



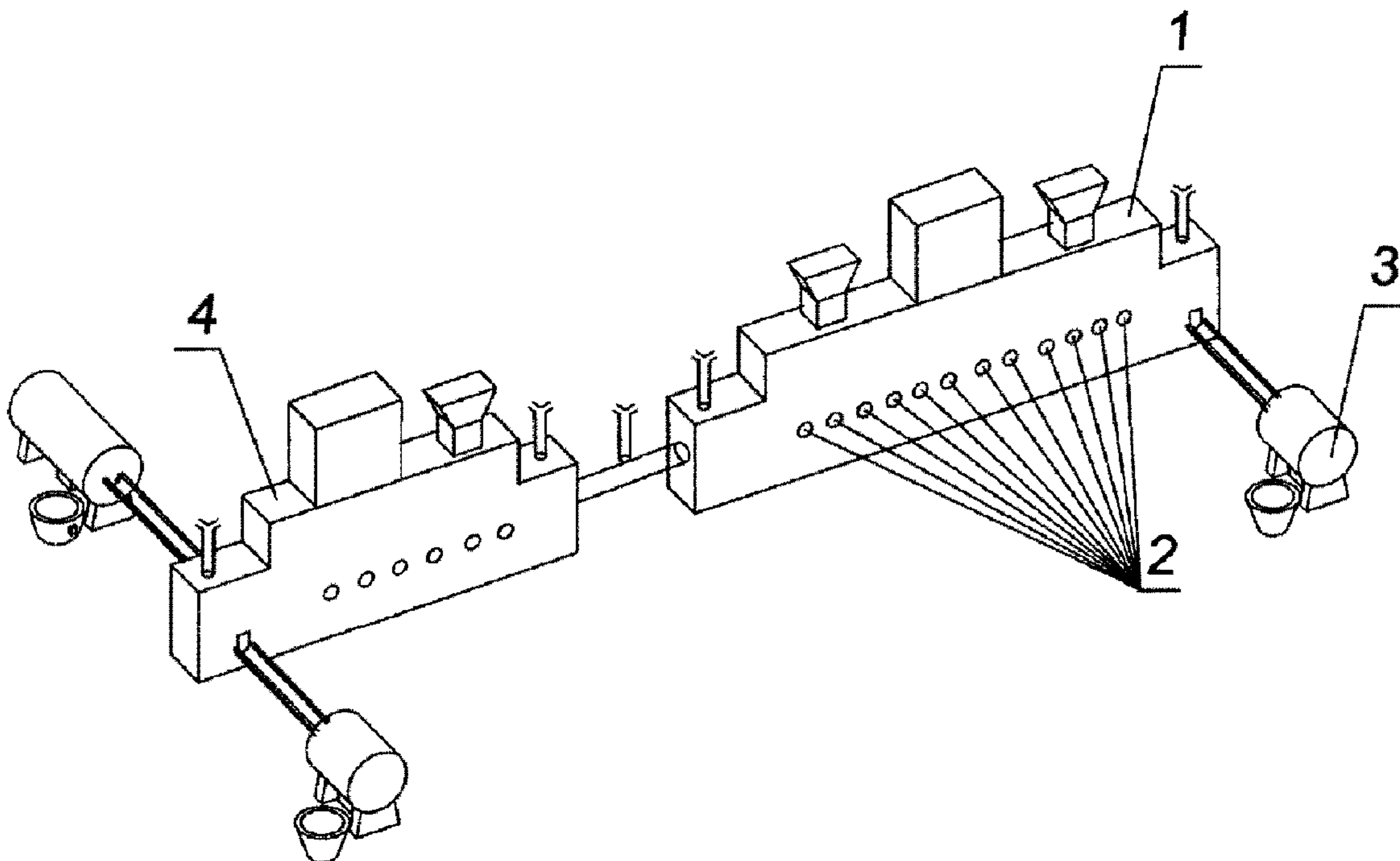
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(54) Titre : PROCEDE DE TRAITEMENT CONTINU DE MATERIAUX SULFURES CONTENANT DU CUIVRE ET DU NICKEL
(54) Title: METHOD FOR CONTINUOUSLY CONVERTING NICKEL-CONTAINING COPPER SULPHIDE MATERIALS



Фиг. 1

(57) Abrégé/Abstract:

The present method can be used for converting nickel-containing copper sulphide materials. A method for continuously converting nickel-containing copper sulphide materials into blister copper, waste slag and a copper-nickel alloy includes smelting the materials

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(57) **Abrégé(suite)/Abstract(continued):**

together with SiO_2 and CaO-containing fluxes and coal in a Vanyukov converting furnace to produce blister copper, gases with a high concentration of SO_2 , and slag with an SiO_2/CaO concentration ratio of from 3:1 to 1:1, in which the sum of the iron, nickel and cobalt concentrations is not more than 30 wt%, at a specific oxygen consumption in the range of 150-240 nm^3 per ton of dry sulphide material for conversion, and depleting the slag in a separate unit, namely a Vanyukov reduction furnace, using a mixture of an oxygen-containing gas and a hydrocarbon fuel at an oxygen consumption coefficient (α) in a range of from 0.5 to 0.9, together with coal, to produce waste slag and a copper-nickel alloy. The technical result is the production of blister copper, waste slag and a copper-nickel alloy using a continuous method, while separating the processes of conversion and reduction into separate units, namely two single-zone Vanyukov furnaces.

ABSTRACT

The present method can be used for converting nickel-containing copper sulphide materials. A method for continuously converting nickel-containing copper sulphide materials into blister copper, waste slag and a copper-nickel alloy includes smelting the materials together with SiO₂ and CaO-containing fluxes and coal in a Vanyukov converting furnace to produce blister copper, gases with a high concentration of SO₂, and slag with an SiO₂/CaO concentration ratio of from 3:1 to 1:1, in which the sum of the iron, nickel and cobalt concentrations is not more than 30 wt%, at a specific oxygen consumption in the range of 150-240 nm³ per ton of dry sulphide material for conversion, and depleting the slag in a separate unit, namely a Vanyukov reduction furnace, using a mixture of an oxygen-containing gas and a hydrocarbon fuel at an oxygen consumption coefficient (α) in a range of from 0.5 to 0.9, together with coal, to produce waste slag and a copper-nickel alloy. The technical result is the production of blister copper, waste slag and a copper-nickel alloy using a continuous method, while separating the processes of conversion and reduction into separate units, namely two single-zone Vanyukov furnaces.

