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(54) **HIGH-BONDING STRENGTH COPPER-ALUMINUM COMPOSITE CONDUCTIVE MATERIAL AND PREPARATION METHOD THEREFOR**

(57) Provided is a high-bonding strength copper-aluminum composite conductive material and a preparation method thereof. The high-bonding strength copper-aluminum composite conductive material includes a clad copper layer and an aluminum core matrix; an interatomic bonded metallurgical bonding layer is formed between the clad copper layer and the aluminum core matrix; the thickness of the bonding layer is 5~35 μ m, and the bonding strength is ≥ 40 MPa; a copper-aluminum intermetallic compound is dispersedly distributed in the bonding layer; the components of a diffusion layer close to the clad copper layer are uniform, and a thickness is narrow; and a diffusion layer close to the aluminum core matrix is of a reticular structure formed by a mixture of two or more

component phases, and a thickness is wide. The bonding between copper and aluminum in the copper-aluminum composite material achieves a metallurgical bonding state, and the corresponding bonding strength is greater than 40 MPa; a thickness of a side copper layer of the copper-aluminum composite material is about 1.6-2 times of a thickness of a planar copper layer; the thickness of the side clad copper layer is sufficient enough for large current impact and heat dissipation; and the elongation rate of the copper-aluminum composite material is greater than 30%; and the high-bonding strength copper-aluminum composite conductive material may carry out processing such as torsion, spiraling and side bending which are applied to the new field.

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Description

Technical Field

[0001] The present disclosure belongs to the technical field of composite materials, and in particular to a high-bonding strength copper-aluminum composite conductive material and a preparation method thereof.

Background

[0002] A copper-aluminum composite material is also named as a copper-clad aluminum bar or a copper-clad aluminum bus composited by copper on an outer layer and aluminum on a core. For an existing copper-aluminum composite material, the copper on the outer layer and the aluminum on the core are bonded mechanically in general, which is the so-called copper-clad aluminum. The copper on the outer layer and the aluminum on the core are bonded together via a pressure force under a solid-state action. With such a bonding manner, the bonding strength of a copper-aluminum interface is lower, and it is easy for the copper and the aluminum to appear a separation phenomenon under the action of an external force. By observing under a high-power microscope, it is not founded that a mutual diffusion layer is present between the copper and the aluminum. By amplifying the microscope to 500-1000 times and observing, an obvious gap exists at the copper-aluminum interface, which indicates that the bonding strength of the copper-clad aluminum material under a mechanical bonding manner is lower. According to a patent entitled as Improved Copper-Clad Aluminum Bar and Preparation Method Thereof (Application No.: CN201010591239.2), the operation of passing an aluminum rod through a molten copper solution to form a copper-aluminum composite is difficult. Since the melting point of the aluminum is 660°C and is far lower than the melting point 1083°C of the copper, when the aluminum rod passes through the molten copper solution, the aluminum rod may be molten and cannot be composited. With a copper-clad aluminum bar having such a structure, the bonding strength of the copper-aluminum interface cannot be guaranteed macroscopically and microscopically.

[0003] The existing copper-aluminum composite material in various application fields needs to be conventionally bent, punched, milled, hank hnotting, riveted and the like. Along with the continuous improvement of the use requirement of the product, machining manners such as torsion, spiraling and side bending are pushed forward, which requires that the copper-aluminum composite material can have better deformability and higher bonding strength and a copper-aluminum interface when the machining is completed is not damaged. However, the elongation rate of the common copper-aluminum composite material is 3-20%, so that the machining requirement of the torsion, spiraling and side bending is met difficultly. Moreover, it is easy for a surface of the

machined product to occur an orange peel defect, and the copper-aluminum interface easily occur a cracking separation phenomenon. For such a poor product, the density of a current on the surface of the product is extremely uneven in use. The density of a current at a cracking separation site is relatively large, so that the separation site is heated and even is burnt through. In addition, the copper and the aluminum at the cracking separation site may further be corroded electrochemically to cause a safety accident.

[0004] As mentioned above, the existing copper-aluminum composite material has the following defects: (1) the bonding performance between the copper and the aluminum is poor, the metallurgical bonding state fundamentally required by the composite material is not achieved, and the corresponding bonding strength is also lower; (2) for a flat wide copper-aluminum composite material, a thickness of a clad copper layer has a design problem; the thickness of a clad copper layer on a narrow surface is smaller and the current density is larger, which are not sufficient to allow high-current impact; and moreover, the clad copper layer on a narrow surface is easily heated and the heat dissipation performance is poorer; and (3) with the machining performance of the existing copper-aluminum composite material, only machining such as conventional bending, punching, milling, riveting and tapping can be implemented, and the machining such as torsion, spiraling and side bending applied in the new field cannot be implemented.

[0005] There are following several methods to produce the copper-aluminum composite material approximately at present: (1) clad welding method: a copper sheet is coated on an outer surface of an aluminum rod, a joint of the copper sheet is welded by a welding method, and then drawing and moulding are performed for multiple times; (2) sleeve rolling method: an aluminum rod is sleeved to a copper pipe, and the copper pipe and the aluminum rod are solid-phase bonded and moulded by rolling; (3) core-filled casting method: a bottom end of a copper pipe is sealed, a molten aluminum solution is poured into the copper pipe and after the aluminum solution is solidified, a copper-aluminum composite bar billet is formed; and then, rolling, drawing and moulding are performed; (4) hydrostatic extrusion method: a large-diameter copper pipe and a pure aluminum rod are extruded and are moulded under a large pressure by using a large extrusion device; and (5) a copper layer is electroplated on a surface of an aluminum core and then drawing and moulding are performed.

