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(54) FLAT ROLLED PRODUCT MADE OF A COPPER ALLOY COMPRISING SILVER

(57) A flat rolled product made of Cu-Ag alloy, made of Cu-Ag alloys containing copper in the amount of 92-99%wt., silver in the amount of 1-8%wt.Ag and impurities in the form of iron < 4ppm, lead < 1.5ppm, zinc < 4ppm, arsenic < 0.4ppm and others in the amount of < 10ppm, whose physicochemical properties and structure are constant on its whole length.

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Description

[0001] The object of the invention is a flat rolled product, which is characterized by a set of high mechanical and electrical properties, made of a Cu-Ag alloy which is processed in appropriately selected sequences of heat treatment and cold working.

[0002] Continuous development of materials based on copper and silver and technology of processing them into products with rectangular or round cross-sections, including wires, conductors, bunches or sheets, considering their high mechanical and electrical properties and specialist character of their application, result in the fact that they are in the center of attention of leading research centers and the biggest production plants in the world. High global standards concerning quality, safety, health protection, as well as usage and recycling are reflected in material design solutions which, thanks to innovative technologies of production and processing of materials for products, are able to ensure the required level of mechanical and electrical properties, while minimizing production costs.

[0003] Products made of Cu-Ag alloys are characterized by above-standard mechanical strength and electrical properties. They are applied as responsible elements conducting electric current and transferring significant mechanical loads. Products made from Cu-Ag alloys can be applied especially as sheets used for construction of strong magnetic field generators. They can be used to build cores of Bitter electromagnets. The method of operation of the above-mentioned generators requires the application of highly conductive materials. This is because flow of an electrical current of high intensity is necessary in order to achieve a magnetic field with the highest possible strength, whereas high mechanical strength properties are necessary to transmit very strong Lorentz forces that are generated by high magnetic fields being created.

[0004] Specific character of application of these elements impose the necessity of having above-standard operational properties, i.e. high fatigue strength, impact strength, thermal resistance, current-carrying capacity and stability of electrical and mechanical properties in time. The requirements set for these materials are connected with the demand generated by the global industry. Products made of Cu-Ag alloys, apart from the widely applied wires, microprinting and sheets made of copper, but with addition of other elements, i.e. niobium, zircon, chromium and tin, are part of the group presenting the highest mechanical strength properties of the ones mentioned above. However, the presented group of mechanical strength properties can be shaped by plastic working, but it is connected with a simultaneous considerable decrease of electrical properties. Silver, as an element with the highest electrical conductivity among all metals (62 MS/m, 103% IACS), influences the growth of copper resistivity in the least harmful way. Therefore, flat rolled products made from Cu-Ag alloys with a structure formed by conducting thermo-mechanical treatment take the shape similar to a micro-composite structure. Thanks to that, the final product acquires high mechanical and electrical parameters.

[0005] One example of the application of highly durable and highly conductive elements made from copper and silver alloys (up to 8% w/w Ag) are sheets used i.a. as cores of high magnetic fields generators.

[0006] Strict requirements for the materials used in the construction of electromagnets result from the unconventional work conditions such as high mechanical stress and electrical load. The outcomes produced as a result of the influence of high magnetic fields contribute to the occurrence of discontinuities in the structure of sheets creating the core, which causes an excessive growth of stresses and it's damage. Experiments conducted with the application of the highest possible magnetic field strength provide us with new information concerning the required operational parameters of the materials used, and give us inspiration to carry out studies regarding the possibility of introducing new materials and shaping their high properties.