METHOD FOR CONTINUOUSLY CONVERTING NICKEL-CONTAINING COPPER SULPHIDE MATERIALS

FIELD OF THE INVENTION

The present invention relates to a field of non-ferrous metallurgy, in particular to
5 methods for converting nickel-containing copper sulphide materials.

The method can be used for converting nickel-containing copper sulphide materials
to produce a blister copper, a waste slag and a copper-nickel alloy.

PRIOR ART

A method for continuously converting nickel-containing copper sulphide materials is
10 represented as a complex, which consists of two furnaces, for instance of two Vanyukov
furnaces. Oxidizing smelting of nickel-containing copper sulphide material is carried out in
a Vanyukov converting furnace along with SiO_2 and CaO -containing fluxes to produce
blister copper, gases with a high concentration of SO_2 and slag enriched with copper and
nickel oxides, which is continuously entering through the overflow chute to the second
15 furnace of the continuous converting complex, namely into a Vanyukov reduction furnace,
where it is treated with a reducing gas mixture using a mixture of oxygen-containing gas, a
hydrocarbon fuel and coal at an oxygen consumption coefficient (α) in a range of from 0.5
to 0.9 to produce waste slag and the copper-nickel alloy. Besides nickel-containing copper
sulphide material, copper- and nickel-containing by-products are added into the Vanyukov
20 converting and reduction furnaces.

Main products of a continuously converting complex consisting of two Vanyukov
furnaces are blister copper, gases with the high concentration of SO_2 , waste slag and the
copper-nickel alloy. The chemical composition of waste slag allows to use it in a building
industry or for stowing of mines, and the composition of copper-nickel alloy is a basis for
25 producing commercial products.

Known is a method for continuously converting liquid and solid sulphide materials
(RU №2071982) which comprises feeding sulphide materials in a furnace, supplying an
oxygen-containing blast into layer of matte-metal-slag emulsion through horizontal blowing
devices disposed evenly in side walls of furnace, and removing liquid products of
30 conversion from a furnace. The disadvantage of aforesaid method is possibility of periodic
formation of an intermediate matte layer between layers of slag and copper. Presence of the

intermediate matte layer inevitably causes formation of semi-blister copper instead of blister copper. As a periodic production of semi-blister copper is allowed, the given technology of continuously converting should also provide an operation of final conversion, required in this case. The disadvantages of this conversion method are formation of folded nickel slags and inexpediency of sulphur utilization at operation of final conversion. In case of producing in the furnace not semi-blister, but blister copper there should be taken into consideration such disadvantage of the technology as a low direct copper recovery to blister copper because an operation of depletion of slag formed during oxidizing smelting, is not provided by this method.

It is also known a method (RU №2169202) for copper concentrate converting to a blister copper, comprising charge feeding, melt scavenging with formation of the slag and blister copper and releasing of the smelting products. Oxidizing smelting of concentrate is wherein carried out at ratio of loaded concentrate and oxygen-containing gas feeding in a range of 1.0-1.3 of that theoretically required to oxidize a whole sulphur and impurities (Fe, Ni, Co) to oxides, and before releasing the slag, that is performed periodically, the slag depleting is conducted with change of the ratio of loaded concentrate and oxygen-containing gas feeding to 0.3-1.0 of that theoretically required to oxidize the whole sulphur and impurities (Fe, Ni, Co) to oxides, herewith achieving decrease of copper oxide content in the slag from 35 to 22%. The disadvantage of this blister copper production method is rather high content of copper remained in the slag after depletion process. This is because iron, cobalt and nickel are transferred from the concentrate to the slag via exchange reactions during the reduction of the slag by sulphide concentrate that results in substantial increase of iron and nickel concentrations in the slag on background of decreasing copper concentration. Concentrations of iron and nickel in the slag are increasing even more when attempting to reduce copper in the slag more deeply and the sedimentation of solid nickel-iron spinel occurs as a result of homogeneous silicate melt saturation. The consequence of the presence of significant amount of solid spinel in the slag is known to be inevitable slag foaming and creation of emergency.

Combination of two processes (oxidative and reductive) in one furnace space causes inconstancy of smelting products composition (copper, slag and waste gases) and makes it rather complicated to control such technology automatically.

Inconstancy of slag and copper levels implies a periodic contact of molten slag, which is aggressive due to a high content of copper oxide (at the stage of oxidation the copper concentration reaches 35 wt %) with refractory lining with rapid wear of the latter.

The closest to the proposed invention on technical and technological essence is a method for continuously converting copper- and nickel-containing sulphide materials with SiO₂ and CaO-containing fluxes (RU № 2359046) with production of blister copper, process slag, gases with a high concentration of SO₂ in a furnace with two zones - oxidizing smelting is carried out in oxidizing zone while slag depletion is carried out continuously in reducing furnace zone using a mixture of oxygen-containing gas and hydrocarbon fuel at the oxygen consumption coefficient (α) in a range of from 0.5 to 0.9. CaO-containing flux is added along with SiO₂-containing flux during the oxidizing smelting to obtain the slag with SiO₂:CaO ratio from 3:1 to 1:1, and total flux consumption for oxidizing smelting is determined to maintain the sum of iron, nickel and cobalt concentrations in the slag not more than 30 wt %. At the stage of slag reduction a solid fuel, for instance coal, is added along with hydrocarbon one. There is a significant disadvantage in this method: the oxidizing smelting slag without any changes of conditioned properties of blister copper according to nickel content cannot be deeply reduced because of active nickel and iron recovery from the slag on a certain stage of the process, followed with their transfer to blister copper, thereby making it substandard for further flame refining. Accordingly, the slag obtained in two-zone Vanuykov furnace contains plenty of copper and nickel oxides (more than 11% and more than 6% respectively), that makes it a rich product, which needs to be processed at the stage of additional recovery of copper and nickel. The converting of this slag causes additional burden on the pyrometallurgical nickel-producing circuit, where the slag is directed to additional copper and nickel recovery. This method has been considered as the closest analogue.

