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(54) **THE METHOD OF MANUFACTURING A WIRE FROM CU-AL-MN-NI-FE ALLOY, ESPECIALLY FOR THE USE IN ADDITIVE MANUFACTURING**

(57) The method of manufacturing a wire from Cu-Al-Mn-Ni-Fe alloy conducted by a multi-stage heat treatment in a protective atmosphere **characterized in that** after annealing at the temperature of 700-800°C anneal-

ing of the semi-finished product at the temperature of 450-750°C for 45 - 60 minutes is conducted, then it is etched in a pickling bath at the temperature of 50-60°C for 50-60 minutes, and next it is rinsed and cleaned.

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Description

[0001] The field of the invention is the method of manufacturing a wire from Cu-Al-Mn-Ni-Fe alloy, especially for the use in additive manufacturing, for 3D printing in the WAAM process (Wire Arc Additive Manufacturing). The technology of the wire manufacturing uses the continuous casting process and drawing of the semi-finished product in single stages.

[0002] A solution US3942582 is known from the prior art, which presents the method of copper rod manufacturing in which liquid copper is cast in a continuous casting device with inclined mould cavity, which ensures obtaining a continuous copper rod. After leaving the casting device, the rod is directed to the horizontal rolling mill.

[0003] Another solution is P.427654, which presents a multi-step method of producing solid welding wires comprising cleaning of the wire rod, drawing of the rod with winding, unwinding of the semi-product, dry drawing, copper plating, washing-cleaning and packing. This method is characterized by the fact that the wire rod is cleaned with a high-pressure water jet, the speed of dry drawing of the semi-finished product is controlled by using an additional loop at the back of the drawing drum instead of the tension roller, the wire is rinsed with hot water under pressure, electro-chemical etching in sulfuric acid (H₂SO₄), rinsing three times, and copper plating in a solution of copper sulphate (CuSO₄), water and sulfuric acid.

[0004] The essence of the solution is the method of obtaining a wire from the Cu-Al-Mn-Ni-Fe alloy carried out by a multi-stage heat treatment in a protective atmosphere, characterized by the fact that after annealing at a temperature of 700-800°C, the semi-finished product is annealed at a temperature in the range of 450-750°C for 45-60 min, then it is etched in a pickling bath at 50-60°C for 50-60 minutes, then it is rinsed and then cleaned. The protective atmosphere is nitrogen or a vacuum.

[0005] The etching of the semi-finished product is carried out in an 18-20% solution of citric acid (C₆H₈O₇). Cleaning is done thermochemically.

The method is presented by an example of implementation

Example I:

[0006] In the example of manufacturing the solid wire, especially for the use in additive manufacturing, a charge of a copper alloy containing aluminium, manganese, nickel, iron, with the mass content of aluminium 9.0%, manganese 1.5%, nickel 4.0% and iron 4.0%, the balance being copper, is melted in an open tilting melting furnace, and then, under a carbon cover, the metal bath is stabilized at 1160°C for 40 minutes. After the temperature is stabilized, the liquid metal is poured into the foundry furnace maintaining the set temperature. The finished mol-

ten bath is continuously cast into a semi-finished product with a round cross section with a diameter of 8.0 mm, maintaining the stability of the main process parameters. The feed value of the material leaving the mould in the horizontal system is 12.0 mm with the speed of 20.0 mm/s and acceleration of 300.0 mm/s². The standstill is 0.0 s, whereas the reverse feed is 1.0 mm. Cooling is conducted in the primary system with the medium flow of 2.0-4.0 l/min depending on the structure of the medium circulation in the system, the temperature of the cooling medium leaving the system is in the range of 60-80°C. Additionally there is secondary cooling applied in the form of a water curtain. The prepared semi-finished product in the form of coiled rod undergoes plastic processing in the cold drawing process. The cast semi-product requires a calibrating drawing operation on a drum drawing machine to the diameter of 7.6 mm. Soap powder with the addition of calcium is used as a lubricant. After cross-section calibration the semi-finished product is subjected to high temperature heat treatment at a temperature of 750°C. The heat treatment is conducted for 60 minutes in the nitrogen protective atmosphere. After completing the process, the material cools down together with the furnace. After annealing the material is skinned to the diameter of 7.4 mm. In the case of skinning the container at the entrance to the drawing machine is rebuilt into a skinning linear system with the installation of an insert and the guide dies. It is required to apply synthetic grease to the first guide die, to pour a cooling and lubricating emulsion on the product and cyclical removal of chips, which may block proper heat dissipation by the cooling medium. The result of this operation is the removal of residual oxides and contamination after annealing as well as residues after continuous casting. After levelling the surface of the top layer, the semi-finished product is drawn with a total draft of 35% of the deformation value, using a draft of 12% in single runs. For larger cross sections of the semi-finished product, it is favourable to use a soap powder with the addition of calcium as a lubricant. However, for wires below 2.0 mm in diameter, the process should be carried out on a wet drawing machine, using a cooling-cleaning-lubricating emulsion with a concentration of 8%. In order to prepare the material for heat treatment, before the next annealing process, it is useful to tie the material using binding wire made of the same alloy as the processed material. Next the tied coil is rinsed with warm water under pressure to remove the remains of lubrication from the surface after drawing, and then dried with compressed air.

