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ANALYSIS OF COPPER-CONTAINING PRODUCTS FOR THE CONTENT OF NOBLE METALS

Abstract: In the article we are presenting the results of electron microscopy study of the samples of blister copper taken from copper production. It was shown significant amount of noble metals – silver and gold. As a result, silver was found in the range of 0.29-0.59%, gold – up to 0.66%. The methodof assay-gravimetric detection of gold and silver in samples of blister copper is described.

Keywords: copper, noble metals, melting, gold, silver, electron microscopy, impurity.

Introduction

Kazakhstan is one of the largest producers of copper in the world meanwhile more than half of produced refined copper is exported. That is why copper as well as aluminum, nickel and ferrous metals are ones of the key export products. Exported copper is represented by copper concentrate, refined copper and copper wire rod.

Blister copper contains impurities, which deteriorate quality of copper (sulfur, oxygen et al.), and therefore to be removed, as well as impurities non-affecting the quality of copper, but extracted because of their value (silver and gold) [1-4].

In present time for determination of gold and silver content in samples of blister copper of copper production assay-gravimetric method of analysis is widely used [5-9]. Related to bulk up of copper production necessary of using more express method of analysis emerges not giving up by accuracy to assay-gravimetric method. Thus, the development and implementation of appropriate methods of blister copper analysis is an important issue.

Methods and materials

Normally used methods of assay-gravimetric detection of gold and silver in samples of blister copperare described, for example, in standards [10, 11].

The method is based on melting of blister copper samples with furnace charge containing lead (as a collector of noble metals) and borax as a flux at temperature of 1000±50°C. A lead bullion (werkblei, lead alloy containing silver and gold) and slug are obtained after sherber melting. Lead is separated from gold and silver by cupellation of alloy on cupel in muffle furnace at temperature of 950±50°C with obtaining of gold-silver regulus. Gold is separated from silver by solvation of silver in nitric acid. Mass of silver is calculated as difference between mass of gold-silver regulus and mass of the gold.

The method is designed for identification of mass fraction of gold from 20 to 400 g./ton and silver from 500 to 12000 g./ton.

The sample of blister copper (5.00 g.) isweighed on precision (technical) scales, placed in a borax glazed sherber. Above the sample components of furnace chargeare poured. The components are weighed on electronic scales, they contain 80 g. of granulated lead and 8 g. of borax.

Sherbering is carried on in the muffle furnace at a temperature of 1000±50°C. During sherbering oven door is slightly opened up for access of air oxygen. In the presence of oxygen, melt is oxidized and after interaction with borax it gives a slug, in which base-metal oxides move. The slug is shifted to sherber periphery, and melted lead forms center or «eye» of the melt. When lead «eye» will be covered with slug, the sherber stays in the muffle from five to 8 minutes and then melt is poured into a mould. Cooled lead alloy is separated from the slug, forged as a cube and cupelled.

Cupelling is carried on in the muffle furnace at a temperature of 950±50 °C. Werkblei is placed in the muffle furnace onto a cupel with diameter from 35 to 42 mm. Preliminary heated muffle furnace stays with closed door from 2 to 3 minutes until complete melting of the werkblei. After disposal of last remains of lead that can be signed with fulguration, following darkening and solidification of reguluses, cupels are taken off from the furnace, cooled; reguluses are got off from the cupels using forceps, cleaned from adhered particles of cupel mass, flatten out on stithy obtaining thin plates and weighed on microscales. Obtained mass represents total mass of gold and silver. Golden-silver reguluses are parted.

Parting of reguluses is carried on on the electric stove. Solution of nitric acid (ρ = 1.06 g/cm^3) is poured into the porcelain crucible filling it to three-quarters of volume. Then, crucibles are set on the stove and heated until emergence of bubbles. Flattened reguluses are placed into crucibles and solved until full solvation of silver not bringing the solution to a boil. After solvation, solution is drained into reservoir for collection of silver nitrate and hot solution of nitric acid (ρ = 1.21 g/cm^3) is poured into the crucibles up to two thirds by volume. Crucibles are stood on the stove until full discontinuation of nitrogen oxides releasing. Then, the solution is also drained into a reservoir for collection of silver nitrate and gold beads are washed triple with hot water by decantation. Crucibles with gold beads are carefully dried on the stove and annealed in the muffle oven at a temperature of 550±50 °C for 5 minutes. After cooling gold bead is weighed on microscales. The difference between mass of golden-silver regulus and mass of gold bead is the mass of silver.