[0006] A solid-state bonding method is substantially adopted by the above first method and second method, i.e., solid-state copper and aluminum are bonded mechanically by virtue of an external pressure, no obvious mutual diffusion layer is present between the copper and the aluminum, and the bonding strength is very low. In the above third method, the process of pouring the aluminum solution is not continuous and stable, so that the copper pipe is easily burnt through. Moreover, the length

in one casting is limitable, so the problems of low yield, low production efficiency and unstable product performance are caused. There is no report for the fourth method in China. However, a hydrostatic extrusion technology has an application in British. The copper and the aluminum are solid-phase bonded by Bruker by using a large hydrostatic extrusion machine to extrude and deform the copper pipe and the core aluminum rod, and then are moulded into the copper-aluminum composite material via various moulds. Such a method is highly demanding on a use device, cannot implement continuous production, has low production efficiency, large loss, complex process requirement and high manufacturing cost, and thus is not suitable for large batch production. For the fifth method, a thickness of the electroplated copper layer is limitable, and the general electroplated thickness is far smaller than the thickness of a copper pipe used by other methods; and moreover, the copper layer is dropped easily, so that the quality problem of the product cannot be guaranteed.

Summary

[0007] In order to solve the above problems, the present disclosure provides a high-bonding strength copper-aluminum composite conductive material and a preparation method thereof.

Solutions for problems

Technical solutions

[0008] The technical solutions of the present disclosure are implemented as follows: a high-bonding strength copper-aluminum composite conductive material includes a clad copper layer and an aluminum core matrix; an interatomic bonded metallurgical bonding layer is formed between the clad copper layer and the aluminum core matrix; a thickness of the bonding layer is 5~35 μm , and a bonding strength is $\geq 40\text{Mpa}$; a copper-aluminum intermetallic compound is dispersedly distributed in the bonding layer; the components of a diffusion layer close to the clad copper are uniform, and a thickness is narrower; a diffusion layer close to the aluminum core matrix is of a reticular structure formed by a mixture of two or more component phases, and a thickness is wider; and a thickness of a side copper layer of the flat wide copper-aluminum composite material is about 1.6~2 times of a thickness of a planar copper layer.

[0009] A method for preparing a high-bonding strength copper-aluminum composite conductive material includes the following technological steps.

1) Aluminum melting

[0010] Adding a raw material of an aluminum ingot into an aluminum melting furnace for melting, according to a proportion of 0.15‰~0.5‰ of AlB_3 and 0.3‰~0.7‰ of

NH_4Cl , adding the AlB_3 and the NH_4Cl to the aluminum melting furnace; performing high-purity impurity removal and degassing, wherein a furnace addition amount at each time is 100 kg~400 kg and a rotational speed of a corresponding degassing stirring rod is 100~400 r/min; controlling a flow of a high-purity argon gas to a degassing stirrer at 0.1~0.5 L/min, controlling the degassing time at 15~20 min, and an aluminum solution after deslagging and degassing can be used; and controlling a temperature of the aluminum solution at 770~820° C and at this moment, controlling a power of the aluminum melting furnace at 50~70 kw.

2) Copper melting

[0011] Adding a raw material of a standard cathode electrolytic copper plate to an oxygen-free copper melting furnace, and polishing verdigris and pollutant on a surface of the electrolytic copper plate by a polishing machine, wherein a furnace body of the copper melting furnace is divided into three portions that are a melting area, a heat preservation area and a standing area; 3~5 mins per material feeding interval, keeping a temperature of the copper solution at 1150~1180° C and flowing the molten copper solution to the heat preservation area; and at this moment, there is a need for temperature adjustment, and flowing the copper solution after heat preservation to the standing area to leach out the copper for use.

3) Copper-aluminum compositing

[0012] compositing the copper solution in the step 2 and the aluminum solution in the step 2 via a respective flowing channel, wherein the copper solution enters a composition cavity via a copper flowing pipeline, the aluminum solution enters the composition cavity via an aluminum flowing pipeline at core, the copper solution and the aluminum solution in a composition furnace pass through a composition mould, a peripheral crystallizer, a twice-triple cooling device to form a copper-aluminum composite bar billet of which the outer layer is the copper and the core is the aluminum, controlling a composite casting temperature at $1200 \pm 5^\circ \text{C}$, controlling a temperature of the returned water of cooling water of the crystallizer at 50~60° C, controlling a flow at 4~8 L/min, the twice-triple cooling device is connected with the crystallizer, a flow of the cooling water of the twice-triple cooling device is 12~25 L/min, and a pulling speed of the bar billet is 110~180 mm/min.

4) Copper-aluminum composite bar billet rolling

[0013] rolling the copper-aluminum composite bar billet prepared in the step 3, , a rolling is a two-roll reversing rolling mill, wherein a material reversing device is mounted at two sides of the rolling mill respectively, the rolling mill may reverse a material automatically, and rolls are of a box-type pass shape; rolling the copper-aluminum

composite bar billet having a rectangular cross section into a copper-aluminum composite intermediate product having a flat wide cross section, wherein a roll gap during rolling is generally set as 2~3 mm and a rolling speed is 10~40 m/min.

5) Side surface layer treatment

[0014] rotating incoming material at a side of a rolled copper-aluminum composite material at a constant speed in a pressed state under the transmission of a transfer roll, and entering a side surface layer treatment device, wherein a grinding wheel of the device contacts the side of the rolled copper-aluminum composite material, and with the high-speed rotation of the grinding wheel, polishing and grounding a surface layer of a contact surface of the incoming material.

6) Planar surface layer treatment

[0015] for a semi-finished copper-aluminum composite bar treated in the step 5, after a side edge is polished and ground, upper and lower surface still needs to be treated. Sending the incoming material enters a planar treatment device via a pull roll leader and pressing the incoming material via upper and lower rolls so as to prevent the incoming material from swinging up and down, wherein the transmission speed of the incoming material is 3~5 m/min, and performing the incoming material move forward at a constant speed under the pull of a transmission device; and milling surface layers of copper layers on upper and lower planes via machining devices on upper and lower planes, wherein a amount of feed of a milling cutter is 0.10~0.15 mm, and a milled amount of the copper layers is 0.1~0.15 mm.