[0007] From the published patent application EP 1201782 A1 a method of production of sheets characterized by high electrical conductivity and tenacity is known. Representatives of Tanaka Kikinzoku Kogyo in the above mentioned patent application focused their studies on sheets made of Cu-Ag alloys with a chemical of composition 4-32% at. of the alloy addition which was silver. In their case, the process of producing sheets consists of the following stages:

1) casting of an ingot with a specific chemical composition with immediate cooling,
2) cold straining through the process of rolling with a draft of between 49 and 76%, then annealing in the temperate range of between 300 and 500°C for the duration of 0.5-5h in vacuum or in a shielding gas atmosphere,
3) possible repeating of the actions from point 2), namely straining and annealing,
4) straining in the process of rolling to a fixed and final sheet thickness,
5) finishing heat treatment conducted in the temperature range of between 150 and 400°C for the duration of 0.5-5h.

[0008] Each stage of conducted studies makes it necessary to analyze the changing mechanical strength and electrical properties of the material. In the case of presented patent application, a key element of the process of producing is the heat treatment conducted at different stages of the production technology of cold-rolled sheets. According to the authors, the final heat treatment in the temperature range of 150-400°C is the most important element. Correlations of changes of electrical conductivity and tenacity in a function of temperatures of annealing presented in the document, aim at indicating the optimal temperature scope which will enable to preserve mechanical strength properties at a stable level, not allowing for the recrystallization of the material. At the same time, this temperature scope is meant to enable for the maximum growth of electrical conductivity to improve the final working properties of the sheets. Materials presenting offset of both high electrical and mechanical strength properties belong to the group of highly sought-after by the electrical and power industry.

[0009] A wide range of applications of copper-silver alloys encourages one to do continuous searches and modifications of new products, such as wires, bars, pipes and sheets with even higher electrical and mechanical strength properties. Working requirements concerning thermal resistance, corrosion resistance and electrical conductivity grow incessantly.

[0010] In another patent application CN 101428304 A, we can find examples of industrial applications of Cu-Ag alloy products in electronics, the aircraft industry and radio broadcasting. With regard to silver, because of it's high cost, the authors present the possibility of producing Cu-Ag alloys with an optimal content of alloy addition, that is 1.6-2% at. Ag, without the necessity of increasing its content in order to enable it to achieve high mechanical strength and electrical properties, fulfilling all design requirements set by the industry. The authors of the discussed solution optimize production costs through the modification of the production process of sheets, plates, bars and pipes with a smaller content of silver. The process entails straining by hot-rolling with the prior application of a one-stage heat treatment in the temperature of 650-680°C lasting 4-5h.

[0011] The common fault of the presented solutions is not fully exploring possibilities of advantageous forming of the Cu-Ag alloys' microstructure, given by the connection of the phase system of Cu-Ag alloys and the possibility of producing flat rolled products with an even higher mechanical strength and electrical properties. Another flaw of the presented solutions is the lack of a system of the continuous obtaining of alloys in the form of casts, but only of ingots with a finite length, which lengthens the production process and increases production costs. The next drawback is a disadvantageous diversification of the chemical composition, the microstructure between particular ingots, which can in effect result in the lack of repeatability of their mechanical and electrical properties.

[0012] Multisequential processes of thermo-mechanical treatment, with disadvantageously selected ranges of temperatures in connection with excessively prolonged duration of heat treatment, do not effectively influence the maximization of mechanical strength and electrical properties. Moreover, additional interoperational procedures of heat treatment (necessarily connected with generating of the total production costs), applied on the wrong stage of production of flat rolled products, do not translate into high mechanical strength and electrical properties of the final product. The presented solutions lack the possibility of shaping the properties of Cu-Ag alloys through the selection of an optimal level of other alloy additions, especially zircon, which allow for an advantageous modification of the microstructure, the shaping of high mechanical properties, as well as a high thermal, rheological, fatigue and impact resistance.

[0013] The invention pertains a flat rolled product made from Cu-Ag alloy containing copper in amount of 92-99% wt., silver in the amount of 1-8%wt.Ag and impurities in the form of iron < 4ppm, lead < 1.5ppm, zinc < 4ppm, arsenic < 0.4ppm and others in the amount of < 10ppm, whose physicochemical properties and structure are constant on the whole length.

