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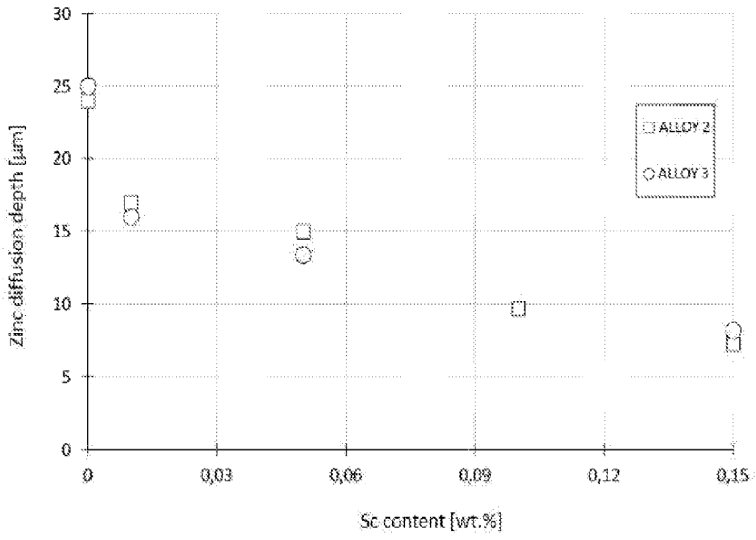
(54) Title: COPPER-CHROMIUM ALLOY, METHOD OF MANUFACTURING THEREOF, THE USE OF THIS ALLOY FOR MAKING CAP ELECTRODES AND A METHOD OF MANUFACTURING A CAP ELECTRODE USING THIS ALLOY

Fig. 1



(57) Abstract: The object of the invention is a copper-chromium alloy containing 99.1-99.49 wt.% of copper, 0.3-0.7 wt.% of chromium, 0.05-0.1 wt.% of zirconium and 0.01-0.15 wt.% of scandium, the use of this alloy for making cap electrodes. Also the object of the invention is a method of manufacturing the copper-chromium alloy and a method of making a cap electrode using this alloy.

WO 2023/003481 A1

[Continued on next page]

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Copper-chromium alloy, method of manufacturing thereof, the use of this alloy for making cap electrodes and a method of manufacturing a cap electrode using this alloy

The object of the invention is a copper-chromium alloy with a scandium additive, a method of manufacturing thereof, the use of this alloy for making cap electrodes and a method of manufacturing a cap electrode using this alloy.

New alloys based on copper and chromium are currently being sought as substitutes for previously used materials for cap electrodes used mainly in the car industry. Due to the development of resistance welding technology as one of the methods of cheap and effective joining of metals, research on the development of a new material solution for the structural components of automatic welding machines becomes important. Requirements are made for materials with a high set of mechanical and electrical properties, thermal conductivity, heat resistance, erosion resistance, etc. In practice, resistance welding technology provides for the use of cap electrodes made of copper-based alloys with chromium or zirconium, the service life of which is determined by the phenomena occurring at the point of the tool (electrode)/material contact mainly due to the flow of electricity and the release of excessive amounts of Joul's heat.

Currently used electrodes made of CuCrZr alloys have insufficient wear resistance, which means that they must be replaced frequently in the production cycle of welded joints. The copper alloys with a beryllium additive used, despite their high performance characteristics, are gradually being eliminated from use due to the harmful effects of beryllium on living organisms. Therefore, new alloys based on copper and chromium are being sought as substitutes for previously used materials for cap electrodes mainly for the car industry. Due to the development of resistance welding technology as one of the methods of cheap and effective joining of metals, research on the development of a new solution for the structural components of automatic welding machines becomes important.

From the European patent application EP1650317A2, a solution is known which deals with the possibility of appropriate selection of alloying additives increasing strength properties and resistance to annealing of copper alloys with Ni, Si, Zn, Al, Mn and Cr additives. The object of this application is a method of obtaining, which includes heat treatment, namely precipitation hardening processes, which makes it possible to obtain high electrical conductivity above 85% IACS (about 49 MS/m). An important element is the phosphorus additive used in the amount of 100÷550 ppm, which is responsible for high level of electrical properties and hardness of alloys such as Cu-Cr, Cu-Ti, Cu-Zr, Cu-Cr-Zr.