7) Drawing

[0016] drawing the incoming material after being treated in the step 6, wherein the machining rate for a drawing amount at the first time is controlled at 25%~30% and the machining rate is $\leq 30\%$; and coiling or sawing the pulled material into a straight material having a certain length, wherein the whole drawing, coiling and sawing processes all are controlled automatically and may work continuously.

8) Annealing

[0017] annealing is the most important procedure before moulding; an annealing temperature is 295~345° C and an annealing heat preservation time is 3~4.5 h; and then, spraying water to a tank to cool to a room temperature.

9) Surface cleaning

[0018] placing a copper-aluminum composite bar in

the step 8 into a guide groove via an automatic loading mechanism, starting a device, and under the driving of a delivery wheel, first passing the copper-aluminum composite bar through an alkali washing box, wherein a hairbrush and an air knife are provided in a box body, the hairbrush is configured to brush surface oil stain and the air knife blows a surface of the copper-aluminum composite bar to be dry; then, passing the copper-aluminum composite bar through a water spraying device, and washing a residual alkali solution on the surface with water and blowing the copper-aluminum composite bar to be dry to enter an acid cleaning box, wherein a hairbrush and an air knife are also provided in the acid cleaning box; after acid cleaning treatment, washing the copper-aluminum composite bar with the water and blowing be dry again to enter a passivation box, wherein a passivation solution is prepared with a passivation process in the passivation box; after spraying and passivation, drying the copper-aluminum composite bar automatically, and discharging from the passivation box under the pull of a conveyor belt; and then, placing the copper-aluminum composite bar after surface cleaning and passivation onto a receiving rack via an automatic material receiving device.

[0019] Preferably, the machining rate in the drawing process is as follows: when thickness $h \geq 10$ mm, $25\% > \text{machining rate} \leq 30\%$; when $6 \text{ mm} \leq \text{thickness } h < 10$ mm, $20\% > \text{machining rate} \leq 25\%$; when $3 \text{ mm} \leq \text{thickness } h < 6$ mm, $15\% > \text{machining rate} \leq 20\%$; and when thickness $h < 3$ mm, $\text{machining rate} \leq 15\%$.

[0020] Preferably, tank annealing and online induction annealing are adopted by the annealing process.

[0021] Preferably, the online induction annealing is adopted by a copper-aluminum composite bar of which the width of the specification above 80 mm; and the tank annealing is adopted by a copper-aluminum composite bar of which the specification below 80 mm.

[0022] Preferably, the rolling process is a pass type nine-course rolling process.

[0023] Preferably, a coil drawing process, a hydraulic drawing process and a crawler drawing process may be adopted by the drawing process. When the width ≤ 30 mm, the coil drawing or hydraulic drawing or crawler drawing is adopted; when $30 \text{ mm} < \text{width} \leq 120 \text{ mm}$, the hydraulic drawing or crawler drawing is adopted; $6 \text{ m/min} \leq \text{coil drawing speed} \leq 60 \text{ m/min}$; $50 \text{ m/min} \leq \text{crawler drawing speed} \leq 80 \text{ m/min}$, and hydraulic drawing speed $\leq 8 \text{ m/min}$.

Beneficial effects of the disclosure

Beneficial effects

[0024] The present disclosure has the following beneficial effects: the bonding between copper and aluminum in the copper-aluminum composite material achieves a metallurgical bonding state, and the corresponding bonding strength is greater than 40 MPa; a thickness of a side copper layer of the copper-aluminum composite material

is thicker than a thickness of a planar copper layer, and is about 1.6~2 times of the thickness of a planar copper layer; the thickness of the side clad copper layer is sufficient enough for large current impact and heat dissipation; and the elongation rate of the copper-aluminum composite material is greater than 30%; and the high-bonding strength copper-aluminum composite conductive material may carry out processing such as torsion, spiraling and side bending which are applied to the new field.

1) With special treatment and formulated degassing process on the aluminum solution, the purified aluminum with a high purity and low gas content is obtained from the aluminum solution; and meanwhile, for the control of the cooling amount of the furnace body, the energy consumption and the heat loss are reduced by 6-8%.

2) The verdigris and the pollutant on the surface of the electrolytic copper plate are polished by the polishing machine, and the furnace body of the melting furnace is divided into the three portions, so that a melting, adjusting and stabilizing state is implemented; with a sealing furnace cover, the surface layer of the molten copper solution is covered by graphite beads and charcoal to prevent oxidation and thus the effects of low hydrogen and low oxygen are achieved; and by controlling the hydrogen and oxygen contents to below 10 PPM and reducing the gas content of the copper solution, a subsequent product may be prevented from appearing a potential bubble.

3) The temperature of the copper-aluminum composite is controlled at $1200 \pm 5^\circ \text{C}$, so it may be assured that the flowability of the copper solution and the aluminum solution is the best and the degree of superheat meets the solidification requirement; the twice-triple cooling flow is about 3 times of the cooling flow of the crystallizer and the cooling water flow is about 12~25 L/min, so the crystallization potential heat produced in solidification of an aluminum core is brought away and the cooled bar billet is in a normal temperature state.

4) The obvious diffusion layer, i.e., the metallurgical bonding layer which present between copper and aluminum matrixes is implemented with the cooperation of a casting temperature and cooling, and the interatomic bonding is implemented between the copper and the aluminum; the composite casting temperature is controlled at $1200 \pm 5^\circ \text{C}$, the pulling speed is controlled at 110~180 mm/min, the temperature of the returned water of the cooling water of the crystallizer is controlled at $50 \sim 60^\circ \text{C}$, the flow is controlled at 4~8 L/min, the thickness of the bonding layer is required to be controlled at $5 \sim 35 \mu\text{m}$ in terms of the thickness of the copper-aluminum bonding layer.