[0007] Depending on the size of the product diameter, a high-temperature treatment or low-temperature treatment is performed. This is to reduce the amount of undesirable tarnish forming on the wire surface. For the multi-stage annealing, the following scheme for carrying out the heat treatment was adopted, depending on the size of the cross-section:

- $d > \varnothing 6 \text{ mm}$ - annealing at 750°C for one hour,

- $d < \varnothing 6$ mm - annealing at 650°C for one hour,
- $d < \varnothing 4$ mm - recovering at 450°C for 60 minutes,
- $d < \varnothing 2$ mm - recovering at 450°C for 45 minutes.

Where: d - product diameter

[0008] Following the heat treatment at each of the multiple steps in the process, the wire is etched in a 20% citric acid solution for approximately at the temperature of 55°C for 60 minutes in order to remove the tarnish formed on the surface of the product. It is necessary for the wire to be placed in a heated pickling bath. The coil of wire placed in the bath should be loose and not tied to obtain a better end result of the process. After etching, the wire is rinsed intensively with water to remove the remains of citric acid and then, before the next drawing stage, it is rinsed in a cooling, cleaning, and lubricating emulsion. To ensure a shiny surface of the product of an appropriate quality, linear mechanical cleaning is applied during drawing on the uncoiled part of the wire using abrasive material on cloth with a grit of P80 and P120. In case of observing casting defects in the form of microcracks or misruns during drawing additional skinning process of the surface layer of the product is done. This process is conducted necessarily on soft material, before drawing, cutting the appropriate value of the thickness of the layer around the perimeter of the cross-section of the product, ensuring the removal of visible defects. Following the adopted scheme, the wire is drawn until obtaining the final diameter of the final value of $\varnothing 1.0$ mm. Before winding the wire on a spool, the surface of the wire is cleaned of the residue after the production processes, including the lubrication left on the surface after the drawing process. First, the wire bundle is rinsed with water under pressure and next in a special emulsion using ultrasounds for 40 minutes in 40°C using an ultrasonic cleaner. In the next operation the wire bundle is rinsed in 10% solution of isopropyl alcohol with distilled water. The purpose of this procedure is to clean the surface of the emulsion used in the ultrasonic cleaner, which after drying may leave discolouration and unattractive appearance of the wound spool. The finished product is wound on a SD 300 K spool.

Example II

[0009] Production of the wire according to the described method can take place also for copper alloy containing aluminium, manganese, nickel, iron with the mass content of aluminium 8.0%, 8.0% of manganese, 2.0% of nickel, and 2.5% of iron, the balance being copper. In this example the semi-finished product with a round cross-section shape is cast continuously in a horizontal casting system, and prepared for plastic working in the cold drawing process like in example I. After preparing the semi-finished product it is drawn with a maximum total draft of 40% of the deformation value, using 14% draft in single runs. All the operations related to drawing

the wire are the same as in example I. Following the adopted scheme, the wire is drawn with maintaining the multi-stage intermediate procedures, until the final diameter of the final value $\varnothing 1.0$ mm is obtained. Before winding the material on the spool, the surface of the wire is cleaned of residues from production operations, including lubrication left on the surface after drawing, as in example I. The finished product is wound on an SD 300 K spool.

Claims

1. The method of manufacturing a wire from Cu-Al-Mn-Ni-Fe alloy conducted by a multi-stage heat treatment in a protective atmosphere **characterized in that** after annealing at the temperature of 700-800°C annealing of the semi-finished product at the temperature of 450-750°C for 45 - 60 minutes is conducted, then it is etched in a pickling bath at the temperature of 50-60°C for 50-60 minutes, and next it is rinsed and cleaned.
2. The method of producing a wire according to claim 1 **characterised in that** the protective atmosphere is nitrogen.
3. The method of producing a wire according to claim 1 **characterised in that** the protective atmosphere is a vacuum.
4. The method of producing a wire according to claim 1 **characterised in that** the etching of the semi-finished product is conducted in an 18-20% solution of citric acid ($C_6H_8O_7$).
5. The method of producing a wire according to claim 1 **characterised in that** cleaning is done thermo-chemically.



EUROPEAN SEARCH REPORT

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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			

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**ANNEX TO THE EUROPEAN SEARCH REPORT
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5 This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
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For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

REFERENCES CITED IN THE DESCRIPTION

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