The authors Watanabe S., Kleppa O.J. have already in 1984 investigated the thermodynamic properties in materials, i.e. CuSc, with 0.2, 0.33 and 0.5 wt.% of scandium content.

Numerous literature reports indicate the possibility of using Cu-Cr alloys, as in applications CN110202159 and CN107598172, or alloys with high chromium content (30wt.%), as in application CN108559867, for producing electrical contacts from powder in ball mills with the use of sintering technology. High-purity materials are used as a charge for the process, and the resulting castings are subjected to precipitation hardening operations in order to shape the structure. The products obtained in the solutions presented in the state of the art have an oxygen content of about 500 ppm. Oxygen content in copper alloys at the indicated level can have a negative impact on the further effective conduct of the process of plastic processing of castings.

The solutions known from the patent literature assume the use of a limited number of alloying additives and focus on elements such as chromium and zirconium, while omitting the possibility of additional chemical modification which allows materials with preferable functional properties to be obtained.

Another patent application no. RO125605A0 presents a solution for the production of semi-finished products made of CuCr and CuCrZr alloys, chromium in the amount of 1 wt.%, Zr in the amount of 0.15 wt.%. The patent covers only the

horizontal continuous casting process and the authors point to the problem of oxidation of chromium and zirconium due to the strong affinity of these two elements for oxygen.

The latest research by the authors K. Franczak, P. Kwaśniewski, G. Kiesiewicz et all in Archives of Civil and Mechanical Engineering titled "Research of mechanical and electrical properties of Cu-Sc and Cu-Zr alloys" carried out on Cu-Sc alloys containing 0.16 wt.% of scandium makes it possible to modify their properties by supersaturation and artificial ageing. Under the influence of the temperature of 500°C for 45 minutes, the hardness of the CuSc0.16 alloy measured on the Vickers scale increased from 55 HV10 to the value of 109 HV10, for an alloy with a higher scandium content in identical conditions, the hardness on the Vickers scale was 95HV10.

The object of the invention is to develop a new copper-chromium alloy, a method of manufacturing thereof and the use of this alloy for making cap electrodes, as well as a method of manufacturing a cap electrode using this alloy. As a result of using the alloy according to the invention, an increase in the service life of the cap electrode products was unexpectedly achieved by using a copper-chromium based material with a scandium additive. An alloying additive in the form of scandium effectively reduces zinc absorption into the surface of the produced cap electrodes, ultimately increasing their service life.

The essence of the solution according to the invention is that the copper-chromium alloy contains 99.1-99.49 wt.% of copper, 0.3-0.7 wt.% of chromium, 0.05-0.1 wt.% of zirconium and 0.01-0.15 wt.% of scandium. Preferably it contains 0.1 wt.% of nickel.

The essence of the solution according to the invention also relates to the use of the above-described copper-chromium alloy for producing cap electrodes.

The object of the invention is also a method of producing a copper-chromium alloy, which comprises the following:

- in the first step, copper is melted at a temperature of 1100-1300°C,

- in the second step, 0.3-0.7 wt.% of chromium and 0.05-0.1 wt.% of zirconium and 0.01-0.15 wt.% of scandium are added, and the surface is sprinkled with graphite sprinkles and stirred with a graphite lance until the alloying components are completely melted.

Preferably, in the second step, 0.1 wt.% of nickel is additionally added.

Preferably, in the third step, a casting process is carried out using a crystalliser made of boron nitride or boron nitride and graphite, at a casting speed of 1-20 mm at a standstill time of 0.1-30 s.

The object of the invention is also a method of making a cap electrode as indicated above, which further comprises the following:

- in the fourth step, a forging process is carried out under the following conditions: die temperature 25-200°C, minimum forging speed 5 mm/s, minimum force 20 t, separator: boron nitride;

- and in the fifth step, the forgings are subjected to an ageing process at a temperature of 450-550°C for 1-5 h;

- in the sixth step, the electrode surface is cleaned, preferably by polishing or smoothing.

Preferably, the fourth step of this method may include:

- a hot forging process consisting of heating the charge to a temperature of 800-950°C; or

- a cold forging process under the following conditions: die at ambient temperature, minimum forging speed 5 mm/s, minimum force 20 t, separator: boron nitride.

Preferably, in the sixth step, flashes are additionally trimmed if necessary.

By selecting an appropriate scandium content in copper-chromium alloys, materials resistant to excessive zinc absorption into their surfaces were obtained.