SUMMARY OF THE INVENTION

An object of the invention is development of a method for continuously converting nickel-containing copper sulphide materials to produce blister copper, slag which composition correspond to that of spoil standards slag, i.e. waste slag, and copper-nickel alloy. In order to achieve the intended purpose, conversion and recovery processes must be separated by separate units, namely two single-zone Vanyukov furnaces connected via overflow chute.

A technical result is production of blister copper, waste slag and copper-nickel alloy by continuous method, wherein conversion and recovery processes are separated by separate units, namely two single-zone Vanyukov furnaces.

The technical result is achieved due to the fact that in contrast to the closest analogue, in the method for continuously converting nickel-containing-copper sulphide materials into blister copper, waste slag and the copper-nickel alloy, comprising oxidizing smelting along with SiO_2 and CaO -containing fluxes and coal to produce blister copper, gases with a high concentration of SO_2 , slag with an SiO_2 : CaO concentrations ratio of from 3:1 to 1:1 in which the sum of iron, nickel and cobalt concentrations is not more than 30 wt %, at a specific oxygen consumption in a range of 150-240 nm^3 per ton of dry sulphide material for conversion, and depleting this slag using a mixture of oxygen-containing gas and a hydrocarbon fuel at an oxygen consumption coefficient (α) in a range of from 0.5 to 0.9 along with coal, the slag depletion is conducted in a separate unit, namely a Vanyukov reduction furnace, wherein producing waste slag and copper-nickel alloy.

The method can be characterized in that copper-nickel alloy, being a basis for producing commercial products, is produced during depletion of molten slag.

Moreover, the method can be characterized in that CaO -containing flux is added along with SiO_2 -containing flux during the oxidizing smelting to produce slag with SiO_2 : CaO concentrations ratio from 0,4:1 to 3:1.

In addition, the method can be characterized in that the reduction is supplied with coal in an amount of up to 15% of the weight of the slag obtained at the oxidation stage.

The method can also be characterized in that by-products contain copper and nickel.

BRIEF DESCRIPTION OF THE DRAWINGS

The claimed method for continuously converting nickel-containing copper sulphide materials in a complex of two furnaces, namely two Vanuykov furnaces, is presented as shown in Fig. 1. Nickel-containing copper sulphide materials are added along with SiO_2 and CaO -containing fluxes to a Vanuykov converting furnace 1 of continuously converting complex. Oxygen-air mixture and gaseous fuel are added to Vanuykov furnace 1 through furnace tuyeres 2. Blister copper formed during a smelting process in Vanuykov converting furnace 1 is continuously released into a mixer 3, and slag with a high content of copper, nickel and iron passes to a second furnace of continuously converting complex, namely to Vanuykov reduction furnace 4, where it is depleted by reducing gas-air mixture along with

coal to produce waste slag and copper-nickel alloy. Reducing gas-air mixture is formed as a result of natural gas combustion in oxygen-air mixture under oxygen shortage conditions. A temperature of oxidation and reduction processes is maintained at a level of 1350°C.

Smelting products of converting furnace 1 (blister copper) and of reduction furnace 4 (waste slag and copper-nickel alloy) are assumed to be released continuously. To release the smelting products, siphon-type devices (not shown in the drawing), located in the opposite ends of furnaces, are provided. A continuity of the proposed process in a form of complex of two Vanuykov furnaces 1 and 4 paves the way for maintaining constancy of levels of slag and blister copper in the Vanuykov converting furnace 1, and slag and copper-nickel alloy in the Vanuykov reduction furnace 4, that is an important advantage of this process. Blister copper is continuously released through a siphon-type device into the mixer 3 designed for it and then is sent to anodic refining to produce copper anodes. A specific of the slag composition of the new method oxidizing stage is that it contains copper and nickel at a rate of 4:1–5:1, which is favourable for producing valuable copper-nickel alloy, for instance a ‘melchior’ alloy. Copper-nickel alloy with some content of iron, which is a basis for producing commercial products, is produced as a result of deep reduction of this slag to spoil standards. This copper-nickel alloy can be converted in pyrometallurgical nickel production, or directed to a stage of oxidizing refining in order to remove iron and produce commercial products, which composition is determined for Russia conditions by the State standard (‘melchior’ alloy, ‘neusilber’ etc.).

An important feature of the developed method is the fact that in case of converting materials containing precious and platinum group metals in the Vanuykov converting furnace 1, these metals are almost completely recovered to blister copper and are not transferred to slag, fed in the Vanuykov reduction furnace 4. It provides a production of copper-nickel alloy being almost free from precious, platinum group metals in the Vanuykov reduction furnace 4.

It is obvious that the alloy of the Vanuykov reduction furnace 4 is more preferable to be supplied to a customer as a commercial product after refining and casting operations.

Slag produced in the Vanuykov reduction furnace 4 is the waste one. Its chemical composition allows to use it in the building industry or for the stowing of mines.

All sulphur contained in nickel-containing copper sulphide materials passes to a gaseous phase of the Vanuykov converting furnace 1.

EMBODIMENT OF THE INVENTION

Since oxidation stage of continuously converting process, conducted in the Vanuykov converting furnace with production of blister copper has passed extensive studies and currently is sufficiently investigated (Tsymbulov L.B., Knyazev M.V., Tsemekhman L, Sh. A method for converting copper sulphide materials to blister copper // The patent of the Russian Federation № 2359046 of 09.01.2008. Pigarev S.P. Structure and features of slag melts of the continuously converting nickel-containing copper sulphide materials. Abstract of PhD dissertation St-Petersburg. 2013. 21 p.), the proposed invention is based on data of experimental studies of the reduction stage of the new method, with searching conditions providing production of waste slag and copper-nickel alloy, which is a basis for producing commercial products, for instance 'melchior' alloy, which is widely used nowadays in industries as the alloy with high anticorrosion properties, and also for producing household products and jewelry.

A methodology of the experimental studies was as follows. An alundum reactor with an alundum crucible inside, which contains an initial slag, namely oxidative stage slag, with a following composition, wt %: Cu-17,9; Ni-5,6; Fe-23,1; Co-0,135; SiO₂-27,5; CaO-11,9; Al₂O₃-3,1; MgO-0,79. Then the furnace was run with changing an inductor voltage, and heated up to operating temperature of 1350°C.