5) The box-like pass shape is adopted by the rolls, so the interface bonding strength of the copper-alu-

minum composite bar is enhanced and the bonding strength is greater than 40 Mpa (the bonding strength of a copper-aluminum composite bar prepared with other methods is difficultly achieved); and meanwhile, the rolling reduction in subsequent rolling at each time may be alleviated, and the cracking phenomenon due to large rolling reduction and material hardening in subsequent rolling is prevented.

6) The side treatment and the planar treatment replace the traditional surface treatment manner, the machining speed is improved by 2.2 times, the defects such as indentation, casting line and triangular crack on the surface of the material are completely eliminated.

7) The drawing process may work automatically and continuously; moreover, rolling and unrolling devices are provided; a roll material may be rolled; when a straight material is provided, it may be sized and sawn according to a production requirement; and theoretically, a limitless long material may be unloaded.

Detailed Description of the Embodiments

Detailed Description of the Embodiments

[0025] For better understanding and implementation, the high-bonding strength copper-aluminum composite conductive material and the preparation method thereof provided by the present disclosure will be described below in detail. The high-bonding strength copper-aluminum composite conductive material provided by the present disclosure includes an aluminum bar matrix and a copper layer; an interatomic bonded metallurgical bonding layer is formed between a clad copper layer and an aluminum core matrix; the thickness of the bonding layer is controlled at $25 \mu\text{m}$; the bonding layer is different from common copper-aluminum bonding and requires that the bonding strength is 40 MPa; and copper-aluminum intermetallic compounds CuAl_2 , Cu_9Al_4 and CuAl are dispersed in the bonding layer.

[0026] Casting moulds having unequal thicknesses of copper layers are designed. According to a manner of alternatively rolling a horizontal hole and a vertical hole in subsequent machining, a product having a narrow surface copper with a thicker layer is produced, wherein the thickness of a side copper layer of a copper-aluminum composite bar is 1.8 times of the thickness of a planar copper layer. The product meets an electrical theory such as "skin effect", and the problems of difficult heat dissipation and insufficient current carrying of a narrow surface of a flat wide copper-aluminum composite material are solved.

[0027] The preparation method of the high-bonding strength copper-aluminum composite conductive material in the present disclosure includes the following steps.

I. Copper-aluminum composite bar billet casting

1. Aluminum melting

[0028] A raw material of a 1070 model (or equivalent 1060 model) aluminum ingot is added to an aluminum melting furnace for melting, wherein according to a proportion of 0.3% of AlB_3 and 0.5% of NH_4Cl , adding the AlB_3 and the NH_4Cl to the aluminum melting furnace, the aluminum melting furnace is a medium-frequency induction melting furnace, a rated power of the aluminum melting furnace is 500 KW, a furnace addition amount at each time is 200 kg and a rotational speed of a corresponding degassing stirring rod is 200 r/min; a high-purity argon gas is charged to a degassing stirrer till a flow is controlled at 0.2 L/min, wherein a degassing time is controlled at 18 min, and with corresponding parameter matching, a gas of the aluminum solution in each furnace may be removed completely; and a temperature of the aluminum solution is controlled at 780°C and at this time, the power of the aluminum melting furnace is adjusted to 60 kw. The temperature in the control range may meet the temperature requirement of a continuous casting process; and in addition, by reducing the cooling water, the heat loss may be decreased and the energy consumption is lowered to the greatest extent.

2) Copper melting

[0029] A raw material of a standard cathode electrolytic copper plate is added to a melting area of an oxygen-free copper melting furnace, and verdigris and pollutant on a surface of the electrolytic copper plate are polished by a polishing machine, 3-5 mins per material feeding interval, a molten copper solution is flowed to a heat preservation area, and the copper solution after heat preservation is flowed to a standing area to leach out the copper for use; a furnace body of the copper melting furnace is divided into three portions that are the melting area, the heat preservation area and the standing area. The electrolytic copper plate is added to the melting area, a temperature of the copper solution is kept at $1150\sim 1180^\circ\text{C}$ and a temperature of the heat preservation area and the standing area is kept at $1200\pm 10^\circ\text{C}$. With such a control, a crystallization potential required for a solidification process of the copper solution may be compensated; and in addition, a heat energy required for a copper-aluminum composition process may be supplemented and the metallurgical bonding is implemented.

[0030] The furnace body of the whole copper melting furnace is provided with a sealed furnace cover, and a surface layer of the molten copper solution is covered by graphite beads and charcoal for protection to prevent the copper solution from oxidizing and sucking gas, so that the effects of low hydrogen and low oxygen are achieved; and by controlling the hydrogen and oxygen contents to below 10 PPM and reducing the gas content of the copper solution, a subsequent product may be prevented from

appearing a potential bubble.

3. Copper-aluminum compositing

[0031] The copper solution and the aluminum solution in the step 1 and the step 2 are composited via a respective flowing channel, wherein the copper solution is cooled by a crystallizer to form a solidified copper pipe, the core aluminum solution enters the copper pipe via an aluminum flowing pipeline and then passes through a copper sleeve inside the crystallizer, and the copper pipe is cooled to form the solidified core aluminum; and at last, the copper pipe and the core aluminum are cooled by a twice-triple cooling device to form a copper-aluminum composite bar billet. The copper solution enters a composition cavity via a copper flowing pipeline, and a composition casting temperature is controlled at 1205°C ; the aluminum solution enters the composition cavity via an aluminum flowing pipeline at core, and the copper solution and the aluminum solution in a composition furnace pass through a composition mould, a peripheral crystallizer, the twice-triple cooling device to form the copper-aluminum composite bar billet of which the outer layer is the copper and the core is the aluminum.