The analysis of the phenomenon was developed on the basis of tests on the thickness of the zinc diffusion layer on the surface of copper-chromium-scandium alloys. In addition, charge materials in the form of the highest purity copper and Cr- and scandium-containing mortars are subjected to a melting process at a temperature of 1120-1400°C with preservation of the protective atmosphere and cooling conditions in the primary and secondary systems. An appropriate combination of the casting process temperature with the performance of the primary and secondary systems for cooling the copper-chromium-scandium alloys made it possible to obtain, after casting, materials with a structure characterising the supersaturated state. Not having to use an additional supersaturating operation on castings is an improvement to the entire technological process of cap electrode production. As a result of the use of high quality charge materials, as well as the selection of parameters for the melting and casting process, it was possible to obtain a high purity semi-finished product in which the oxygen content was within 0-100 ppm, usually around 25 ppm.

The solutions according to the invention are shown in the following implementation examples and in Tables 1-2 and Fig. 1:

Table 1 electrical and mechanical properties of materials produced according to examples 1 to 5 after casting, forging and ageing processes

Table 2 change in the zinc diffusion depth depending on the scandium content in the copper-chromium alloys (alloys 2 and 3)

Fig. 1 shows the results of tests on the influence of the scandium content in copper-chromium alloys (alloys 2 and 3) on the zinc diffusion depth

Example 1:

The material in the form of CuETP copper granules was melted at the temperature of 1120°C in a graphite crucible of an induction furnace. In the next step, chromium CuCr8 and zirconium CuZr10 mortars were added together with alloying additives in the form of Ni in the amount of 0.1 wt.% with 99% purity and Sc

in the amount of 0.01 wt.%. A graphite lance was used to mix the alloying components during the melting process, and the surface was sprinkled with lamellar graphite with a gradation of 0.3-0.5 mm, providing deoxidising conditions for the liquid bath. When the temperature of the liquid metal reached 1200°C, the horizontal casting process was initiated. In the horizontal casting process, a crystallisation system was used which was made of boron nitride with a threaded connection to the crucible of the casting furnace system. The casting speed was maintained at 1 mm per 0.1 s of standstill. The flow rate of the cooling medium in the crystallisation system, i.e. the primary cooling system, was 0.4 l/min and in the secondary cooling system was 1 l/min. 14mm diameter castings were subjected to electrical and mechanical property tests which showed that the obtained material was in a supersaturated state. This process resulted in a copper-scandium alloy (indicated in Fig. 1 and in Tables 1 and 2 as alloy 1). The oxygen content of the casting was estimated at 25 ppm. Scandium content of 0.01 wt.% allowed zinc diffusion to be reduced from 24 to 17 um by immersion in liquid pure zinc at the temperature of 450°C for 1 min. The measured value of zinc diffusion refers to the depth of its penetration into the scandium-copper structure, determined by linear EDS chemical composition measurement. The castings are subjected to a cutting process to the lengths required by the forging process. The single-operation forging process was carried out under the following conditions: die temperature 200°C, minimum forging speed 10mm/s, minimum force 20 t, separator: boron nitride, charge heating to 950°C. The forging operation was followed by the operations of flash trimming, ageing at 450°C for 5 hours and centrifugal smoothing with a pyramidal abrasive.

Example 2:

The material in the form of CuETP copper granules was melted at the temperature of 1120°C in a graphite crucible of an induction furnace. In the next step, chromium CuCr8 and zirconium CuZr10 mortars were added together with alloying additives in the form of Ni in the amount of 0.1 wt.% with 99% purity and Sc

