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(54) **Method of manufacturing wires of Cu-Ag alloys**

(57) A method of manufacturing wires, including microwires, of Cu-Ag alloys, in particular of alloys of Cu-(3÷7.9)% Ag by weight, consisting in that the materials in the form of high chemical purity copper and silver are melted at a temperature of 1083÷1300 C in a graphite crucible placed in a furnace, and subsequently continu-

ously cast at a temperature of 1083÷1300 C, in an inert gas atmosphere, using a graphite mould, at primary cooling conditions (mould cooling) and secondary cooling conditions (the solidified alloy after leaving the mould). Thus obtained casting is subjected to the thermo-mechanical treatment.

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## Description

**[0001]** This invention concerns a method of manufacturing wires, including micro-wires, of Cu-Ag alloys, in particular of an alloy comprising Cu-((3÷7.9)% Ag by weight. These alloys having the form of rods and coming from a continuous melting and casting line are subject to properly selected heat treatment sequences and drawing into wires, featuring a set of excellent mechanical and electrical properties.

**[0002]** According to recent reports, Cu-Ag alloys may be used as conductors in power supply applications, in the automotive industry, in power supply and signalling systems of high speed railways, in medical appliances and as power supply components of strong magnetic field generator windings.

**[0003]** So far, copper-based conductor alloys, which may also contain Nb, Be, Zn, Sn, Zr, Cr, etc. have been applied in the analysed fields of technology. However, these alloys, apart from their relatively high mechanical properties, are characterized by low electrical conductivity. Apart from their high mechanical properties, Cu-Ag alloys also show exceptionally high values of electrical conductivity. A number of global solutions focus on developing these properties by selecting an appropriate technology of obtaining and processing materials. Research in scientific centres and research institutes worldwide is aimed at obtaining wires with excellent mechanical properties and, at the same time, the highest electrical conductivity possible. Production of ingots with various cross-section shapes and limited lengths, and continuous melting and casting systems ensuring that a material with theoretically endless length can be obtained, are amongst commonly known engineering solutions applied to obtain alloys.

**[0004]** An analysis of global solutions indicates that alloys obtained with those methods are subsequently processed by application of various technologies, in particular by plastic working, e.g. rolling, forging, drawing, extruding, in addition heat treatment operations are applied at various stages of mechanical processing in order to increase mechanical and electrical properties of the products.

**[0005]** A method for obtaining micro-wires of an alloy with the chemical composition of Cu-(2÷14)% Ag by weight is known from a Japanese patent application JP 2000-199042. The description provides for a method of manufacturing microwires with a diameter of 0.01÷0.1 mm using eight variants of treatment. The research findings presented in the patent description have focused on a material in the form of cast rods with a diameter of 8mm and containing silver as an alloying constituent in the amount of 5 and 10% Ag by weight. The scheme for obtaining microwires according to the referred description provides for executing the following treatment sequences. Cast rods of the alloy of Cu-10% Ag by weight were subjected to diameter reduction in the drawing process from 10mm to 5 mm, at a set reduction of 61%. Next, the deformed material was heat treated at 450 C for 10 h, in order to apply subsequent overall reduction of either 94.2% or 99%. The final wire diameter was 1.2mm and 0.5mm, respectively. The wires with such a development history of thermo-mechanical treatment reached mechanical and electrical properties at a high level of 1530 MPa and 76% IACS (100% IACS = 58.0 MS/m). A separate treatment variant of cast rods with a bit lower silver content than in the previous version (6% Ag by weight) according to this solution, provided for the application of heat treatment conducted in the same conditions: 450 C/10 h applied to the initial material, i.e. the cast rod. Next, the overall reduction reaching 98.4% (for a diameter of 1.0mm) was set, which finally enabled a tensile strength of 1320MPa to be achieved. The electrical conductivity reached 78% IACS. Apart from the treatment variants described above, the authors of this patent introduced an additional stage of holding at 370 C/15 h. Beginning with a rod with an as-cast diameter of 8mm, the subsequent stages involved the overall reduction of 61 % (to a diameter of 5mm), a heat treatment (450 C/10 h), again overall reduction of 84% (to a diameter of 2mm).