After the slag smelting a melt was scavenged via beryllium oxide tube with a reducing gas mixture of the following composition, vol%: CO-44; CO₂-38; H₂-18. Oxygen and the reducing gas mixture partial pressure corresponded that of oxygen in a mixture produced during natural gas combustion at the 'alpha' value (α) = 0,6.

In laboratory experiments a duration of the melt scavenging by the gas mixture was varied from 0 to 50 minutes. A gas mixture flow rate was 0.8 l/min. After completion of scavenging, the melt was allowed to settle for 15 minutes and then the furnace was turned off. After that the crucible with the melt was removed out of the furnace and cooled, and slag was separated from metal alloy.

After appropriate sample preparation, slag and metal alloy have been analyzed by methods of atomic absorption spectrometry and inductively coupled plasma atomic emission spectrometry.

Chemical compositions of metal alloy and slag, produced as a result of conducted experimental studies, are presented in TABLE 1.

At first, we consider changes in the slag composition according to copper and nickel content when changing a time of the molten slag scavenging by the reducing gas mixture. This dependency is presented in Fig. 2.

As can be seen at the Fig.2, with the increase of time of molten slag scavenging by reducing gas mixture, there is a sharp decrease in copper content in slag, and starting from the 17th minute of scavenging there is also a substantial decrease in nickel content in molten slag on the background of decreasing copper content. After 35th minute of the molten slag scavenging the decrease in copper and nickel concentrations in slag becomes extremely insignificant.

As can be seen from the graph presented in Fig. 3, a decrease of copper (a) and nickel (b) content in the slag is accompanied by an increase a nickel content in metal alloy, reaching a maximum of its content at a level of 21,5% at copper and nickel concentration in slag at a level of 0,8% and 0,4% respectively. Further decrease of copper and nickel content in molten slag to standard values is characterized by a decrease of nickel content in metal alloy, that is associated with a start of active iron recovery and its transfer to metal alloy. This will be discussed subsequently in details.

As the proposed new method for continuously converting nickel-containing copper sulphide materials assumes simultaneous production of, on the one hand, an alloy with a certain rate of copper and nickel and with a certain standard content of iron in it, and on the other hand, waste slag, it is necessary to choose optimum technological parameters to focus on while implementing thereof.

So let's consider dynamics of changes in slag and copper-nickel alloy composition during scavenging by reducing gas mixture (Fig. 4).

Fig.4 illustrates a line graph, which characterizes changes in nickel and iron content in metal alloy depending on time of molten slag scavenging by reducing gas mixture. Changes in copper and nickel content in slag depending on time of molten slag scavenging by reducing gas mixture are also plotted on the considered graph.

First of all, an attention on the presented line graphs should be paid to a correlation between copper and nickel content in waste slag and nickel and iron content in metal alloy, produced as a result of reduction. There is a significant decrease in concentrations of both copper and nickel in slag during active nickel reduction from 5th to 30th minutes of

scavenging, but this residual content is still rather high (Cu – 0,8%; Ni – 0,4%) and slag cannot be considered as a waste one.

Only when active iron reduction starts, it becomes possible to decrease copper and nickel concentrations to spoil contents.

5 Thereby, on the one hand, in order to obtain a standard iron content in copper-nickel alloy, particularly, in ‘melchior’ ($\text{Fe} \leq 0,5\%$), it is necessary to strive for a minimal rate of iron reduction during the depletion process.

On the other hand, deep reduction of slag according to copper and nickel contents is only possible when producing an alloy with an iron concentration of 5% or more, that will
10 require additional expenditures at a stage of refining when producing trademark copper-nickel alloys. In this regard, it is recommended to conduct the depletion process until the iron concentration in the copper-nickel alloy reaches $\sim 6\%$. In this case, waste slag with a following composition will be obtained, wt %: Cu-0,45; Ni-0,17; Fe-30,3; SiO_2 -37,5; CaO-16,2; Al_2O_3 -5; MgO-1. A composition of copper-nickel alloy will be as follows, wt %: Cu-
15 73,2; Ni-20,5; Fe-6,1.

To produce commercial products from this alloy, for instance in a form of ‘melchior’ alloy, it is necessary to carry out a stage of refining, at which iron content in copper-nickel alloy can be decreased to standard values. Cu:Ni ratio in produced refined metal alloy will be in range of 4:5-5:1, that matches the composition of commercial products. Slag formed
20 during the oxidative refining process, which base are iron oxides, is supplied to a continuous converting complex, namely to an oxidative stage of the process to the Vanuykov converting furnace 1. It is possible to produce other types of products, which composition is determined for Russia conditions by the State standard. A specific feature of the developed method, as was stated above, is fact that precious and platinum group metals, presented in a raw
25 material, are almost completely transferred into blister copper at a converting stage, and production of new types of products will not cause additional losses of these metals.

INDUCTRIAL APPLICABILITY

The developed method has a significant advantage – possibility to produce new commercial products according to a short flow chart, that in general substantially reduces metallurgical
30 plant’s expenses on the commercial products production.

TABLE 1:

№ exp.	Duration of scavenging, min	Content in alloy, wt %			Content in slag, wt %						
		Cu	Ni	Fe	Ni	Cu	Fe _{general}	SiO ₂	CaO	Al ₂ O ₃	MgO
1	5	98.97	0.89	0.01	5.11	17.26	23.0	27.1	11.7	3.6	0.82
2	10	98.90	1.05	0.01	5.09	12.12	24.8	28.9	12.5	3.9	0.88
3	15	95.62	4.24	0.02	4.40	10.60	25.4	29.6	12.8	4.0	0.90
4	21	92.85	7.00	0.03	3.06	6.85	26.9	31.3	13.5	4.2	0.95
5	25	90.87	8.99	0.04	1.49	5.19	27.5	32.1	13.8	4.3	0.97
6	27	87.70	12.18	0.05	1.32	4.29	28.4	33.1	14.3	4.4	1.01
7	29	80.46	17.79	0.49	0.40	1.54	30.5	38.7	15.4	4.7	1.09
8	30	76.72	21.50	1.72	0.42	0.82	30.9	36.4	15.8	4.9	1.11
9	31	75.68	21.49	2.73	0.29	0.67	30.8	36.9	15.9	4.9	1.12
10	32	74.93	21.37	3.68	0.23	0.58	30.7	37.2	16.0	5.1	1.13
11	35	74.06	21.20	4.72	0.19	0.52	30.5	37.4	16.1	4.9	1.14
12	37	73.30	21.02	5.66	0.16	0.48	30.3	37.6	16.2	5.3	1.14
13	40	72.82	20.26	6.27	0.15	0.25	30.2	37.7	16.3	5.4	1.21
14	45	70.03	20.24	9.61	0.11	0.43	29.4	38.4	16.5	5.3	1.18
15	50	67.95	19.67	12.37	0.09	0.40	28.72	39.1	16.3	5.6	1.23