in the amount of 0.05 wt.%. A graphite lance was used to mix the alloying components during the melting process, and the surface was sprinkled with lamellar graphite with a gradation of 0.3-0.5 mm, providing deoxidising conditions for the liquid bath. When the temperature of the liquid metal reached 1200°C, the horizontal casting process was initiated. In the horizontal casting process, a crystallisation system was used which was made of boron nitride with a threaded connection to the crucible of the casting furnace system. The casting speed was maintained at 1 mm per 0.1 s of standstill. The flow rate of the cooling medium in the crystallisation system, i.e. the primary cooling system, was 0.4 l/min and in the secondary cooling system was 1 l/min. 14mm diameter castings were subjected to electrical and mechanical property tests which showed that the obtained material was in a supersaturated state. This process resulted in a copper-scandium alloy (indicated in Fig. 1 and in Tables 1 and 2 as alloy 1). The oxygen content of the casting was estimated at 25 ppm. Scandium content of 0.01 wt.% allowed zinc diffusion to be reduced from 24 to 17 um by immersion in liquid pure zinc at the temperature of 450°C for 1 min. The measured value of zinc diffusion refers to the depth of its penetration into the scandium-copper structure, determined by linear EDS chemical composition measurement. The castings are subjected to a cutting process to the lengths required by the forging process. The single-operation forging process was carried out under the following conditions: die temperature 200°C, minimum forging speed 10mm/s, minimum force 20 t, separator: boron nitride, charge heating to 800°C. The forging operation was followed by the operations of flash trimming, ageing at 450°C for 5 hours and centrifugal smoothing with a pyramidal abrasive.

Example 3:

The material in the form of CuOFE copper granules was melted at the temperature of 1100°C in a graphite crucible of a resistance furnace. In the next step, the temperature of the liquid bath was raised to 1200°C and chrome CuCr8 and zirconium CuZr10 mortars and Sc were added in the amount of 0.15 wt.%. A

graphite lance was used to mix the alloying components during the melting process, and the surface was sprinkled with crushed graphite with a gradation of 1-5 mm, providing deoxidising conditions for the liquid bath. When the temperature of the liquid metal reached 1250°C, the horizontal casting process was initiated. In the horizontal casting process, a crystallisation system was used which was made of graphite with an internal insert of boron nitride. The internal insert of boron nitride was embedded inside the graphite crystalliser through a threaded connection. The connection between the crystalliser structure and the crucible is effected by pressing the crystalliser to the crucible. The casting speed was maintained at 20 mm per 30 s of standstill. The flow rate of the cooling medium in the crystallisation system, i.e. the primary cooling system, was 3 l/min and in the secondary cooling system was 1 l/min. 14mm diameter castings were subjected to electrical and mechanical property tests which showed that the obtained material was in a supersaturated state. As a result of these processes, a copper-chromium alloy with a Sc additive was obtained (indicated in Fig. 1 and in Tables 1 and 2 as alloy 1). The oxygen content of the casting was estimated at 7 ppm. Scandium content of 0.15 wt.% allowed zinc diffusion to be reduced from 24 to 7.3 um by immersion in liquid pure zinc at the temperature of 450°C for 1 min. The measured value of zinc diffusion refers to the depth of its penetration into the scandium-copper alloy structure, determined by linear EDS chemical composition measurement. The castings are subjected to a cutting process to the lengths required by the forging process. The single-operation forging process was carried out under the following conditions: die temperature 40°C, minimum forging speed 10 mm/s, minimum force 60 t, separator: boron nitride. The forging process is flashless. The forgings were subjected to the ageing process at the temperature of 480°C for 2 h, followed by a sandblasting operation.

Example 4:

The material in the form of CuETP copper granules was melted at the temperature of 1300°C in a graphite crucible of a casting furnace. In the next step,

alloying additives in the form of chromium CuCr8 and zirconium CuZr10 mortars and Sc in the amount of 0.1 wt.% were added. A graphite lance was used to mix the alloying components during the melting process, and the surface was sprinkled with charcoal with a gradation of 4-5 mm, providing deoxidising conditions for the liquid bath. The casting speed was maintained at 5 mm per 0.6 s of standstill. The flow rate of the cooling medium in the crystallisation system, i.e. the primary cooling system was 4 l/min and in the secondary cooling system was 2 l/min. 21 mm diameter castings were subjected to electrical and mechanical property tests which showed that the obtained material was in a supersaturated state. As a result of these processes, a copper-chromium alloy with a Sc additive was obtained (indicated in Fig. 1 and in Tables 1 and 2 as alloy 2). The oxygen content of the casting was estimated at 50 ppm. Scandium content of 0.01 wt.% allowed zinc diffusion to be reduced from 25 to 16 um by immersion in liquid pure zinc at the temperature of 450°C for 1 min. The measured value of zinc diffusion refers to the depth of its penetration into the scandium-copper alloy structure, determined by linear EDS chemical composition measurement. The castings are subjected to a cutting process to the lengths required by the forging process. The five-operation forging process without flash was carried out under the following conditions: die temperature 25°C, minimum forging speed 5 mm/s, minimum force 20 t, separator: boron nitride. The forgings were subjected to the ageing process at the temperature of 550°C for 1 h, followed by polishing operations with the use of an abrasive.