[0014] Preferably, the flat rolled product according to the invention is made from Cu-Ag alloy enriched with other alloy additions, especially in the form of zircon, whose total content does not exceed 0.5%wt.

[0015] Preferably, the flat rolled product according to the invention has an ultimate tensile strength of over 900MPa and an electrical conductivity above 69% IACS scale, measured in the temperature of 20°C.

[0016] The solution according to the invention is based on the observation that Cu-Ag alloys have an ability of mutual incomplete miscibility in solid state of silver in copper and copper in silver. The alloy microstructure is composed of a matrix, composed mainly of copper containing a certain amount of unprecipitated silver, as well as precipitations enriched with silver containing also a small amount of unprecipitated copper.

[0017] Flat rolled products according to the invention, flat rolled are produced by way of an integrated method comprising:

a) obtaining the starting material in the form of cast plates by way of a continuous melting and casting technology,

b) thermal pretreatment of the casting in the form of a solution treatment process with homogenization in the range of 600÷779.1°C (779.1°C is the temperature of eutectic reaction for Cu-Ag alloy) for a time of 0.1÷100h, concluded by rapid cooling,

c) preforming of casting in the process of cold rolling with total a true strain of $\ln\lambda=0.1\div0,6$, where $\lambda=S_0/S_k$ (S_0 - field of casting cross-section, S - field of casting cross-section after straining),

d) a two-stage thermal treatment where the first stage is contained in the range of 150÷300°C for a time of 0.5÷100h, and the second stage is contained in the range of 300÷600°C for a time of 0.5÷20h, and subsequently slow cooling,

e) plastic strain through cold rolling to the final size without additional inter-operational thermal treatment,

f) straining through rolling to gauge combined with one or more inter-operational thermal treatment of the material in a temperature in the range of 100÷500°C for a time of 0.1÷1000h ending with slow cooling.

[0018] This way the following technical and utility effects are obtained:

a) a possibility of forming a set of high electrical and mechanical properties of the product,

b) a possibility of alloy microstructure modification and changing its mechanical properties, thermal and rheological resistance as well as fatigue and impact strength through the procedure of introducing alloy additions and the optimization of thermal and plastic working conditions,

c) a possibility of lowering the costs of manufacturing of flat rolled products thanks to properly selected and connected thermo-mechanical treatment operations,

d) a possibility of a selection of optimal conditions for thermo-mechanical treatment in order to obtain the required mechanical strength and electrical properties,

e) an advantageous weight factor in relation to mechanical strength parameters of the obtained products.

[0019] By way of applying of a multistage thermal-mechanical treatment of the casting and by properly selecting the temperature and duration of the thermal treatment (solution treatment and aging procedures) it is possible to precipitate within the total volume of the supersaturated solution of silver in copper numerous, small silver precipitations. In the case of the addition of other elements to the Cu-Ag base alloy modification of the microstructure is possible. This modification could pertain grain size change, the presence of precipitations containing alloy elements, increase of mechanical properties and growth of thermal and rheological resistance as well as fatigue and impact strength of the products made from the alloys. An application of a significant plastic strain causes strong extension of precipitations arisen as a result thermo-mechanical treatment of the alloy. The structure on the longitudinal section of the obtained product consists of numerous, thin, strongly extended fibers, e.g. of silver or other alloy addition, against a background of a matrix composed of almost entirely of copper. The diameter of the fibers can be measured in nanometers.

[0020] The obtained microstructure causes substantial strengthening of the alloy through the presence of many grain boundaries and their straining. A kind of composite structure of the alloy is formed, whose reinforcing phase are numerous fibers, e.g. silver fibers, giving the alloy high mechanical strength properties. At the same time, possibly intensive silver precipitation (or of another alloy addition) from the solution causes its purification (almost only pure copper remains). In connection with this many strongly extended silver fibers (or of another alloy addition) together with copper form a peculiar parallel connection of perfect current conductors, which finally results in reaching very high electrical conductivity of the obtained products.