CLAIMS

1. A method for a continuously converting nickel-containing copper sulphide materials comprising oxidizing smelting along with SiO_2 and CaO-containing fluxes and coal at a specific oxygen consumption in a range of 150-240 nm^3 per 1 ton of dry sulphide material for conversion to produce blister copper, gases with a high concentration of SO_2 and slag with a sum of iron, nickel and cobalt concentrations not more than 30 wt %, and depleting the slag, obtained by reduction, using a mixture of oxygen-containing gas and a hydrocarbon fuel at an oxygen consumption coefficient (α) in a range of from 0.5 to 0.9 along with coal, characterized in that the depletion of the slag is conducted in separate single-zone Vanyukov converting and reduction furnaces, wherein supplying a CaO-containing flux to the oxidizing smelting stage along with a SiO_2 -containing flux to produce slag with SiO_2 :CaO concentrations ratio of from 0.4:1 to 3:1, and on the stage of depletion of the slag supplying coal in an amount of up to 15% of weight of slag produced at the oxidation stage, wherein depleting of the slag is performed by scavenging within 17 to 35 minutes, thereby producing a waste slag and a copper-nickel alloy.

2. The method of claim 1 characterized in that supplying by-products to the Vanuykov converting and reduction furnaces.

3. The method of claim 2 characterized in that the by-products contain copper and nickel.

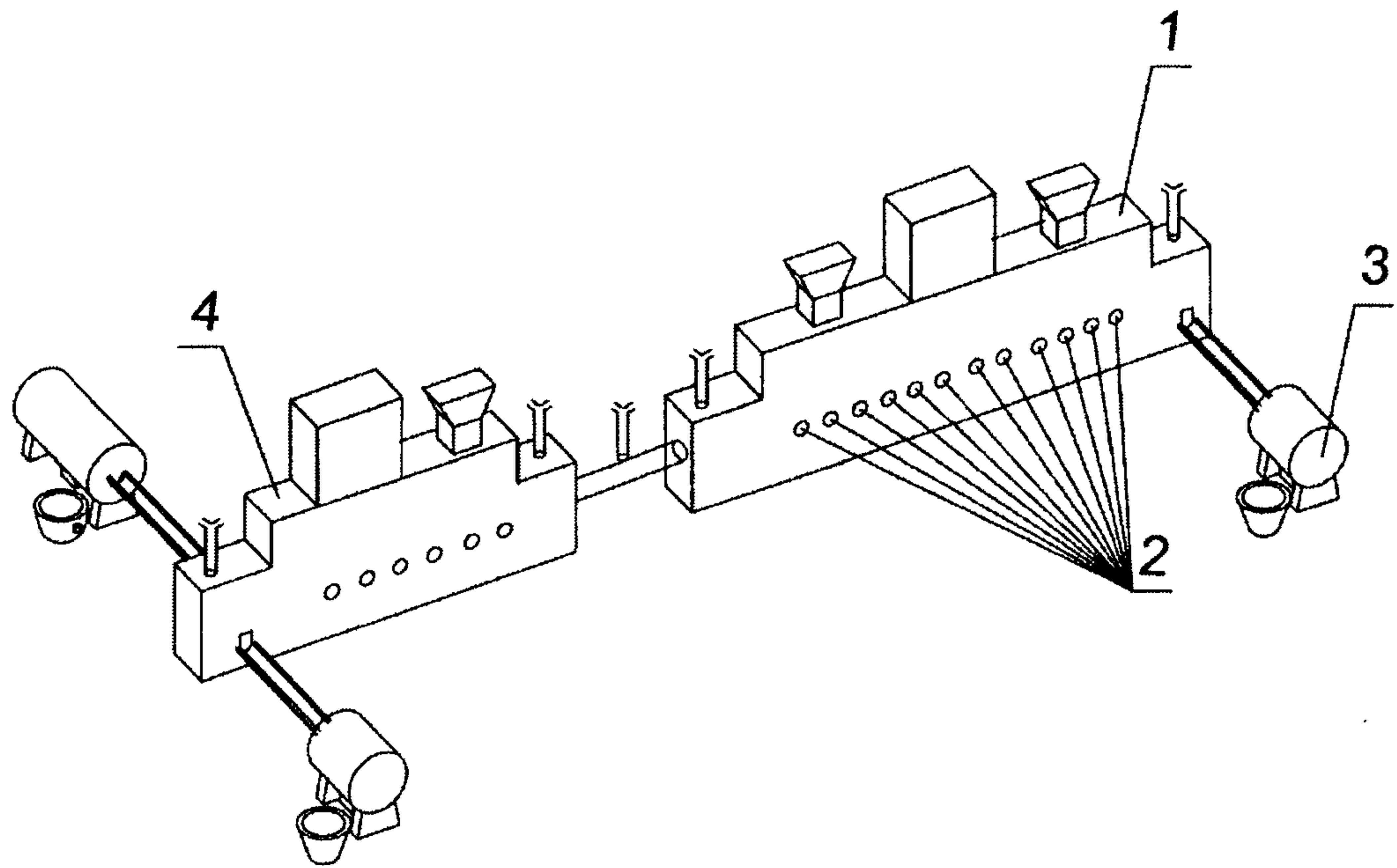


Fig. 1

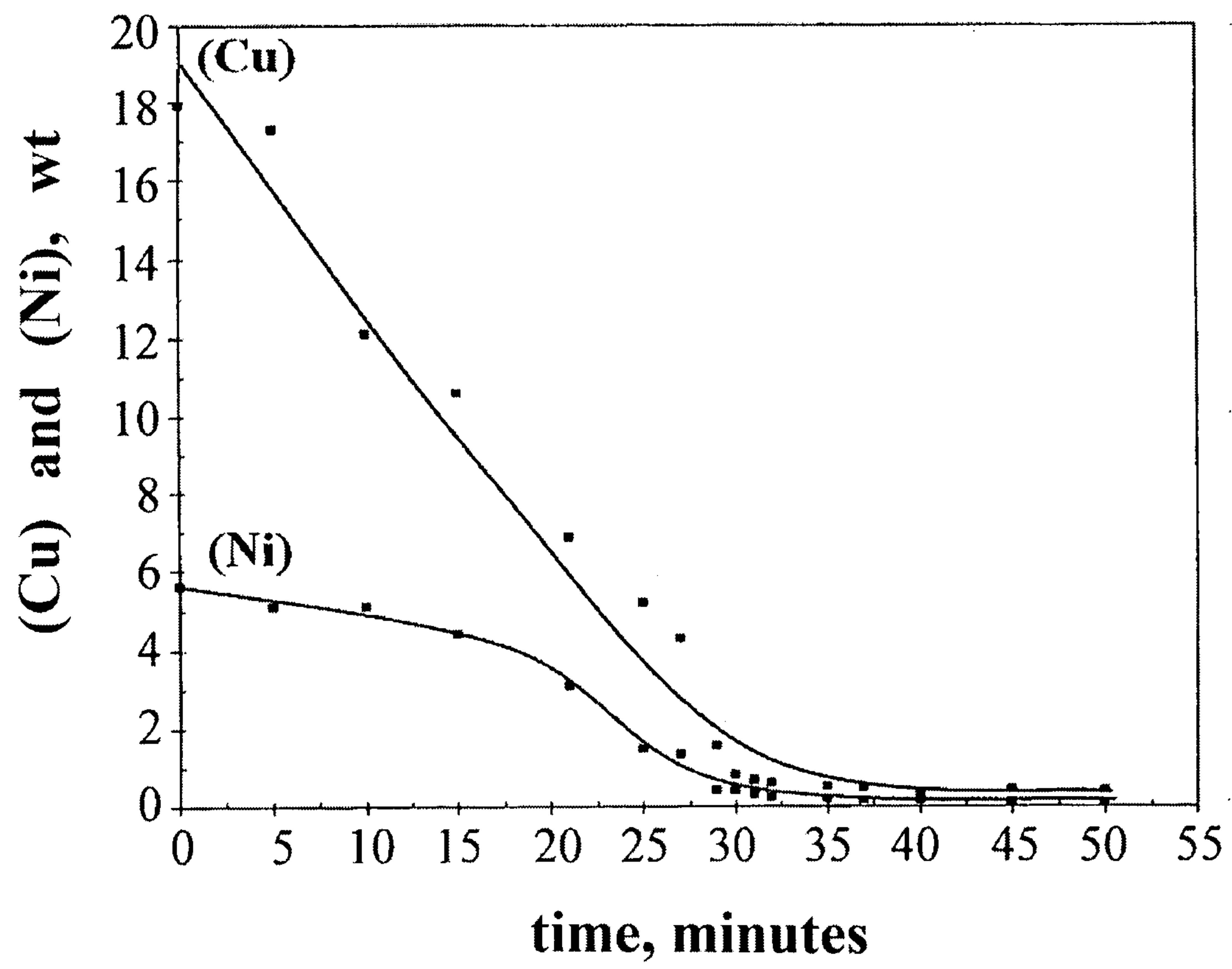


Fig. 2

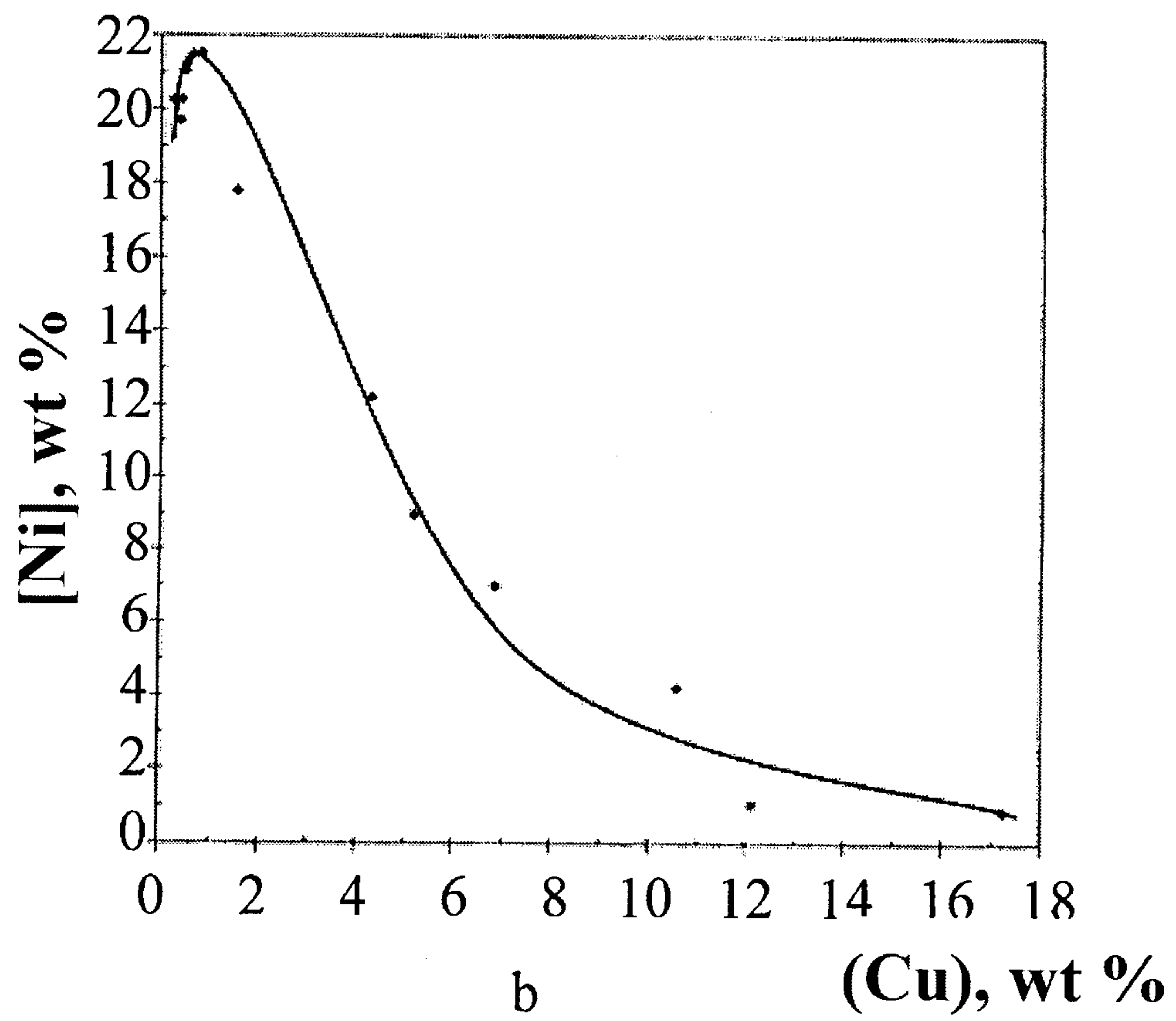
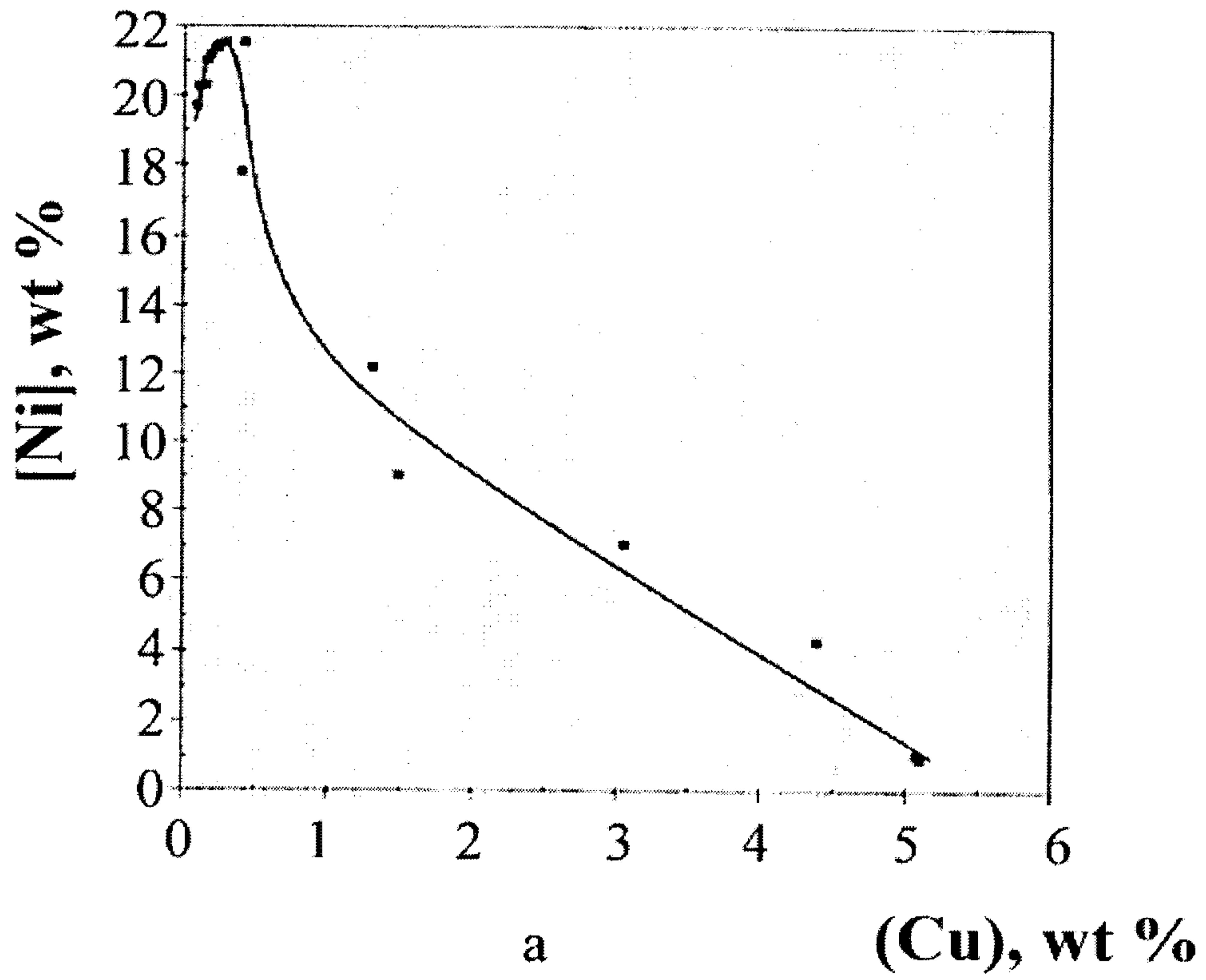