**[0006]** Next, additional one or two stages of heat treatment (370 C/15 h) was applied. One of the variants assumed, after the overall reduction of 84%, a heat treatment (370 C/15 h) and further working to diameters of 0.05÷0.03 mm (total reduction of 99,3÷99,8%). Such a procedure allows for a significant increase of mechanical properties within the range of 1420÷1735 MPa and an increase of electrical conductivity to 60÷65% IACS. The second of the variants expected, after the initial overall reduction of 61%, a heat treatment at 450 C /10h, the overall reduction of 84%, a heat treatment at 370 C/15 h, followed by the overall reduction of 97.8% to a diameter of 0.3mm, and a subsequent heat treatment 370 C/60 h, and the final overall reduction of 99.6% to a diameter of 0.02mm. Such a method of proceeding allowed the wires to achieve the tensile strength of 1250 MPa and the electrical conductivity of 71 % IACS.

**[0007]** Another method for obtaining materials from a Cu-Ag alloy is presented in the international application description no. WO 2007-046378. The input material was a Cu-Ag alloy ingot with dimensions of 10x10x30mm, obtained by melting in an electric Tamman furnace at a temperature of 1250 C. Alloys from the range of Cu- (1÷10)% Ag by weight, Cu-(2÷6)% Ag by weight were subjected to a reduction in the drawing process. The heat treatment processes applied in the central phase of the reduction were carried out at temperatures of 400÷500 C for a period from 1 to 50 hours in a vacuum or an inert gas atmosphere to avoid oxidation of the material surface. The relationships presented in the patent description refer to alloys mainly from the range of Cu-(1÷10)% Ag by weight. A Cu-Ag ingot with dimensions as mentioned above and a silver content of first 1%, 2% and 3% Ag by weight was subjected to a heat treatment at 450 C/20 h, and subsequently to an overall reduction with a logarithmic measure 0.6 (true strain is the natural logarithm of the elongation coefficient in the wire drawing process, the elongation coefficient means a square of the quotient of the

initial wire diameter and the final wire diameter).

**[0008]** Then the material of Cu-4% Ag by weight was subjected to holding at 450 C/10 h and drawing with a strain of 0.6 in the logarithmic scale. As the silver content in the alloy increased, the time of the applied heat treatment decreased. An ingot of Cu-10% Ag by weight was subjected to holding at 450C for 5 hours. Each alloy described, at the subsequent stage of processing was subjected to a true strain of 8 or 12. As a result of the research, wires with a tensile strength of 1400MPa, and an electrical conductivity of 76.4% IACS were obtained, as well as with a tensile strength of 1200MPa and a conductivity of 81.7% IACS. In the opinion of the author of this solution, the quotient of strength of the Cu-Ag alloys exceeding 10% Ag by weight to the Ag content is disadvantageous, thus the selected range of the alloys tested was between 1 and 10% Ag by weight.

**[0009]** In the description of the American application no. US 2008/0202648 A1 research findings of Cu-Ag alloys with the silver content within the range of 1 ÷ 3.5% Ag by weight are presented. In this case, the initial material is an ingot with the maximum content of impurities of 10 ppm or less, obtained in the process of mould casting. The metal during casting is cooled at a cooling rate of 400 ÷ 500 C/min. The product according to this solution is further processed by e.g. drawing, rolling, etc. The heat treatment operations following the plastic working processes are carried out at 300 ÷ 350 C for 10 ÷ 20 h, 350 ÷ 450 C for 5 ÷ 10 h, or at temperatures of 450 ÷ 550 C for 0.5 ÷ 5 h in an inert gas atmosphere. After the holding processes, the schedule of obtaining products of the Cu-(1 ÷ 3.5)% Ag by weight according to this invention provides for drawing to a diameter of 0.05mm or less. According to the referred-to description the tensile strength of the final material is within the range of 800 ÷ 1200 MPa, while the electric conductivity is within the range of 80 ÷ 84% IACS. This solution also assumes, at a certain stage of obtaining wires from the alloy of Cu-(1 ÷ 3.5)% Ag by weight, an additional holding process at temperatures of 600 ÷ 900 C for a very short time, i.e. from 5 to 120 seconds.

**[0010]** A disadvantage shared by the solutions is underutilization of a possibility to advantageously develop the microstructure of Cu-Ag alloys, and a related possibility to manufacture wires with an even higher set of mechanical and electrical properties.