If the mass fraction of silver in the samples of blister copper is 600 g/ton or more, check sample is prepared from silver with mass corresponding to it's mass fraction in the sample for taking into account silver loss after cupelling. For that samples of silver are placed into pockets of lead foil, compressed tightly and placed in the muffle oven on the cupels preliminary heated up to a temperature of 950±50 °C. In the cupel along with the pocket the granulated lead is placed granulated in the amount at which total mass of lead with a mass of leaden pocket would correspond to mass of sample of werkblei obtained after sherber melting, and then it is cupelled.

Cupelling of check samples is carried on straight after analysis of the samples in the same muffle under the same conditions.

The values of metrological characteristics and standards for determining the mass fraction of gold must not exceed the values given in tables 1 and 2, respectively.

Table 1 - Numerical values of the limits of the absolute error of silver content (g/ton)

Mass fraction of silver	Standard deviation of repeatability σ_r	Repeat limit at n = 3 r_3	Standard deviation of reproducibility σ_R	Reproducibility limit at t = 2 R	Limits of absolute error ±Δ
500 « 1000	10,6	35,0	15,2	42,0	30,0
1000 « 2000	21,1	70,0	30,0	83,0	59,0
2000 « 3000	30,2	100,0	43,3	120,0	85,0
3000 « 4000	45,3	150,0	65,0	180,0	128,0
4000 « 6000	60,4	200,0	86,6	240,0	170,0
6000 « 8000	75,5	250,0	108,3	300,0	213,0
8000 «10000	90,6	300,0	130,0	360,0	256,0
10000 « 12000	105,7	350,0	151,6	420,0	298,0

Table 2 - Numerical values of the limits of the absolute error of gold content (g/ton)

Mass fraction of gold	Standard deviation of repeatability σ_r	Repeat limit at n = 3 r_3	Standard deviation of reproducibility σ_R	Reproducibility limit at t = 2 R	Limits of absolute error ±Δ
20 « 30	0,91	3,0	1,30	3,6	2,6
30 «45	1,21	4,0	1,73	4,8	3,4
45 « 70	1,36	4,5	1,95	5,4	3,8
70 « 100	1,51	5,0	2,17	6,0	4,3
100 « 150	1,81	6,0	2,56	7,1	5,0
150 « 250	2,11	7,0	3,00	8,3	5,9
250 « 400	2,42	8,0	3,43	9,5	6,7

Results and discussion

The method of scanning electron microscopy is intended primarily for the study of the surface structure.

Scanning electron microscopes have 10^3 times greater depth of field than optical instruments, which provides a much higher image quality and allows you to successfully apply the technique of obtaining stereo pairs. The resulting images allow you to recreate a three-dimensional picture of the surface of the sample.

The scanning method allows for sequential analysis and element-by-element scanning of multiple sites in automatic mode and processing of data in relation to the corresponding observation points [12, 13].

We have applied the SEM method to prove the presence of micro-and macro-quantities of gold and silver, respectively, in the samples of blister copper of copper production.

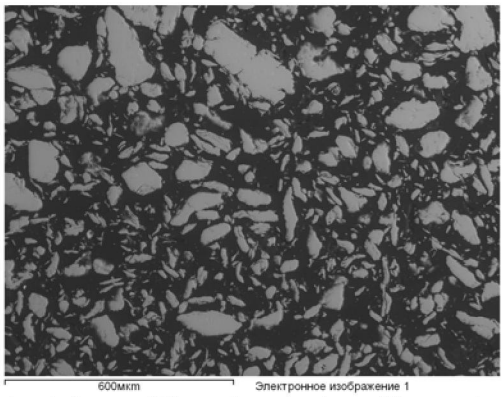

Figure 1. An electronic image of the surface structure of the sample of blister copper