Fig. 3

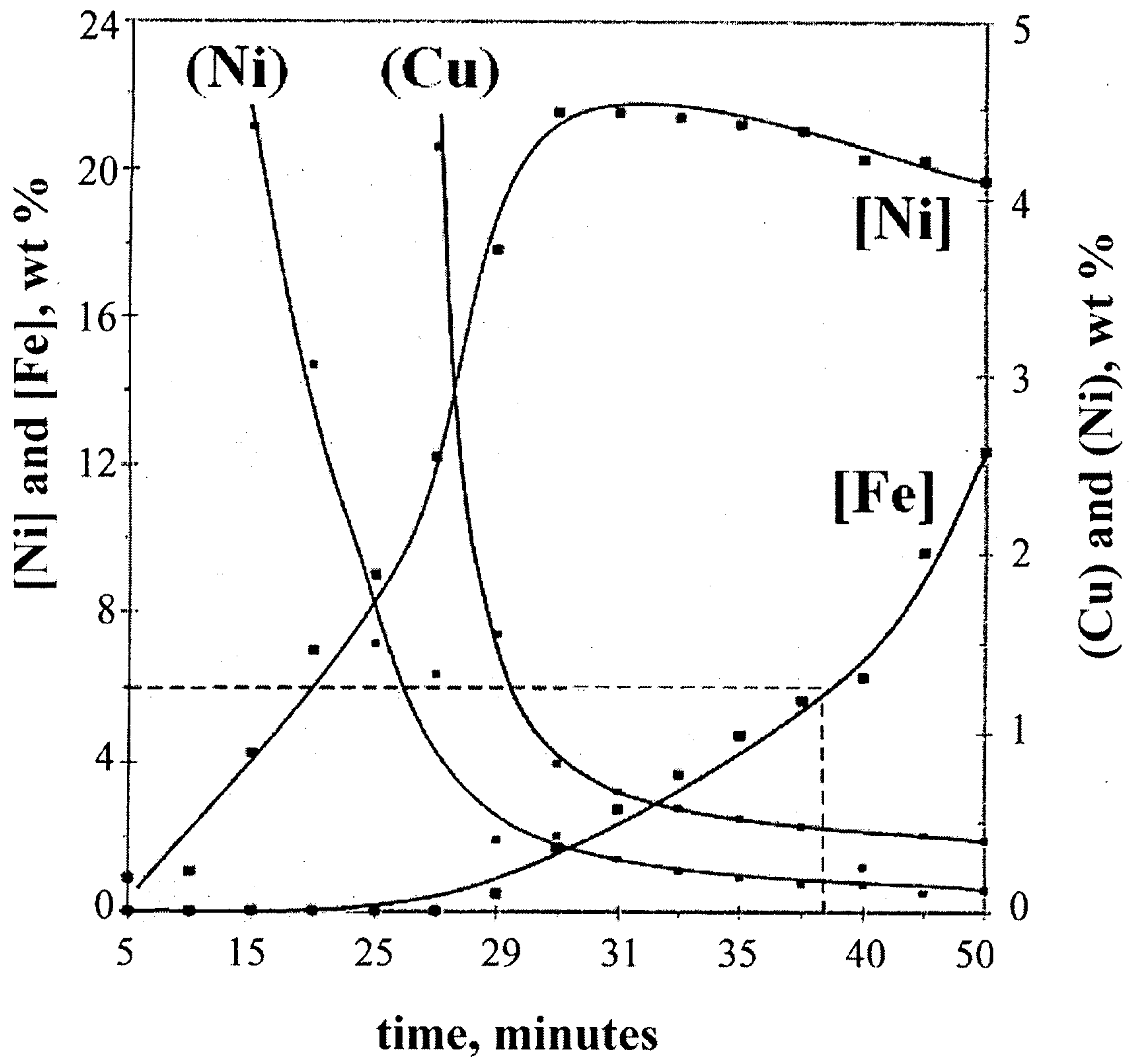
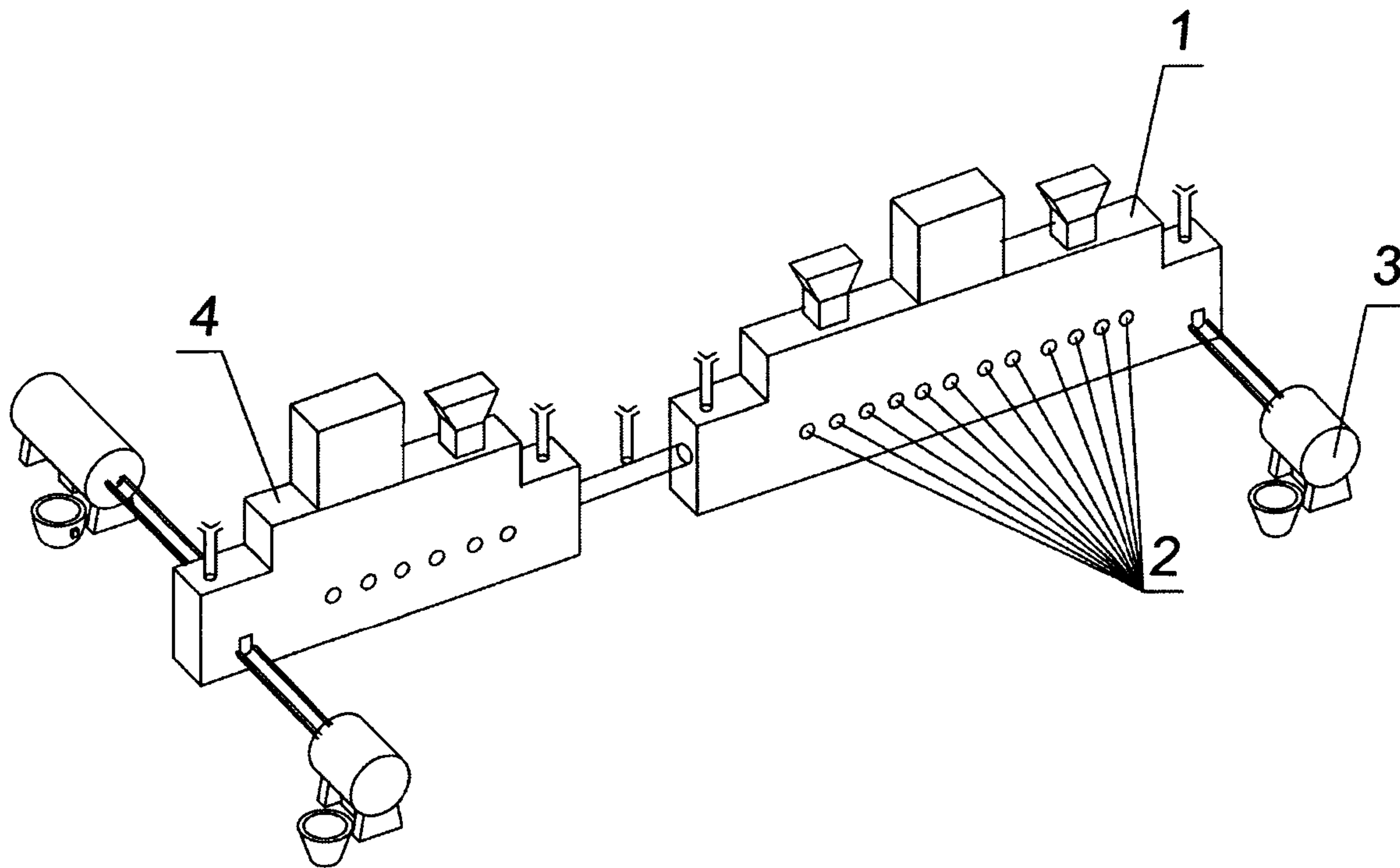


Fig. 4



ФИГ. 1