[0032] A temperature of the returned water of cooling water of the crystallizer is controlled at 55°C , a flow is controlled at 6 L/min, the twice-triple cooling device are connected with the crystallizer, a flow of the cooling water of the twice-triple cooling device is about 18 L/min and is three times of a flow of the cooling water of the crystallizer, and a pulling speed of the bar billet is controlled at 150 mm/min. An obvious mutual diffusion layer, i.e., the metallurgical bonding layer, is present between the copper matrix and the aluminum matrix; the interatomic bonding is implemented between the copper and the aluminum; intermetallic compounds CuAl_2 , Cu_9Al_4 and CuAl are dispersedly distributed in the bonding layer; the components of a diffusion layer close to the copper matrix are uniform, and the thickness is narrower; a diffusion layer close to the aluminum matrix is of a reticular structure formed by a mixture of two or more components, and the thickness is wider.

II. Rolling

1) Cogging down and rolling

[0033] The A1 is reversed for 90° via a material reversing device of a reversing mill, an appropriate roll gap is adjusted, vertical pass type E rolling is adopted, and according to different billet specifications and rolling specifications, a reduction rate is also obviously different. Generally, when a small billet is used for rolling a large copper-aluminum composite bar, since the rolling material needs to be sufficiently broadened, the reduction rate is smaller. When a large billet is used for rolling a small copper-aluminum composite bar, since the rolling material needs to be narrowed, the reduction rate is relatively

large and the reduction rate is 5%~23%. The inclination of a sidewall of the vertical pass type E generally is 3°~9°. The larger the inclination of the sidewall, the higher the demand on the material reversing device; moreover, after the material is reversed, the operation of the rolling material is unstable and the rolling material is aligned difficultly when entering a next pass; and when the rolling material is gripped, it is easy to occur distortion. Besides, with the larger inclination, the wear of the rolling material on the pass sidewall is more serious and it is easier to attach the copper on the pass sidewall and is disadvantageous for the bonding strength of the rolling material, which is mainly manifested in vertical rolling. For horizontal pass, since the groove depth is smaller, such a condition is not obvious in horizontal rolling. Additionally, the inclination of the sidewall is not too small because the excessively small inclination of the sidewall prevents the rolling material from being gripped and thrown out and is disadvantageous for redressing of the rolls to cause poor utilization rate of the rolls.

2) First vertical pass type rolling (vertical rolling)

[0034] The A1 is reversed for 90° via the material reversing device of the reversing mill, the vertical pass type E rolling is adopted, the reduction rate is between 20%, the inclination of the sidewall of the vertical pass type E is between 7° generally, and the rolling material after the first vertical rolling is called as A2.

3) Second horizontal rolling

[0035] The A2 is reversed for 90° via the material reversing device of the reversing mill, an appropriate roll gap is adjusted, the horizontal pass type F rolling is adopted, the reduction rate is between 55% and the inclination of the sidewall of the horizontal pass type F is between 14°. The surface of the rolling material after this time of rolling becomes smooth from a rough state, and at this moment, the prepared rolling material is called as A3.

4) Second vertical rolling

[0036] The A3 is reversed for 90° via the material reversing device of the reversing mill, an appropriate roll gap is adjusted, the vertical pass type G rolling is adopted, the reduction rate is between 15% and the inclination of the sidewall of the horizontal pass type G is between 5°. At this moment, the prepared rolling material is called as A4.

5) Third horizontal rolling

[0037] The A4 is reversed for 90° via the material reversing device of the reversing mill, an appropriate roll gap is adjusted, the horizontal pass type H rolling is adopted, the reduction rate is between 22% and the inclination of the sidewall of the horizontal pass type H is

between 13°. At this moment, the prepared rolling material is called as A5.

6) Third vertical rolling

[0038] The A5 is reversed for 90° via the material reversing device of the reversing mill, an appropriate roll gap is adjusted, the vertical pass type I rolling is adopted, the reduction rate is between 8% generally and the inclination of the sidewall of the vertical pass type I is between 5°. At this moment, the prepared rolling material is called as A6.

7) Fourth horizontal rolling

[0039] The A6 is reversed for 90° via the material reversing device of the reversing mill, an appropriate roll gap is adjusted, the horizontal pass type J rolling is adopted, the reduction rate is between 16% and the inclination of the sidewall of the horizontal pass type J is 8°~10°. At this moment, the prepared rolling material is called as A7.

8) Fourth vertical rolling

[0040] The A7 is reversed for 90° via the material reversing device of the reversing mill, an appropriate roll gap is adjusted, the vertical pass type K rolling is adopted, the reduction rate is between 6% generally and the inclination of the sidewall of the vertical pass type K is between 3°. This time is the last time of vertical rolling and thus it is necessary to strictly control the narrowing size of the rolling material. At this moment, the prepared rolling material is called as A8.

9) Fifth horizontal rolling

[0041] The A8 is reversed for 90° via the material reversing device of the reversing mill, an appropriate roll gap is adjusted, the horizontal pass type L rolling is adopted, the reduction rate is between 15% generally and the inclination of the sidewall of the horizontal pass type L is between 12°. This time is the last time of rolling before drawing and thus it is necessary to strictly control the discharge size of the rolling material, i.e., an appropriate drawing amount is reserved, and obvious influence will be occurred on a surface state of the drawing material. At this moment, the prepared rolling material is called as A9.