**[0011]** Multi-sequential thermo-mechanical treatment processes conducted at unfavourably selected temperature ranges, combined with an overly extended heat treatment time, do not influence effectively the maximisation of mechanical and electrical properties. In addition, additional intermediate heat treatments (inherent to the whole production cost generation), used at an improper stage of wire production, do not translate fully into a high set of mechanical and electrical properties of the final product.

**[0012]** The objective of the invention is to present a consistent, integrated method for manufacturing wire components, including microwires, comprising the continuous melting and casting process of rods of Cu-Ag alloys and a sequential heat treatment combined with drawing, enabling wires, including micro-wires to be obtained with a tensile strength  $R_m$  within the range of 1100 ÷ 1400 MPa and simultaneously an electrical conductivity within the range of 68 ÷ 84% IACS.

**[0013]** The Cu-Ag alloys have the possibility of mutual limited solubility in the solid state of silver in copper and copper in silver. The alloy microstructure consists of a matrix comprising mainly copper containing a certain amount of not precipitated silver, and precipitates rich in silver, containing also a small amount of not precipitated copper. By using a multi-stage thermo-mechanical treatment of castings and properly selected temperature and time of the heat treatment (quenching and ageing), very numerous, fine silver precipitates may precipitate within the whole volume from the supersaturated silver solution in copper. The application of a significant plastic strain contributes to a substantial elongation of the precipitates formed as a result of the thermo-mechanical treatment of the alloy. The structure at a longitudinal section of the wires (microwires) consists of very numerous, thin, considerably elongated fibres almost wholly comprising silver with a small admixture of copper and the matrix comprising almost wholly of copper. The diameter of these fibres has nanometric dimensions.

**[0014]** In the solution according to this invention, the materials in the form of copper and silver with a high chemical purity are melted at a temperature of 1083 ÷ 1300 C in a graphite crucible placed in a furnace, and subsequently continuously cast at a temperature of 1083 ÷ 1300 C, in an inert gas atmosphere using a graphite mould, at primary cooling conditions (mould cooling) and secondary cooling conditions (the solidified alloy after leaving the mould), and the casting obtained with this method is subjected to a thermo-mechanical treatment.

**[0015]** Preferably, during the thermo-mechanical treatment, the obtained casting is solution annealed at a temperature of 600 ÷ 779.1 C for 0.5 ÷ 100 hours, and subsequently quenched and, subsequently, it is drawn, with a true strain measure of 0.1 ÷ 1, and next it is subject to processes of another two-stage heat treatment, followed by a deformation in the drawing process into final cross-section wires.

**[0016]** Preferably, during the thermo-mechanical treatment the obtained casting is solution annealed at a temperature of 600 ÷ 779.1 C for 0.5 ÷ 100 hours, and subsequently quenched, and next it is subjected to processes of a further two-stage heat treatment, followed by drawing into final cross-section wires.

**[0017]** Preferably, in the two-stage heat treatment, the first stage involves holding at 150 ÷ 300 C for 0.1 ÷ 100 hours, followed by the second stage which is holding at 300 ÷ 500 C for 0.1 ÷ 20 hours followed by slow cooling.

**[0018]** Preferably, when deforming the material into the final cross-section wires, at least one intermediate heat treatment occurs within 200 ÷ 600 C for 0.1 ÷ 50 hours, followed by slow cooling.

**[0019]** Preferably, during the deformation of the material into the final cross-section wires at least one intermediate heat treatment occurs at  $600 \div 900$  °C for  $0.1 \div 1000$  seconds, followed by quenching.

**[0020]** Preferably, final cross-section wires are subjected to a heat treatment at a temperature of  $50 \div 300$  °C for  $0.1 \div 1000$  hours.

**[0021]** Preferably, after the solution annealing, the casting is water quenched. Preferably, after the solution annealing, the casting is oil quenched.

**[0022]** Preferably, after the solution annealing, the casting is liquid nitrogen quenched. Preferably, after the solution annealing, the casting is emulsion quenched.

**[0023]** Preferably, the graphite crucible is made of a high purity graphite, wherein alloying constituents are placed under a charcoal or graphite layer.