[0021] The product according to the invention, is characterized by high electrical and mechanical properties. The finished product has also an advantageous weight factor in relation to mechanical strength parameters.

[0022] The products according to the invention are described in the following examples.

[0023] Example 1. Materials in the form of a silver granulate with a high purity of 99.99% and oxygen-free copper in proportion enabling the obtaining of the CuAg3 alloy, were subjected to a melting process in the temperature of 1180°C in a graphite melting pot placed in a vacuum induction furnace. The casting process was conducted in the temperature of 1220°C in an inert gas atmosphere. The process of plate casting with the application of a graphite crystallizer was conducted in the conditions of primary cooling (crystallizer cooling) and secondary cooling (solidified alloy after being taken out of thecrystallizer). Castings in the form of plates, obtained in the process of continuous casting, had following measurements: 25 x 300 x 5000 mm. Thusly obtained material was subjected to a thermal treatment process coupled with mechanical treatment. The casting was subjected to solution treatment in the temperature of 750°C for a period of 20h, and then it was rapidly cooled in water to preserve a homogenous structure of the material. The material after the stage of solution treatment was characterized by following properties: 188MPa ultimate tensile strength, and 88% IACS - electrical conductivity. The subsequent scheme of procedure included small straining in the process of rolling, with measure of true strain in the amount of 0.4. After this process conducting two-stage processes of aging was necessary, that was aimed at introducing the maximum amount of silver from the homogenous solid solution of Cu-Ag. Primary aging of the castings (the first stage) was conducted in the temperature of 300°C for a period of 20h. Secondary aging of the castings (the second stage) was conducted in the temperature of 500°C for a period of 8h and it enabled a significant growth of mechanical strength properties to 430MPa, with a small change of electrical conductivity, growth of 4.5MS/m to the amount of 96% IACS. Next, the material was strained in the process of cold rolling into plates. To improve final electrical properties, the plates of the final size were subjected to thermal treatment in the temperature of 220°C for a time of 3h. Eventually, the plates with a true strain of 4.2 (thickness of 0.4mm) had a tenacity of 910MPa and electrical conductivity of 46.7MS/m, that is 80.51% in IACS scale. The analysis of chemical composition indicated content of silver 3.05%wt. and impurities in the form of iron < 4ppm, lead < 1.5ppm, zinc < 4ppm and arsenic < 0.4ppm. The remaining impurities did not exceed 10ppm. Copper comprised the rest of the alloy. The physicochemical properties and structure of the obtained products were constant on the whole length of the casting.

[0024] Example 2. Materials in the form of a silver granulate with a high purity of 99.99% and oxygen-free copper in proportion enabling the obtaining of the CuAg8 alloy, were subjected to a melting process in the temperature of 1180°C in a graphite melting pot placed in a vacuum induction furnace. The casting process was conducted in the temperature of 1220°C in an inert gas atmosphere. The process of plate casting with the application of a graphite crystallizer was conducted in conditions of primary cooling (crystallizer cooling) and secondary cooling (solidified alloy after being taken out of the crystallizer). Castings obtained in the process of casting, had following measurements: 25 x 300 x 5000mm. The obtained material was subjected to a thermal treatment process coupled with mechanical treatment. The casting was subjected to solution treatment in the temperature of 750°C for a period of 100h, and then it was rapidly cooled in water to preserve a homogenous structure of the material. After this process conducting two-stage processes of aging was necessary, that was aimed at introducing the maximum amount of silver from the homogenous solid solution of Cu-Ag. Primary aging of the castings (the first stage) was conducted in the temperature of 300°C for a period of 50h. Secondary aging of the castings (the second stage) was conducted in the temperature of 500°C for a period of 12h. Next, the material was strained in the process of cold rolling into plates. To improve the final electrical properties, the plates of the final size were subjected to thermal treatment in the temperature of 170°C for a time of 20h. Eventually, the plates with a true strain of 4.4 (thickness of 0.3mm) had an ultimate tensile strength of 960MPa and electrical conductivity of 40.1MS/m, that is 69.1% in IACS scale. The analysis of chemical composition indicated the content of silver 7.9%wt. and impurities in the form of iron < 3.5ppm, lead < 1.0ppm, zinc < 3.6ppm and arsenic < 0.3ppm. The remaining impurities did not exceed 10ppm. Copper comprised the rest of the alloy. The physicochemical properties and structure of the obtained products were constant on the whole length of the casting.