Example 5:

The material in the form of CuETP copper granules was melted at the temperature of 1300°C in a SiC crucible of a casting furnace. In the next step, alloying additives in the form of chromium CuCr8 and zirconium CuZr10 mortars and Sc in the amount of 0.05 wt.% were added. A graphite lance was used to mix the alloying components during the melting process, and the surface was sprinkled with charcoal with a gradation of 4-5 mm, providing deoxidising conditions for the liquid

bath with additional protection with an inert gas, i.e. argon, with a flow rate of min. 3 l/min. through the furnace chamber. Once the chemical composition has been obtained, the alloy is poured into a cooled mould with a diameter of 40 mm and a length of 60 mm. Castings were subjected to electrical and mechanical property tests which showed that the obtained material was in a supersaturated state. As a result of these processes, a copper-chromium alloy with a Sc additive was obtained (indicated in Fig. 1 and in Tables 1 and 2 as alloy 2). The oxygen content of the casting was estimated at 100 ppm. The scandium content of 0.05 wt.% allowed zinc diffusion to be reduced from 25 to 13.4 um by immersion in liquid pure zinc at the temperature of 450°C for 1 min. The measured value of zinc diffusion refers to the depth of its penetration into the scandium-copper alloy structure, determined by linear EDS chemical composition measurement.

The tables below show the electrical and mechanical properties of the materials produced according to examples 1 - 5 after the casting, forging and ageing processes, as well as the results of tests on the influence of zirconium content on the zinc diffusion depth.

Table 1

Example		**1**	**2**	**3**	**4**	**5**
Alloy		1	2	3	4	5
Cu	wt.%	99.49	99.49	99.0	99.59	99.2
Cr		0.3	0.3	0.7	0.3	0.7
Zr		0.1	0.1	0.05	0.1	0.05
Ni		0.1	0.1	0	0	0
Sc		0.01	0.05	0.15	0.1	0.05
Casting properties	Hardness HV 10	53	63	95	68	87
	Electrical conductivity γ, MS/m	30	24	21	23	23
Ageing conditions	**°C/h**	**450/5**	**450/5**	**480/2**	**550/1**	**-**
Properties after forging and ageing	Hardness HV 10	140	155	185	160	-
	Electrical conductivity γ, MS/m	47	45	43	41	-

Table 2

ALLOY 2	
Sc [wt.%]	D [µm]
0	24
0.01	17
0.05	15
0.1	9.7
0.15	7.3

ALLOY 3	
Sc [wt.%]	D [µm]
0	25
0.01	16
0.05	13.4
0.15	7.3

Claims

1. A copper-chromium alloy **characterised in that** it contains 99.1-99.49 wt.% of copper, 0.3-0.7 wt.% of chromium, 0.05-0.1 wt.% of zirconium and 0.01-0.15 wt.% of scandium.

2. The copper-chromium alloy according to claim 1, **characterised in that** it contains 0.1 wt.% of nickel.

3. The use of the copper-chromium alloy according to claim 1 for making cap electrodes.

4. A method of manufacturing the copper-chromium alloy according to claim 1, **characterised in that**

in the first step, copper is melted at a temperature of 1100-1300°C,

in the second step, 0.3-0.7 wt.% of chromium and 0.05-0.1 wt.% of zirconium and 0.01-0.15 wt.% of scandium are added, and the surface is sprinkled with graphite sprinkles and stirred with a graphite lance until the alloying components are completely melted.

5. A method of manufacturing the copper-chromium alloy according to claim 4, **characterised in that**

in the second step 0,1 wt.% of nickel is additionally added.

6. The method of manufacturing the copper-chromium alloy according to claim 4 or 5, **characterised in that**

in the third step, a casting process is carried out using a crystalliser made of boron nitride or boron nitride and graphite, at a casting speed of 1-20 mm at a standstill time of 0.1-30 s.

7. A method of making a cap electrode according to claim 4 or 5, or 6, **characterised in that**

in the fourth step, a forging process is carried out under the following conditions: die temperature 25-200°C, minimum forging speed 5 mm/s, minimum force 20 t, separator: boron nitride;

in the fifth step, the forgings are subjected to an ageing process at a temperature of 450-550°C for 1-5 h;

in the sixth step, the electrode surface is cleaned, preferably by polishing or smoothing.