**[0024]** Preferably, the graphite crucible is placed in protective atmosphere.

**[0025]** Preferably, the graphite mould is cooled with a system that is mounted on It, through which a cooling agent flows (the primary cooling system).

**[0026]** Preferably, the casting leaving the mould is additionally cooled by a cooling agent fed directly onto the casting (the secondary cooling system).

**[0027]** Thanks to the application of the method according to the invention, the following technical and functional effects have been obtained, namely a possibility to form a set of excellent electrical and mechanical properties of the product, reduction of manufacturing costs thanks to properly selected thermo-mechanical treatments, a possibility to select the optimum conditions of the thermo-mechanical treatment sequence in order to obtain the required mechanical and electrical properties, an advantageous ratio of weight to mechanical parameters of the obtained products.

**[0028]** The solution according to the invention is presented in the embodiment examples in Table 1, wherein with an example of three Cu-Ag alloys with various silver contents within the range of this invention, the method of obtaining wires (including micro-wires) is presented, along with a list of mechanical and electrical properties at different stages of product manufacturing.

Table 1

Ag content in the alloy [% by weight]		3	5	7
Diameter [mm]		9.5		
Casting properties	$R_m$ , MPa	190	210	240
	%IACS	89	87	84
Heat treatment [°C/h] (solution annealing)		750/20-oil quenching	750/10-water quenching	750/20-emulsion quenching
True strain $\varepsilon_{rz}$		0.4	none	0.4
Properties	$R_m$ MPa	230	not applicable	260
	%IACS	94	not applicable	83
Heat treatment [°C/h] (primary ageing)		300/20-air cooling	200/20-air cooling	300/20-air cooling
Heat treatment [°C/h] (secondary ageing)		450/10 - air cooling		
True strain $\varepsilon_{rz}$		2.7		
Properties	$R_m$ MPa	510	540	570
	%IACS	90	87	83
Heat treatment [°C/h]		400/2-air cooling	none	none
Properties	$R_m$ MPa	400	not applicable	not applicable
	%IACS	95	not applicable	not applicable
True strain $\varepsilon_{rz}$		7.7	6.5	7.7
Final diameter of round wire [mm]		0.2	0.37	0.2
Final heat treatment [°C/h]		240/2	180/10	150/100
		air cooling		

(continued)

Ag content in the alloy [% by weight]		3	5	7
Properties	R <sub>m</sub> MPa	100	1220	1250
	%IACS	82	74	75

**[0029]** The method for obtaining microstructures from Cu-Ag alloys is described with the embodiment examples below.

#### Example 1

**[0030]** Materials in the form of high purity silver pellets of 99.99% and OFE copper were melted at the temperature of 1200 °C in a graphite crucible placed in an induction furnace. Continuous casting process was conducted at a temperature of 1200 °C in an inert gas atmosphere. The continuous casting of rods with a chemical composition of Cu-3% Ag by weight using a graphite mould was performed in primary cooling (mould cooling) and secondary cooling (the solidified alloy after leaving the mould) conditions. Round rods obtained as a result of the continuous casting process had a diameter of 9.5mm and a tensile strength R<sub>m</sub>=190 MPa, and the electric conductivity of 89% IACS. The material was then subjected to the thermo-mechanical treatment processes. The casting was solution-annealed at a temperature of 750 °C for 20 hours, and subsequently oil quenched to preserve the homogeneous structure of the material. The further procedure included setting a strain in the drawing process, with the true strain measure of 0.4. After this process, the rods demonstrated the tensile strength of R<sub>m</sub>=230 MPa, and the electric conductivity of 94% IACS. Next, a two-stage ageing process was carried out in order to extract as much silver as possible from the homogeneous solid solution of Cu-Ag. The primary ageing (the first stage) was conducted at 300 °C for 20 hours. The secondary ageing (the second stage) was conducted at the temperature of 450 °C for 10 hours. After the completed preliminary heat treatments, the alloy microstructure consisted of very numerous fine silver precipitates in the copper matrix. Next, the material was drawn into wires with a true strain of 2.7, followed by an intermediate heat treatment that consisted in holding at a temperature of 400 °C for 2 hours. Next, the material was drawn into the final diameter wires. In order to enhance the electric properties, the final diameter wires were subjected to a heat treatment at a temperature of 240 °C for 2 hours. In the end, wires with a diameter of 0.2mm and a true strain of 7.7 had a tensile strength R<sub>m</sub>=1100 MPa, and an electric conductivity of 82% IACS. The final microstructure of the wire, as observed on its longitudinal section, presented very numerous, elongated, thin silver bands and copper matrixes, favourable to obtain a set of high mechanical properties and a high electrical conductivity of the product.

