given by 250ppm ≤ Si + 10Mg ≤ 750ppm.

10. Alloy according to any of the previous claims, comprising no Rhenium (Re) and/or no Ruthenium (Ru) and no Yttrium (Y).

11. Method to heat treat an alloy according to any of the previous claims,

wherein a temperature level is especially **characterized by** increasing the temperature to his desired temperature, holding time and decreasing the temperature, especially near or to room temperature,
wherein four different temperature levels, especially three different temperature levels, are used.

12. Method according to claim 11,
wherein only three different temperature levels are used.

13. Method according to any of the previous claims 11 or 12,

wherein the temperature of each subsequent temperature level is decreased,
especially by at least 130°C.

14. Method according to any of the previous claims 11, 12 or 13,

wherein the temperature of the first level to the second level is decreased,
by at maximum 190°C.

15. Method according to any of the previous claims 11, 12, 13 or 14,

wherein the temperature of the second level to the third level is decreased
at least by 170°C and
preferably at maximum 250°C.

16. Method according to any of the previous claims 11, 12, 13, 14 or 15

wherein the holding duration at the stabilization temperature level for the stabilization treatment,
which is preferably 100min to 140min,
is least 40% shorter than the holding duration at the first temperature level,
which is preferably 220min to 260min,
which is the solution treatment.

Europäisches Patentamt
European Patent Office
Office européen des brevets

EUROPEAN SEARCH REPORT

Application Number
EP 22 21 4482

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 Y	EP 3 572 623 A1 (SIEMENS AG [DE]) 27 November 2019 (2019-11-27) * paragraph [0054] * * paragraph [0066] *	1-16 3,4	INV. C22C19/05 C22F1/10
X Y	US 2020/030883 A1 (MUELLER RALF [DE] ET AL) 30 January 2020 (2020-01-30) * paragraph [0040] *	1-10 3,4, 11-16	
X Y	WO 2021/234368 A1 (RENISHAW PLC [GB]) 25 November 2021 (2021-11-25) * claims 1-3 * * page 6 - page 7 *	1-10 3,4, 11-16	
X Y	KIM IN SOO ET AL: "Effect of heat treatment on microstructural evolution and creep behaviors of a conventionally cast nickel-based superalloy", MATERIALS CHARACTERIZATION, ELSEVIER, NEW YORK, NY, US, vol. 165, 11 May 2020 (2020-05-11), XP086190814, ISSN: 1044-5803, DOI: 10.1016/J.MATCHAR.2020.110378 [retrieved on 2020-05-11] * abstract * * Section 2; page 3 * * Section 4; page 9 * -/--	1-16 3,4, 11-16	TECHNICAL FIELDS SEARCHED (IPC) C22C C22F

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
The Hague	8 May 2023	Neibecker, Pascal

1

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

Europäisches Patentamt
European Patent Office
Office européen des brevets

EUROPEAN SEARCH REPORT

Application Number
EP 22 21 4482

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
Y	BOR H Y ET AL: "The influence of magnesium on carbide characteristics and creep behavior of the mar-M247 superalloy", SCRIPTA MATERIALIA, ELSEVIER, AMSTERDAM, NL, vol. 38, no. 2, 22 December 1997 (1997-12-22), pages 329-335, XP004324973, ISSN: 1359-6462, DOI: 10.1016/S1359-6462(97)00444-2 * example B; table 1 * * abstract * * Conclusions; page 334 * -----	3,4	

TECHNICAL FIELDS SEARCHED (IPC)

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
The Hague	8 May 2023	Neibecker, Pascal

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

1

EPO FORM 1503 03.82 (P04C01)

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO.

EP 22 21 4482

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.

08-05-2023

Patent document cited in search report		Publication date	Patent family member(s)		Publication date
EP 3572623	A1	27-11-2019	NONE		
US 2020030883	A1	30-01-2020	DE 102018212625	A1	30-01-2020
			US 2020030883	A1	30-01-2020
WO 2021234368	A1	25-11-2021	CN 115702052	A	14-02-2023
			EP 4153371	A1	29-03-2023
			WO 2021234368	A1	25-11-2021

EPO FORM P0459

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