III. Side polishing

[0042] The copper-aluminum composite rolling material after being rolled enters side polishing machines under the transmission of a transfer roll, where the side polishing machines are divided into four groups, and the former two groups of the side polishing machines grind the upper side and the later two groups of the side pol-

ishing machines grind the lower plane; the polishing material is a sandpaper flap wheel; the grinding amount for narrow edges is controlled at 0.12 mm; each of the side polishing devices that are used is provided with a pressing device, which may prevent the copper-aluminum composite rolling material from swinging up and down or left and right; the grinding amount of each of the narrow edges is performed in groups so as to prevent excessively large grinding amount at each single time; and the grouped side grinding refers to that two narrow edges are ground alternatively.

IV. Milling

[0043] The incoming material is a rolled copper-aluminum composite bar, and enters a mill via a pull roll leader; the incoming material is pressed via upper and lower rolls so as to prevent it from swinging up and down; the transmission speed of the incoming material is 4 m/min; a milling cutter is mounted on a circular roll cutting tool; a spiral blade is provided on a surface of a roll cutter, and the roll cutter is a circular roll milling cutter. The milling cutters are divided into two groups, where the first group machines the upper plane and the second group machines the lower plane; the amount of feed of each of the milling cutters is 0.13 mm; the milled amount of the copper layer is 0.12 mm; and copper scales on a milling surface is recycled by a blower via a pipeline.

V. Drawing

[0044] A drawing process includes the following steps.

1) Rolling a head. The rolled head of the incoming material is 250 mm, the copper and the aluminum at the head rolling end of the incoming material are bonded, and the separation phenomenon between the copper and the aluminum cannot be observed by visual inspection; the optimal thickness of the rolled head is 0.3 mm smaller than a thickness of a mould; and the optimal length of the rolled head is 120 mm exposed out after the rolled head enters the mould, so that the rolled head is drawn easily and no snap phenomenon is occurred.

2) Drawing. The drawing amount at the first time may be large; it is appropriate to control the machining rate at about 25% and the machining rate is not greater than 30% at maximum. When the thickness is 12 mm, the machining rate ϕ ($\phi = (1 - F1/F0) * 100\%$) should be controlled at 25%. However, it is noted that the drawing amount of the thickness should not be greater than 4 mm as much as possible; and moreover, with the smaller and smaller thickness, and the more and more drawing times, the machining rate should be smaller.

3) Receiving material. Automatic sawing is adopted by material receiving, and it is required that the blanking length is between 6 m; after the straight materials

are drawn, three straight materials are selected at random to check a flatness, a length and a performance, so that the flatness, the length and the performance of each of the straight materials meet the production requirement. It is required by the flatness that the curvature of a narrow edge within any 1 m length should not be greater than 2 mm, and a curvature of a wide edge should not be greater than 5 mm; and a length tolerance is required to be $\pm 0.3\%$ of the blanking length.

VI. Annealing

[0045] Online induction annealing is adopted by a copper-aluminum composite bar of which the width of the specification is above 80 mm. For example, a copper-aluminum composite bar of which the width is 100 mm passes through an induction coil area via a delivery bearing to generate an induction current inside the copper-aluminum composite bar to heat, an induction annealing current is set at 140 A, and the copper-aluminum composite bar is quickly cooled by a water-spray cooling device at an outlet to achieve the quick-heating and quick-cooling annealing effect. A transmission speed of the incoming material in induction annealing is 45 mm/s. In the online induction annealing, the temperature of the copper-aluminum composite bar can be monitored timely via an infrared temperature measurer at a discharge port, and an annealing temperature is approximately set at 295-345°C.

[0046] Tank annealing is adopted by a copper-aluminum composite bar of which the width is below 80 mm. For example, for a copper-aluminum composite bar of which the width is 60 mm, the copper-aluminum composite bar is sized at 6.3 m, then put onto a material rack and placed into a heated tank via a gantry crane. An annealing heat preservation time of the tank bright annealing is about 4.2 h according to different charge batches, the composite bar is delivered to a heating hearth via a control cabinet button, the vacuum is pumped for 12 min, an argon gas is charged to 0.12 MPa, an annealing temperature is set at 330°C according to the specification of the copper-aluminum composite bar, the heating heat preservation time is set according to the charge batch and the tank bright annealing is performed. With tank water-spray cooling, the water is sprayed all around via spray cooling pipelines, so that the tank is guaranteed to be cooled quickly and uniformly.

[0047] By changing a heat treatment method, the plastic property of the material is improved. With the online induction annealing, a temperature of the material is improved to about 350°C within a very short time (6~10 s in general); and then, the material is cooled by water quickly to a normal temperature. With such an annealing method, crystal particles inside the copper layers are recrystallized again and it is too late to grow the crystal particles; and meanwhile, the bonding layer on the copper-aluminum interface is not damaged. Therefore, the

plastic machining property of the material is good. With such an annealing method, the elongation rate of the copper-aluminum composite material may be controlled at 30~35%, and the requirements of machining manners such as torsion, spiraling and side bending may be met.

VII. Surface cleaning

[0048] The copper-aluminum composite bar is placed on a platform of an automatic loading mechanism; automatic loading and material receiving devices suck the surface of the copper-aluminum composite bar via vacuum suction plates, and are moved up and down or left and right via lead screws. The copper-aluminum composite bar is placed into a guide groove, and under the driving of a delivery wheel, the copper-aluminum composite bar first passes through an alkali washing box, where a hairbrush and an air knife are provided in a box body, the hairbrush is configured to brush surface oil stain and the air knife blows the surface of the copper-aluminum composite bar to be dry; then, the copper-aluminum composite bar passes through a water spraying device, and a residual alkali solution on the surface is cleaned with water and the copper-aluminum composite bar is blown to be dry to enter an acid cleaning box, where a hairbrush and an air knife are also provided in the acid cleaning box; after acid cleaning treatment, the copper-aluminum composite bar is washed with the water and blown to be dry again to enter a passivation box; in the passivation box, a passivation solution is sprayed to the surface of the copper-aluminum composite bar; after spraying and passivation, the copper-aluminum composite bar is dried automatically, and is discharged from the passivation box under the pull of a conveyor belt; and then, the copper-aluminum composite bar after surface cleaning and passivation is placed onto a receiving rack via the automatic material receiving device; and therefore, the whole surface cleaning process is completed.