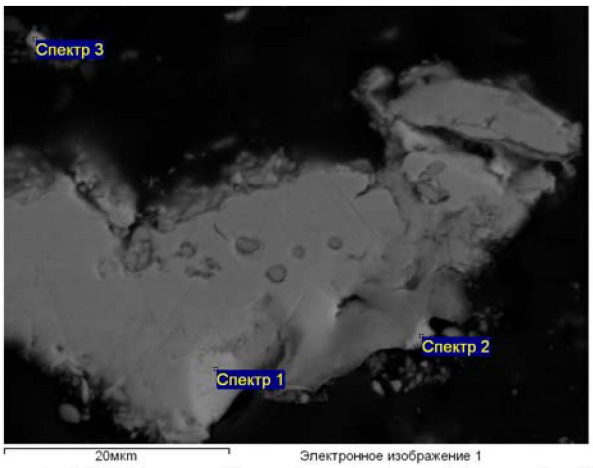

Figure 2. Fragment of SEM image of the surface structure of the sample of blister copper on the impurity content (C, O, Al, Si, Au, Sn, Fe)

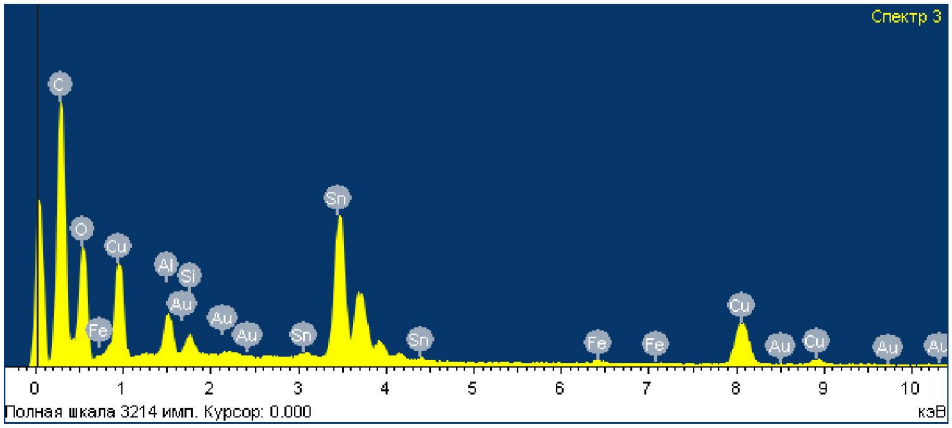

Figure 3 - Spectrum of the analysis site (site №1)

Table 3. Processing parameters of the site №1 for the analysis of all elements (all results in weight %)

Spectrum	O	Al	Si	Fe	Cu	Ag	Sn	Au	Total
Spectrum 1	4.37				95.63				100.00
Spectrum 2	3.85				95.56	0.59			100.00
Spectrum 3	44.29	3.48	1.25	0.74	17.12		32.44	0.66	100.00
Max.	44.29	3.48	1.25	0.74	95.63	0.59	32.44	0.66	
Min.	3.85	3.48	1.25	0.74	17.12	0.59	32.44	0.66	

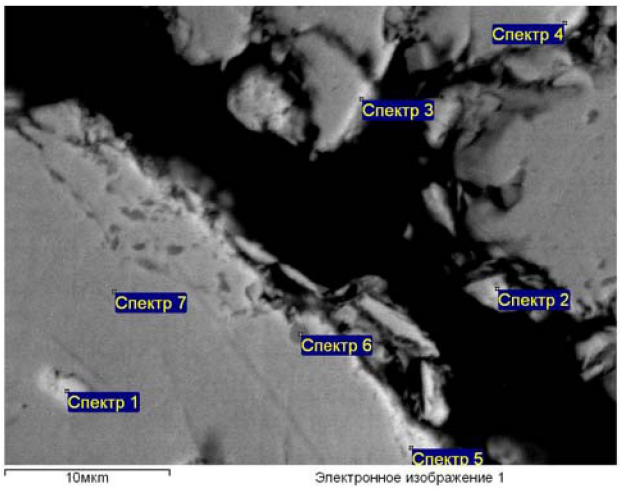

Figure 4 - Fragment of SEM image of the surface structure of the sample of blister copper on the impurity content (C, O, As, Pb, Ag, Sb)