[0025] Example 3. Materials in the form of a silver granulate with a high purity of 99.99%, oxygen-free copper and Cu-Zr prealloy in proportion enabling the obtaining of the CuAg3Zr0,2 alloy, were subjected to a melting process in the temperature of 1200°C in a graphite melting pot placed in a vacuum induction furnace. The casting process was conducted after the alloy in the melting pot reached the temperature of 1240°C in an inert gas atmosphere. The process of plate casting with the application of a graphite crystallizer was conducted in conditions of primary cooling (crystallizer cooling) and secondary cooling (the solidified alloy after being taken out of the crystallizer). The casting obtained in the process of casting, had the following measurements: 25 x 300 x 5000mm. The obtained material was subjected to a thermal treatment process coupled with mechanical treatment. The casting was subjected to solution treatment in the temperature of 750°C for a period of 0.5h, and then it was rapidly cooled in water to preserve a homogenous structure of the material. After this process conducting two-stage processes of aging was necessary, that was aimed at introducing maximum amount of silver from the solid solution of Cu-Zr-Ag. Primary aging of castings (the first stage) was conducted in the temperature of 250°C for a period of 48h. Secondary aging of castings (the second stage) was conducted in the temperature of 450°C for a period of 20h. Next, the material was strained in the process of cold rolling. To improve the final electrical properties, flat products of the final size were subjected to thermal treatment in the temperature of 150°C for a time of 48h. Eventually, the obtained products with a true strain of 4.27 (thickness of 0.35mm) had an ultimate tensile strength of 980MPa and electrical conductivity of 43.8MS/m, that is 75.51% in IACS scale. The analysis of the chemical composition indicated content of silver 3.0%wt., zircon 0.2%wt., and impurities in the form of iron < 3.4ppm, lead < 1.2ppm, zinc < 3.4ppm and arsenic < 0.35ppm. The remaining impurities did not exceed 10ppm. Copper comprised the rest of the alloy. The physicochemical properties and structure of the obtained products were constant on the whole length of the casting.

Claims

1. A flat rolled product made of Cu-Ag alloy containing copper, silver and impurities, especially in the form of iron, lead, zinc and arsenic, **characterized in that** it is made of a Cu-Ag alloy containing copper in the amount of 92-99%wt., silver in the amount of 1-8%wt. Ag and impurities in the form of iron < 4ppm, lead < 1.5ppm, zinc < 4ppm, arsenic < 0.4ppm and others in the amount of < 10ppm, whose physicochemical properties and structure are constant on its whole length.

2. The flat rolled product according to claim 1, **characterized in that** the Cu-Ag alloy is enriched by other alloy additions, especially in the form of zircon, whose total content does not exceed 0.5% wt..

3. The flat rolled product according to claim 1 or 2, **characterized in that** its ultimate tensile strength is above 900MPa and its electrical conductivity is above 69% in IACS scale measured at the temperature of 20°C.

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EUROPEAN SEARCH REPORT

Application Number
EP 15 46 1531

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Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
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The present search report has been drawn up for all claims

1

Place of search	Date of completion of the search	Examiner
Munich	20 October 2015	von Zitzewitz, A

CATEGORY OF CITED DOCUMENTS

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