Claims

1. A high-bonding strength copper-aluminum composite conductive material, comprising a clad copper layer and an aluminum core matrix, wherein an interatomic bonded metallurgical bonding layer is formed between the clad copper layer and the aluminum core matrix; the thickness of the bonding layer is 5~35 μm , and the bonding strength is $\geq 40\text{Mpa}$; a copper-aluminum intermetallic compound is dispersedly distributed in the bonding layer; the components of a diffusion layer close to the clad copper layer are uniform, and a thickness is narrow; a diffusion layer close to the aluminum core matrix is of a reticular structure formed by a mixture of two or more component phases; and a thickness is wide; and a thickness of a side copper layer of the wide flat copper-aluminum composite material is about 1.6~2

times of a thickness of a planar copper layer.

2. A preparation method of a high-bonding strength copper-aluminum composite conductive material as claimed in claim 1, comprising the following technological steps:

1) aluminum melting

adding a raw material of an aluminum ingot to an aluminum melting furnace for melting, according to a proportion of 0.15‰~0.5‰ of AlB_3 and 0.3‰~0.7‰ of NH_4Cl , adding the AlB_3 and the NH_4Cl to the aluminum melting furnace; performing high-purity impurity removal and degassing, wherein a furnace addition amount at each time is 100 kg~400 kg and a rotational speed of a corresponding degassing stirring rod is 100~400 r/min; controlling a flow of a high-purity argon gas to a degassing stirrer at 0.1~0.5 L/min, controlling the degassing time at 15~20 min, and an aluminum solution after deslagging and degassing can be used; and controlling a temperature of the aluminum solution at 770~820° C and controlling the power of the aluminum melting furnace at 50~70 kw;

2) copper melting

adding a raw material of a standard cathode electrolytic copper plate to an oxygen-free copper melting furnace, and polishing verdigris and pollutant on a surface of the electrolytic copper plate by a polishing machine; then, adding the electrolytic copper plate to a melting area, keeping a temperature of a copper solution at 1150~1180° C, flowing the molten copper solution to a heat preservation area, and flowing the copper solution after heat preservation to a standing area to leach out the copper for use;

3) copper-aluminum compositing

compositing the aluminum solution in the step 1 and the copper solution in the step 2 via a respective flowing channel, wherein the copper solution enters a composition cavity via a copper flowing pipeline, the aluminum solution enters the composition cavity via an aluminum flowing pipeline at core, the copper solution and the aluminum solution in a composition furnace pass through a composition mould, a peripheral crystallizer, a twice-triple cooling device to form a copper-aluminum composite bar billet of which the outer layer is the copper and the core is the aluminum, controlling a temperature of compositing casting at 1195~1205° C, controlling a temperature of the returned water of cooling water of the crystallizer at 50~60° C, controlling a flow at 4~8 L/min, the twice-triple cooling device is connected with the crystallizer, the flow of the cooling water of the twice-triple cooling device is 12~25 L/min, and controlling a pulling speed

of the bar billet is 110-180 mm/min.

4) copper-aluminum composite bar billet rolling
rolling the copper-aluminum composite bar billet
prepared in the step 3, a rolling mill is two-roll
reversing rolling mill, wherein a material reversing
device is mounted at two sides of the rolling
mill respectively, the rolling mill may reverse a
material automatically, and rolls are of a box-
type pass shape; rolling the copper-aluminum
composite bar billet having a rectangular cross
section into a copper-aluminum composite in-
termediate product having a flat wide cross sec-
tion, wherein setting a roll gap during rolling as
2~3 mm and the rolling speed as 10~40 m/min;
5) side surface layer treatment

rotating an incoming material at a side of a rolled
copper-aluminum composite material at a con-
stant speed in a pressed state under the trans-
mission of a transfer roll, and entering a side
surface layer treatment device, wherein a grind-
ing wheel of the device contacts the side of the
rolled copper-aluminum composite material,
and with the high-speed rotation of the grinding
wheel, polishing and grounding a surface layer
of a contact surface of the incoming material;

6) planar surface layer treatment
for a semi-finished copper-aluminum composite
bar treated in the step 5, after a side edge is
polished and ground, upper and lower surface
still needs to be treated; sending the incoming
material enters a planar treatment device via a
pull roll leader and pressing the incoming ma-
terial via upper and lower rolls so as to prevent
the incoming material from swinging up and
down, wherein a transmission speed of the in-
coming material is 3~5 m/min, and performing
the incoming material move forward at a con-
stant speed under the pull of a transmission de-
vice; and milling surface layers of copper layers
on upper and lower planes via machining devic-
es on upper and lower planes, wherein an
amount of feed of a milling cutter is 0.10~0.15
mm, and a milled amount of the copper layers
is 0.1~0.15 mm;

7) drawing

drawing the incoming material after being treat-
ed in the step 6, wherein a machining rate for a
drawing amount at the first time is controlled at
25%~30% and the machining rate is $\leq 30\%$; and
coiling or sawing the pulled material a straight
material having a certain length, wherein the
whole drawing, coiling and sawing processes all
are controlled automatically and may work con-
tinuously;

8) annealing

annealing is the most important procedure be-
fore moulding; an annealing temperature is
295~345° C and an annealing heat preservation

time is 3~4.5 h; and then, spraying water to a
tank to cool to a room temperature;