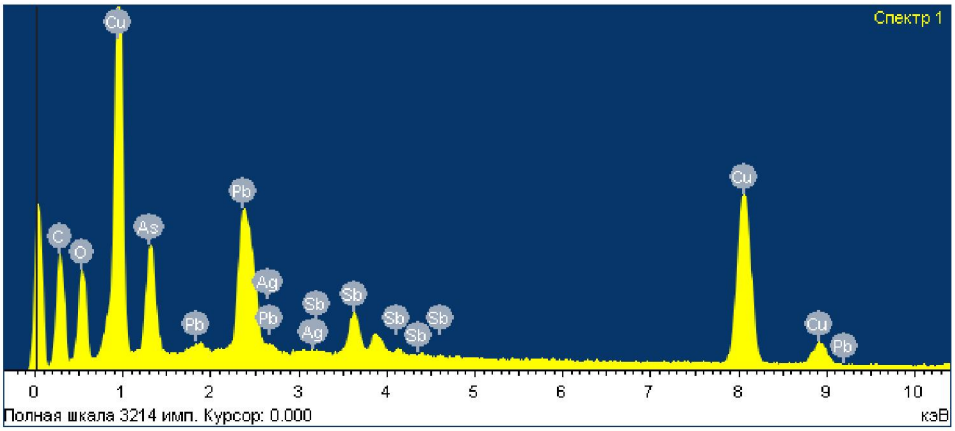

Figure 5 - Spectrum of the analysis site (site №2)

Table 4 - Processing parameters of the site №2 for the analysis of all elements (all results in weight %)

Spectrum	O	Si	Cu	As	Ag	Sb	Pb	Total
Spectrum 1	15.00		41.71	13.94	0.29	7.40	21.67	100.0
Spectrum 2	7.96	0.57	91.47					100.0
Spectrum 3	5.60	1.33	93.06					100.0
Spectrum 4	12.73		62.99	11.92		4.19	8.17	100.0
Max.	15.00	1.33	93.06	13.94	0.29	7.40	21.67	
Min.	5.60	0.57	41.71	11.92	0.29	4.19	8.17	

Figure 6 - A fragment of the SEM image of silver on the surface of the sample of blister copper

Conclusion

Thus, studying of structure surface of samples using SEM we have revealed presence of impurities (C, O, As, Pb, Ag, Sb, Al, Si, Au, Sn, Fe) in blister copper of copper production. Herewith, there was a significant presence of precious metals. So, silver was found in the range of 0.29-0.59%, gold – up to 0.66%.

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ҚҰРАМЫНДА МЫС БАР ӨНІМДЕРДІ АСЫЛ МЕТАЛДАРҒА ТАЛДАУ

Аннотация: Бұл мақалада мыс өндірісінің бастапқы қара мыс үлгілерін электронды-микроскопиялық зерттеу нәтижелері берілген. Асыл металдар – күміс пен алтынның елеулі мөлшері көрсетілген. Нәтижесінде 0.29-0.59% шамасында күміс, 0.66% – ға дейін алтын табылды. Қара мыс үлгілерінде алтын мен күмісті анықтаудың сынамалы-гравиметриялық әдісі сипатталған.

Түйін сөздер: мыс, асыл металдар, балқыту, алтын, күміс, электронды микроскопия, қоспалар.

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АНАЛИЗ МЕДЬ-СОДЕРЖАЩИХ ПРОДУКТОВ НА СОДЕРЖАНИЕ БЛАГОРОДНЫХ МЕТАЛЛОВ

Аннотация: В данной статье представлены результаты электронно-микроскопического исследования образцов черновой меди медного производства. Показано значимое количество благородных металлов – серебра и золота. В результате серебро было обнаружено в пределах 0.29-0.59%, золото – до 0.66%. Описан пробирно-гравиметрический метод обнаружения золота и серебра в образцах черновой меди.

Ключевые слова: медь, благородные металлы, плавление, золото, серебро, электронная микроскопия, примеси.

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