8. The method of making a cap electrode according to claim 6 or 7, **characterised in that**

in the fourth step, a hot forging process is carried out by heating the charge to a temperature of 800-950°C.

9. The method of making a cap electrode according to claim 4 or 5, or 6, **characterised in that**

in the fourth step, a cold forging process is carried out under the following conditions: die at ambient temperature, minimum forging speed 5 mm/s, minimum force 20 t, separator: boron nitride;

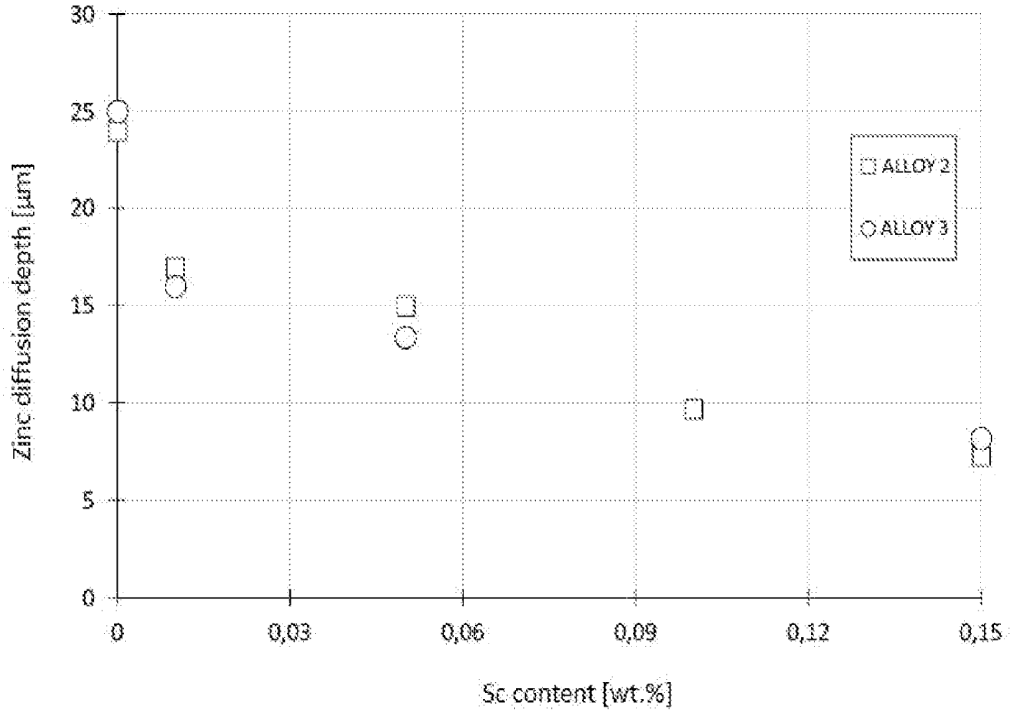
in the fifth step, the forgings are subjected to an ageing process at a temperature of 450-500°C for 1-5 h;

in the sixth step, the electrode surface is cleaned, preferably by polishing or smoothing.

10. The method of making a cap electrode according to claim 7 or 9, **characterised in that**

in the sixth step, flashes are additionally trimmed if necessary.

Fig. 1


30
25
20
15
10
5
0
Zinc diffusion depth [µm]
0
0,03
0,06
0,09
0,12
0,15
Sc content [wt.%]
ALLOY 2
ALLOY 3

INTERNATIONAL SEARCH REPORT

International application No
PCT/PL2021/050074

A. CLASSIFICATION OF SUBJECT MATTER
INV. C22C1/02 C22C9/00 C22F1/08
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C22C C22F B23K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CN 110 317 970 A (CHINA FAW GROUP CORP) 11 October 2019 (2019-10-11) claims 1,3, 4, 9; example 3	1-10
A	CN 109 385 555 B (GUANGDONG HUAXING HEAT EXCHANGE EQUIPMENT CO LTD ET AL.) 17 November 2020 (2020-11-17) paragraph [0022]; claim 1; examples 1-3	1-10
A	CN 110 747 365 B (UNIV CENTRAL SOUTH) 15 January 2021 (2021-01-15) claims 1-10; examples 1,2	1-10

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
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1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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