9) surface cleaning

placing a copper-aluminum composite bar in the
step 8 into a guide groove via an automatic load-
ing mechanism, starting a device, and under the
driving of a delivery wheel, first passing the cop-
per-aluminum composite bar through an alkali
washing box, wherein a hairbrush and an air
knife are provided in a box body, the hairbrush
is configured to brush surface oil stain and the
air knife blows a surface of the copper-aluminum
composite bar to be dry; then, passing the cop-
per-aluminum composite bar through a water
spraying device, and washing a residual alkali
solution on the surface with water and blowing
the copper-aluminum composite bar to be dry
to enter an acid cleaning box, wherein a hair-
brush and an air knife are also provided in the
acid cleaning box; after acid cleaning treatment,
washing the copper-aluminum composite bar
with the water and blowing be dry again to enter
a passivation box, wherein a passivation solu-
tion is prepared with a passivation process in
the passivation box; after spraying and passiva-
tion, drying the copper-aluminum composite bar
automatically, and discharging from the passiv-
ation box under the pull of a conveyor belt; and
then, placing the copper-aluminum composite
bar after surface cleaning and passivation onto
a receiving rack via an automatic material re-
ceiving device.

3. The preparation method of the high-bonding
strength copper-aluminum composite conductive
material as claimed in claim 2, wherein the machin-
ing rate in the drawing process is as follows: when
thickness $h \geq 10$ mm, $25\% > \text{machining rate} \leq 30\%$;
when $6 \text{ mm} \leq \text{thickness } h < 10$ mm, $20\% > \text{machining}$
rate $\leq 25\%$; when $3 \text{ mm} \leq \text{thickness } h < 6$ mm,
 $15\% > \text{machining rate} \leq 20\%$; and when thickness $h < 3$
mm, machining rate $\leq 15\%$.

4. The preparation method of the high-bonding
strength copper-aluminum composite conductive
material as claimed in claim 2, wherein tank anneal-
ing or online induction annealing is adopted by the
annealing process.

5. The preparation method of the high-bonding
strength copper-aluminum composite conductive
material as claimed in claim 4, wherein the online
induction annealing is adopted by a copper-alumi-
num composite bar of which the width of the speci-
fication above 80 mm; and the tank annealing is
adopted by a copper-aluminum composite bar of
which the specification below 80 mm.

6. The preparation method of the high-bonding strength copper-aluminum composite conductive material as claimed in claim 2, wherein the rolling process is a pass type nine-course rolling process.

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7. The preparation method of the high-bonding strength copper-aluminum composite conductive material as claimed in claim 2 or 3, wherein a coil drawing process, a hydraulic drawing process or a crawler drawing process may be adopted by the drawing process; when the width ≤ 30 mm, the coil drawing or the hydraulic drawing or the crawler drawing is adopted; when $30 \text{ mm} < \text{width} \leq 120 \text{ mm}$, the hydraulic drawing or the crawler drawing is adopted; $6 \text{ m/min} \leq \text{coil drawing speed} \leq 60 \text{ m/min}$; $50 \text{ m/min} \leq \text{crawler drawing speed} \leq 80 \text{ m/min}$, and hydraulic drawing speed $\leq 8 \text{ m/min}$.

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2016/110430

A. CLASSIFICATION OF SUBJECT MATTER

H01B 1/02 (2006.01) i; B21C 37/04 (2006.01) i

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)

H01B; B21C

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)

CNTXT; CNABS; DWPI; Google Scholar: 烟台孚信达双金属股份有限公司, 王连忠, 董晓文, 结合强度, 复合, 金属间化合物, 厚度, 铜包铝, 退火, 表面, aluminum, bonding strength, wire, copper, core, interface, diffusion, layer, component?, thickness

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	苏亚军 等, “水平连铸直接复合成形铜包铝复合材料的组织与性能”, 特种铸造及有色合金, 30 September 2011 (30.09.2011), 31(9), ISSN: 1001-2249, pages 786-790, (SU, Yajun et al., “Microstructure and Properties of Copper Cladding Aluminum Rod Fabricated by Horizontal Core-filling Continuous Casting”, Special casting & non-ferrous alloys)	1-7
X	SU, Yajun et al., “Interfacial Microstructure and Bonding Strength of Copper Cladding Aluminum Rods Fabricated by Horizontal Core-Filling Continuous Casting”, Metallurgical and Materials Transactions A, 31 December 2011 (31.12.2011), vol. 42, ISSN: 1073-5623, pages 4088-4099	1
A	CN 102161088 A (ZHANG, Jiyun), 24 August 2011 (24.08.2011), description, paragraphs 6-10	1-7
A	CN 105170689 A (YANTAI FISEND BIMETAL CO., LTD.), 23 December 2015 (23.12.2015), description, paragraphs 3-6	1-7

☒ Further documents are listed in the continuation of Box C.☒ See patent family annex.

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“P” document published prior to the international filing date but later than the priority date claimed

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“&” document member of the same patent family

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2016/110430

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2010294537 A1 (RH ONOVATION), 25 November 2010 (25.11.2010), abstract	1-7
A	吴永福 等, “矩形断面铜包铝复合材料的水平连铸直接复合成形”, 中国有色金属学报, 30 September 2012 (30.09.2012), 22(9), ISSN: 1004-0609, pages 2501-2507, (WU, Yongfu et al., “Copper Cladding Aluminum Composite Materials with Rectangle Section Fabricated by Horizontal Core-Filling Continuous Casting”, The Chinese Journal of Nonferrous Metals)	1-7

Form PCT/ISA/210 (continuation of second sheet) (July 2009)

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/CN2016/110430

5	Patent Documents referred in the Report	Publication Date	Patent Family	Publication Date
	CN 102161088 A	24 August 2011	None	
10	CN 105170689 A	23 December 2015	None	
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			WO 2007147872 A3	16 October 2008
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Form PCT/ISA/210 (patent family annex) (July 2009)

REFERENCES CITED IN THE DESCRIPTION

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