#### Example 2

**[0031]** Materials in the form of high purity silver pellets of 99.99% and OFE copper were melted at a temperature of 1200 °C in a graphite crucible placed in an induction furnace. The continuous casting process was conducted at a temperature of 1210 °C in an inert gas atmosphere. The continuous casting of rods with a chemical composition of Cu-5% Ag by weight, using a graphite mould was performed in the primary cooling (mould cooling) and secondary cooling (of the solidified alloy after leaving the mould) conditions. The round rods obtained as a result of the continuous casting process had a diameter of 9.5mm and a tensile strength R<sub>m</sub>=210 MPa, and an electric conductivity of 87% IACS. Thus obtained material was subjected to the thermo-mechanical treatment processes. The casting was solution-annealed at a temperature of 750 °C for 10 hours, and subsequently it was water quenched in order to preserve the homogeneous structure of the material. After this process, it was necessary to conduct a two-stage ageing processes, in order to extract as much silver as possible from the homogeneous solid solution of Cu-Ag. The primary ageing (the first stage) was conducted at 200 °C for 20 hours. The secondary ageing (the second stage) was conducted at a temperature of 450 °C for 10 hours. After the preliminary heat treatments, the alloy microstructure consisted of very numerous fine silver precipitates in the copper matrix. Next, the material was drawn into the final diameter wires. In order to enhance the electric properties, the final diameter wires were subjected to a heat treatment at a temperature of 180 °C for 10 hours. Finally, the wires with a diameter of 0.37mm and a true strain of 6.5 had a tensile strength R<sub>m</sub>=1220 MPa, and an electric conductivity of 74% IACS. The final wire microstructure, as observed on its longitudinal section, presented very numerous, elongated, thin silver bands and copper matrixes, favourable to obtain a set of high mechanical properties and a high electrical conductivity of the product.

#### Example 3

**[0032]** The materials in the form of high purity silver pellets of 99.99% and OFE copper were melted at a temperature

of 1220 C in a graphite crucible placed within an induction furnace. The continuous casting process was conducted at a temperature of 1220°C in an inert gas atmosphere. The continuous casting of rods with a chemical composition of Cu-7% Ag by weight, using a graphite mould was performed in primary cooling (mould cooling) and secondary cooling (of the solidified alloy after leaving the mould) conditions. The round rods obtained as a result of the continuous casting process had a diameter of 9.5mm and a tensile strength  $R_m=240$  MPa, and an electrical conductivity of 84% IACS. Thus obtained material was subjected to the thermo-mechanical treatment processes. The casting was solution-annealed at a temperature of 750 C for 20 hours, and then quickly water quenched in order to preserve the homogeneous structure of the material. The further procedure included setting a strain in the drawing process, with the true strain measure of 0.4. After this process the rods had a tensile strength  $R_m=260$  MPa, and an electrical conductivity of 83% IACS. Next, the two-stage ageing process was carried out, which was to extract as much silver as possible from the homogeneous solid solution of Cu-Ag. The primary ageing (the first stage) was conducted at 300 C for 20 hours. The secondary ageing (the second stage) was conducted at a temperature of 450 C for 10 hours. After the preliminary heat treatments, the alloy microstructure consisted of very numerous fine silver precipitates and a copper matrix. Next, the material was drawn into wires of the final diameter. In order to enhance the electric properties, the wires of the final diameter were subjected to heat treatment at a temperature of 150°C for 100 hours. Finally, the wires with a diameter of 0.2mm and a true strain of 7.7 had a tensile strength  $R_m=1250$  MPa, and an electric conductivity of 75% IACS. The final microstructure of the wire, as observed on its longitudinal section, presents very numerous, elongated, thin silver bands on the background of a copper matrix, favourable for obtaining a set of high mechanical properties and a high electrical conductivity of the product.

**[0033]** The solution according to the invention is a previously unknown, consistent, integrated method of manufacturing finished rods as a result of the continuous melting and casting process of Cu-Ag alloys that feature a high chemical purity with an allowable oxygen content in the alloy of 3 ppm or less and other impurities up to max. 20 ppm. The chemical composition and the structure of Cu-Ag alloy rods obtained on the basis of the solution according to the invention are constant along the whole length of the casting. The final product in the form of wires (including micro-wires), is only obtained by drawing of continuously cast rods, using dies with a round profile or other.

## Claims

1. A method of manufacturing wires, including microwires, of Cu-Ag alloys, in particular of alloys with Cu-(3÷7.9)% Ag by weight **characterised in that** the materials in the form of copper and silver with a high chemical purity are melted at a temperature of 1083÷1300 C in a graphite crucible placed in a furnace, and subsequently continuously cast at a temperature of 1083÷1300 C, in an inert gas atmosphere using a graphite mould, in primary cooling (mould cooling) and secondary cooling conditions (the solidified alloy after leaving the mould), and then the casting thus obtained is subjected to a thermo-mechanical treatment.
2. A method as claimed in the claim 1 **characterised in that** during the thermo-mechanical treatment the obtained casting is solution annealed at a temperature of 600÷779.1 C for 0.5÷100 hours, and subsequently quenched at a rate faster than the process of precipitating of its constituents from the solid solution, and then it is drawn, with a true strain measure of 0.1÷1, whereupon it is subjected to further two-stage heat treatment processes, followed by drawing into wires of the final cross-section.
3. A method as claimed in the claim 1 **characterised in that** during the thermo-mechanical treatment the obtained casting is solution annealed at a temperature of 600÷779.1 C for 0.5÷100 hours, and subsequently quenched at a rate faster than the process of precipitating of its constituents from the solid solution, and then it is subjected to a further two-stage heat treatment processes, followed by drawing into wires of the final cross-section.
4. A method as claimed in claim 1 **characterised in that** in the two-stage heat treatment at the first stage there is holding at 150÷300 C for 0.1÷100 hours, followed by - at the second stage - holding at a temperature of 300÷500 C for 0.1÷20 hours, and then slow cooling.
5. A method as claimed in claim 1 **characterised in that** during drawing of the material into wires of the final cross-section, at least one intermediate heat treatment occurs within the range of 200÷600 C for 0.1÷20 hours, followed by either slow cooling or quenching.
6. A method as claimed in claim 1 **characterised in that** during the drawing of the material into wires of the final cross-section, at least one intermediate heat treatment occurs within 600÷900 C for 0.1÷1000 hours, followed either by slow cooling or quenching.

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7. A method as claimed in claim 2 or 3 **characterised in that** the wires of the final cross-section are subjected to a heat treatment at a temperature of  $50 \div 250^{\circ}\text{C}$  for  $0.1 \div 1000$  hours.
8. A method as claimed in claim 2 **characterised in that** after the solution annealing the casting is water quenched.
9. A method as claimed in claim 2 **characterised in that** after the solution annealing the casting is oil quenched, in particular with a process oil.
10. A method as claimed in claim 2 **characterised in that** after the solution annealing the casting is liquid nitrogen quenched.
11. A method as claimed in claim 2 **characterised in that** after the solution annealing the casting is emulsion quenched, with the oil in water concentration of between 3 and 25%.
12. A method as claimed in claim 1 **characterised in that** the graphite crucible is made of a high purity graphite, wherein alloying constituents are placed under a charcoal or graphite layer.
13. A method as claimed in claim 1 **characterised in that** the graphite crucible is placed in a protective atmosphere.
14. A method as claimed in claim 1 **characterised in that** the graphite mould is cooled with a system that is mounted on it, through which a cooling agent flows (the primary cooling system).
15. A method as claimed in claim 1 **characterised in that** the casting leaving the mould is additionally cooled by a cooling agent applied directly onto the casting (the secondary cooling system).



## EUROPEAN SEARCH REPORT

Application Number

EP 14 46 1523

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The present search report has been drawn up for all claims			
Place of search Munich		Date of completion of the search 10 April 2015	Examiner Lombois, Thierry
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